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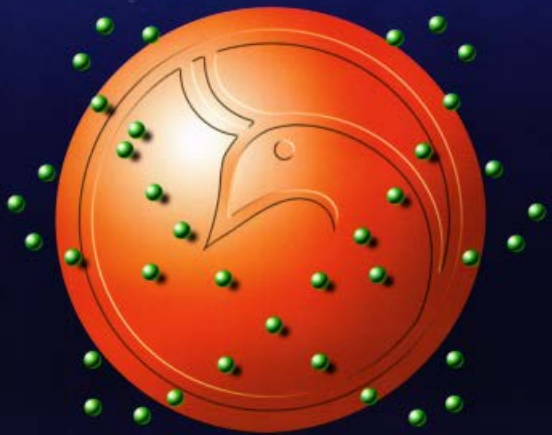

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CONTENTS

Anti-tumor Effect of Honey Against HEP-2 and AMN-3 Cancer Cell Lines *in vitro*

Khalid M. Salih
Department of Biology, College of Science, Al-Mustansiriyah University

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الخلاصة

يعد العسل من اقدم النتجات الطبيعية ذات الاستخدامات المتعددة حيث يمتاز بخصائصه التغذوية و المضادة لكل من المكروبات, الاكسدة, الالتهابات و الاورام. لقد صممت هذه الدراسة للتحري عن تأثير استخدام تراكيز مختلفة من العسل (2.5-15٪ وزن/حجم) على نوعين من خطوط الخلايا الورمية HEP-2 و AMN-3 و كذلك خط واحد من الخلايا الطبيعية REF, و ذلك باستخدام تقنيات الزرع النسيجي. لقد اظهر العسل تأثيراً معتدلاً على التصاق خلايا خط HEP-2 (30.9٪) و خلايا خط AMN-3 (17.1٪), لكن بدون اي تأثير معنوي يذكر على خلايا خط REF. بينما اعطى العسل تثبيطاً قوياً ضد تكاثر خلايا خط HEP-2 (85.2٪) و خلايا خط AMN-3 (82.5٪) بالمقارنة مع التأثير الطفيف على تكاثر خلايا خط REF (26.4٪). كما ابدى العسل تأثيراً معدلاً للمحتوى البروتيني الموجود في افرازات خطي الخلايا الورمية و ذلك من خلال نقصانه بحوالي 96.3٪ في افرازات HEP-2 و 87.6٪ في افرازات AMN-3 و من دون اي تأثير معنوي على المحتوى البروتيني لافرازات خط خلايا REF. كذلك سبب العسل تأثيراً قوياً في حث آلية الموت المبرمج في خلايا الخطوط الورمية, حيث كانت نسبة الموت المبرمج في خلايا خط HEP-2 حوالي 93.3٪ و في خلايا خط AMN-3 73٪ بالمقارنة مع تلك الحاصلة في مجاميع السيطرة غيرالمعاملة بالعسل و التي كانت 10٪ و 18.3٪ على التوالي. ان نتائج هذه الدراسة التي اجريت في الزجاج *in vitro* تشير بشكل واضح الى امتلاك العسل للخاصية المضادة للاورام, لكن نحتاج الى دراسات اكثرداخل الجسم الحي *in vivo* لتأكيد امتلاكه هذه الخاصية.

ABSTRACT

Honey is one of the oldest natural product that characterized by multifunctional effects including nutritional, antimicrobial, anti-oxidant, anti-inflammatory and anti-tumor activities. This study was designed to investigate the effect of various concentrations of honey (2.5-15% wt/v) against two tumor cell lines, HEP-2 and AMN-3 and one normal cell line REF, by using tissue culture techniques. Honey revealed a moderate anti-adhesive effect against both tumor cell lines, HEP-2 (30.9%) and AMN-3 (17.1%), but without significant effect on REF cell line. However, very potent anti-proliferative effect of honey was demonstrated in HEP-2 (85.2%) and AMN-3 (82.5%) in comparison to the moderate effect on REF (26.4%). Honey also showed a modulating effect on protein content in the secretions of both tumor cell lines by decreasing it about 96.3% in HEP-2 and 87.6% in AMN-3 secretions. Furthermore, honey caused a potent apoptotic effect in HEP-2 (93.3%) AMN-3 (73%) in comparison to their untreated controls, 10% and 18.3% respectively. The results of this *in vitro* study clearly indicated the anti-tumor activity of honey, but need further investigation to support this activity *in vivo*.

INTRODUCTION

One of the best known properties of honey is its anti-microbial activity due to various factors which contribute to this activity (1). In recent years there has been a growing interest in the use of honey in wound management, particularly when there is delayed healing and local infection such as leg and pressure ulcers, burns and infected skin

graft donor sites (2,3,4). With regard to the stimulation of tissue growth, honey is not only used as nutrition but also used as an alternative treatment for clinical conditions ranging from gastro-intestinal tract problems to ophthalmic conditions, and as wound barrier against tumor implantation in laparoscopic oncological surgery (5). It has been demonstrated *in vitro*, that the phenolic compounds in honey contributed very significantly to its anti-oxidant capacity (6,7). Therefore, oral supplementation of honey in experimental obstructive jaundice model rats diminished the oxidative stress and hepatocyte apoptosis caused by ligation and division of the common bile duct (8). Also the phenolic acids and flavonoids found in honey were the main causes of the protective effect through their synergistic action that enable it to lower the risks and effects of acute and chronic free radical-induced pathologies such as atherosclerosis, diabetes and cancer (9). Thus supplementation of diets with honey and *Nigella sativa* grains revealed a protective effect against methylnitrosurea-induced oxidative stress, inflammatory response and carcinogenesis in Sprague Dawely rats (10). Very few studies have been carried out to investigate the anti-tumor properties of honey, for instances, using five strains of rat and murine tumors, honey showed moderate anti-tumor and pronounced anti-metastatic effect and potentiated the anti-tumor activity of 5-fluorouracil and cyclophosphamide (11). Furthermore, honey is an effective agent for inhibiting the growth of three human bladder cancer cell lines (T24, 253J and RT4) and one murine bladder cancer cell line MBT-2 (12).

The aim of this work was to study the cytotoxic effects of honey against two cancer cell lines and one normal cell line to detect its anti-adhesive, anti-proliferative and apoptotic activities by using tissue culture techniques.

MATERIALS AND METHODS

Preparation of Honey

Natural unprocessed honey, dark yellow in color, multifloral origin was used for experimentation. Honey was collected from Khan Dhari farm, Baghdad city, Iraq. The initial honey solution in a ratio of 15% (wt/v) was prepared by dissolving 15 grams honey in 100 ml serum-free RPMI-1640 medium (Sigma) supplemented with penicillin G (100U/ml) and Streptomycin (100µg/ml), and then sterilized by filtration with 0.22µm filter. A series of six concentrations (15, 12.5, 10, 7.5, 5 and 2.5%) were prepared just before using in the experiments under aseptic conditions.

Cell Lines and Cell Culture

Murine mammary gland adenocarcinoma (AMN-3), epithelial cell carcinoma of human larynx (HEP-2) and normal rat embryonic fibroblast (REF) cell lines were obtained from Iraqi Center of Cancer Research and Medical Genetics. All cell lines were routinely kept in RPMI-1640 medium supplemented with 10% fetal calf serum and Penicillin G (100u/ml) / streptomycin (100µg/ml) at 37˚c in a humidified 5% CO2- 95%air incubator under standard conditions.

Cell viability was measured by counting, excluding those cells stained with 0.1% trypan blue, and cell suspension should be prepared at a concentration of 1×10^6 cells/ml to carry out cell culture experiments (13).

Short-Term Toxicity Assay

Cell suspension 1×10^6 cells/ml was incubated in one ml of phosphate buffer saline containing various concentrations of honey solutions (2.5, 5, 7.5, 10, 12.5 and 15%) at 37˚c for 3 hours. Cell viability was determined by hemocytometer using trypan blue exclusion method (14).

Cell Adherence Assay

Cell adherence was assessed by crystal violet staining method as described by Mather and Roberts (15). The cells were plated (1×10^5 cells/well) in 96-well flat bottom plates and treated at the same time with various concentrations of honey solution (should be prepared at twice the final concentration) and incubated at 37˚c for 24 hours. The cells washed and stained with crystal violet, then the absorbance (O.D.) of each well was determined at 492 nm by using an Elisa plate reader.

Long-Term Cytotoxicity Assay

Cytotoxicity was assessed by crystal violet staining method as described by Willson (16). The cells were seeded (2×10^5 cells/well) in 96-well plates for 24 hours, then treated with different concentrations of honey solution for 48 hours. After treatment, the cells were washed as stained as described above to determine their absorbance at 492 nm by using Elisa plate reader.

Determination of Protein Content

The cells were plated (4×10^5cells/well) in 24-well plates and incubated at 37˚c for 24 hours, then treated with various concentrations

of honey solution for 48 hours. After treatment the medium of each well was aspirated and transferred into eppendroff tubes to be centrifuged and to eliminate the associated cells. The supernatant was referred as cell line secretion, and the protein content was determined by using Bradford method (17).

Apoptosis Assay

This assay was carried out according to mitochondria bioassay kit (US. Biological Company) described by Chen *et al.* (18). The cells were plated (5×10^5cells/well) in 8-chamber tissue culture slide and incubated at 37°c for 24 hours, then the cells were treated with the highest concentration of honey solution (15%) for 36 hours. After treatment, the cells were treated with mitocapture reagent for 20 min and examined under fluorescent microscope to count the number of apoptotic cells (green) and healthy cells (red).

Statistical Analysis

All data were expressed as mean ± S.E. and the validity was tested by linear correlation (r) between the treatment and each parameter. However the statistical significance of differences between treated and control groups was carried out by using Mann-Whitney test at $p < 0.05$.

RESULTS AND DISCUSSION

The percent changes in cell viability were plotted in figure-1, in which a significant reverse correlation between the 3 hours exposure to different concentrations of honey and cell viability was demonstrated particularly for REF ($r = -0.7$) and HEP-2 ($r = -0.79$) at $p < 0.001$, but not for AMN-3 cell line. However, only the highest concentration of honey solution (15%) caused significant reduction in the cell viability of REF (11.9%) and HEP-2 (13.1%) at $p < 0.02$.

The percent change in optical density (O.D.) of cells after 24 hours exposure to six concentrations of honey solution were compared to those of their controls and referred as cell adhesion (figure 2). Only HEP-2 and AMN-3 cell lines showed significant reverse correlation ($r = -0.6$, -0.65 at $p<0.001$ respectively). Two concentrations of honey (12.5% and 15%) caused significant reduction ($p<0.02$) in cell adhesion of HEP-2 (20.1% and 30.9% respectively), while three concentrations of honey solution (10%, 12.5% and 15%) caused significant reduction ($p<0.006$) in cell adhesion of AMN-3 (15.8%, 16.4% and 17.1% respectively).

The percent change in O.D. of cells after 48 hours exposure to 6 concentrations of honey were illustrated in figure 3 and referred as cell

proliferation. All three cell lines showed significant reverse correlation; REF (r = -0.74), HEP-2 (r = -0.61) and AMN-3 (r = -0.85) at $p < 0.001$. Otherwise, both tumor cell lines revealed significant reduction in cell proliferation at concentrations of 10%, 12.5% and 15% which are 34.7%, 48.2% and 85.2% for HEP-2 and 25.6%, 32.9% and 82.5% for AMN-3 respectively. However, only the highest concentration of honey (15%) caused significant reduction in cell proliferation of REF cell line (26.4%).

Figure (4) demonstrates the protein content in secretions of 3 cell line cultures, in which there is clearly and gradual elevation in protein content of REF (r = 0.5, $p<0.001$). In contrast, the protein content in the secretions of HEP-2 and AMN-3 were declined (r = -0.89, -0.93 at $p<0.001$ respectively). Nearly, all concentrations of honey treatment caused significant reduction in protein content of AMN-3 that decreased from 483.2 µg/ml (control) down to 60 µg/ml at the highest concentration of honey treatment (15%). However, only three concentrations of honey (10%, 12.5% and 15%) were significantly decreased the protein content in the secretion of HEP-2 from 403.2 µg/ml (in control) down to 287, 49 and 15 µg/ml respectively.

Finally, apoptotic effect of the highest concentration of honey solution (15%) was demonstrated in both tumor cell lines (figure 5). The apoptosis % of treated HEP-2 (93.3 ± 1.45) was significantly varied from related control (10 ± 2.89) at $p<0.009$. Also honey treatment cause significant induction of apoptosis in treated AMN-3 cells (73 ± 4.04) in comparison to its control (18.3 ± 4.41).

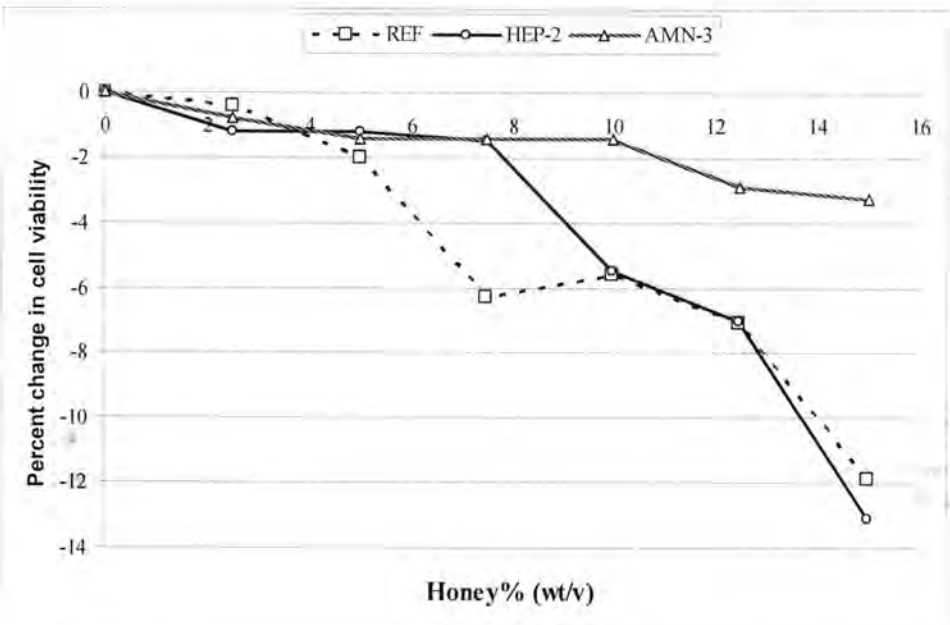

Figure- 1: Effect of 3 hours exposure to different concentrations of honey on the cell viability of normal and tumor cell lines

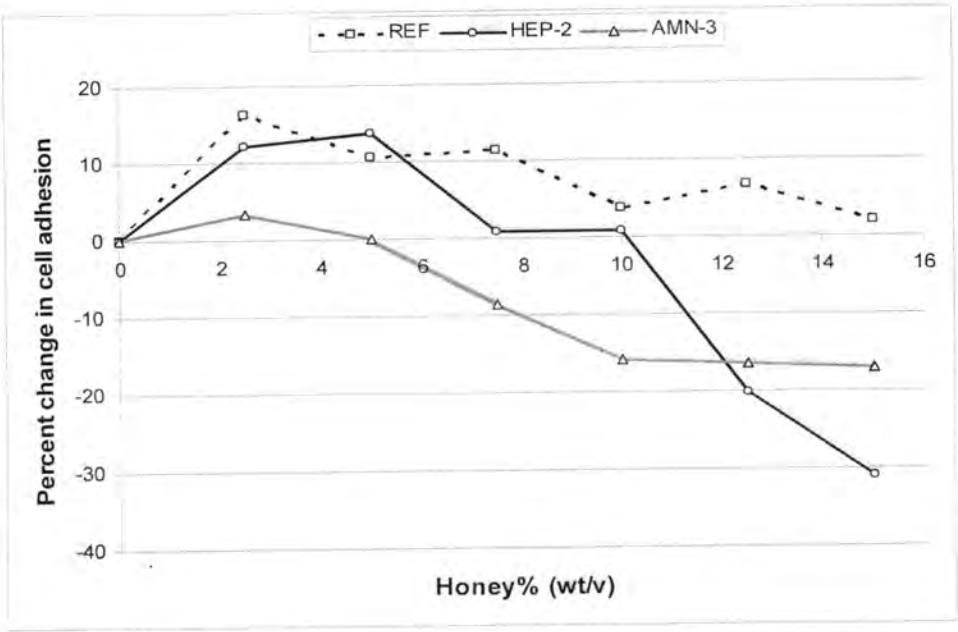

Figure- 2: Effect of 24 hours exposure to different concentrations of honey on the cell adhesion of normal and tumor cell lines

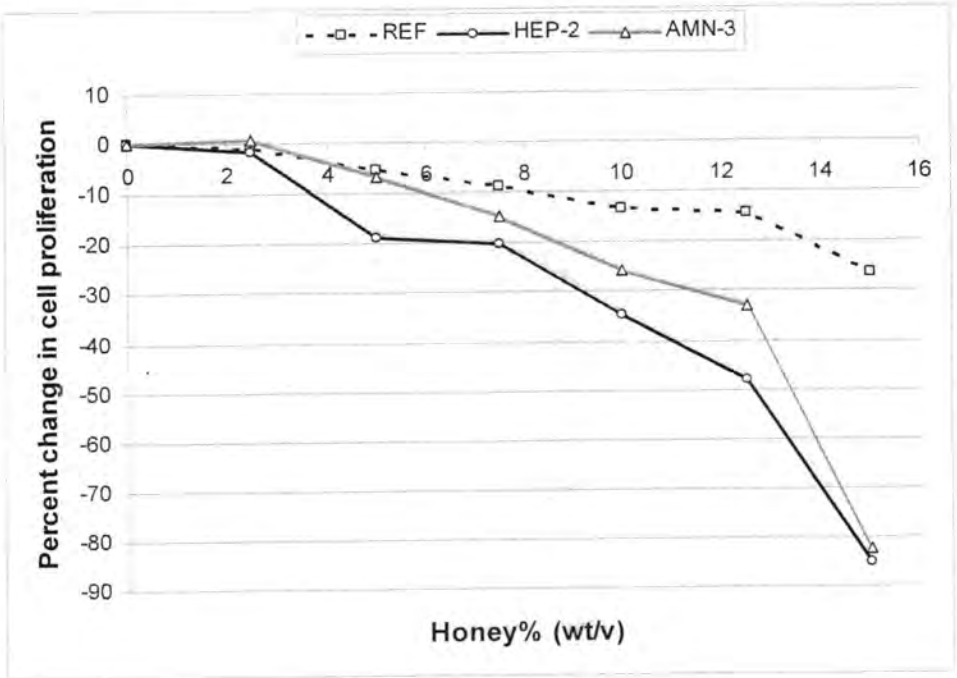

Figure- 3: Effect of 48 hours exposure to different concentrations of honey on the cell proliferation of normal and tumor cell lines.

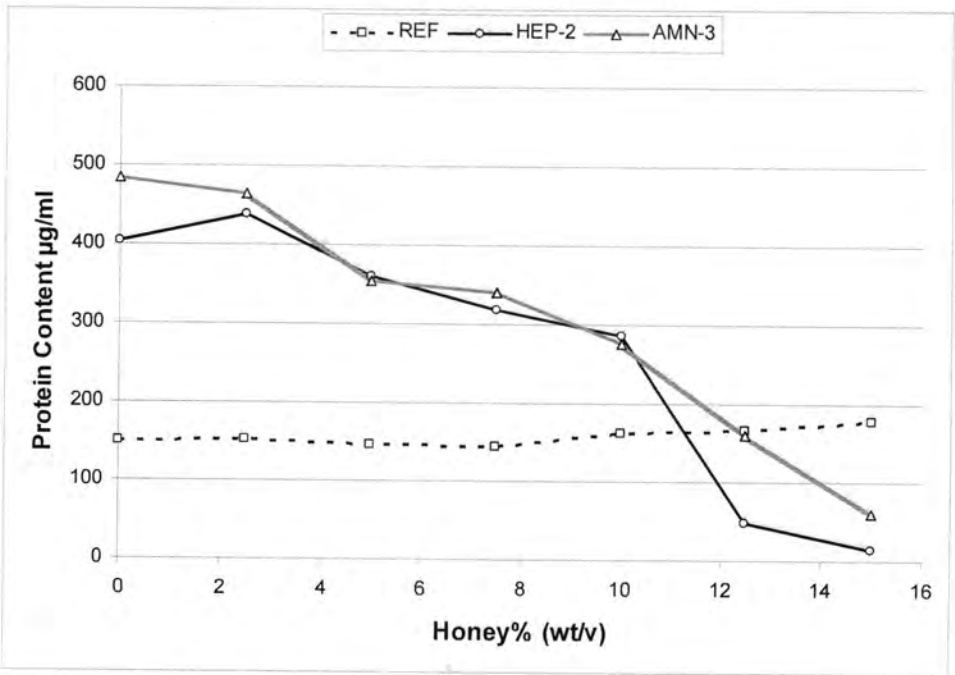

Figure -4: Effect of 48 hours exposure to different concentrations of honey on the protein content in the secretions of normal and tumor cell lines.

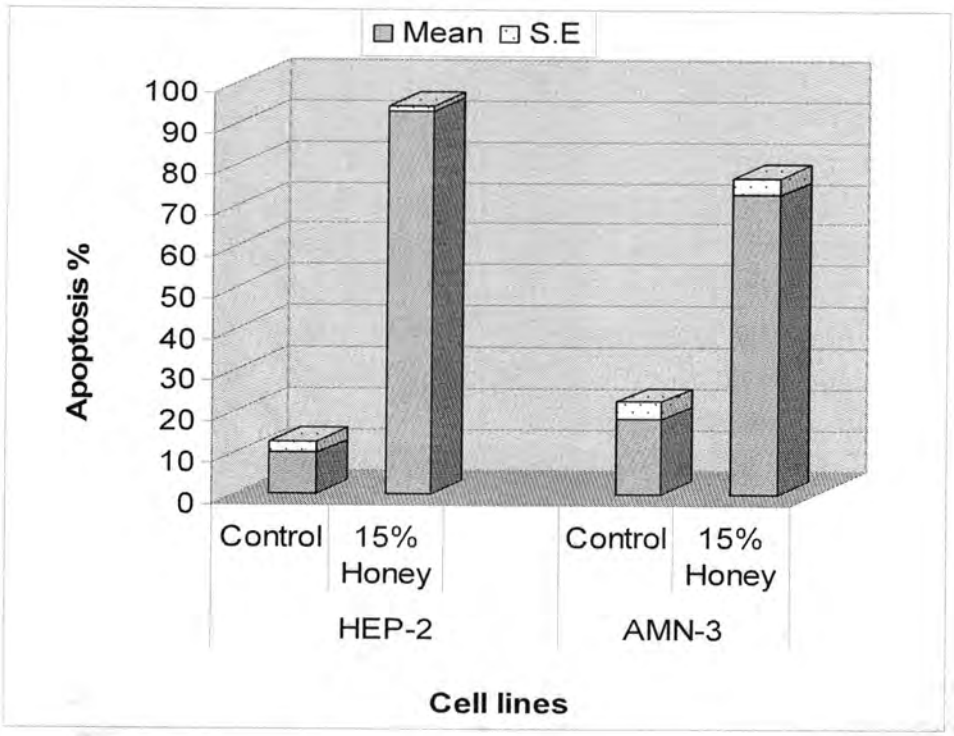

Figure- 5: Apoptotic effect of 36 hours exposure to 15% honey solution in two tumor cell line.

Cell viability of all cell lines was slightly decreased after 3 hours exposure to different concentrations of honey solutions (figure 1), because honey is a supersaturated solution of sugars that make it hygroscopic (osmotic effect) as well as its low pH 3.5-3.9 (acidic effect) (19).

Honey revealed an inhibitory effect on cell adhesion of HEP-2 (30.9%) and AMN-3 (17.1%) tumor cell lines, but without significant effect on the normal cell line REF (Figure 2). These results indicated that honey has one or more constituents that are capable to interfere with the adhesion process of cells leading to detach from plate and not involved in the measurement of optical density (13). The most compatible suggestion that interpret this selectively anti-adhesive action of honey may be due to interfering of honey either with cell substrate adhesion molecules "integrins" (20), cell-cell adhesion molecules "cadherins" (21), or cell-substrate adhesion molecules which are transmembrane proteoglycans (22).

It was found that the 48 hours exposure to different concentrations of honey solution caused anti-proliferative effect up to 85.2% and 82.2% in HEP-2 and AMN-3 tumor cell lines respectively in comparison to 26.2% in the normal cell line REF (figure 3). This result together with those obtained by other investigators (11, 12) showed that honey possess a potent anti-proliferative activity against different tumor cell lines *in vitro*.

The present study demonstrated for the first time that the 36 hours exposure to 15% honey caused a potent apoptotic effect against HEP-2 tumor cell line (93.3%) and AMN-3 (73%) (figure 5). This fact needs more investigation to determine the constituent that is responsible for this activity and the mechanism by which it acts. However, earlier publications suggested that the phenolic acids and flavonoids found in the honey were the main causes of its protective effect against some pathological conditions such as cancer (9). Also sulphorafane component found in the honey, which is enzymatically released from the glucosinolate, play an important role in the anti-tumorigenic activity (23). Hamzaoglu *et al.* (2000) implanted cancer cells into the neck wounds of mice, a marked decrease in wound cancer tumors were found in the group of mice that had surgical wounds coated with honey pre- and post- operatively (24). Furthermore, pasteurized honey has a potential to decrease cancer growth or used as an adjuvant with cancer therapy (25).

On the other hand, honey clearly decreased the protein content in the secretion of HEP-2 from 403.3 µg/ml (in control) down to 15 µg/ml and from 483.2 µg/ml (in control) down to 60 µg/ml in the secretion of AMN-3 cell line, while honey treatment had no significant effect on that

of REF cell line (figure 4). The present study showed that honey might partly affect either the synthesis or the release of certain secretory protein molecules, which may be growth factors or cytokines. Many investigators showed that some epidermoid carcinomas secrete complex molecules "Haptoglobin" to suppress the activity of natural killer cells (26), while other tumor cells secrete different cytokines such as IL-10 to suppress immune response against them (27, 28). Also Al-Shammery (2003) demonstrated that murine mammary gland adenocarcinoma cells (AMN-3) still consist of secretory acini filled with milk-like secretions (29), therefore, the reduction that occurred in the protein content of AMN-3 cell line may be due to the ability of honey to modulate certain gene expression that is responsible for this milk-like secretion.

According to the results obtained from this preliminary study, it can be concluded that honey caused significant anti-adhesive, anti-proliferative and apoptotic activities against tumor cell lines HEP-2 and AMN-3, but with negligible effect on normal embryonic fibroblast cell line REF. Also, it has been found that honey was able to modulate the protein content in the secretions of only tumor cell lines that may be due to regulation in certain gene expression. Therefore, it is necessary to investigate its cytotoxic effect in other tumor cell lines as well as to analyze the nature of protein molecules found in their secretions particularly those that act as growth factors or involved in cell adhesion.

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The Effect of Lead Contamination on Some Physiological Parameters of Newzland Rabbits Males *

Hassony J . Abdulla
Biology Department , College of Science , AL Mustansyria University

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الخلاصة

اجرّي هذا البحث في قسم علوم الحياة – كلية العلوم – الجامعة المستنصرية في الفترة من 2003 - 2005 لدراسة تأثير التلوث بالرصاص على بعض المعاير الفسيولوجية لذكور الأرانب النيوزلندية (*Lepus lepus*)أجريت تجربتين , تجربة حقن وتجربة تجريع الحيوانات عن طريق الفم, اخذ 70 حيوان في كل تجربة وعشرة أرانب لكل معاملة من المعاملات (ماء مقطر، 30 و 60, 90 غم/ كغم رصاص Pb) بمجموع 140 معاملة.

بينت النتائج انخفاض معنوي في عدد كريات الدم الحمراء ومكداس الدم ومستوى الكلوكوز في الدم في كل المعاملات . وزيادة معنوية لخلايا الدم البيضاء وزيادة في حجم كرية الدم وتركيز أنزيميGOT, GPT .

ولوحظ انخفاض معنوي في وزن الجسم للحيوانات المختبرية في تجربة الحقن من بداية الأسبوع الثاني والى نهاية الأسبوع الخامس ولوحظ انخفاض في وزن بعض الأعضاء مثل الكليتين , المعدة , القلب ، الطحال ، الكبد . زيادة معنوية في سرعة التنفس , معدل النبض , ودرجة حرارة الجسم تنخر من نوع الموضعي المنتشر مع ارتشاح دموي وتغير في لون الكبد خاصة في تركيز 60 و 90 ملغم / كغم رصاص .أن تأثير الرصاص في تجربة الحقن كان اكبر من تأثيره في تجربة التجريع عن طريق الفم .

ABSTRACT

This investigation has been conducted in the biology department / college of science / university of AL- Mustansyria in the period from 2003 – 2005 to study the effect of lead pollution on some physiological parameters of Newzland rabbits(*Lepus lepus*) .

Seventy (70) rabbits males have been taken in each experiment (exposure experiment and oral experiment) Ten(10) rabbits males for each treatment have been injected with distilled water only, with 30 mg / kg Pb, with 60 mg / kg Pb and with 90 mg / kg Pb. The same treatments have been given to the oral treated animals. A total of 140 male rabbits were involved in this work .

The results show significant difference decrease in red cells a count, packed cell volume and glucose level in blood for all Pb treatments .

The result has significant increase Glutamic oxalo – transminase and Glutamic pyruvic – transminase have been found in all pb treatments .The increase was 49.7 % and 58% for Glutamic oxalo – transminase and Glutamic pyruvic – transminase respectively .

The result shows increase in heart beats , temperatures and rate of breathing with Pb exposure or injection from the first week in all Pb treatments.

The result shows significant difference decrease in animal weights with pb injection from the second week to the fifth week.

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*Compiled from Al- Ragihi , S . J . H .(2005) , The effect of Cadmium and lead on some physiological parameters of Newzealand rabbit males(in Arabic)
Ph . D thesis University of AL Mustansyria, Baghdad, Iraq.

The necrosis , conjunction ,of blood vessel, change in color tissue in liver and change in kidney cortex glomerular have been found in animals treated with 60 and 90 mg / kg pb .

In general , the results of exposure experiment is more effective than oral treated experiment .

INTRODUCTION

The world these days has many problems due to the need of increasing rate of population, technology, and agriculture developments .Human development effect the ecosystem, practically it's biotic individuals which have had standard criteria along last centuries . The industry an agriculture have not been overused and pollution problem have not been known until 1960 [5] . In the present days , the deterioration is clear in the ecosystem and the decrease in the quality of biotic elements of the water and wild live .

Lead is used in many industrial fields that have direct relation in daily present live . It is used in dyes , compound , sinks , batters , petrol industry and derivatives and some of it used for cleaning large fuel tanks and other important utilizations[6].

Lead contamination cause blood anemia , weakness , epilepsy fast rate of breathing , death , death of embryo[13]. An American study[1] indicates that the lead contamination causes moving a lot of youth and little people out of the law , the symptomatic lead poison in stomach pain and lead colic due to lead pollution[7].The children in the age of 2 – 3 years are more effect by lead pollution[9][10]

Rocyle and Needleman , 1993[12] have divided lead poisonings to little poisoning (50 µg / 100 ml) , moderate poisoning (60 µg / 100 ml) and high poisoning (100 µg / 100 ml).

In the present time in Iraq , there is little information on lead pollution and its effect on human and animals live . Therefore , this investigation has been conducted to study the effect of lead on some physiological parameters of Newzealand rabbit males.

MATERIALS AND METHODS

This investigation has been conducted in the biology department / college of science / university of AL- Mustansyria in the period from 2003 – 2005 .

In order to study some physiological parameters of Newzland rabbit males *(Lepus lepus)* . The measured parameters are :

- Red RBC and white cells count (WBC)
- Packed cell volume (PCV).
- Hemoglobin (Hb).

- Mean corpuscular volume (MCV).
- Level of glucose in blood.

Weights of animals (fifth and sixth weeks animal weights are neglected because the death of the animals) .

- Weights of brain, kidney heart , liver , lungs and testes.
- Some physiological parameters such as heart beats , temperatures and rate of breathing .
- Prepare some tissue slides.

The differences between treatments and control is shown by giving LSD values in addition some parameters explain more by giving percentage decrease or increase from control:

For example hemoglobin decrease (b) $\% = \frac{\text{control} - 90\ (\text{mg}/\text{kg})}{\text{control}} \times 100$

$\frac{9.9 - 7.31}{9.9} \times 100 = 29.4\ \%$ (see table 1)

The above measurements have been done according[8][11]. Seventy (70) rabbits males have been taken for each of the two experiments , a total of 140 male rabbits were involved in this work :

1 - Exposure experiment , ten(10) rabbits males for each treatment have been injected with distilled water only, with 30 mg / kg Pb, with 60 mg / kg Pb and with 90 mg / kg Pb.

2 - Oral experiment , ten(10) rabbits males for each treatment have been watered by moth with distilled water only, with 30 mg / kg Pb, with 60 mg / kg Pb and with 90 mg / kg Pb.

RESULTS AND DISCUSSION

Table (1) shows significant difference decrease in red cells a count, packed cell volume and glucose level in blood for all Pb treatments .The decrease was 40 % , 16.12 % and 29.4 % for red cells a count , packed cell volume and Hemoglobin respectively. This agrees with the result that obtained by Albahary , 1972[2] and Block et al 1992[4] .However , there are significant increase in white cells count. This was 35% in 90 mg /kg treatment compare to untreated . It means that white cells active out of diapedsis system.

In table (2) significant increase in Glutamic oxalo – transminase and Glutamic pyruvic – transminase have been found in all pb treatments .The increase was 49.7 % and 58 for Glutamic oxalo – transminase and Glutamic pyruvic – transminase respectively .This due to the damage in animals livers.

Table (3) shows increase in heart beats , temperatures and rate of breathing with Pb injection from the first week in all Pb treatments .They were 200 beat / min , 37 C° and 37 breath / min for the untreated animals .However , for the animals treated with 90 mg/ kg lead were 218.10 beat / min , 37 C° and 44 breath / min for the above parameters.

The result in figure (1 a) shows significant difference decrease in animal weights with pb injection from the second week to the fifth week . In 60 gm / kg treatment after 28 days the animals have been perished and then in 35 days died. But , in 90 gm / kg after 28 days the animals have been died .

In figure (1 b) , also there is decrease in the weights of brain, kidney, spleen , stomach , lungs, heart ,and liver . For example , the different in weight between the untreated and the 90 mg/ kg was 0.24 gm and 2.7 gm for Kidney and stomach respectively . This because the decrease of glycogen in liver .

The necrosis , conjunction ,of blood vessel, change in color tissue in liver and change in kidney cortex glomerular have been found in animals treated with 60 and 90 mg / kg pb (plates 1a , b , c, and d) .

In general , the results of exposure experiment (a) are more effective than oral experiment (b) see tables 1 , 2 , 3 , figure 1 a and b .

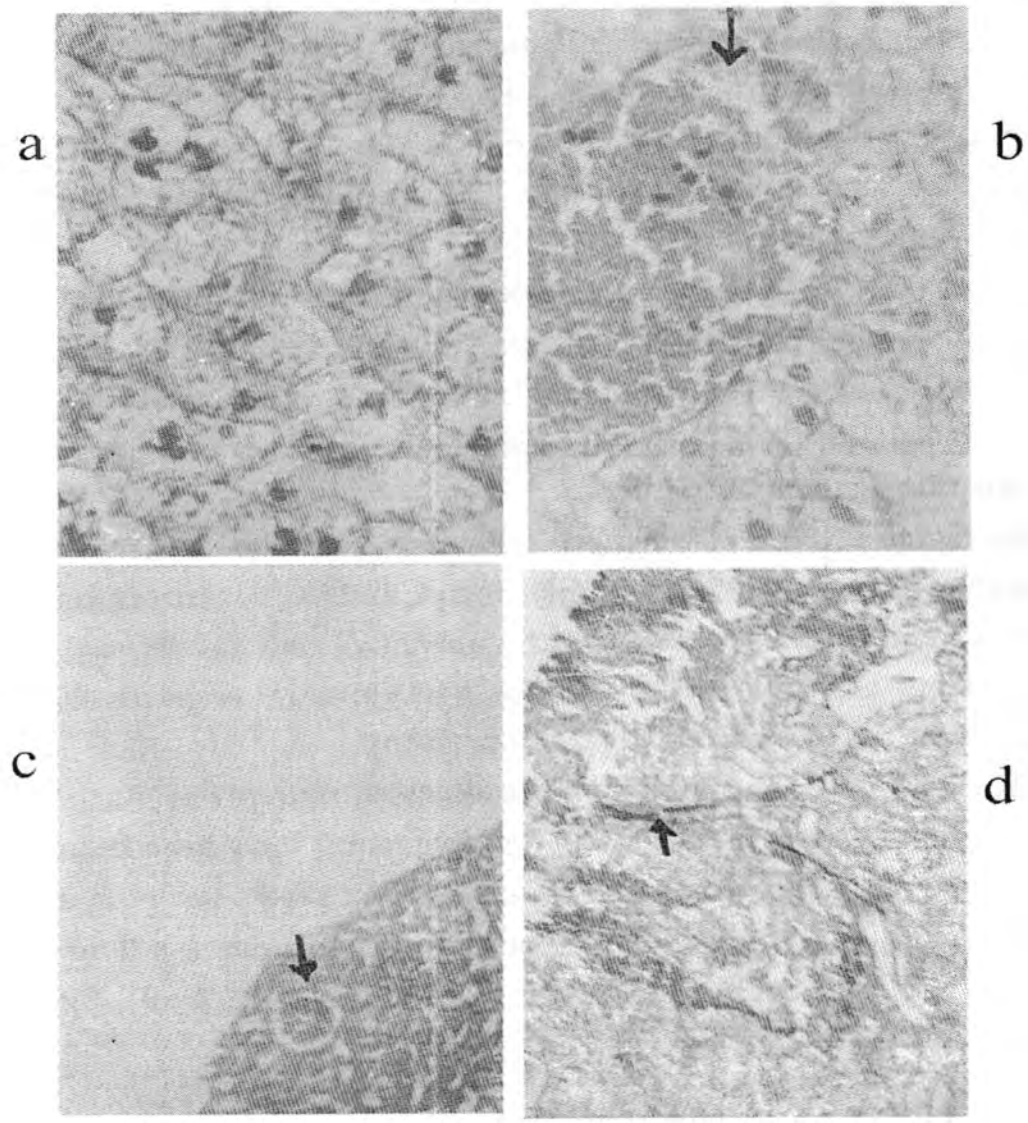


Plate 1. a- Untreated (Control)animal liver cells . b-Animal liver cells treated with 90 mg/kg pb. c-Untreated animal kideny cells. d-Animal kidey cells treated with 90 mg / kg pb.

Table – 1: The mean blood components RBC , WBC , PCV , MCV and Hb of rabbit males as effected by Pb .

Treatment	Blood components				
	RBC X 10 (12) / L	WBC X 10 (9) / L	PCV %	MCV (FI)	Hb (g/dI)
Control a b	6.9 5.8	3.63 3.0	36.48 31.4	52.86 50.2	11.90 9.9
30(mg / kg) a b	5.2 5.0	4.41 3.9	33.7 30.8	64.40 59.4	9.50 9.4
60(mg / kg) a b	4.0 4.0	6.81 6.5	32.0 31.0	70.20 71.1	8.0 7.5
90(mg / kg) a b	4.14 4.1	5.69 5.9	33.5 32.4	83.45 72.3	8.40 7.31
5% LSD a b	1.1 1.3	1.3 1.2	2.1 3.5	10.7 13.8	1.2 1.0

a=Injection experiment.
b= Treated by moth experiment.
5% LSD= least significant difference at 5 % level .

Table – 2: The mean of some biochemical indicators(GOT , GPT and Glucose)of rabbit males as effected by Pb .

Treatment	GOT (IU / L)	GPT (IU / L)	Glucose (mg / dL)
Control			
a	34.9	24.6	169.7
b	30.8	22.5	175.8
30(mg / kg)			
a	35.5	32.3	160.4
b	30.8	22.5	175.8
60(mg / kg)			
a	41.0	48.8	142.0
b	31.5	29.5	155.4
90(mg / kg)			
a	69.4	58.5	159.0
b	40.0	45.8	146.0
5% LSD			
a	1.3	3.1	1.5
b	4.1	11.5	15.9

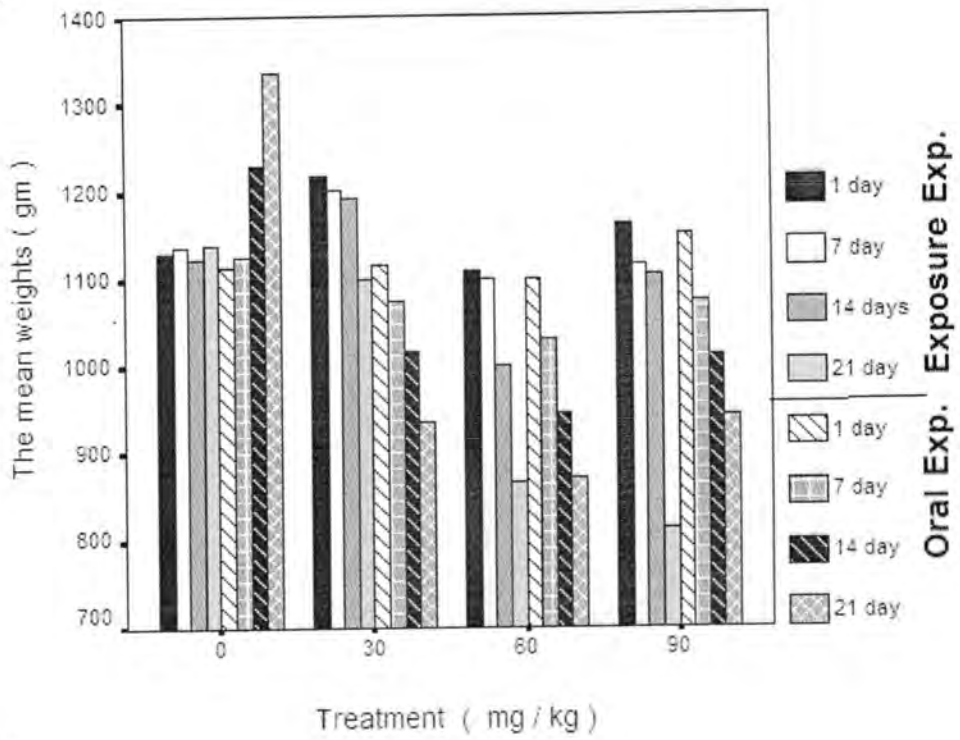
a=Injection experiment.
b= Treated by moth experiment.
5% LSD= least significant difference at 5 % level .

Table -3:mean some physiological parameters heart beats , temperatures and rate of breathing of rabbit males as effected by Pb .

Treatment	heart beats (beat / min)	temperatures (C°)	rate of breathing (breath / min)
Control			
a	200.0	37.00	37.0
b	210.0	37.1	37.0
30(mg / kg)			
a	211.0	37.00	37.00
b	215.0	37.2	39.0
60(mg / kg)			
a	216.0	38.00	38.00
b	213.0	38.0	38.0
90(mg / kg)			
a	218.0	37.10	44.0
b	217.0	37.7	45.0
5% LSD			
a	4.2	0.6	8.0
b	4.1	0.7	3.6

a=Injection experiment.
b= Treated by moth experiment.
5% LSD= least significant difference at 5 % level .

(a)



(b)

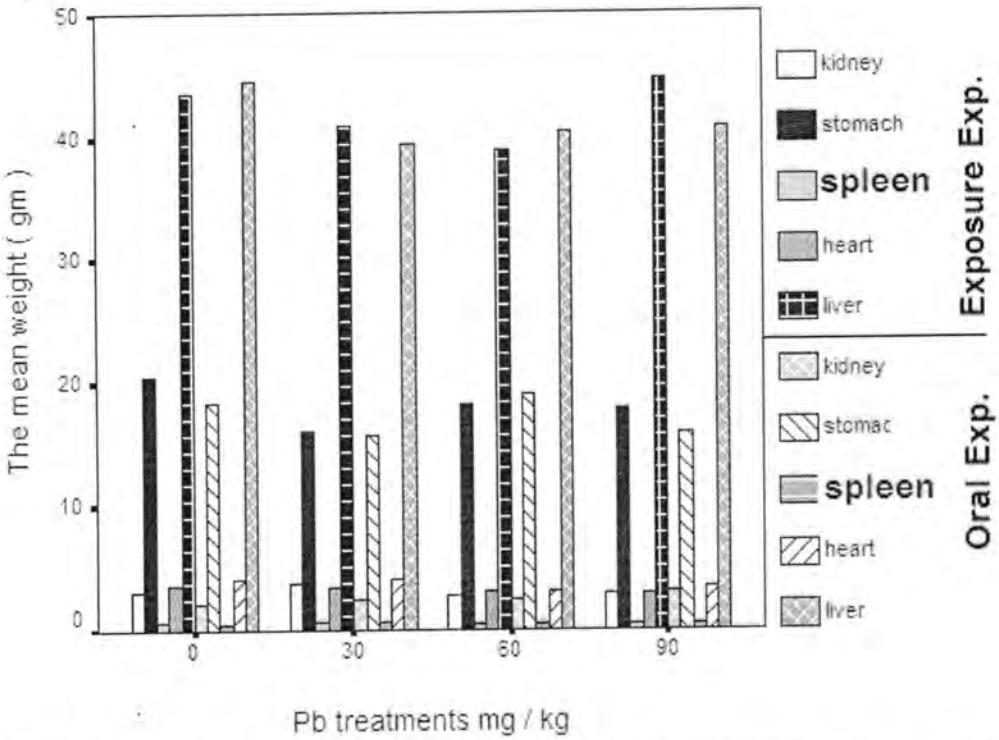


Figure -1: (a) the mean weights of rabbit males (primary weight (1 day) ,7 , 14 ,21 days) (b) the mean weights of kidney , spleen , stomach , heart and liver of rabbit males as effected by Pb .

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Assessment of Different Immunological Parameters in Human Immunodeficiency Virus (HIV)-Infected Patients in Baghdad

Nawal M. Utba[1], Majid M. M. Al-Jewari[2], Saad H. Mohammed [3]
[1]College of Science/Baghdad University
[2]College of Science Al-Mustansiriya University
[3]College of Medicine /Baghdad University

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الخلاصة

شملت الدراسة 43 فردا من مرضى HIV المراجعين للمركز الاستشاري والعلاجي في مستشفى ابن زهر للفترة من حزيران 2004 الى اذار 2005. اضافة الى 113 من الاصحاء ظاهريا كافراد سيطرة.اجري تقييم كمي لتركيز مستضد البروتين 24 في 36 حالة،كانت 3 منها (8.3%) حالات مشتبهة و7 (0.194%) منها ذات نتائج موجبة لهذا المستضد. قيست مستويات الحركيات الخلوية المتظمنة بين بضاضي 1 و2 و4 و6 و8 والانترفيرون-كاما وعامل نخر الورم-الفا، وتبين من النتائج انخفاض مستويات IL8 معنويا (pθ.001) وارتفاع مستويات TNFα معنويا (pθ.022) في امصال مرضى HIV مقارنة بمستوياتها عند الاصحاء، و لم تسجل مثل هذه الفروقات في مستويات الحركيات الاخرى. انخفضت اعداد WBCs ولمفاويات الدم معنويا (p=0.048وpθ.001) عند مرضى HIV، اذ سجل انخفاض معنوي (p=0.037و pθ.001 و p=0.018) على التوالي في اعداد الخلايا اللمفاوية المحيطية CD3وCD4وCD56 لمرضى HIV فيما كان الانخفاض طفيفا في خلايا CD8 وذلك عندالمقارنة بالاصحاء . وكانت النسبة CD4/CD8 منخفضة معنويا (pθ.001) عند المرضى. اما الخلايا CD38 فقداخذت منحى اخر اذ ارتفعت معنويا (p=0.03) عند مرضى HIV . من جانب اخر سجل ارتفاع معنوي (pθ.001) في تراكيز IgG وIgM في امصال المرضى مقارنة بالاصحاء، فيما لم تسجل فروقات معنوية في مستويات IgA. وانخفضت مستويات جزئي المتمم C3 وC4 معنويا (pθ.001) في امصال المرضى. واخيرا سجل ارتفاع معنوي (pθ.001) في مستويات β2μ عند مرضى HIV مقارنة بمستوياته عند الاصحاء.

ABSTRACT

Forty three HIV-positive patients who attended Baghdad Consultative and Treating Center in Ibn-Zhr hospital from June 2004 to march 2005, in addition to 113 apparently healthy controls were included in this study.

Quantitative estimation of serum p24 antige n concentration was done by ELFA for 36 HIV cases. Among the examined patients, 3 cases (8.3%) had equivocal result whereas 7 cases (19.4%) had shown positive p24 antigen in their sera. Some cytokine levels were measured by using (EIA), they include Interleukin -1, IL -2, IL -4, IL -6, IL-8, Interferon–gamma, and tumor necrosis factor –alpha. The serum IL-8 concentration was significantly lower (Pθ.001) in HIV cases, whereas the TNF- α was significantly higher (P= 0.022) in them when compared to control group. The remaining selected cytokines had shown statistically insignificant differences between HIV cases and healthy controls.

The total WBC and total blood lymphocytes counts in HIV cases were significantly lower (Pθ.001 and P = 0.048, respectively) th an those in controls. The peripheral blood CD3+ CD4+and CD56+lymphocytes counts were significantly lower (P =0.037, 0.001, 0.018, respectively), while the count of CD8+lymphocytes were lower insignificantly in HIV cases. Among HIV cases, the CD4/CD8 ratio was significantly lower (Pθ.001) th an that noted in healthy controls. On the other hand, CD38+lymphocytes showed different beha vior, as their counts were significantly higher (P=0.03).

The serum IgG and IgM concentrations were found to be significantly higher ($P< 0.001$) in HIV cases as compared to controls. No statistically difference was found in IgA concentrations. The serum complement (C3, C4) components concentrations were significantly lower ($P<0.001$) among HIV cases. The concentration of serum beta 2-microglobulin was significantly higher ($p<0.001$) in HIV cases compared to controls.

INTRODUCTION

In Iraq, and during 1986, a group of young hemophiliacs in Baghdad began to complain of high fevers and unexplained bleeding and sustained ill health after receiving a tainted clotting agent bought from the French pharmaceutical company (Merieux). The original number of victims was around 220, mostly hemophiliacs' children, and their blood was tested for HIV, they all showed to be positive [1].

According to the Iraqi AIDS research center, a total number of 448 HIV/AIDS cases, including those who died of disease, have been detected since 1987. However, in 2005, only 72 of them were living with HIV/AIDS, but have not yet developed full-blown AIDS [2].

Individuals infected with HIV show both cellular and humoral immune responses to this virus. However, these responses are unable to prevent the ultimate progression of disease in the great majority of infected individuals. The cellular responses mediated by cytotoxic T lymphocytes (CTLs) (CD8 cells) inhibit HIV replication both directly, by recognizing and killing infected cells, and indirectly, by producing soluble chemokine antiviral factors [3]. Helper T lymphocytes (CD4 cells) responses to HIV are important in viral control, and strong HIV-specific CD4 responses are associated with lower HIV viral loads [4]. Humoral immunity appears to be less effective in controlling viremia than cellular responses; Antibodies to envelope, core protein, reverse transcriptase (RT), or regulatory proteins can be detected in HIV – infected individuals [5]. Neutralizing antibodies, which are possibly responsible for the initial clearance of virus from the peripheral blood, have been detected in variable titers in most infected individuals [6].

In addition; patients at all stages of HIV infection have been found to have detectable ADCC which is directed against the gp 120 molecule, and the effecter cell is primarily the NK cell and monocytes [7].

In view of mentioned introduction, this study is designed and conducted to explore different humoral and cellular immune responses associated with Iraqi HIV infected patients.

MATERIALS AND METHODS

Forty three (27 males and 16 females) HIV infected patients who attended Baghdad Consultative and Treating Center in Ibn- Zhr Hospital were investigated, their ages range was 9 - 53 years. All of them were diagnosed by ELISA and confirmed by western blot technique in the Laboratory of Communicable Diseases Center (CDC) in Baghdad, those included 23 hemophiliacs, 19 acquired the disease by sexual transmission and only 1 by vertical transmission. In addition, 113 apparently healthy individuals (59 males and 54 females) were included for comparison. All controls sera were tested for HIV antibodies by ELISA to ensure serum negativity for HIV antibodies.

The procedures involved were:

1- Determination of P24 Ag concentration of HIV-1 in serum by using the (ELFA) technique.

2- Determination of serum IL-1α, IL-2, IL-4, IL-6, IL-8, INF-γ, TNF-α concentration by enzyme immunoassay method.

3- Studying the cell mediated immune response, by isolation and characterization of PBL, using lymphocyte CD marker labeled with immunofluorescence staining, including (CD3, CD4, CD8, CD56, CD38) cell count and CD4CD8 ratio.

4- Studying the humoral immune response by quantitative measurement of serum immunoglobulins IgG, IgM, IgA and complement components C3, C4 concentrations estimation in serum by SRID test.

5- Determination of β 2 microglobulin concentration in serum by using the ELFA technique.

Statistical analysis

Data were translated into a computerized database structure. Statistical analysis assisted using (Statistical Package for Social Sciences). The performance characteristics include; sensitivity, specificity, positive predictive value, negative predictive value, the ROC method and multiple regression analysis.

RESULTS AND DISCUSSION

The most frequently reported modes for acquiring HIV infection among the studied cases were; contact with blood and blood products that comprised (23) 53.5%, followed by sexual contact in (19) 44.2%, while vertical mode of transmission (from mother to her child) was reported in only one case (2.3%) .

The duration of HIV disease was ranged between 1 to 22 years. those with less than 10 years duration constituted (14) 32.6% of the patients,

while those between 10 to 19 years duration constituted (23) 53.5% and lastly those with more than 20 years constituted (6)13.9 %.

In this study males were more frequent among HIV cases, they constituted 62.8% of the patients whereas the remaining 37.2% of the patients were female (Table 1).

Table- 1: Frequency distribution of HIV cases and healthy controls according to their Genders.

	Healthy controls		HIV cases	
Gender	**No**	**%**	**No**	**%**
Male	69	61	27	62.8
Female	44	39	16	37.2
M/F ratio	1.6/1	1.6/1	1.7/1	1.7/1
Total	**113**	**100**	**43**	**100**

Contact with blood and blood products was the most frequently reported mode for acquiring the disease, comprised 53.5% of cases, followed by sexual contact in 44.2%, while vertical mode was (2.3%) (Table 2).

Table -2: Frequency distribution of HIV cases by the mode of acquiring this infection

Mode of acquiring infection	**No**	**%**
Sexual	19	44.2
Vertical	1	2.3
Blood and blood products transfusion	23	53.5
Total	**43**	**100**

The duration of acquiring HIV disease was as in (Table.3).

Table -3: Frequency distribution of HIV cases by duration of acquiring the infection.

Duration of HIV disease(years)	**No**	**%**
<10	14	32.6
10-19	23	53.5
20+	6	13.9
Total	**43**	**100**

Quantitative estimation of serum P24 Antigen concentration in HIV cases showed about 20% of these cases had positive serum P24 Antigen .(Table 4). This result was in agreement with the results of [8], who found that P24 Ag was present in only 21% of person infected with HIV, while it was present in 54% of the AIDS patients. These results

also in agreement with the results of [9], who found that P24 Ag was consistently present in only 25% of persons infected with HIV. The presence of P24 Ag in those patients reflects intense multiplication of the virus and unfavorable progression of HIV infection.

Table-4: Frequency distribution of HIV cases according to concentration of serum P24 antigen.

Serum P24 Antigen concentration (pg/ml)	N	%
Negative (3 pg/ml)	26	72.2
Equivocal (3-4.9 pg/ml)	3	8.3
Positive (5 pg/ml))	7	19.4
Total	36	100

The concentration of P24 antigen in HIV patients sera had showed a statistically significant correlation with the CD4/CD8 ratio. The rate of positive P24 antigen was significantly higher in subjects with the lowest CD4/CD8 ratio compared to no positive P24 antigen in sera of subjects with highest CD4/CD8 ratio (Figure 1).

These results are in agreement with the results of [10], who found that P24Ag concentration was significantly correlated with the initial stage of HIV disease, as well as CD4 count and CD4/CD8 ratio.

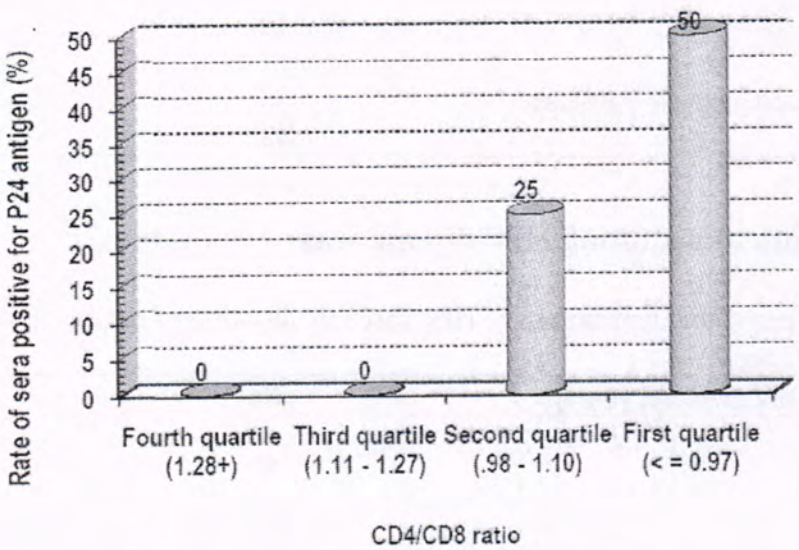

Figure -1: Bar chart showing the rate of positive P24 antigen in serum of HIV cases by CD4/CD8 ratio.

The HIV virus either stimulates or inhibits the production of various cytokines. Thus HIV appears capable of increasing the production of certain cytokines as well as utilizing the production of certain cytokines to increase its own replication.

Some cytokines levels were measured in this study. There were no important differences between serum IL-1, IL-2, IL-4, IL-6, INF- γ in HIV cases & healthy control. Serum IL-8 level was significantly lower in HIV cases, while serum TNF-α level was significantly higher in HIV cases (Table 5).

Table- 5: The results of serological Cytokines concentration in the group with HIV as compared to healthy control.

The cytokines	Healthy controls	HIV cases	P
Median IL-1 α concentration (pg/ml)	4.1	3.6	0.3 *[NS]*
Median IL-2 concentration (pg/ml)	1	0	0.05 *[NS]*
Median IL-4 concentration (pg/ml)	0.5	0.1	0.86 *[NS]*
Median IL-6 concentration (pg/ml)	0	1.2	0.39 *[NS]*
Median IL-8 concentration (pg/ml)	86.7	59.8	<0.001
Median IFN – γ concentration (IU/ml)	0	0	0.11 *[NS]*
Median TNF- α concentration (pg/ml)	14	25.2	0.022

Regarding the results of total WBC and blood lymphocytes as well as selective CD markers in this table it has been found that the cellular immunity was depressed in HIV cases than healthy controls (Table 6). In addition, the present results are consistent with results of [11], who reported that the low WBC count may be due to bone marrow problem resulting of either chronic disease –like HIV itself or from drugs used for HIV infection in those patients like AZT, ganciclovir, and other. Also the results of this study are in agreement with the results of [12], [13], who reported that when AIDS was first identified, CD4 T cell - reduction was shown to be a major feature of the disease.

Table- 6: The difference between mean count of total WBC and lymphocytes-positive for selected CD markers in study groups.

The count X0 ^{6} L	Healthy controls	HIV cases	P
Mean Peripheral blood total WBC count)	6797	4623	0.001
Mean Blood Lymphocytes count	2061	1702	0.048
Mean Count of CD4 positive lymphocytes	858	599	0.001
Mean Count of CD8 positive lymphocytes	580	539	0.44[NS]
Mean Count of CD3 positive lymphocytes	1426	1145	0.037
Mean Count of CD56 positive lymphocytes	196	140	0.018
Mean Count of CD38 positive lymphocytes	480	630	0.03
Median CD4CD8 ratio	1.49	1.1	0.001

The association of lymphocytes count and specific CD markers with P24 Ag status in HIV cases showed the mean lymphocyte and CD markers count were significantly lower in HIV cases who had positive serum P24 antigen compared to those case who were negative (Table 7).

Table -7: The difference in mean counts of total lymphocytes and lymphocytes positive for selected CD markers between HIV cases with positive P24 antigen and those with negative or equivocal tests.

The count X0 ^{6} L	Serum P24 Antigen Negative/equivocal (5- pg/ml)	Positive (5+ pg/ml))	P
Mean Blood Lymphocytes count	1823	1200	0.01
Mean Count of CD4 positive lymphocytes	648	393	0.002
Mean Count of CD8 positive lymphocytes	563	442	0.06[NS]
Mean Count of CD3 positive lymphocytes	1233	783	0.02
Mean Count of CD56 positive lymphocytes	151	95	0.09[NS]
Mean Count of CD38 positive lymphocytes	651	542	0.32[NS]
Median CD4CD8 ratio	1.13	0.94	0.01

The humoral immunity was activated in HIV cases his was represented by IgG and IgM which were significantly higher in HIV cases than healthy control, and by C3, C4 which were significantly lower in HIV cases than healthy control (Table 8). [14] found that in AIDS patients, functional abnormalities of B cells, including polyclonal B cell activation, hypergammaglobulinemia, raised titer of antibodies to various pathogens and autoantigens were documented early in AIDS epidemic. Serum Ig concentration was also reported to increase in asymptomatic HIV infection.

Table -8: The difference in mean serum immunoglobulins and complement components between HIV cases and healthy controls.

	Healthy controls	HIV cases	P
Mean Serum IgG (mg/dl)	1429	2099.6	<0.001
Mean Serum IgM (mg/dl)	109.9	161.5	0.001
Mean Serum IgA (mg/dl)	311.2	298	0.79[NS]
Mean Serum C3 (mg/dl)	147.4	107.9	0.001
Mean Serum C4 (mg/dl)	42.4	23.2	<0.001

The level of serum beta 2-microglobulin (which is an immune cell-activation marker) was determined in this study and was significantly higher in HIV cases than the control. This was in agreement with [15] results who found that serum β - 2 M level in HIV – seropositive patients was mostly higher than upper normal limit value and was significantly increased with time.

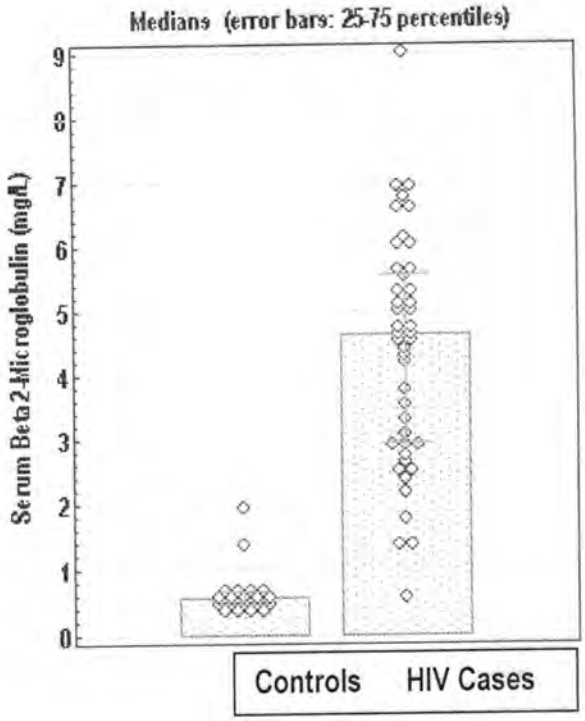

Figure- 2: Dot diagram with error bars comparing the distribution of serological median values, (and its interquartile range) of Beta2-Microglobulin in HIV cases to healthy controls.

HIV cases positive for serum P24 Ag have shown a significantly higher serum β - 2 M concentration compared to those with negative or equivocal serum P24 Ag (Table 9).

Table- 9: The difference between the mean serum Beta2-Microglobulin concentration in HIV cases with positive P24 antigen and those with negative or equivocal tests.

Serum Beta2-Microglobulin (mgL)	Serum P24 Antigen Negative&equivocal (5 pg/ml)	Positive (5 pg/ml))	P
			0.002
Median	4.52	6.1	

Serum β 2M has shown statistically significant negative linear correlation with CD4/CD8 ratio in HIV cases (Figure 3).

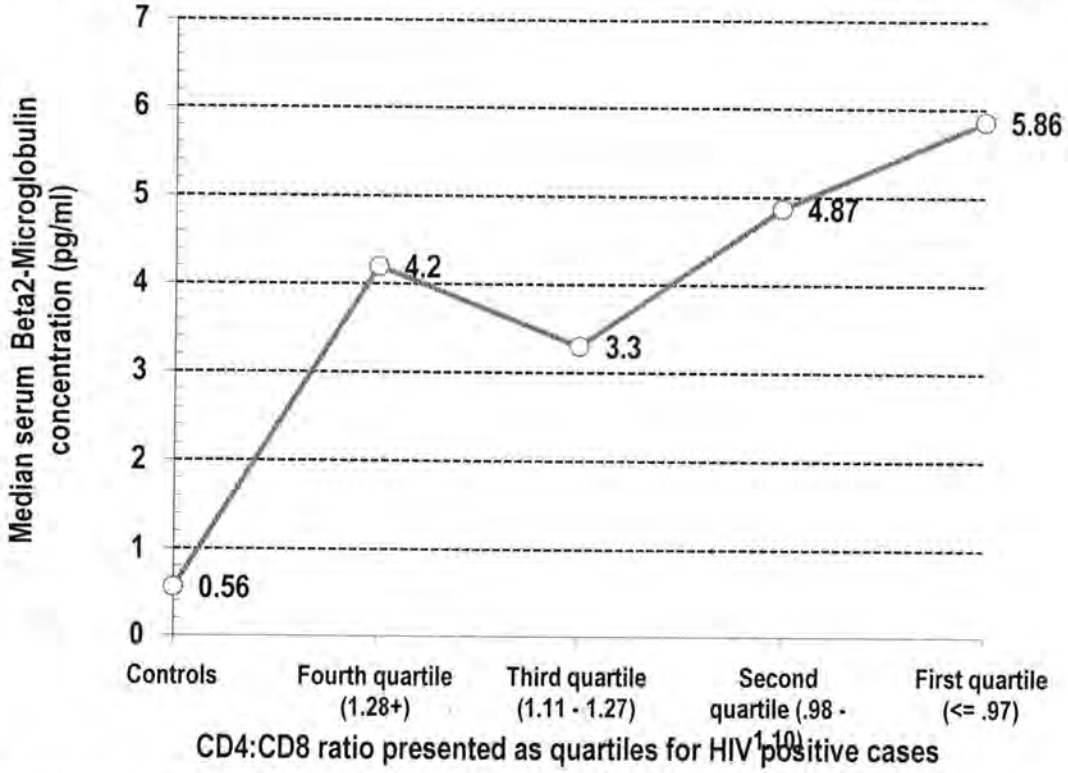

Figure -3: Linear graph showing the changes in median level of serum Beta2 Microglobulin concentration between different gradients of CD4/CD8 ratio of HIV cases comparing them to controls group.

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Synthesis and Spectroscopic Study of Benzotriazole Derivatives

Aoras A.K. Al- Rubaay
Department of Chemistry, College of Science, Al-Mustansiriya University

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الخلاصة

تم في هذا البحث تحضير عدد من مشتقات المركب بنزوترايازول. حيث تم مفاعلة البنزترايازول مع المركب α- كلورو خلات الاثيل لتحضير المشتق (Bz1) ومن ثم تحويل الأخير إلى مشتق الهيدرزايد(Bz2) بمفاعلته مع الهيدرازين المائي (99%) في الايثانول. استخدم المركب (Bz2) في تحضير العديد من المشتقات الحلقية غير المتجانسة والمفتوحة حيث تم تحضير المشتق 1، 2، 4- ترايزول (Bz4) من خلال مفاعلة مشتق الهيدرازايد مع 4- كلورو فنيل ايزوثايوسيانيد ومن ثم إجراء الغلق باستخدام القاعدة. كما تم تحضير مشتقين لحلقة 1، 3 ، 4- اوكساديازول (Bz5-6) باستخدام المركب (Bz2) وفي ظروف تفاعل مختلفة.

ان تفاعل المركب(Bz2) مع 4- كلورو حامض البنزويك بوجود $POCl_3$ لمدة ثلاث ساعات أعطى مشتق السميكارباز ايد للبنزوترايزول(Bz7). اما قواعد شيف (Bz8-9) فقد تم تحضيرها من خلال مفاعلة (Bz2) مع الديهايدات وكيتونات أروماتية. شخصت المركبات المحضرة من خلال دراسة خواصها الفيزيائية واستخدام بعض الطرق الطيفية إضافة إلى حساب عامل الإعاقة (Rf).

ABSTRACT

Ethyl benzotriazoacetate (Bz1) was prepared from the reaction of benzotriazol with α- chloro ethyl acetate in presence of sodium hydroxide. (Bz1) was then treated with hydrazine hydrate (99%) in ethanol to give 1-benzotriazoacetyl hydrazide (Bz2). (Bz2) can be used for the preparation of many heterocyclic rings or open derivatives. (Bz3) was prepared by the reaction of the hydrazide (Bz2) with 4- chloro phenylisothiocyanate then cyclized with sodium hydroxide to produce Substituted 1, 3, 4- triazol (Bz4) .

1,3,4-Oxadiazoles derivatives (Bz5-6) were obtained by the reaction of carbondisulfide in potassium hydroxide solution and triethoxymethane in dimethylformamide with (Bz2). While reaction of (Bz2) with arylcarboxylic acid in the presence of phosphorus oxychloride gave arylsemicarbazide (Bz7). Treatment of (Bz2) with arylaldehyde or ketone afforded the corresponding Schiff's bases (Bz8-9).

The synthesized compounds have been characterized and identified via of their physical properties and spectral data analysis (IR, UV) in addition to the determination of the retardation factor (Rf).

INTRODUCTION

Benzotriazol and its derivatives comprise an important class of corrosion inhibitors, and typically used as trace additives in industrial chemical mixtures fluid.[1] Recent studies have shown that benzotriazol derivatives are a major component of aircraft deicing fluids (ADFs) responsible for toxicity to bacteria.[1]

On the other hand the five membered ring hetrocyclic compounds which may contain three hetero-atoms such as 1, 3, 4- oxadiazoles and 1, 3, 4- triazole derivatives are well known to possess various biological activities,[2] controlling blood pressure[3] and can affect central nervous system.[4]

These facts encouraged the idea of incorporation of benzotriazole with an oxadiazole or triazole moieties which might result in potential biologically active agents.

MATERIAL AND METHODS

The melting points were measured on a Callenkamp MFB-600 and were uncorrected. The I R spectra were recorded by KBr discs with PYE UNICAM SP3-100 and PYE UNICAM SP3-300 infrared spectrophotometer. UV spectra were recorded on UV- 160 and UV-VISIBLE recording spectrophotometer, using ethanol as a solvent. And the retardation factor (Rf) were measured by thin layer chromatography on a silica plate as stationary phase and acetone as eluent.

All the chemical substances were supplied by B.D.H or Fluka.

Synthesis of 1- Ethyl benzotriazoacetate (Bz1) [4]

A mixture of benzotriazol (0.01 mole) and anhydrous sodium carbonate (0.01 mole) and ethyl chloroacetate (0.01 mole) in absolute ethanol (25 ml) was refluxed for 6hrs. The hot reaction mixture was then filtered, cooled and poured onto crushed ice, the precipitate obtained was filtered off and washed with water several times and recrystallized from water. The physical properties are listed in table (1), and the spectral data in table (2).

Synthesis of 1- Benzotriazoacetyl hydrazide (Bz2) [5]

A mixture of (Bz1) (0.01 mole) and hydrazine hydrate (0.013 mole,99%) in ethanol (50 ml) was refluxed for 4hr. On cooling, the solid product was filtered off, and recrystallized from chloroform. The physical properties are listed in table (1), and the spectral data in table (2).

Synthesis of 1- Benzotriazoacetyl –N`–(4- chlorophenyl) thiosemicarbzide (Bz3) [6]

A mixture of (Bz2) (0.01 mole) and 4-chlorophenylisothiocyanate (0.01 mole) in absolute ethanol (30 ml) was refluxed for 2hr. The solid obtained was filtered off and recrystallized

from methanol. The physical properties are listed in table (1), and the spectral data in table (2).

Synthesis of 1- (4- Chlorophenyl)-2-mercapto -5-(1-methylbenzotriazo) 1, 3, 4-triazol (Bz4) [6]

The thiosemicarbazide (0.01 mole) was dissolved in aq. NaOH (4%,50 ml)and refluxed gently for 2hr. The resulting solution was adjusted to pH 5-6 with dil. Acetic acid (10%) and the solid precipitated was filtered off, washed with water and recrystallized from methanol. The physical properties are listed in table (1), and the spectral data in table (2).

Synthesis of 1- (2`,3`- Dihydro-2`-thione-1`, 3`, 4`- oxadiazol- 5- yl) methylbenzotriazol (Bz5) [7]

To a cold stirred solution of (Bz2) (0.01 mole) in ethanol (30ml) and KOH (0.01 mole), carbon disulphide (0.05 mole) was added drop wise. The reaction mixture was refluxed on steam bath for 8hr. Ethanol was removed by distillation under vacuum and the residue was stirred with (10 ml) of water, filtered and the filtrate was neutralized with 10% HCl. The precipitate product was filtered, washed thoroughly with water, dried and recrystallized from methanol. The physical properties are listed in table (1), and the spectral data in table (2).

Synthesis of 1-(1`,3`,4`- oxadiazol-5-yl) methylbenzotriazol (Bz6) [8]

A mixture of (Bz2) (0.01 mole) and triethoxymethane $HC(OC_2H_5)_3$ (0.03 mole) in DMF (10ml) was refluxed for 5hr. Addition of water (10ml) to the cold reaction mixture afforded a solid, which was filtered off and recrystallized from water. The physical properties are listed in table (1), and the spectral data in table (2).

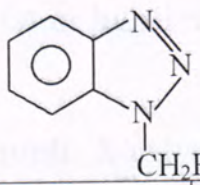
Synthesis of 1- Benzotriazoacetyl –N`–(4- chlorophenyl) semicarbzide (Bz7)

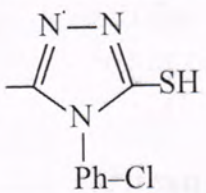
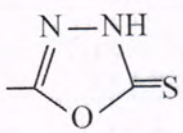
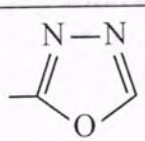
Compound (Bz2) (0.01 mole) was treated with 4-chlorobenzoic acid (0.01 mole) and phosphorus oxychloride (10 ml) under reflux for 3hr. The reaction mixture was cooled and then poured onto ammonium hydroxide solution. The precipitate was filtered off, washed with water, dried and crystallized from methanol. The physical properties are listed in table (1), and the spectral data in table (2).

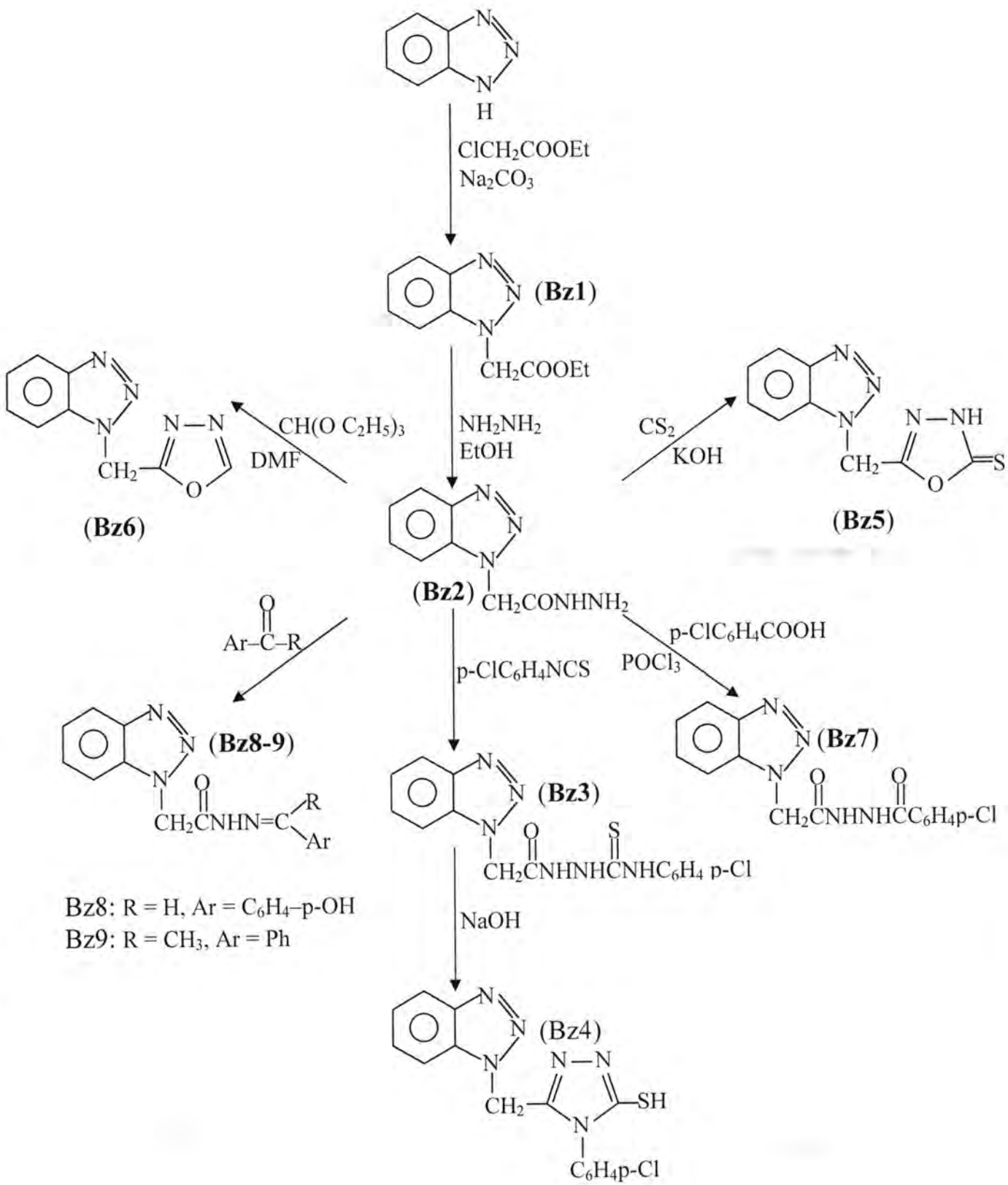
Synthesis of Benzotriazol-1-yl-acetyl-N`- arylidene hydrazines (Bz8-9) [9]

A mixture of (Bz2) (0.01 mole) and 4-hydroxybenzaldehyde or acetophenone (0.01 mole) in ethanol (30ml) with drops of acitic acid was refluxed for 2-3hr. The solid precipitate obtained on cooling was filtered off and recrystallized from methanol. The physical properties are listed in table (1), and the spectral data in table (2).

Table -1: Physical properties for compounds which have structure:



No. of Comp	R	Molecular Formula	Yield %	Purification solvent	M.P °C	Rf
Bz1	$-COOC_2H_5$	$C_{10}O_2N_3H_{11}$	54	H_2O	50-52	0.79
Bz2	$-CONHNH_2$	$C_8ON_5H_9$	70	$CHCl_3$	150-153	0.92
Bz3	–CONHNHCSNH–Ph– p-Cl	$C_{15}ON_6SClH_{13}$	45	MeOH	177-180	0.8
Bz4		$C_{15}N_6SClH_{11}$	75	MeOH	250-253	0.62
Bz5		$C_9ON_5SH_7$	50	MeOH	181-184	0.39
Bz6		$C_9ON_5H_7$	70	H_2O	130-132	0.85
Bz7	–CONHNHCO–Ph– p-Cl	$C_{15}ON_5ClH_{10}$	88	MeOH	215-217	0.41
Bz8	–CONHN=CH–Ph– p-OH	$C_{15}O_2N_5H_{13}$	60	MeOH	240-243	0.51
Bz9	$-CONHN=C(CH_3)-Ph$	$C_{16}ON_5H_{10}$	70	MeOH	169-171	0.54


H
ClCH2COOEt
Na2CO3
(Bz1)
CH2COOEt
NH2NH2
EtOH
CH(O C2H5)3
DMF
(Bz6)
CS2
KOH
(Bz5)
(Bz2)
CH2CONHNH2
Ar–C–R
p-ClC6H4NCS
p-ClC6H4COOH
POCl3
(Bz8-9)
(Bz3)
(Bz7)
Bz8: R = H, Ar = C6H4–p-OH
Bz9: R = CH3, Ar = Ph
NaOH
(Bz4)

Scheme 1

RESULTS AND DISCUSSION

1-Ethyl benzotriazoacetate is prepared by the reaction of benzotriazole with α- chloro ethyl acetate. The reaction is followed by disappearance of NH absorption band and appearance of (C=O) absorption band at 1750 cm^{-1} in their IR spectra. The ethyl ester (Bz1) was converted into acid hydrazide (Bz2) by its reaction with hydrazine in ethanol, the hydrazide (Bz2) showed absorptions at 3300 cm^{-1} for (N–H) and 1660 for (C=O).

The hydrazide was refluxed with 4-chlorophenylisothiocyanate to give the expected thiosemicarbazide (Bz3), which was identified by (N–H) absorption bands at 3260-3310 cm^{-1},weak band of (S–H) absorption at 2620 cm^{-1} and (C=O) absorption at 1700 cm^{-1}. Treatment of thiosemicarbazide with base yielded triazole (Bz4) which showed absorption of weak band at 3280 cm^{-1} for (N–H), (S–H) absorption at 2520 cm^{-1} in addition to disappearance of (C=O) absorption.

The hydrazide (Bz2) was refluxed with carbon disulfide in alcoholic potassium hydroxide solution to give substituted oxadiazole (Bz5). Compound (Bz5) showed absorption at 3270 cm^{-1} for (N–H), 2600 cm^{-1} for (S–H) and 1640 cm^{-1} for (C=N).

Refluxing (Bz2) with ethylorthoformate in DMF afforded oxadiazole derivative (Bz6). The IR spectrum of (Bz6) was devoid of both amide and amino bands of (Bz2). Treatment of hydrazide (Bz2) with 4-chlorobenzoic acid in the presence of phosphorous oxychloride for 3hr resulted in the formation of 1- benzotriazo acetyl- N`- (4-chlorophenyl) semicarbazide (Bz7). The IR spectrum of (Bz7) was showed absorption at 3300 cm^{-1} for (N–H) and 1680 cm^{-1} for (C=O).

The Schiff`s bases (Bz8-9) have been prepared by the reaction of (Bz2) with 4-hydroxybenzaldehyde or acetophenone and acid catalyst. The structures of these derivatives have been identified by their IR spectrum which showed absorption at 1640 cm^{-1} for (C=N).

The UV spectra of the synthesised compounds showed the expected electronic transitions ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$). The UV absorption of compound (Bz2) with λmax 280nm compared with (Bz1) of 289nm there is a hypsochromic shift which results from the exchange of (–OEt) group with ($–NHNH_2$) group. While there is a bathochromic shift in the λmax of compound (Bz3) which results from introducing (C=S) group. On the other hand there is an increased in λmax of compound (Bz4)

which may be resulted from the extension of the double bond conjugation with the aromatic and oxadiazole rings.

On the same basis compound (Bz5) has λmax 287nm due to the two factors, the first one is the conjugation of oxadiazole ring, second the presence of sulfur atom may also play an important rule in bathochromic shift in oxadiazole (Bz5) as compared with (Bz6) which absorbed at λmax 284nm.

Compound (Bz7) λmax showed an increase into till 293 nm due to the introducing (C=O) group. While the shiff's bases showed increasing in λmax may resulted from the presence of (PhCH=N) group. Spectral data were listed in (table 2).

Table -2: IR and UV spectral data for compounds ($M_2 - M_9$)

No. of Comp	U.V λmax ($CHCl_3$) nm	Characteristic IR bands Cm^{-1}						
		C=O	C–H al.	C–H ar.	C=N	C=C	N–H	Other
Bz1	289,251 245	1750	2970 2990	3000	–	1510	–	(N=N) 1570
Bz2	280, 267 251, 245	1660	2908 2812	3057	–	1545	3300	(N=N) 1610
Bz3	290, 251 245, 224	1700	2980 2999	3070	–	1550d	3260 - 3310	(S–H) 2620 (N=N) 1600 (C=S) 1500
Bz4	295, 256 249, 245 232	–	2940 2980	3080 3160	1620	1570	3280w	(S–H) 2540 (C=S) 1520 (C–Cl)ar1070
Bz5	287, 267 251, 244	–	2920 2940	3000	1640	1510	3280	(S–H) 2600w (C=S) 1400
Bz6	284, 245 221	–	2998 2990	3020	1680	1520	–	–
Bz7	293, 257 249, 245 241	1690s	2840 2860	3040	–	1590	3310	(C–Cl)ar1099
Bz8	320, 309 304, 300 292, 267 251, 245	1710	2880 2900	3000	1610	1520	3240	(C–OH)ar 3400 - 3600w
Bz9	309, 292 267, 245	1710	2980 2990	3100	1640	1520	3240	–

ar: aromatic, s: strong, w: weak

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Synthesis and Biological Activities of Some New Twin Compounds Containing Heterocyclic Unit

Ivan H. Roui'l
Department of Chemistry, College of Science, University of Al-Mustansiriya

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الخلاصة

ان تكثيف 4- ميثوكسي فنيل حامض الهيدرازيد مع الحوامض الكاربوكسيلية الثنائية بوجود الفوسفوريل كلورايد يؤدي الى تكوين ثنائي - ω,α - [5- (4- ميثوكسي فنيل) – 4,3,1 – اوكساديازول – 2 – يل] الكان $[V]_n$. كسرت الاصرة الايثرية لهذه المركبات باستخدام الالمنيوم كلورايد في البنزين الجاف لتعطي ثنائي - ω,α - [5- (4 – هيدروكسي فنيل) – 4,3,1- اوكساديازول – 2 – يل] الكان $[VI]_n$.

السلسلة الجديدة $[VI]_n$ تكونت بتكثيف المركبات السابقة $[VI]_n$ مع 4 – (4' – ن – بيوتوكسي بنزلدين إمينو) كلوريد البنزوايل [II] في البيريدين الجاف .

شخصت المركبات المحضرة $[VI]_n$ بواسطة القياسات الطيفية والفيزيائية. كل المركبات الجديدة فحصت لمعرفة فعاليتها البايولوجية تجاه نوعين من البكتيريا (E. Coli و S. Aureus) وفي ثلاثة تراكيز (0,1 , 0,01, و 0,001) mg/mL واظهرت النتائج فعالية بايولوجية جيدة ضد E. Coli لكن لم تظهر اي فعالية بايولوجية ضد S. Aureus .

ABSTRACT

Condensation of 4- methoxy phenyl acid hydrazide with di carboxylic acid in $POCl_3$ leads to the formation of bis – α , ω -[5-(4-methoxyphenyl)-1,3,4-oxadiazole-2-yl) alkanes $[V]_n$. These compounds were demethylated with aluminum chloride in dry benzene to give bis –α ,ω-[5-(4-hydroxyphenyl)-1,3,4-oxadiazole – 2- yl) alkanes $[VI]_n$. The new series $[VII]_n$ was obtained by condensation of the latter compounds $[VI]_n$ with 4(4'-n-butoxybenzylideneimino) benzoyl chloride [II] in dry pyridine.

The synthesized compounds $[VII]_n$ were characterized by spectral and physical data. All new compounds have been screened for their antibacterial activities against two types of bacteria (E. Coli and S. Aureus) in three concentration (0.1, 0.01 and 0.001) mg/mL. The results showed good biological activity against E. Coli, but did not show any antibacterial activity against S. Aureus.

INTRODUCTION

The synthesis of 1, 3, 4-oxadiazoles has considerable interest due to their various biological activities reported among these activities were: antifungal [1] , anticonvulsant [2], antibacterial [3] activities.

Substituted 1, 3, 4-oxadiazoles are associated with many types of biological properties. Antimicrobial activity data of these structures showed their considerable activity against Gram negative and Gram positive bacteria as well as some strains of fungi [4].

Schiff bases are important compounds since they have biological activity against bacteria and fungi [5,6]. Also the Schiff bases posses anticancer [7,8] activity in animal screening.

In this paper, the synthesis and biological activity of some new twin 1, 3, 4-oxadiazole units were reported with the hope that the incorporation of these moieties with imine group might enhance biological activity.

MATERIAL AND METHODS

Materials:

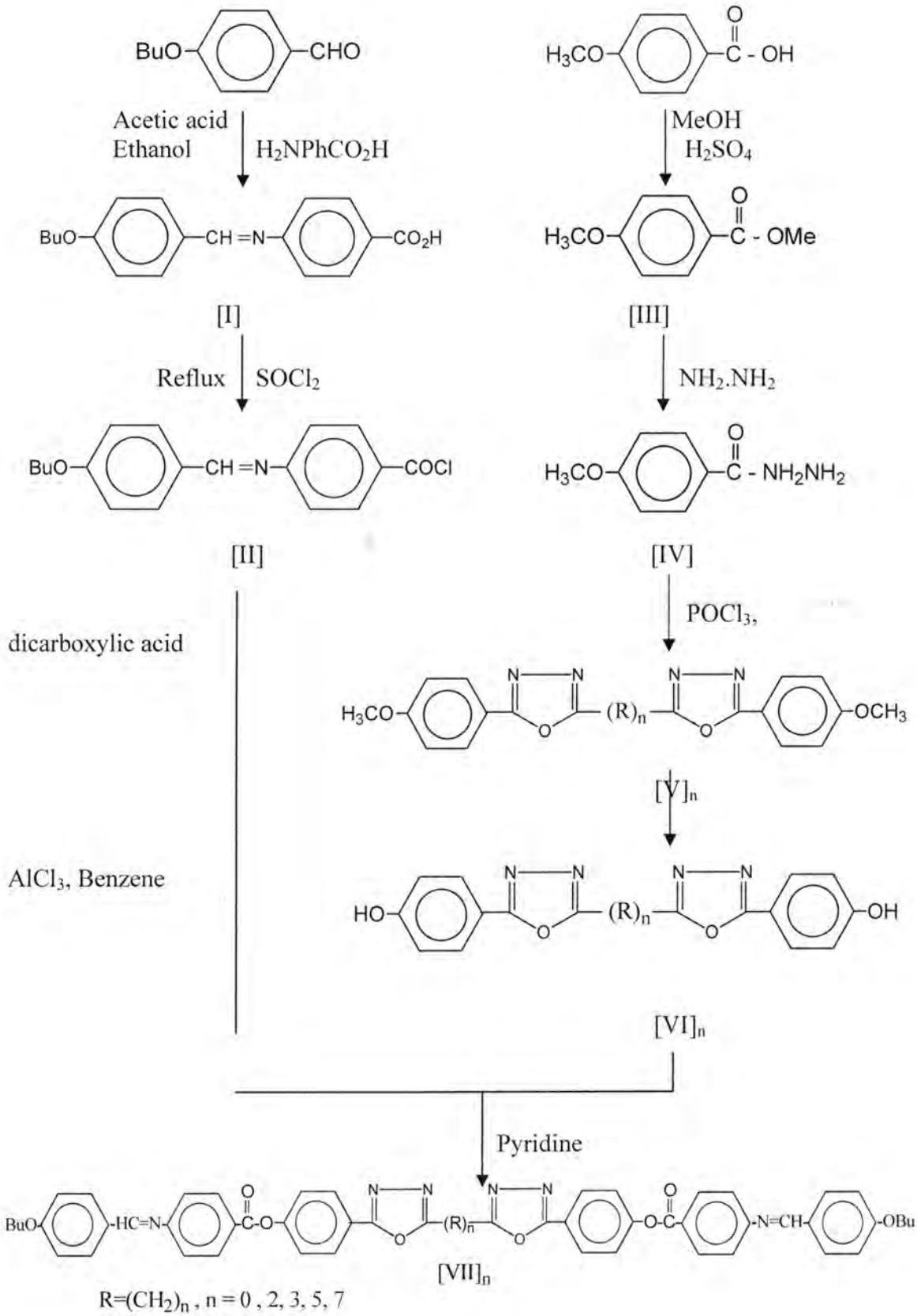
Most of chemicals used were supplied from FLUKA, MERCK and BDH chemicals co. and used as received.

Techniques:

The melting points were determined by using an (electrothermal) melting point apparatus. Elemental analysis was carried out by using carlo-erba 5500 elemental analyzer. The IR spectra were recorded on a PYE-UNICAM type (1310) infrared spectrophotometer using potassium bromide discs. FTIR spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer; mass spectra were recorded on Shimadzu QP1000A gas chromatography spectrophotometer. The ^{1}HNMR spectra recorded on Brucer 60MHz NMR spectrometer. Deuterated dimethylsulfoxide solution was used as internal solvent.

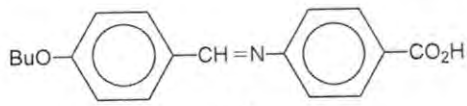
SYNTHESIS

The homologous series of Bis α,ω– { 5 – [4 (4' – n – butoxybenzylideneimino) benzoyloxyphenyl] – 1,3,4 - oxadiazole – 2 – yl } alkanes $[VII]_n$ was prepared according to scheme 1


BuO
CHO
Acetic acid
Ethanol
H2NPhCO2H
BuO
CH =N
CO2H
[I]
Reflux
SOCl2
BuO
CH =N
COCl
[II]
H3CO
C - OH
MeOH
H2SO4
H3CO
C - OMe
[III]
NH2.NH2
H3CO
C - NH2NH2
[IV]
dicarboxylic acid
POCl3,
H3CO
(R)n
OCH3
[V]n
AlCl3, Benzene
HO
(R)n
OH
[VI]n
Pyridine
BuO
-HC=N-
C-O
(R)n
O-C
-N=CH-
-OBu
[VII]n
R=(CH2)n , n = 0 , 2, 3, 5, 7

Scheme 1

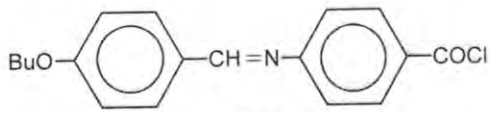
4(4'-n-Butoxybenzylideneimino) benzoic acid [I].



[I]

This compound was prepared following the procedure described by Smith [9]. Yield 88%, m.p 191 - 193° C.

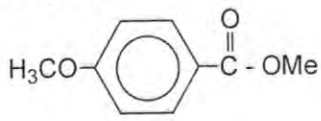
4(4'-n-Butoxybenzylideneimino) benzoyl chloride [II].



[II]

This acid chloride was prepared by refluxing the corresponding carboxylic acid with an excess of thionyl chloride. Unreacted thionyl chloride was removed under reduced pressure, and the acid chloride was distilled under reduced pressure and kept under dry N_2 atmosphere. [10]. Yield 81%, b.p 224 - 225° C.

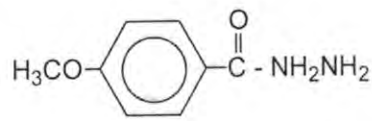
4-Methoxybenzoate [III].



[III]

This compound was prepared following the procedure described by Vogel [10]. Yield 95% m.p 49-51 °C (lit. m.p 49-51 °C)

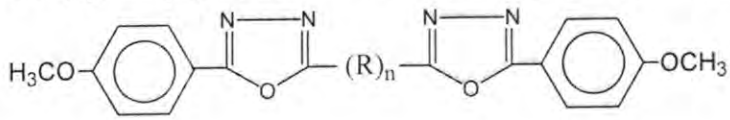
4-Methoxybenzoyl hydrazine [IV].



[IV]

This compound was prepared following the procedure described by Smith [9]. Yield 98% m.p 135-137° C.

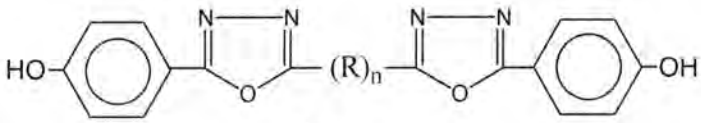
Bis-α,ω -[5-(4-methoxyphenyl)-1, 3, 4-oxadiazole-2-yl) alkanes $[V]_n$.



$[V]_n$

A mixture of 4-methoxybenzoyl hydrazine (0.02 mol), dicarboxylic acid (0.01 mol) and phosphorousoxychloride (5mL) was refluxed for 7 hrs. The cold reaction mixture was poured into ice-water and made basic by adding sodium bicarbonate solution. The resulting solid was filtered, dried and purified by refluxing with ethanol. [11], Table (1) shows the physical properties of compounds $[V]_n$.

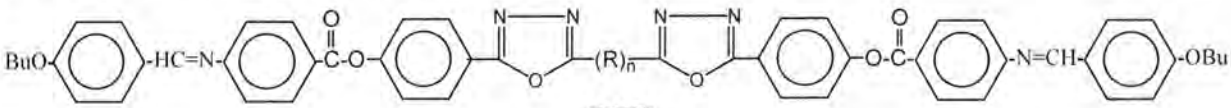
Bis- α,ω -[5(4-hydroxyphenyl)-1, 3, 4-oxadiazole-2-yl]alkanes $[VI]_n$.



$[VI]_n$

To compound [V] (0.033 mol) dissolved in dry benzene (25 mL) was added anhydrous aluminum chloride (2 g). The reaction mixture was refluxed for 10 hrs. The solvent was evaporated and the residue was poured into ice-water. The solid was collected and purified by dissolving in (30 mL) of 10 % NaOH solution. The reminder solid was filtered and the filtrate was neutralized with 10% HCl. The crude product precipitate during the neutralization, washed with water several times and dried to give the desired compounds $[VI]_n$ [12], Table (1) shows the physical properties of compounds $[VI]_n$.

Bis - α,ω - { 5-[4(4'-n-butoxybenzilydeneimino)benzoyloxyphenyl] - 1,3,4-oxadiazole-2-yl} alkanes $[VII]_n$.



$[VII]_n$

To a stirred solution of compound $[VI]_n$ (0.01 mol) in dry pyridine , was added 4(4'-n-Butoxybenzylideneimino) benzoyl chloride [II] (0.02 mol) at (0-4)°C. After the addition had been completed, the resulting was stirred for 3hrs. at room temperature. Afterwards the resulting mixture was poured into (100 mL) of 10% HCl. The precipitate was filtered, washed with solution of 10% $NaHCO_3$ and then with water several times, dried and recrystallized from chloroform. The physical data of this series $[VII]_n$ are listed in Table (1).

RESULTS AND DISCUSSIONS

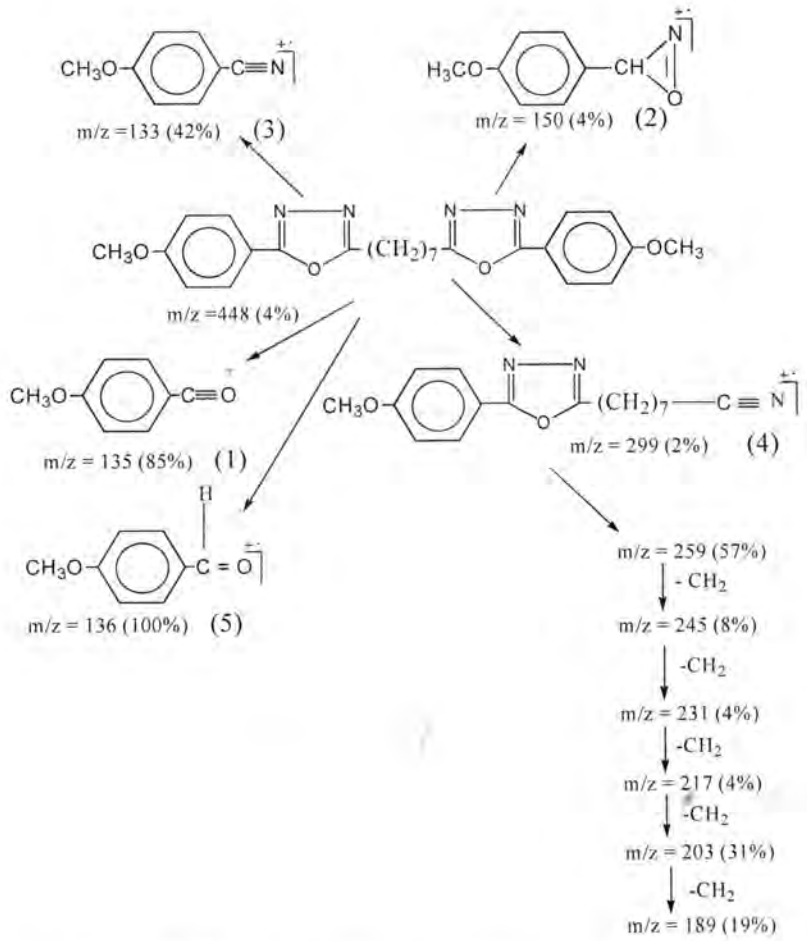
4(4'-n-Butoxybenzylideneimino) benzoic acid [I] was synthesized from the reaction of 4-amino benzoic acid with 4-n-butoxybenzaldehyde in the absolute ethanol with glacial acetic acid as a catalyst. This compound was characterized by melting point (191 - 193° C) and IR spectrum.

The IR spectrum of this compound showed disappearance of absorption band due to C=O stretching of aldehyde at (1700) cm^{-1} and two absorption bands due to NH_2 stretching at 3300 cm^{-1} and 3160 cm^{-1} of hydrazide [IV] together with appearance of a stretching band at (1620)cm^{-1} assignable to C=N stretching. This compound was converted to the corresponding acid chloride by refluxing with $SOCl_2$ for 1 hrs.

Condensation of 4-methoxybenzoylhydrazine [IV] with dicarboxylic acid in $POCl_3$ yielded the compounds $[V]_n$. The structures of these compounds were confirmed by using spectral data (IR Table (2), ^{1}HNMR and mass spectroscopy) and elemental analysis, Table (3). The IR spectrum of compound $[V]_5$, Figure (1) showed disappearance of absorption band due to NH_2 stretching together with appearance a new band at (1600, 1250 and 1020) cm^{-1} due to C=N, Asy. C-O-C and Sy. C-O-C stretching, respectively.

^{1}HNMR spectrum of compound $[V]_2$, Figure (2) showed the following characteristic chemical shifts: pairs of doublet of doublet at δ 7.21- 7.92 that could be attributed to the eight protons of the benzene ring. The ^{1}HNMR spectrum also showed the triplet signal between δ 1.41 – 1.69 that could be assigned to the four protons of methylene group (CH_2-CH_2) while the sharp singlet peak at δ 3.52 suggesting the attribution of the six protons of lateral methoxy group (OCH_3)

The mass spectrum of compound $[V]_7$ as a representative example is shown in Figure (3). The molecular ion peak (m/z = 448) is prominent which corresponds to the molecular weight of the structure suggested to this compound. The ions (1, 2, 3, 4) gives an excellent diagnostic for 1, 3, 4-oxadiazole ring [13], scheme (2). The fragmentation pattern of alkyl chain in this compound is characterized by clusters of peaks (189, 203, 217, 231, 245, and 259), at intervals of 14 units (CH2), that are known in the mass spectra of n-alkanes [14]. Finally, the aromatic nature of this compound is evident as a result of the peaks at masses (39, 50, 51, and 77).



Scheme (2) Fragmentation pattern of compound $[V]_7$

The compounds $[V]_n$ were demethylated with aluminum chloride in dry benzene to give compounds $[VI]_n$. The structures of these compounds $[VI]_n$ were confirmed on the bases of spectral data (IR , Table (2) and ^{1}HNMR) and elemental analysis, Table (3).

The characteristic of IR-absorption bands showed the disappearance of absorption bands due to aliphatic stretching of lateral CH_3 group of compound $[VI]_0$ together with the appearance of a broad band in the range (3160-3435)cm^{-1} due to hydrogen bonding of (OH) group, The other compounds $[VI]_2$, $[VI]_3$, $[VI]_5$, and $[VI]_7$ showed only the appearance of broad of hydroxyl group, Figure (4) .

^{1}HNMR spectrum of compound $[VI]_0$ Figure (5) showed the following characteristic chemical shift were appeared : pair of doublet at δ 6.85 – 7.88 that could be attributed to eight protons of the symmetrical phenyl ring. The spectrum showed a singlet at δ 8.41 that could be assigned the two protons of phenolic hydroxyl group.

Finally, these compounds $[VI]_n$ were condensed with two equivalents of the synthesized compound [II] in dry pyridine to yield a new series bis -α,ω -{5-[4 (4' – n – butoxybenzylideneimino)

benzoyloxyphenyl] 1 , 3 , 4 – oxadiazole -2 – yl }alkanes $[VII]_n$. The structures of these compounds were confirmed on the bases of spectral data, Table (2) and elemental analysis, Table (3).

FTIR absorption bands of these compounds showed the disappearance of absorption band due to (OH) stretching of compound $[VI]_n$ together with the appearance of stretching band in the range (1717-1725) cm^{-1} assignable to carbonyl of ester group and a stretching band around (1675) cm^{-1} due to exocyclic imine group (C=N), Figure (6).

Biological Activity

The compounds of new series $[VII]_n$ have been screened for their antibacterial activity by agar growth technique against two type of bacteria viz ., Escherichia Coli (Gram – negative bacteria) and staphylococcus (Gram – positive bacteria). The diameter of the bacteria colony was measured at three different concentrations 0.1 mg/mL, 0.01 mg/mL and 0.001 mg/mL.

The plates were incubated for 24 hrs. at 37°C. The zones of inhibition formed were measured in mm and are represented by (+), (++), (+++) depending upon the diameter and clarity. The results of the preliminary screening test are listed in Table (4). The data showed, all the tested compounds have biological activity against E.Coli. The biological activity was high at concentration (0.1 and 0.01) mg/mL but a slight active at concentration 0.001 mg/mL. While all these compounds were found to be inactive against staphylococcus aureus.

Table -1: The physical properties of compounds $[V]_n$, $[VI]_n$ and $[VII]_n$

No. of Comp.	Formula	m.p (C°)	Yield (%)	Color
$[V]_0$	$C_{18}H_{14}N_4O_4$	276-278	88	White
$[V]_2$	$C_{20}H_{18}N_4O_4$	155-156	73	White
$[V]_3$	$C_{21}H_{20}N_4O_4$	161-163	79	White
$[V]_5$	$C_{23}H_{24}N_4O_4$	156-158	66	White
$[V]_7$	$C_{25}H_{28}N_4O_4$	137-138	81	White
$[VI]_0$	$C_{16}H_{10}N_4O_4$	> 300	72	Gray
$[VI]_2$	$C_{18}H_{14}N_4O_4$	> 300	56	Yellow
$[VI]_3$	$C_{19}H_{16}N_4O_4$	> 300	68	White
$[VI]_5$	$C_{21}H_{20}N_4O_4$	> 300	74	Gray
$[VI]_7$	$C_{23}H_{24}N_4O_4$	> 300	77	Gray
$[VII]_0$	$C_{52}H_{46}N_6O_8$	180-181	52	Brown
$[VII]_2$	$C_{54}H_{50}N_6O_8$	163-165	48	Brown
$[VII]_3$	$C_{55}H_{52}N_6O_8$	155-157	61	Brown
$[VII]_5$	$C_{57}H_{56}N_6O_8$	207-208	53	Brown
$[VII]_7$	$C_{59}H_{60}N_6O_8$	149-152	44	Brown

Table -2: Characteristic IR and FTIR absorption bands of compounds $[V]_n$, $[VI]_n$ and $[VII]_n$

No. of Comp.	υ C-H aliph.	υ C=C with υ C=N endo.	υ C=N exo.	υ Asy. C-O-C	υ Sy. C-O-C	υ O-H	υ C=O ester
$[V]_0$	2855-2920	1600	-	1245	1020	-	-
$[V]_2$	2815-2980	1595	-	1240	1015	-	-
$[V]_3$	2835-2980	1600	-	1255	1030	-	-
$[V]_5$	2825-2975	1600	-	1250	1020	-	-
$[V]_7$	2860-2965	1595	-	1235	1030	-	-
$[VI]_0$	-	1605	-	1235	1050	3175-3415	-
$[VI]_2$	2820-2970	1600	-	1245	1045	3180-3420	-
$[VI]_3$	2810-2965	1605	-	1260	1060	3170-3435	-
$[VI]_5$	2870-2980	1600	-	1255	1065	3160-3400	-
$[VI]_7$	2840-2950	1615	-	1250	1025	3190-3410	-
$[VII]_0$	2845-2966	1605	1670	1244	1052	-	1721
$[VII]_2$	2825-2968	1608	1674	1243	1045	-	1717
$[VII]_3$	2850-2977	1610	1672	1252	1037	-	1725
$[VII]_5$	2855-2943	1612	1673	1257	1046	-	1723
$[VII]_7$	2856-2927	1606	1678	1272	1012	-	1718

Table -3: Elemental analysis data of compounds $[V]_n$, $[VI]_n$ and $[VII]_n$

No. of Comp.	Theoretical			Experimental		
	C%	H%	N%	C%	H%	N%
$[V]_0$	61.71	4.00	16.00	61.68	3.97	15.97
$[V]_2$	63.49	4.76	14.81	63.42	4.77	14.79
$[V]_3$	64.28	5.10	14.28	63.47	5.33	15.02
$[V]_5$	65.71	5.71	13.33	65.70	5.70	13.30
$[V]_7$	66.96	6.25	13.08	65.93	6.48	13.19
$[VI]_0$	59.62	3.10	17.39	59.59	3.08	17.36
$[VI]_2$	61.71	4.00	16.00	61.65	4.01	15.95
$[VI]_3$	62.63	4.39	15.38	62.62	4.36	15.31
$[VI]_5$	64.28	5.10	14.28	64.25	5.08	14.25
$[VI]_7$	65.71	5.71	13.33	65.69	5.65	13.32
$[VII]_0$	70.74	5.21	9.52	70.71	5.17	9.50
$[VII]_2$	71.20	5.49	9.23	71.15	5.42	9.22
$[VII]_3$	71.42	5.62	9.09	71.41	5.55	9.01
$[VII]_5$	71.84	5.88	8.82	71.81	5.80	8,78
$[VII]_7$	72.24	6.12	8.57	72.20	6.08	8.55

Table -4: Results of antibacterial activity of the tested compounds $[VII]_n$

No. of Comp.	Escherichia coli (G -)			Staphylococcus aureus (G +)		
	Concentration mg / mL			Concentration mg / mL		
	0.001	0.01	0.1	0.001	0.01	0.1
$[VII]_0$	+	++	+++	-	-	-
$[VII]_2$	+	+++	+++	-	-	-
$[VII]_3$	+	++	+++	-	-	-
$[VII]_5$	+	+++	+++	-	-	-
$[VII]_7$	+	++	+++	-	-	-

Highly active (+++)> 15mm, Moderately active (++) 10-14mm, Slightly active (+) 5-9mm, Inactive (-) < 5.

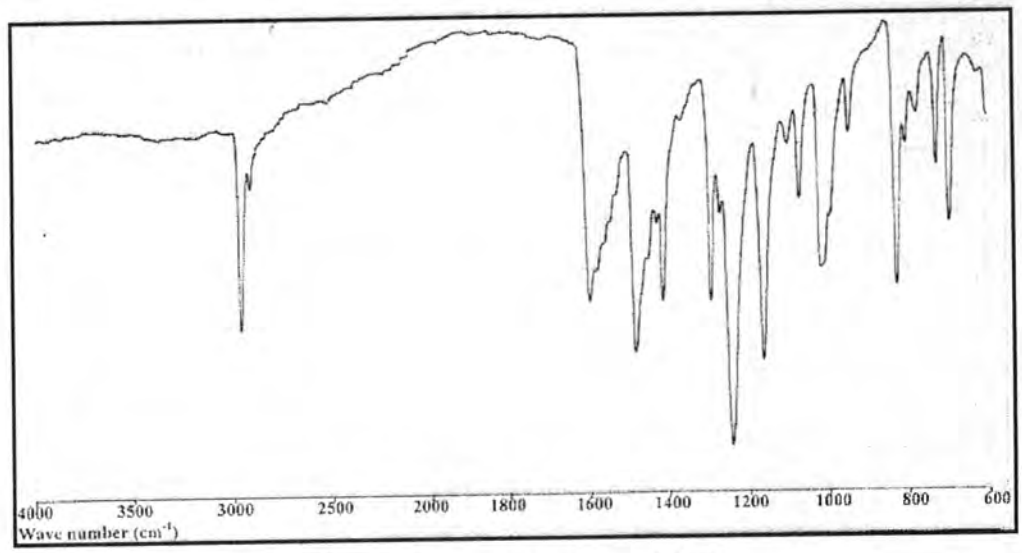


Figure -1: IR spectrum of compound $[V]_5$

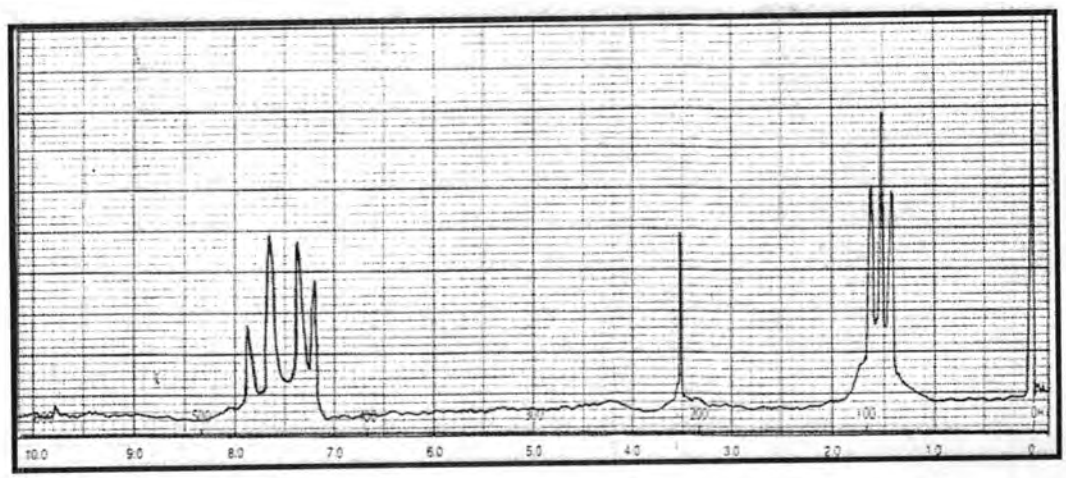


Figure -2: ^{1}HNMR spectrum of compound $[V]_2$

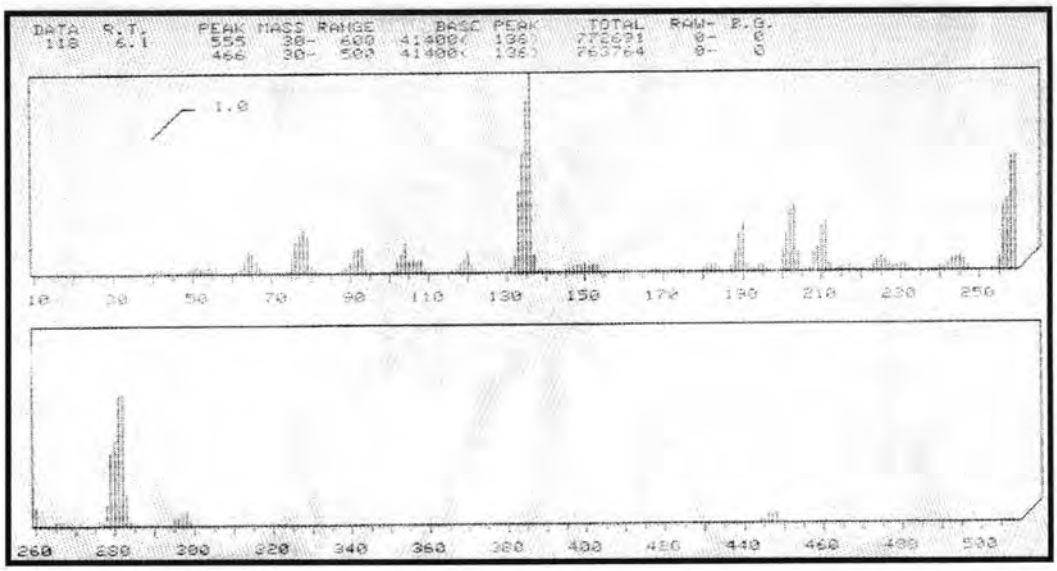


Figure -3: Mass spectrum of compound $[V]_7$

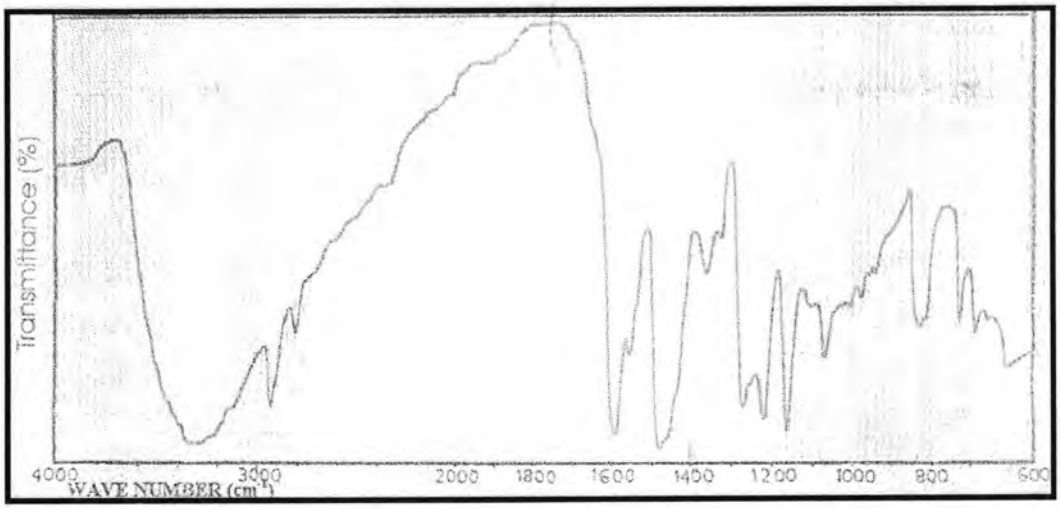


Figure -4: IR spectrum of compound $[VI]_3$

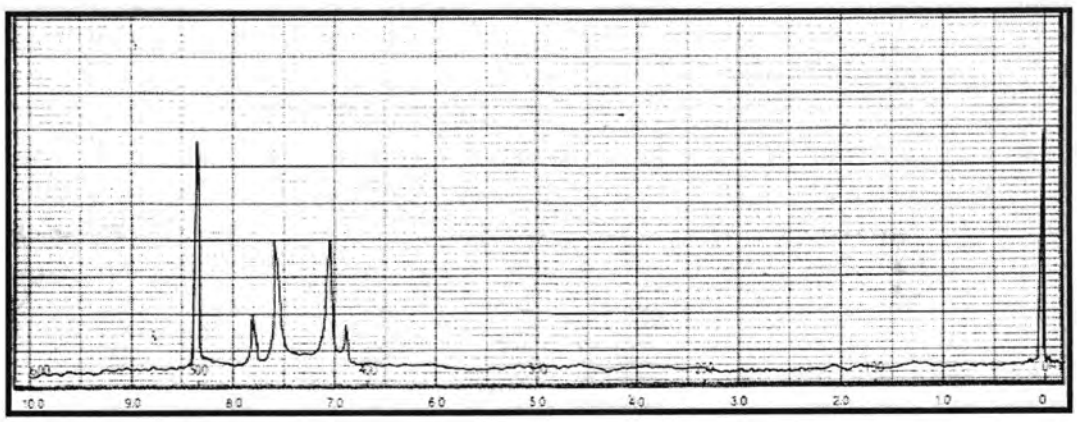


Figure -5: ^{1}HNMR spectrum of compound $[VI]_0$

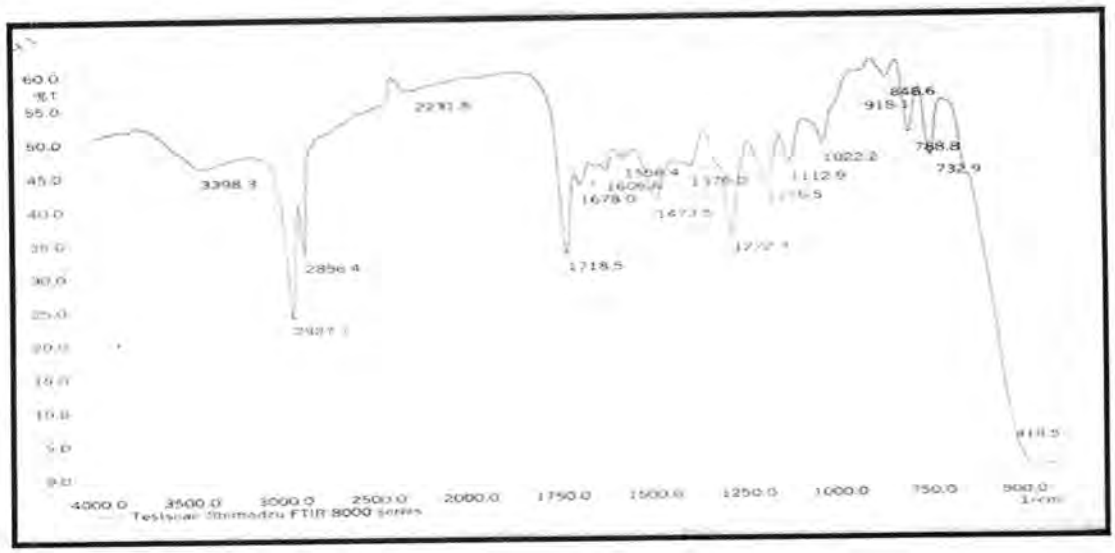


Figure -6: FTIR spectrum of compound [VII]$_7$

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Synthesis and Spectral Studie of the transition metals (Co II, Ni II , Cu II , Cd II, Hg II , pb II) with aniline-2-thiomethylene chloride complexes

Shaymaa H. Naji
Chemistry Dept. College of Education-Ibn-Al-Haitham-University of Baghdad-Iraq

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الخلاصة

تم تحضير الانيلين –2– ثايو مثيلين كلورايد(L)من تفاعل اورثوامينوفنيل ثايول مع ثنائي كلوروميثان وبنسبة 1:1 قد شخص بوساطة تقنية الأشعة تحت الحمراء , الأشعة فوق البنفسجية والمرئية.
وقد حضرت معقداته لأملاح بعض أيونات العناصر (Co , Ni , Cu , Cd , Hg و pb) MX2(L2) وشخصت باستعمال تقنية طيف الأشعة تحت الحمراء, الأشعة فوق البنفسجية , التوصيلية الكهربائية،المطيا ف الذري والخواص المغناطيسية وتم الاستنتاج من التحاليل ان المعقدات لها شكل هندسي ثماني السطوح حول أيون الفلزمع لكاند ثنائي السن (N , S) وقد تم حساب قيم α , kf و Cmax للمعقدات .

ABSTRACT

Aniline 2 - thiomethylenechloride (L) has been prepared from the reaction of orthoaminophenyl thiol with methylene-dichloride in mole ratio1:1at room temperature .The complexes with metal ions(M (II)= Co ,Ni ,Cu ,Cd ,Hg and Pb)of the type MX2 (L2) have been prepared and characterized by molar conductance measurement , IR and UV– Visible data, atomic absorption and magnetic susceptibility .The complexes showed octahedral geometry around the metal ion with the(N,S) ligand coordinated in bidentate mode .α and Kf for the complexes were estimated too.

INTRODUCTION

Self – assembly processes involving metal ions and organic ligands containing multi – basic donor sities have attracted much attention in the field coordination chemistry . Recently, the coordination chemistry of oxadiazol , triazol and orthothioaniline derivates have been of our research interests have been achieved .Many of these ligand and their complexes showed a relation with pharmacetical characters others domenstrate biological activity such as antibacterial and antiflamentery. [1 – 9]

As a part of our continuing reseach in this area , we described herein the synthesis of aniline 2 – thiomethylene chloride , a novel bidentate (N , S) ligand and its complexes with some of metal ions .

EXPERIMENTAL

a- Chemicals ; All reagents used were Analar or chemically pure grade by companies British Drug Houses (BDH), Merk and Fluka .

– The chemical materials :- orthoamino phenyl thiol (C_6H_7NS) methylene dichloride (CH_2Cl_2), potassium hydroxide (KOH), Cobalt chloride ($CoCl_2.6H_2O$), Nickel chloride (Ni $Cl_2.6H_2O$), Copper chloride (Cu $Cl_2.2H_2O$), Cadmium chloride(Cd $Cl_2.2H_2O$), Mercury chloride(Hg Cl_2) Lead nitrate $pb(NO_3)_2$, Ethanol (CH_3CH_2OH) 99% , chloroform (CH Cl_3) 99%, Dimethyl fluoride (DMF) 99.5% ,Dimethyl sulphoxide (DMSO) 99.5% .

b- Instruments;

– Melting points were determined by Gallen-Kamp apparatus .

–IR spectra were recorded as KBr discs in the range (4000-400 cm^{-1}) using Shimadzu-FT IR 8000 series.

–UV – Visible spectra were recorded by SHIMADZU-UV-VIS-160 A Ultra Violet Spectrophotometer at 25 °C, using , 1 cm quartz cell and examined at the range of (200-1100 nm) at 10^{-3} M in DMSO .

– Atomic Absorption (A A) technique using a shimadzu AA 680G atomic absorption Spectro photo meter.

– Molar conductivity of the complexes were measured on pw 9526 digital conductivity in DMSO at 10^{-3} M.

- Magnetic susceptibility were recorded by Balance magnetic susceptibility,model,MsB–MK1.

PREPARATION

Synthesis of aniline 2-thiomethylenechloride (L)

A mixture of orthoaminophenyl thiol (0.13gm , 1.04 mmol) in ethanol (20 cm^3) and potassium hydroxide(0.06 gm ,1.04 mmol) in ethanol

($5cm^3$)was stirred for 30min .A solution of methylene-dichloride (0.1 gm , 1.17 mmol) in ethanol (10 cm) was added dropwise with stirring at room temperature . The mixture was further stirred for two hours, giving white precipitate and brownish filterate . The white precipitate is soluble in water and with silver nitrate solution gave silver chloride. The brownish filterate was washed with water. The organic brownish layer was separated , dried over magnesium – sulphate and evaporated to give brownish oil (L) , mixed with most organic solvent .

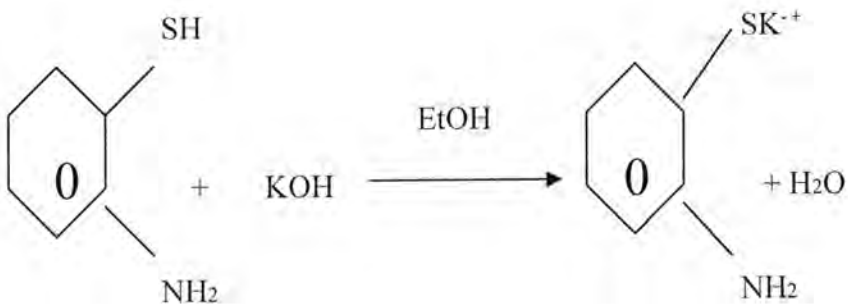
Synthesis of the complexes

Ethanolic solution of each of the following metal ion salt [$CoCl_2.6H_2O$ (0.24gm 1.00 mmol), $NiCl_2.6H_2O$ (0.24gm, 1.00 mmol) , $CuCl_2.2H_2O$ (0.23gm 1.00 mmol) ,$CdCl_2.2H_2O$(0.34gm 1.00 mmol),$HgCl_2$ (0.27gm 1.00 mmol) and pb(NO3)2 (0.31gm 1.00 mmol)] was added to an ethanolic solution (0.35 gm 2.00 mmol) of the ligand L with stirring . The mixture was stirring for two hours during this time a precipitate was formed . Stirring was continued for one hour to ensure a complete reaction . The product in each case was filtered off, washed with hot water and dry under vacuum .The physical data of the ligand and complexes are given in (Table II)

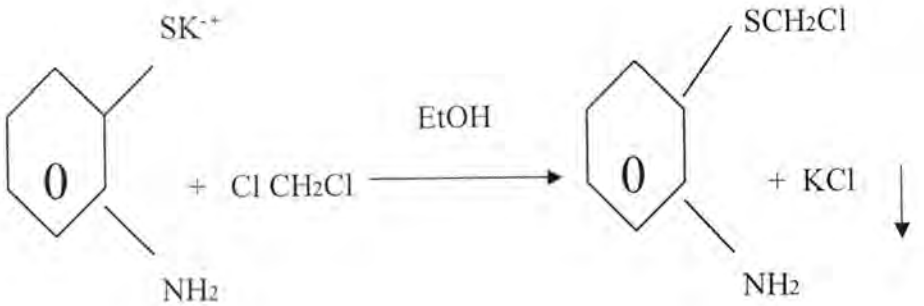
RESULTS AND DISCUSSION

Synthesis and characterization of the ligand aniline 2-thiomethylenechloride . The ligand (L) was considered one of derivatives compound of orthoaminophenyl thiol by the reaction of orthoaminophenyl thiol with methylene dichloride with molar ratio 1:1 in presence of one mole potassium hydroxide ;

(1)



(2)



oily brownish

Using a solution of KCl in water , and a little of solution brownish oily ligand in ethanol are applied to form silver chloride from adding silver nitrate solution to each of them . This clearly indicated that the oily brownish ligand include the one chloride and the other chloride was separated as KCl . The infrared of the ligand and its complexes. The infrared spectrum of the ligand in the KBr disc does not contain the υ (S – H) band which is present in starting material orthoaminophenyl thiol at (2500-2600) cm^{-1} region This indicate the displacement(SH)hydrogen of orthoaminophenyl thiol by means of -Cl-CH_2-. [7]

Furthermore new bands at (2931 cm and 2869 cm^{-1}) due to υ asym and υ sym C – H aliphatic and bands at (1470 cm^{-1}, 1430 cm^{-1}) which are due to bending Cl-CH2- [10]. Two stretching and one bending vibration (3448 cm^{-1}, 3355 cm^{-1} , 1604 cm^{-1}) are diagnostic of the primary amine . Peaks at (1249 cm^{-1} ,1026 cm^{-1}) are attributed to C – S . The infrared spectra of all complexes show ,the multibands in the range (3400-3300) cm^{-1} and split band at (1604 cm^{-1} ,1560 cm^{-1})suggesting the coordination through nitrogen atom of (NH2)group .Bands at (1249 cm^{-1} , 1026 cm^{-1} in the free ligand reappears in all complexes as broaden or split indicating the coordination through sulpher . Bands in the region (520 cm^{-1} ,440 cm^{-1}) which are due to M–N and M – S [12-16]. This account for N,S are coordinate[17] to the metal ion too . The infrared spectra data of the ligand and its complexes in (Table III).

The lead complex showed new band at 817 cm^{-1} which is due to nitrate ion coordinated

The UV – Visible spectrum of the ligand in DMSO solution exhibited strong absorption bands at 254.8 nm (39370 cm^{-1}) and (336.60 nm , 29708 cm^{-1}) .This may attributed to the $\pi - \pi^*$ and n- π^* transition[18] .

The UV – Visible spectrum for Co^{2+} showed[19, 20] two bands in the region (650 nm , 15385 cm^{-1}) and (800 nm , 12500 cm^{-1})are due to T1g ⟶ Eg and T1g ⟶ A2g .

The ratio of these two bands is 1.23 . In Fig . Tanabe – Suguno digram for Co^{2+} ion this ratio fits With Δ o/B =8 corresponds to E/B` = 16.5 .Since E/B` = 12.500 / B` =16.5 , B` = 757.57 cm^{-1} .Δ o/B = 8 , this gives values of E/B for the various transitions as follows

E/B	Transition	Calculated E (cm^{-1})
8	$^4T_{1g} \longrightarrow {}^4T_{2g}$	6060.5
15	$^4T_{1g} \longrightarrow {}^4A_{2g}$	11363.55
20	$^4T_{1g} \longrightarrow {}^4T_{1g}$	15151.40
25	$^4T_{1g} \longrightarrow {}^2A_{1g}$	18939.25

The two bands A2g and T1g are predicted close to the observed band at (12,500 , 15385) cm^{-1} The β for Co complex is 0.780 which is lower than the value of 971 cm for free Co ion ,implying there is some delocalization of the electrons from the Co ion to the ligand .

The UV – Visible spectrum for Ni^{2+} showed one band at (519 nm , 19267.8 cm^{-1}) which is due toA2g ⟶ E1g and for Cu appeared at 626 nm , 15974.4 cm is due to B1g ⟶ Eg

The UV – Visible spectra of Cd^{2+} , Hg^{2+} and pb^{2+} show only tail at (351 nm , 28490 cm+-1) , (456 nm, 21929.8 cm) , (400 nm , 25000 cm) , are due to charge transfer .

The UV – Visible spectra of Cd^{2+},Hg^{2+} and pb^{2+} complexes are located in the region (29411-33330)cm^{-1} due to charge transfer .

General appearance of these bands and their assigned were illustrated in (Table IV) .

The molar conductance of all complexes in DMSO were found to be law which suggested coordination of anion to the metal. (Table IV).

The μeff value of Co , Ni , Cu complexes (Table IV) are within the range(4.70 , 3.00 , 1.90) respectively for spin-free octahedral structures[21, 22] .

Study of complex formation in solution

The complexes of the ligand (L) with the selected metal ions(Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Hg^{2+} , pb^{2+}) were studied in solution using ethanol as solvent , in order to determine (M:L) ratio in the prepared complexes , following molar ratio method[23] . A series of solution were prepared having a constant concentration (c) 10^{-3} M of the hydrated metal salts and the ligand (L) .

The M:L ratio was determined from the relation ship between the absorption of the obsorbed light

and the mole ratio(M:L) found to be (1:2) .The result of complexes formation in solution were listd in table (I) fig(1)

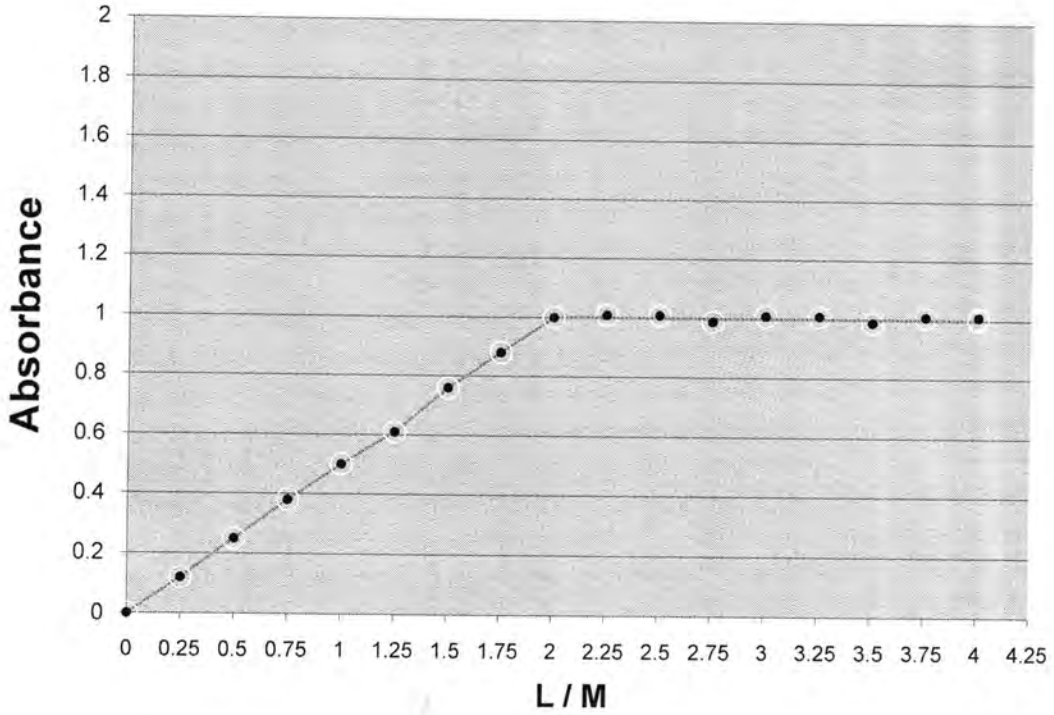


Fig -1:Continuous variation slop for Co^{2+} ions λ (325 nm)

The stability constant of the (1:2) (M:L) complexes was evaluated using the following equation

$$Kf = 1-\alpha / 4\,\alpha^3 c^2 \quad . (3)$$

$$\alpha = Am - As / Am \ldots\ldots (4)$$

where α^3 is the degree of the dissociation and c is the concentration of the complex (10^{-3} M) The absorpance of the solutions were measured at (λmax) of the maximum absorption , further more the molar absorpitivity (ϵmax) for the complexes were calculated from eq (5)

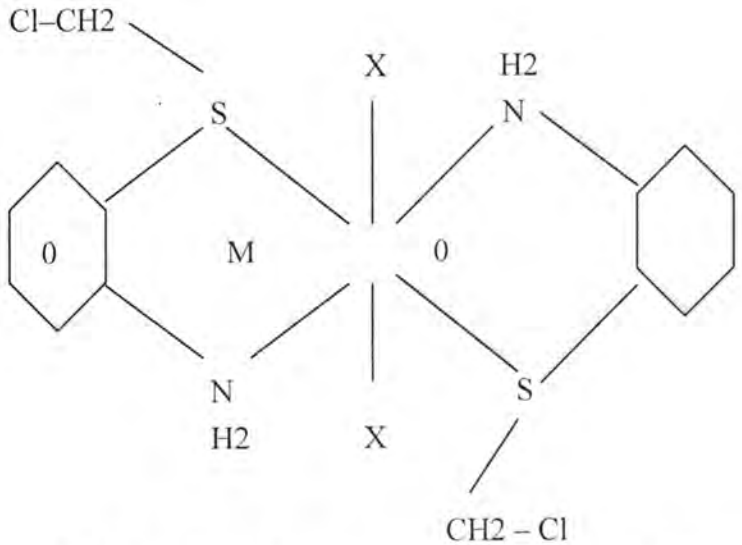
$$A = \epsilon max \,.\, b \,.\, c \quad . (5)$$

Where **A** is the average of three measurement of the absorption containing the same amount of metal ion and three fold excees of ligand and b is the depth of the quartz cell usually equal to 1 cm

Table (I) Stability constants , and molar absorpitivities of the complexes

NO	Compound	As	Am	α	Formation constant (Kf)	Єmax	λ max (nm)
1-	(L)C7 H8 NS Cl	–	—	—	—	—	—
2-	L2 – Co Cl2	0.50	1.01	0.504	9.68x10	1790	325
3-	L2 – Ni Cl2	0.20	0.31	0.354	3.64x10	2426	343
4-	L2 – Cu Cl2	0.36	0.53	0.320	5.18x10	2470	342
5-	L2 – Cd Cl2	0.22	0.50	0.560	6.26x10	1204	275
6-	L2 – Hg Cl2	0.27	0.41	0.341	4.14x10	2075	361
7-	L2 – Pb (NO3)2	0.25	0.60	0.583	5.25x10	2170	299

Where As is the average of three measurements of the absorption of solution containing a stoichiometric amount of ligand and metal ion
The structure of these complexes thus may be represented as follow ;



M(II) = Co , Ni , Cu , Cd and Hg X= Cl

M(II) = Pb X = NO3

Table -2: physical data for the ligand (L) and its complexes

NO	Compound	colour	m.p. °C or (D)	Yield %	M % Found (calculated)	Solubility
1-	(L)C$_7$ H$_4$ NS Cl	brownish	64°C	86	---	EtOH,CHCl$_3$,CH$_2$Cl$_2$ DMF, DMSO
2-	L$_2$ – Co Cl$_2$	Violent	(140) D	72	12.34 (12.36)	CH$_2$Cl$_2$,DMF,DMSO
3-	L$_2$ – Ni Cl$_2$	dark green	152 °C	68	12.32 (12.31)	DMF,DMSO
4-	L$_2$ – Cu Cl$_2$	Violent	126 °C	77	13.16 (13.20)	EtOH,CHCl$_3$,CH$_2$Cl$_2$ DMF,DMSO
5-	L$_2$ – Cd Cl$_2$	green	120 °C	75	21.23 (21.20)	DMF, DMSO CH$_2$ Cl$_2$
6-	L$_2$ – Hg Cl$_2$	dark green	(112) D	78	32.49 (32.45)	DMF,DMSO
7-	L$_2$ – Pb (NO$_3$)$_2$	dark green	126 °C	80	31.50 (31.53)	CHCl$_3$,CH$_2$Cl$_2$ DMF,DMSO

D = Decomposition

Table -3: The IR spectra data of the ligand (L) and its complexes

NO	Compound	(N – H) cm^{-1}	(C-H)cm^{-1} Ar.	(C-H) cm^{-1} Ali.	(C-S)cm^{-1}	(M-N) cm^{-1}	(M-S) cm^{-1}	NO_3^- cm^{-1}
1-	(L)C- HaNSCl	3448(asym) m. br 3355(sym) m. sh 1604 s.s.	3186 , 3062(m.s)	(2931 asym)m.s (2869 sym)m.s 1470w.b , 1430m.s	1249 m.b 1026 m.b	—	—	—
2-	L_2- $Co\,C_{l_2}$	(3440-3340) m. br 1604 s.s , 1558 m.s	3168 , 3062(m.b)	2900w.s , 2805w.s 1470s.s , 1430m.s	1244m.b 1020 m.b	520 m.s	440 m.s.	
3-	L_2- $Ni\,Cl_2$	(3395-3319) m. br 1600 s.s , 1550 m.s	3124 , 3090(s.s)	2914m.s , 2800w.s 1470s.s , 1430m.s	1245 m.b 1025 s.s.	520 m.s	437 m.s.	—
4-	L_2- $Cu\,C_{l_2}$	(3400-3300) m. br 1600 s.s , 1550 s.h.	3110 , 3048(m.s)	2931m.s , 2812w.s 1470s.s , 1430m.s	1245 s.s. 1025 s.s.	520 m.s	440 m.s.	—
5	L_2 CdC_{l_2}	(3375-3300) m. br 1600 s.s , 1550 m.s	3102 , 3050(m.s)	2900m.s , 2812m.s 1470s.s , 1430m.s	1249 m. b 1024 m.b	519 m.s	131 m.s.	—
6-	L_2- $Hg\,C_{l_2}$	(3400-3315) m.br 1600 s.s , 1550 m.s	3100 , 3045 (m.b)	2950m.s , 2825 m.s 1470s.s , 1430m.s	1240 m.b 1026m.b	520 m.s	440 m.s.	—
7-	L_2- $Pb\,(NO_3)_2$	(3380-3300) m. br 1600 s.s , 1550 m.s	3190 , 3055(m.b)	2970m.s , 2885m.s 1470s.s , 1430m.s	1240 m.s 1042 m.s 1026 m.s	517 m.s	437 m.s.	817(m.s)

s = sharp , br = broad , m = medium , s =strong , w = weak
Ar. = aromatic , Ali. = aliphatic , asym = asymmetric , sym = symmetric , sh = shoulder

Table (4): U.V – Visible spectra data of the ligand (L) and its complexes

NO	Compound	λ (nm) $\bar{\upsilon}$ cm^{-1}	Assignment Bands	Λ $s.cm^{-1}$ mol^{-3} DMSO (10^{-3} M)	μ_{eff} (B.M)
1-	(L)$C_{13}H_8NSCl$	39370 (254.8) 29708 (336.6)	$\pi - \pi^*$ $n - \pi^*$	—	—
2-	$L_2 - Co\,Cl_2$	15385 (650) 12500 (800)	$^4T_{1g} \longrightarrow {}^2E_g$ $^4T_{1g} \longrightarrow A_{2g}$	9.32	4.70
3-	$L_2 - Ni\,Cl_2$	19267.8 (519)	$^3A_{2g} \longrightarrow {}^3E_g$	10.30	3.00
4-	$L_2 - Cu\,Cl_2$	15971.1 (626)	$^2B_{1g} \longrightarrow {}^2E_g$	6.82	1.90
5-	$L_2 - Cd\,Cl_2$	28490 (351)	charge-Transfer	5.69	–
6-	$L_2 - Hg\,Cl_2$	21929.8 (456)	==	7.11	–
7-	$L_2 - Pb(NO_3)_2$	25000 (400)	==	6.40	–

B.M = Bohr Magnation

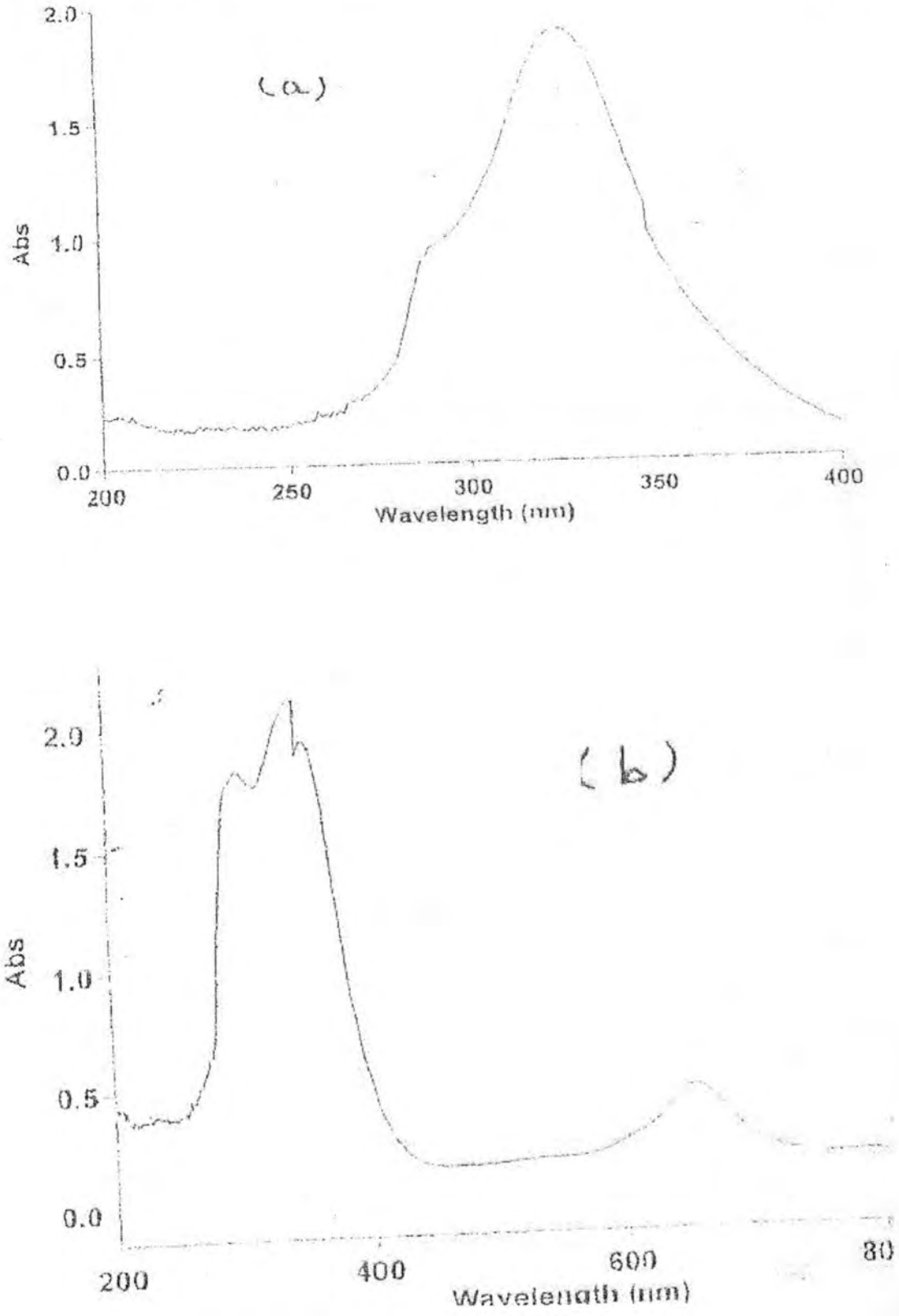


Fig-2: UV Visible spectra of (a)L and (b)L_2CoCl_2

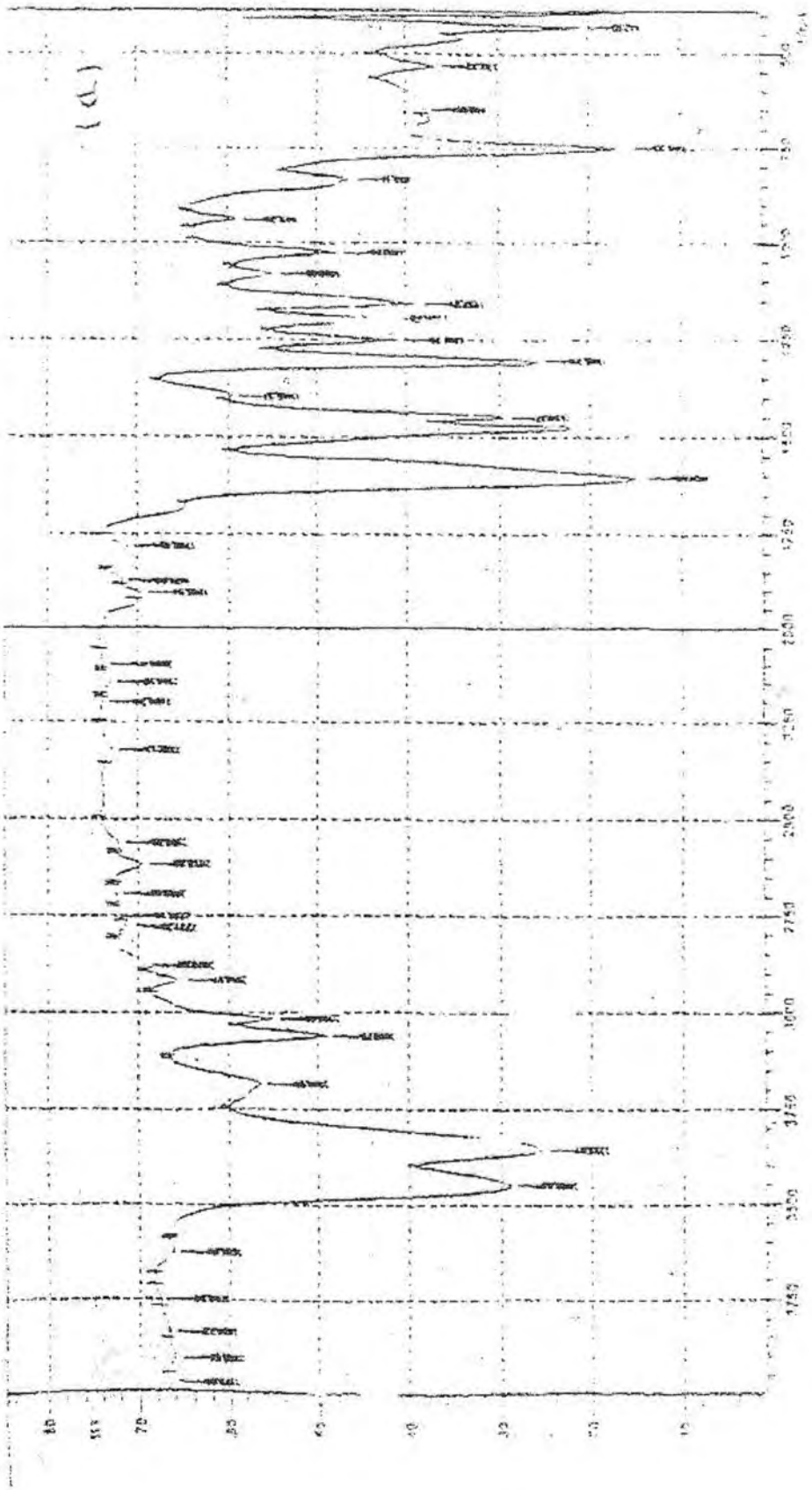


Fig -1: Infrared Spectra of L

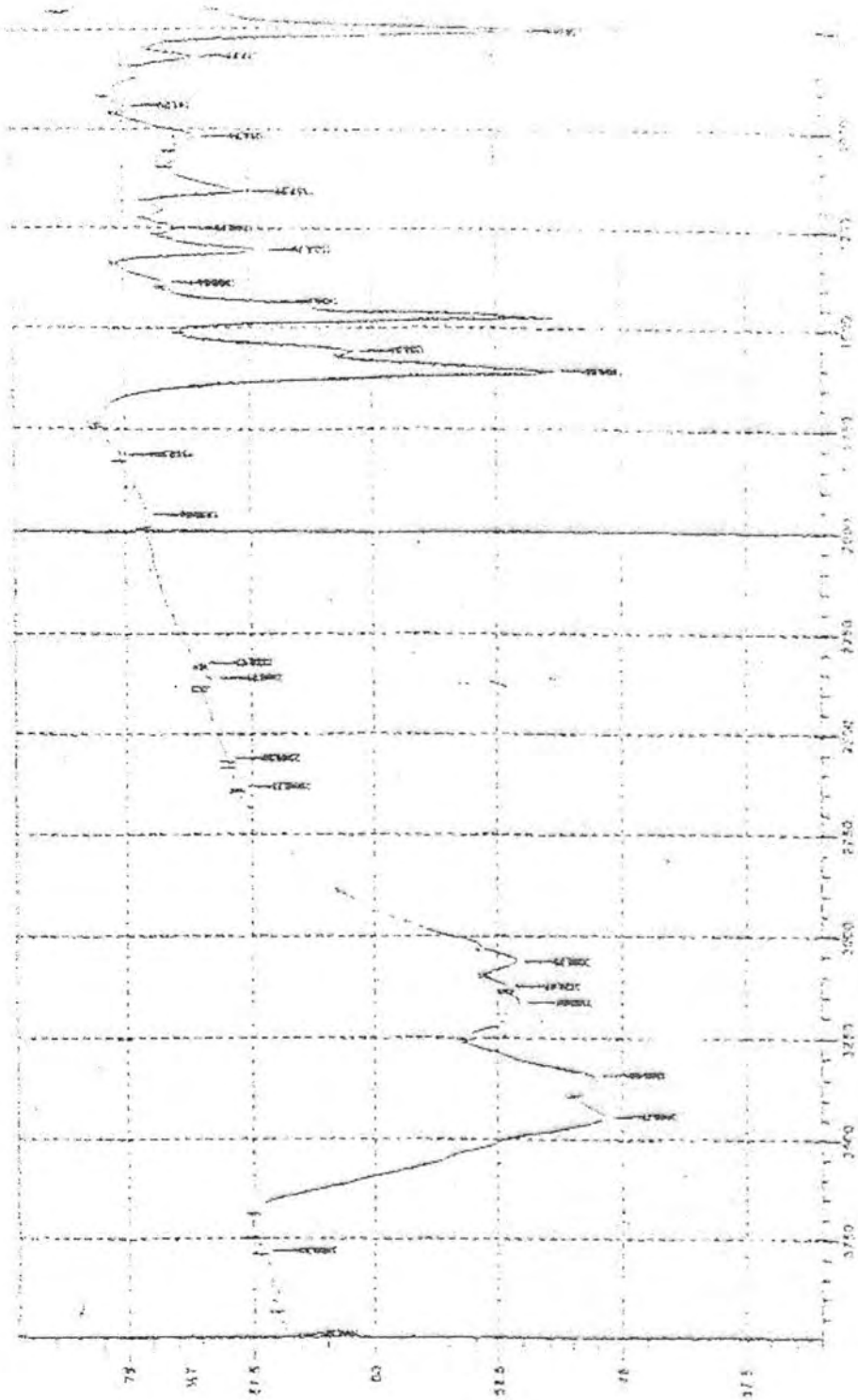


Fig -2: Infrared Spectra of L_2CoCl_2

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Production of Eydrogen By Ca -I Cycle Using Gas-Solid Thermockemical Reaction

Saad T. S. AL-Ashab[1] and Ramzie R. AL-Ani[2]
[1]University of Technology Applied Science Department
[2]Chemistry Department, College of Science, Mustanslriah University
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الخلاصة

باستخـــدام نموذج مختبري لإنتاج Ca - I تم تطبيق دورة أنشطار الغاز الهيدروجين . وبالاستخدام الأمثل لحبيبات السيراميك (الكاؤلين) المفخور CaCo3 , Al2O3والمحتوية على مكونات المواد المتفاعلة بنسب متفاوتة وبإضافة الكرافيت لزيادة المسامية والمساحة السطحية لحبيبات السيراميك لقد تم أجراء التفاعل الغاز – الصلب ، بأمرار غاز اليود على الحبيبات وبظروف مختلفة ، وجد أن أنتاج التفاعل من غاز الهيدروجين قد أزداد بصورة ملموسة وبمعدل 0.38 – 0.46 لتر\ ساعة ضمن النموذج المختبري . ان هذه النتائج من هذا البحث تؤيد أمكانية أجراء نفس النموذج باستخدام المركزات الشمسية لأجراء التفاعل بدل الطاقة الكهربائية نظراً لبساطة النموذج .

ABSTRACT

The Ca-I water splitting cycle was demonstrated on laboratary scale to produce hydrogen . In order to get the best ideal conditions , ceramic pellets were made from the reactant components with different proportions of $CaCO_3$, Al_2O_3, Kaolin and Graphite to increase the porosity of the ceramic . A gas-solid reaction were involved in this sample cyclic system, in which gases were only passed through the reaction . The use of ceramic pellets positively affected the sufficiency of hydrogen production rate from 0.38.*L/h to about 0.46 L/h.

Results of this work indicate the possibility of using solar concentrators instead of the electric oven in splitting water into hydrogen and oxygen gases.

INTRODUCTION

The Ca-I cycle was first proposed by Fujii and others [1] . The Cycle reaction were expressed as:

$$6CaO + 6I_2(C) \xrightarrow{450-650K} 5CaI_2 + Ca(IO_3)_2$$

$$Ca(IO_3)_2(C) \xrightarrow{600-900K} CaO(C) + I_{2(g)} + 2.5\ O_2$$

$$5CaI_2(C) + 5H_2O \xrightarrow{650-1000K} 5CaO(C) + 10HI$$

$$10HI_{(g)} \xrightarrow{550-800K} 5H_{2(g)} + 5I_{2(g)}$$

The developing of this cycle was carried out by a laboratory bench-scale continous hydrogen production model which was constructed to produce 0.38 L/h of hydrogen [2].

Some problems has been arised from this continuous model plant due to the liquid cyclization, which was oparated by using high pressure (30atm). The solution reactions caused the formation of a high amount of slurry .Therefore, in this work the reaction wasmodified to a solid-gas reaction system in order to overcome some of these problems.

The iodine and water vapour was the only gases which passed .through the reactor . Ceramic pellets were made from reaction .material with different components ratio to get the desired pore size and reaction activity for these pellets.

The reactions of the four stages were thermally analysed during the reactions by a specially modified thermal analysis instrument.X-ray powder diffraction pattern of reacted and unreacted pellets, was determined. A porositymeter was used to measure the plugging of the pores of the pellets after reaction.Such pluggings have affected the reactivity of the cycle after few reactions.

METHOD AND MATERIALS

Thermo balance type metler TA3000 system was used for the detection of the charge in weight of the reactants.lt was modified to suit the type of reaction in this work . A quartz tube was employed in the oven of 8 mm I.D., and a quartz holder for the balance was used instead of the steel one.The inlet of N_2 gas was directed to pass through a solid iodine container and in the other stage through a water steam genaration (Fig.1). The outlet of gases formed was passed through 10% NaOH solution trap to get rid of HI and I_2 produced .

The ceramic pellets [3], were prepared from $CaCO_3$, Al_2O_3, Graphite and Kaolin with defferent component ratios (Table 1) , depending on the required size of pores and ratio of the reaction . The ceramic was shaped as a pellets, 5 mm in diameter and calcinated in furnace at 1373 K for 24 h, then it was left in a vacuum oven at 623 k to prevent the absorption of $C0_2$ and H_2O.

A mercury porosity meler was used to measure the size and diameter of the pours.the pore size was found to be 1-3 of the solid ceramic . the active pore size was determined by measuring the size of the pellets befor and after grinding Similarly the plugging of the pore of the ceramic pellets was also measured by the same instrument using the same procedure (Table 1).

The kinetics measurement was carried out by suspending ceramic pellets in a ceramic basket which was placed in the furnace of the therm obalance (Fig. 2). The changing in the weight of the pellets was

detected during the reaction stages, where I_2 vapour with N_2 was were passing through to convert CaO to CaI_2 .In the second stag N_2 gas saturated with water was passed to hydrolys CaI_2 to cao and HI. Both reactions were run at different temperatures in order to improve the results (Table 2), and
(fig. 3,4). .

The solids were analysed by x-ray diffraction before and after each reaction for determining percent yeild . The H_2 gas was analysed by gas chromotography (Pye unicm 304) using molecular sieve coloum (120) cm long and (5) mm diameter at 60°C ,(Fig. 5) .

On basis of the above experimental set up, small bench—scale plant was constructed . The plant consists of two furnace tubes , the first contains a ceramic pellets with CaI_2 at 650-950 K, and the second one contain pellets with CaO components at 450-650 K. N_2 gas saturated with water steam was passed through the first furnace , and N_2 gas saturated with I_2 vapour was passed through the other. The hydrogen gas produced was collected and analysed as shown in (Fig. 2).

RESULTS AND DISCUSSION

The thermal analysis results showed that the gas-solid reaction needed a higher temperature than that of the solution reaction [2] . In the present work the first stage , iodine vapour reacted with, as high as 50-85% of CaO component in the ceramic pellets depending on the temperature of the furnace which ranged between 500 - 700 K (fig. 2). The higher the temperature of the reaction , the more CaO component reacted. This was caused by the ability of I_2vapour to enter the pores of the pellets . The unreacted CaO component corresponded to the unactive pores of the pellets. After repeating the cycle for three times the persence of the converted CaO to CaI_2 was stable at a level of about 62% of CaO in the ceramic pellets .

The second stage was accomplished by passing N_2 gas saturated with water steam over the ceramic pellets containing CaI_2 at 560-800K The CaI was hydrolysed to CaO completely producing HI gas . Consequently , hydrgen gas mixed with HI gas was evolved depending on the temperature of the furnace . About 22-28% of the HI gas split in to hydrogen and iodine when temperature reached 650K .

A traces of oxygen were detected in the gas mixture due to the decomposition of the $Ca(IO_3)_2$. [2]. The 0_2 gas evolved decreased as the reaction temperature of CaO with I_2 increased. This was due to the decrease in the $Ca(IO_3)_2$ produced .

The H_2 gas was produced from HI decomposition at a maximum rate of 0.52 l/ h when the reaction temperature reached 973K . After few cycles , hydrogen production was stable at a rate of 0.46 1/h .

The efficiency of the cycle reactions was calculated according to Funk and Rreiustrom method [4] . This involved the dividing the actual energy needed for splitting water to H2 and O2 gas by the actual heat input of the cycle . All of the heat input was detected thermo analytically , using accurate weight of reactions . The thermal efficiency of the cycle was estimated to be 29.3% which represents the average results of five cycles .

In this study a. thermochemica] hydrogen prodution process using Ca-I cycle was developed . A gas-solid reaction was introduced to overcome the; problem which was arised from the solution reactions.

The kinetics of the bromination of CaO and the hydrolysis of the Ca-l pellets was measured by thermobalcrice. The chemical conversion of the reactions was largly improved due to reducing the amount of lost heat. The reactivity of the pellets was measured and found to be affected by the porosity (pore size) of the pellets .

Changing of the ratio of the reaction components in the ceramic pellets did not greatly affect the hydrogen gas production However , the only main effect was due to the size and diameter of the pores of the pellets.

Hence, ceramic pellet pores are thought to be the key for the reactivity of reaction . The latter is our next investigation.

Table -1: Conversion and hydrolysis of CaO , CaI_2 ceramic .

C / CaO* Conr. %	Pores size $10m^2$ / Kgm	Converision → % CaI_2	Hydrolysis → % CaO
5	0.44	37	81
7.5	0.50	46	85
10	0.60	53	95
12.5	0.65	57	100
15	0.82	62	100
20	0.83	62	100

*** Graphite / $CaCO_3$ After calcinated**

Table -2: Hydrogen prediction (mole)

Temp. K	I_2	H_2	Total I_2 in KOH
300	0.019	----	-----
350	0.026	Trace	Trace
370	0.037	Trace	Trace
400	0.040	0.0011	0.010
420	0.048	0.0020	0.011
450	0.077	0.0042	0.013
500	0.102	0.0087	0.015
550	0.109	0.010	0.018
600	0.107	0.0102	0.019

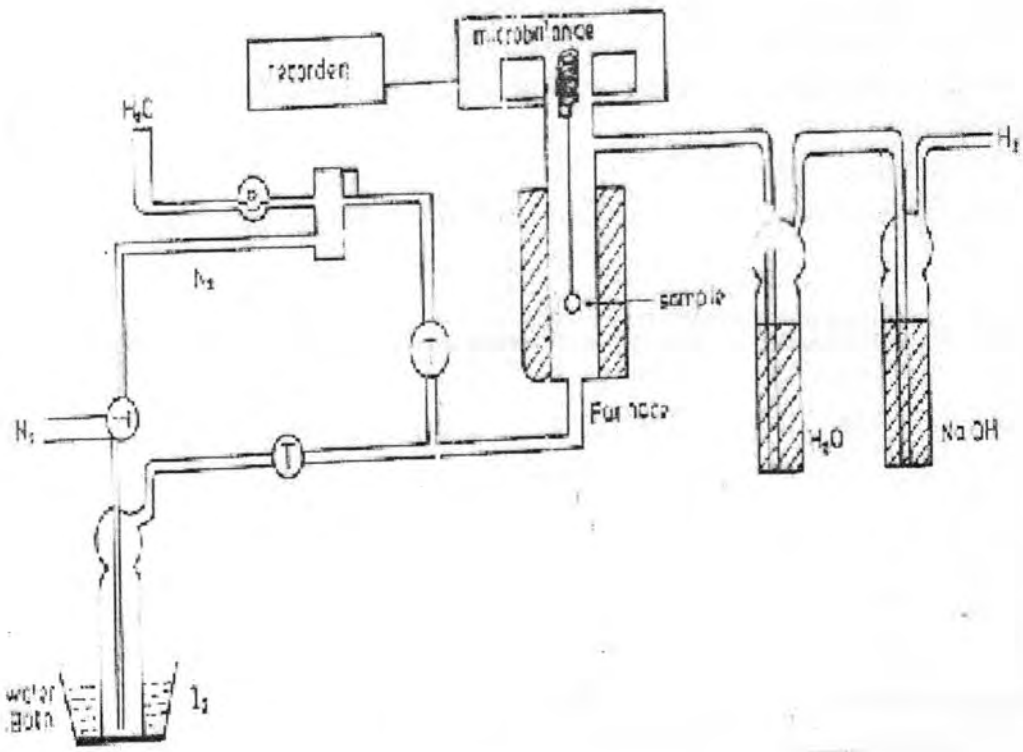

Fig. -1: Experimental set – up for kinetic measurement .

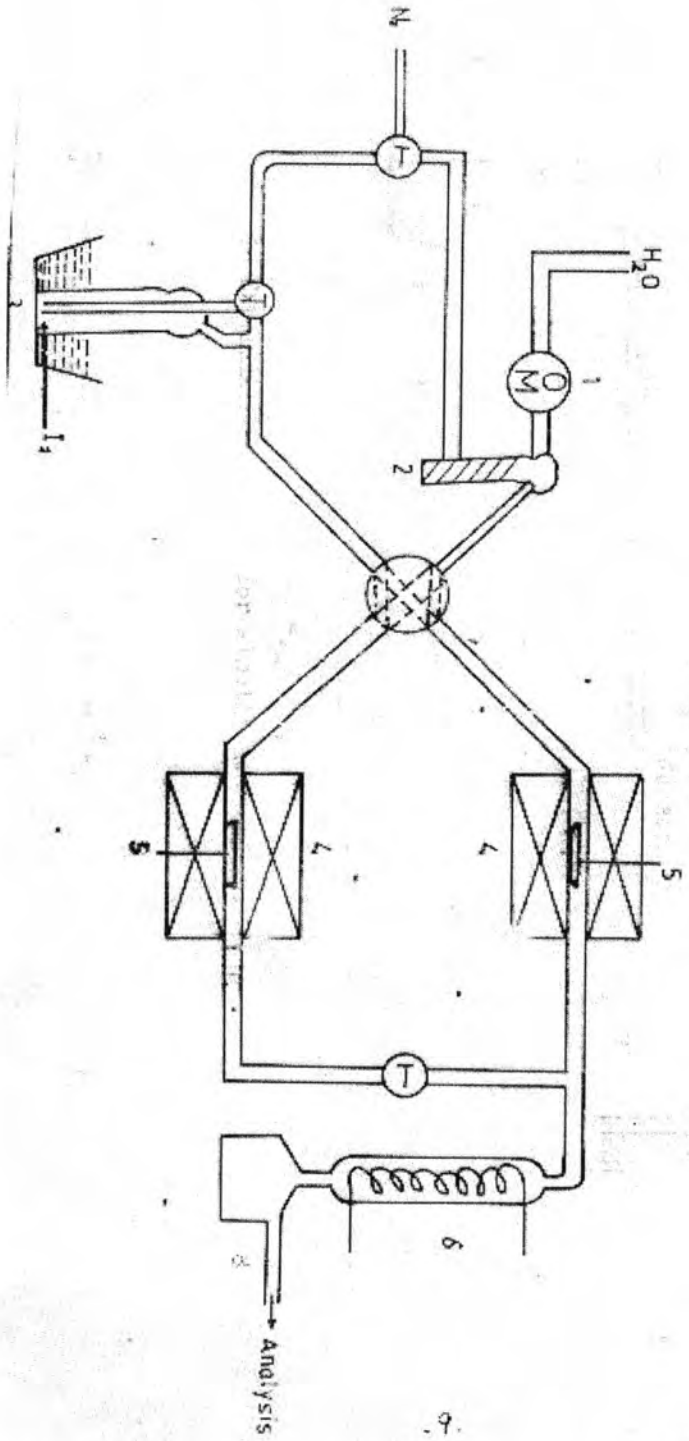

Fig .-2: Laboratory bench scale plant , 1- Rolling pump . 2- Evaporator . 3- Water bath . 4- Tube furnace . 5- Ceramic sample . 6- Condenser .

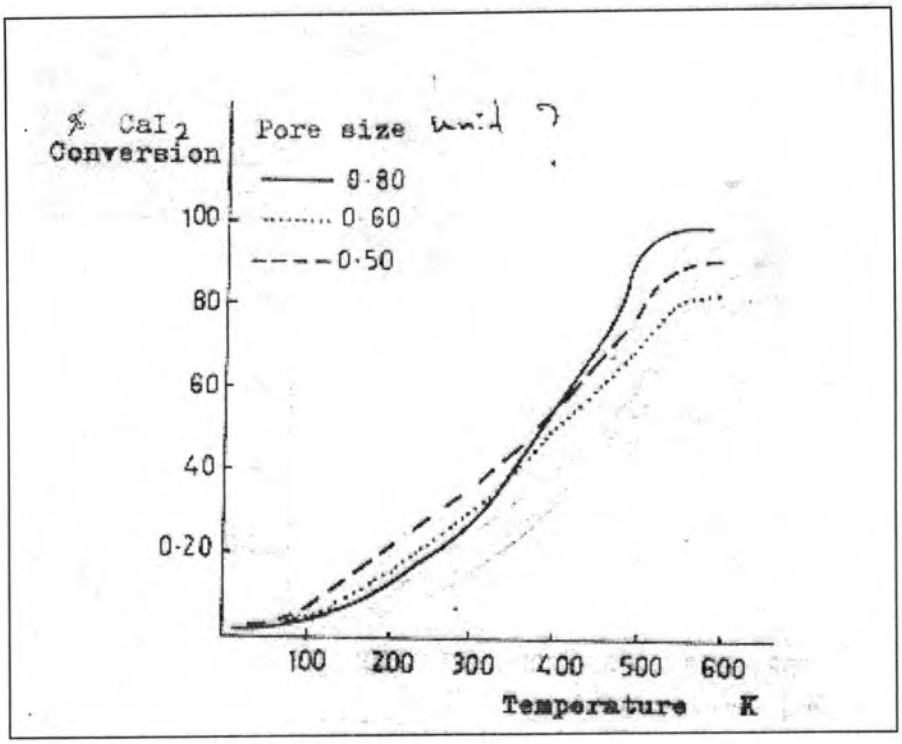

Fig. -3: CaI_2 hydrolysis to CaO

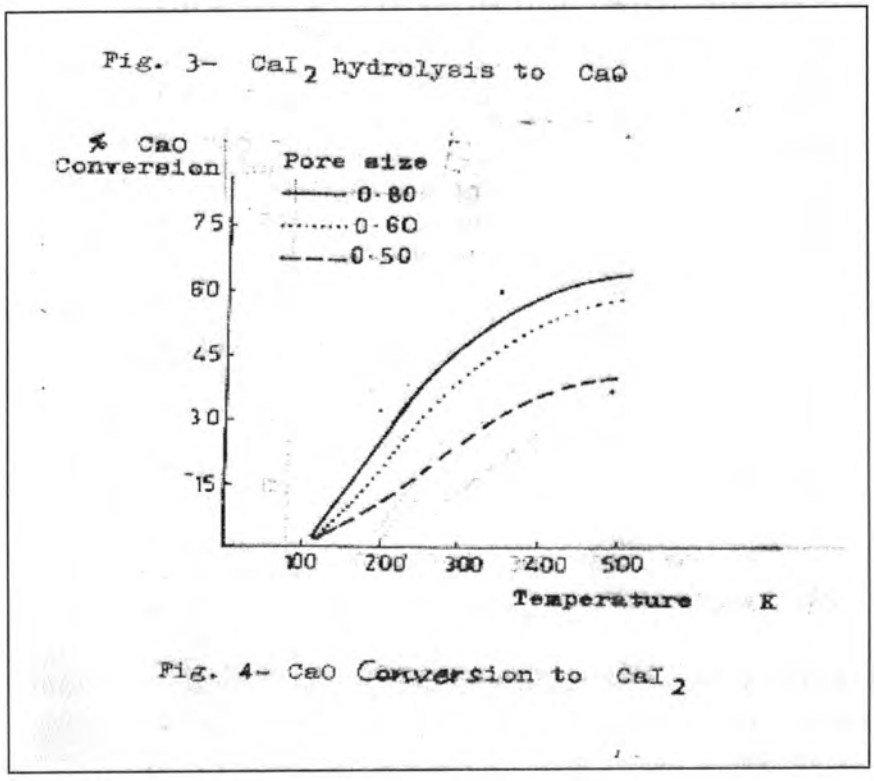

Fig . -4: CaO Conversion to CaI_2

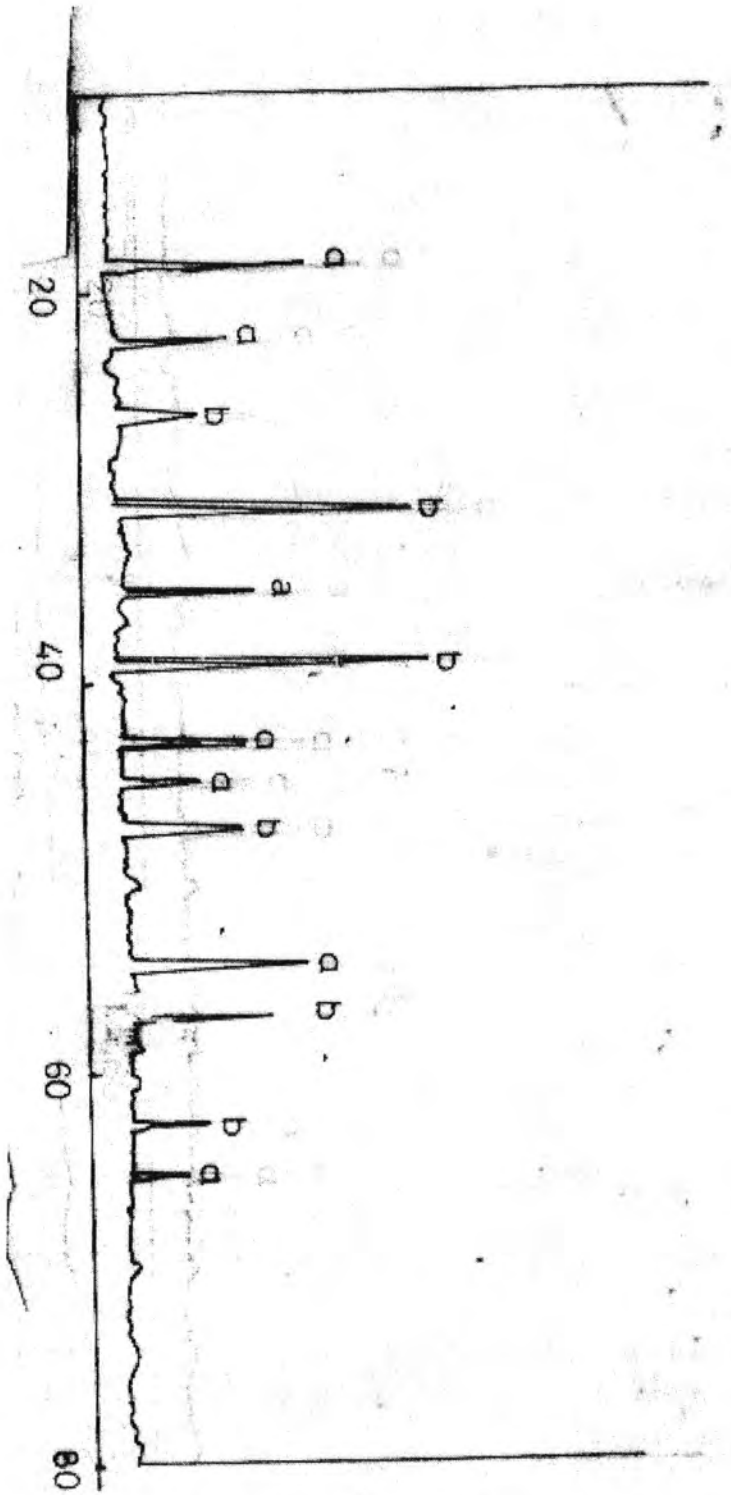

Fig.-5: X-Ray diffraction pattern, a-CaO, b-CaI_2

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Synthesis of New Nitrogenous Coumarin Derivatives

Redha I. Al-Bayati , Abdul-Hussain K. Sharba, Mazin J. Habib
Department of Chemistry , College of Science , Al-Mustansirya University
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الخلاصة

يتناول البحث تحضير سبعة عشر مركبا نيتروجينيا جديدا مشتق من الكيومارين و 6-نايتروكومارين . والتي يتوقع لها فعالية بايولوجية ودوائية، اجري البحث بخطين رئيسيين: تضمن الاول تحضير مجموعة من قواعد مانخ المشتقة من 6-نايتروكيومارين،اما الثاني فتضمن تفاعل 6- نايترو كيومارين مع كلوريد الكلورو استيل ثم معاملة الناتج مع امينات ثانوية مختلفة لينتج مشتقات نايتروجينية جديدة ل 6- نايترو كيومارين. شخصت المركبات المحضرة باستخدام طيف الاشعة تحت الحمراء والاشعة فوق البنفسجية وباستخدام طيف الرنين النووي المغناطيسي وبالتحليل الدقيق للعناصر.

ABSTRACT

In this work seventeen nitrogenous compounds derived from coumarin and 6-nitrocoumarin which have a probable biological activity have been prepared .. Two main lines in this work, the first one includes preparation of "Mannich Bases" for 6-nitro cournarin, the compounds [4a-f]. The second line includes preparation of new serous of nitrogenous derivatives for 6-nitro coumarin . the compounds [7a-cl. The structure of the synthesized compounds has been deduced from their UV, IR ,H-.NMR spectrum and C.H.N. analysis.

INTRODUCTION

Coumarin and its derivatives are a class of organic compounds that have much attention, because of their biological aetivites.The benzopyran-2-ones (coumarin) compounds are quit easily attacked by nucleophilic reagents. some of nucleophilic reaction involve ring opening and occasionally recyclized into another ring. So a number of nitrogenous coumarin derivatives were prepared by "Mannich reaction" .the products of this reaction called "Mannich Bases" which are a nitrogenous molecules prepared by the condensation of compounds having an active hydrogen with formaldehyde and primary or secondary anhines. The increasing popularity of the Mannich reaction has been fueled by the Ubiquitous nature of nitrogen in drugs(I) and natural products as well as by the potential of this multicomponents reaction to generate diversity(2).So a large number of acetylenic amino derivatives having the general formula :

$$-CH_2-C\equiv C-CH_2-N\diagup\diagdown$$

have been prepared using Mannich reaction in order to compare their biological activity with the different structures of this derivatives. Also in this work, A number of acetamide derivatives for 6- nitro coumarin,which have a probable biological activity have been synthesized.

MATERIALS AND METHODS

Instrumentation:

a. Melting points have been determined in open capillary tubes in an electrically heated metal block apparatus and are uncorrected.
b. Infrared spectra are obtained using a Pyc-Unicam SP3-I00 spectrophotonieter. Using KBr discs.
c. Ultra-violet spectra obtained using a Cinta-5-Gbes scientific equipment.
d. Proton NMR spectra have been performed by spectra laboratories in Hanover University (Germany) on a 400 Mhz, with TMS as internal standard.
e. Micro-analysis have been performed by spectra laboratories in Jordan University (Jordan).

Synthesis of compounds

Synthesis of 6-nitro coumarin [1] (10)

This compound was *prepared according to the* method reported in the literature(l0).m.p. 140 -141 C.

Synthesis of 1-amino quinolin-2(IH)-one [2a] 1-amino-6- nitro quinolin-2-(1H)-one [2b](3,4)

A solution of coumarin or 6-nitro coumarin (0.035 mole) and hydrazine hydrate (95%) *(0.035* mole. 1.1 g.) in absolute ethanol was refluxed for (24 hrs.). the solvent was concentrated and the separated solid product was filtered and washed with cold ethanol.

The precipitate was recrystallized from ethanol-water (1:1).

Compound[2a1 mp 130-132c (Lit.131-132),55% yield.. [2b] mp 166-168c .62%.

General Procedure for Preparation of 1-(prop-2-ynyl amino) quinolin-2(lH)-one [3a] and 6-nitro-l-(prop-.2-ynylamino) quinolin-2(1 H)one [3b]

A mixture of compound [2a or 2b] (0.0075 mole) in (20 ml) of absolute methanol and (1.1 ml) of triethyl amine was stirred tr (10 min), then propargyl chloride *(0.0075* mole, 0.56 g.) was added dropwise within (15 min.), the mixture was refluxed for (3 hrs.). After that, the reaction mixture was poured slowly into ice water (20 ml). The precipitate was filtered and recrystallized from ethanol-water (2:1). Compound [3a] mp 175-l77c ,52% yield. [3b] mp l83-l84, 58%.

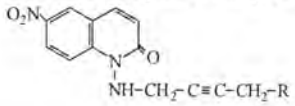
General Procedure for **Preparation of 1-{[4-(dialkylamino)but-2ynyl] amino}-6- intro quinolin-2(1H)-one** [4a-f]

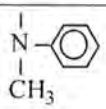
A mixture of compound [3b] (0.005 mole) and formaldehyde (0.005 mole) in (10 ml) of dioxane and cuprous chloride (CuCl) (0.1 g.). were heated in **a** round bottom flask to (70**C**)

At this temperature (0.005 mole) of the suitable secondary amine was added dropwise to the above mixture, which is then heated for (2 hrs,) at *(70c).*the mixture was cooled, and poured on ice water (20 ml). The precipitate was filtered and recrystallized from the appropriate solvent, see table **(1)**

The physical properties are listed in table (1).

Table -1: Physical properties of compounds [4a-f]



Comp. No.	R	M.p. °C	Yield %	Purification solvent	Molecular formula
4a	$-N(C_2H_5)_2$	190-192	58	Ethanol-water (2:1)	$C_{17}H_{20}N_4O_3$
4b	$-N(isobu)_2$	203-205	55	Ethanol-water (2:1)	$C_{22}H_{28}N_4O_3$
4c	$-N(CH_2CH_2CH_3)_2$	195-196	61	Ethanol-water (2:1)	$C_{19}H_{24}N_4O_3$
4d	$-N(CH_2ph)_2$	221-223	65	Chloroform	$C_{27}H_{24}N_4O_3$
4e		189-191	61	Benzene	$C_{17}H_{18}N_4O_3$
4f		199-201 **(decompose)**	57	Benzene	$C_{19}H_{18}N_4O_3$

Preparation of 1-[(4-pyrrolidine-1-ylbut-2-yny amino] quinolin-2(1H)-one [5]

This compound was prepared from the reaction of [3a] (0.0025 mole, 0.49 gm) with pyrrolidine (0.0025 mole, 0.177 gm), in an analogous manner to the preparation method of compounds [4a-f].

The precipitate was recrystalized from ethanol-water (mp 186-188c 53% yield).

Preparation of N-(6-nitro-2-oxoquinolin-1(2H)-yl)-2-acetamide derivatives [7a-e]:

Preparation of 2-chloro-N-(6-nitro-2-oxoquinolin-1(2H)-yl)-2-acetamide [6]:

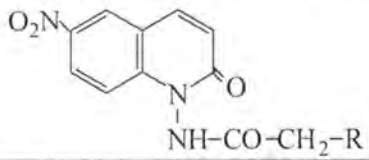
To a mixture of compound [2b] (0.03 mole, 6.15 gm) in benzene (30 ml) and triethyl amine (3 ml), chloro acetyl chloride (98 %) (0.03 mole, 3.39 gm) was added gradually and refluxed for (2 hrs.). The excess of benzene was distilled off under vacuum, and the precipitate was washed with sodium carbonate (2 %) then with distilled water, and recrystallized from ethanol.

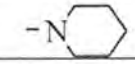
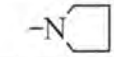
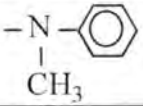
General procedure for Preparation of N-(6-nitro-2-oxoquinolin-1(2H)-yl)-2-acetamide derivatives [7a-e]

To a solution of compound [6] (0.01 mole, 2.81 gm) in ethanol (20 ml), an appropriate secondary amine (0.03 mole) was added, the mixture was refluxed for (6 hrs.).

The excess of ethanol was removed under vacuum, and the precipitate was washed with sodium carbonate (2 %) then with distilled water, and recrystallized from the appropriate solvent, see table (10).
The physical properties of compounds [7a-e] are listed in table (2).

Table- 2: Physical properties of compounds [7a-e]



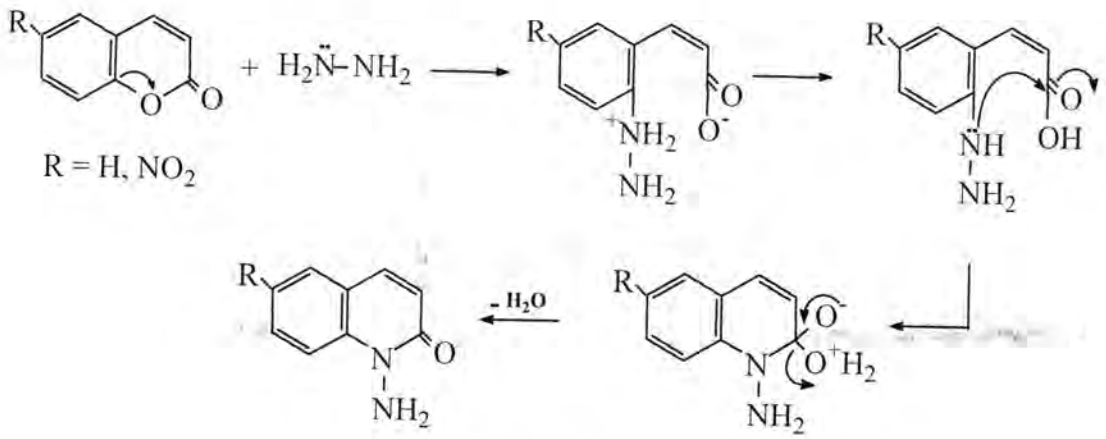
Comp. No.	R	M.p. °C	Yield %	Purification solvent	Molecular formula
7a	$-N(CH_2CH_3)(CH_2CH_3)$	210-212	70	Ethanol	$C_{15}H_{18}N_4O_4$
7b		219-220	61	Ethanol-water (2:1)	$C_{16}H_{18}N_4O_4$
7c		181-182	56	Ethanol-water (2:1)	$C_{15}H_{16}N_4O_4$
7d	$-N(nBu)(nBu)$	213 (decompose)	58	Ethanol-water (2:1)	$C_{19}H_{26}N_4O_4$
7e		221 (decompose)	48	Acetone-water (1:1)	$C_{18}H_{16}N_4O_4$

RESULTS AND DISCUSSION

For the synthesis of the targeted nitrogenous derivatives of coumarin , the reaction sequences are outlined in scheme (4).

Coumarin and 6-nitro coumarin were converted to the N-substituted-2-quinolone derivatives by reaction with hydrazine or primary amines (3,4). Thus compounds [2a and 2b] were prepared by the reaction with hydrazine with coumarin or 6-nitro coumarin [1].

The nucleophilic reaction of coumarins with hydrazine may proceeds through ring opening of the pyron ring and recyclized into the product (5) as shown bellow:



Scheme (1)

This reaction proceeds by attack of the nucleophile to the carbon in position (9) , causing ring opening, then recyclize to form the corresponding 2-quinolone.

The structure of the synthesized compounds have been characterized and identified by U.V. , I.R. and H-NMR spectrum. The I.R. spectrum of compound [2a and 2b] table 3, shows an absorption band at (3400 cm^{-1}) due to (NH_2) stretching vibration, and a band at (1660 cm^{-1}) for amide (C=O) of 2-quinolone, which appeared at (1750 cm^{-1}) in the coumarin compound.

The success of the reaction has been confirmed by comparing between the absorption band for (C=O) of compound [2] and (C=O) of coumarin, also by appearance of (NH_2) stretching vibration band at (3400 cm^{-1}). The spectrum also shows all the absorptions for substrate molecule, table 3.

The U.V. spectra of this compound table 3, has λ_{max} (MeOH) at (277.0 nm) due to (π-π^*) transition.

The ^{1}H-NMR spectrum of compound [2b], shows the following signals:

(d, H3, H) δ_H = 6.3 ppm
(d, H4, H8, 2H) δ_H = 7.5 ppm
(d, H5, H7, 2H) δ_H = 7.7 ppm
(d.d., NH_2, 2H) δ_H = 7.2 ppm
(d = doublet, d.d. = doublet doublet)

The splitting of NH_2 signal may be due to the presence of hydrogen bonding between NH_2 proton and carbonyl oxygen.

The C.H.N. analysis confirmed the structure of compounds [2a and 2b], table7

The data obtained for the minimized geometry, i.e. bond length, bond angle, bond twist angle (bond torsion), were calculated using semi-empirical AMI module in the ACD/Labs products. The determined bond angle and twist angle (the appendix, data 3-1) and the 3D-geometrical for the unsubstituted coumarin (structure-1) indicate that this molecule is planer, which is in a quite agreement with the published results (5,6).

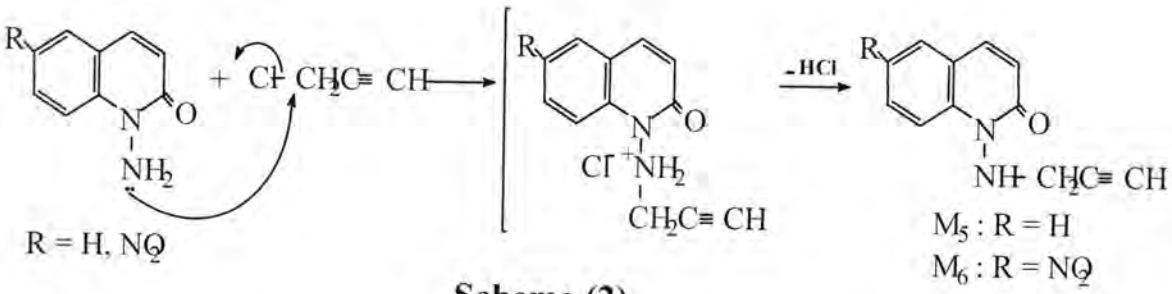
Substitution of (O) in coumarin by hydrazide group to form 1-amino quinolin-2(1H)-one [2a] (structure-2), theoretical calculation shows no appreciable change in the geometrical properties of the coumarin molecule by the presence of 1-hydrazide group.

The 1-amino group is present in the same plane of the molecule, the twist angle of (C_3-C_2-N_1-N_{11}) = 180° and (C_5-C_6-N_1-N_{11}) = 180°.

Compounds [3a and 3b] are key intermediates to the synthesis of many Mannich bases that are prepared in this work. Compounds [3a and 3b] have been prepared by treatment of equimolar quantities of the corresponding 1-aminoquinolone with propargyl chloride in presence of triethyl amine.

This reaction is indicated by nucleophilic attack of the most nucleophilic nitrogen of hydrazide compound on the sp3 carbon of propargyl chloride, via a nucleophilic substitution reaction [7].

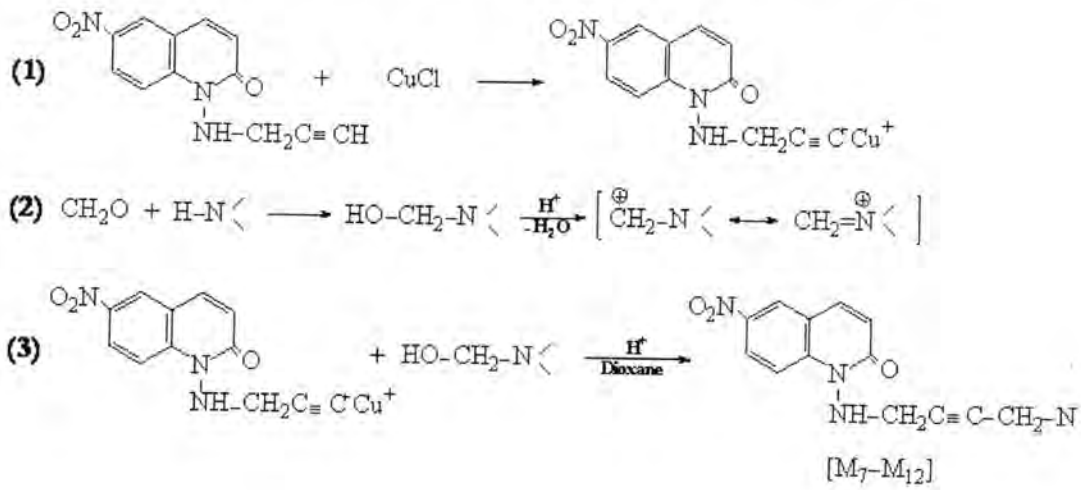
The mechanism of the reaction is believed to be as in scheme (2):



Scheme (2)

The I.R. spectrum of compound [3a], table (4), shows absorption band at (1650 cm^{-1}) for ($\nu_{C=O}$) (amide), (3300 cm^{-1}) for (NH) stretching vibration, (3250 cm^{-1}) for (≡C-H) stretching vibration and (2150 cm^{-1}) for (-C≡C) asymmetrical stretching vibration. Table 4 also lists the absorption bands for compound [3b]

compounds [4a-f] have been obtained by treatment of compound [3b] with the corresponding secondary amines in the presence of formaldehyde and dioxane as a solvent with catalytic amount of cuprous chloride .The mechanism of the reaction is believed to be as follows:



In general, the I.R. spectrum of these compounds [4a-f], shows stretching bands within the following values:

ν_{NH} (stretching vibration) at (3250-3450 cm^{-1}).

$\nu_{C=O\ amide}$ (stretching vibration) at (1660-1720 cm^{-1}).

ν_{NO2} (aromatic stretching vibration) at (1300-1520 cm^{-1}).

$\nu_{C=C}$ (aromatic stretching vibration) at (1400-1600 cm^{-1}).

ν_{C-H} (aromatic bending vibration) at (800-820 cm^{-1}).

ν_{C-H} (aliphatic stretching vibration) at (2900-2950 cm^{-1}).

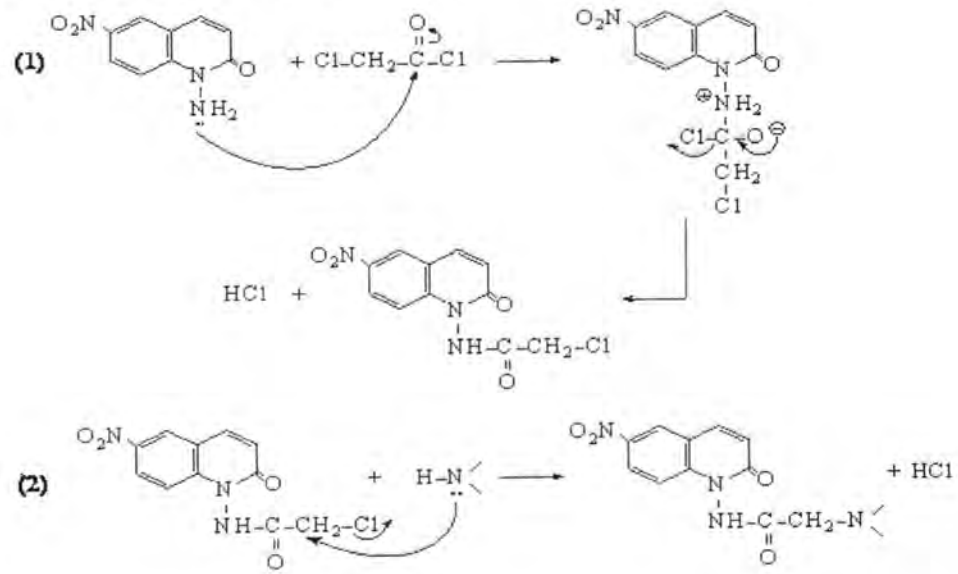
The success of all Mannich reactions have been confirmed by the disappearance of the (≡C-H) stretching vibration band at (≈3200 cm^{-1}). Other bands of the synthesized Mannich bases [4a-f] are listed in table (3).

The C.H.N. analysis confirmed the structure of compounds [4a-f], table (7).

The I.R. spectrum bands of compound [5] shows an absorption band at (1650 cm^{-1} for amide, (3350 cm^{-1}) for (N-H) stretching vibration, (2900 cm^{-1}) due to aliphatic (C-H) stretching vibration and at (3050 cm^{-1}) for aromatic (C-H) stretching vibration.

On the other hand, reaction of 1-amino-6-nitro quinolin-2(1H)-one [2b] with chloro acetyl chloride in benzene as a solvent and triethyl amine as a base afforded 2-chloro-N-(6-nitro-2-oxoquinolin-1(2H)-yl) acetamide [6].

Then, compound [6] was treated with the appropriate secondary amines in ethanol as a solvent. The mechanism of the overall reaction is believed to be as in scheme (3) [9] bellow:



The I.R. spectrum of compound [7a], , table (4) shows absorption bands at (3350 cm^{-1}) due to (NH) stretching vibration, (1710 cm^{-1}) due to amide carbonyl groups stretching vibration. Other bands of compounds [7a-e] are recorded in table (6).

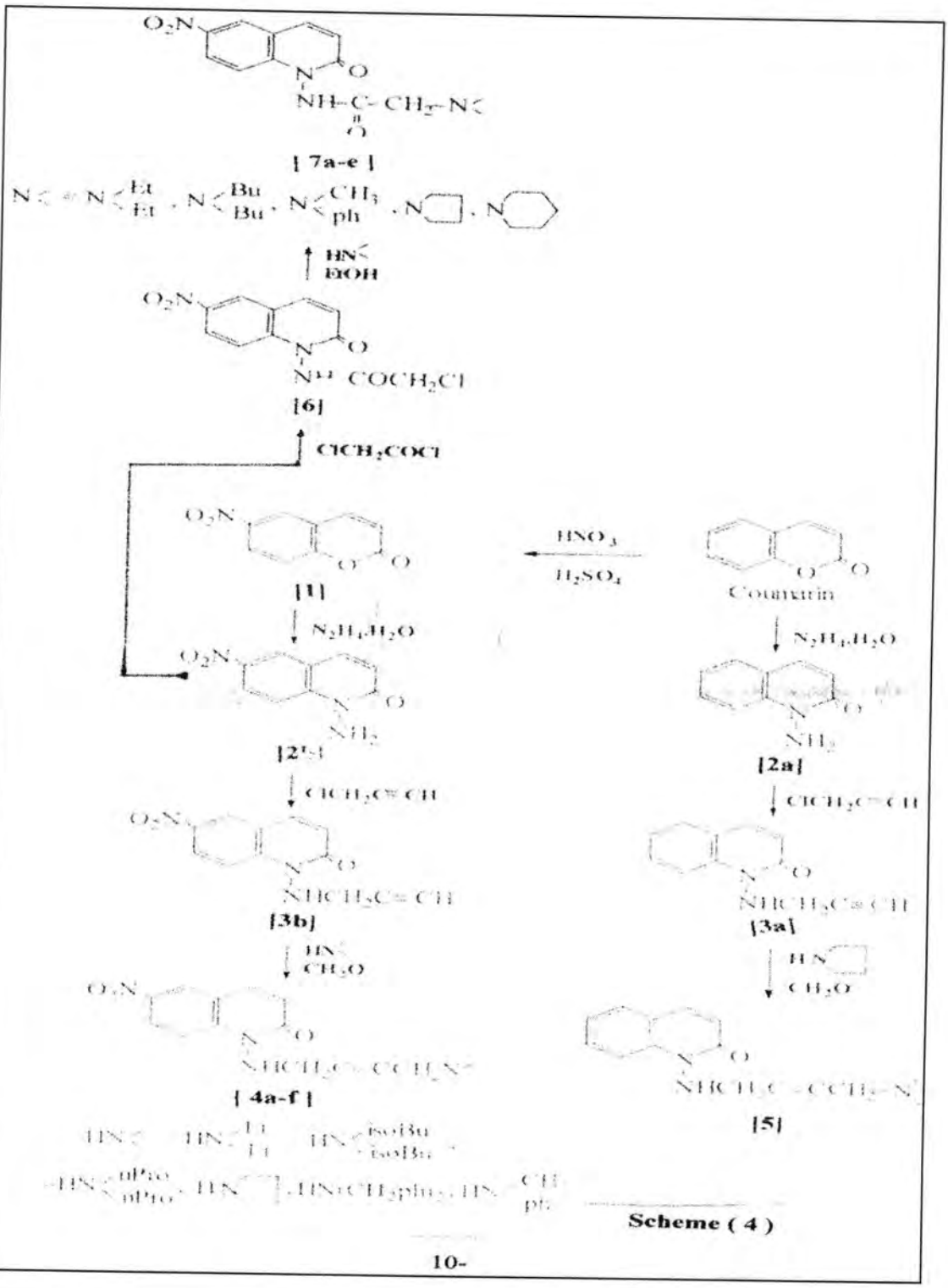


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Table -3: Spectral data of compounds [2a and 2b]

Comp. No.	U.V. λ_{max} (nm)	I.R. (cm^{-1}) KBr						
		υNH_2	$\upsilon C=O$ (amide)	$\upsilon C=C$ (aromatic)	$\upsilon C-H$ (aromatic)	$\upsilon C-H$ (aliphatic)	δ C-H (1,2-arom. sub.)	Others
2a	320.5 277.0 209.0	3400	1660	1420,1450 , 1580	3050	-	790	-
2b	282.0 211.0	3450	1670	1450,1550	3100	-	790	υNO_2 (aromatic) 1320

Table -4: Spectral data of compounds [3a-3b]

Comp. No.	U.V. λ_{max} (nm)	I.R. (cm^{-1}) KBr						
		$\upsilon_s \equiv C-H$	υ_{str} C≡C	υNH	$\upsilon C-H$ (aromatic)	$\upsilon C=C$ (aromatic)	$\upsilon C=O$ (amide)	$\upsilon NO_{2(aromatic)}$
3a	320.5 262.0	3250	2150	3300	3100	1420,1600	1650	-
3b	313.0 258.0	3200	2000	3350	3100	1500,1600	1700	1300

Table -5: Spectral data of compounds [4a-f]

Comp. No.	Amine	U.V. λ_{max} (nm)	I.R. (cm^{-1}) KBr						
			$\upsilon C=O$ (amide)	υNH	$\upsilon C-H$ (aliphatic)	$\upsilon C-H$ (aromatic)	υNO_2 (aromatic)	$\upsilon C=C$ (aromatic)	δ C-H (out of plane)
4a	$-N(Et)_2$	317.5 218.0	1660	3250	2900	3100	1300, 1520	1450, 1550	800,830
4b	$-N(isoBu)_2$	320.0 261.0	1670	3300	2950	3050	1300, 1510	1400, 1500	800
4c	$-N(n-Pro)_2$	310.0 257.0	1700	3300	2950	3000	1310, 1500	1450, 1500	850
4d	$-N(CH_2ph)_2$	311.0 253.0	1660	3320	2900	3100	1320, 1510	1450, 1600	810
4e	-N□	320.0 269.0	1700	3450	2900	3000	1300, 1550	1500, 1550	820,800
4f	$-N(CH_3)-C_6H_5$	330.5 271.0	1680	3250	2920	3100	1320, 1500	1500, 1600	820

Table -6: Spectral data of compounds [7a-e]

Comp. No.	U.V. λ_{max} (nm)	I.R. (cm^{-1}) KBr				
		υN-H	υC=O (amide)	υNO_2 (aromatic)	υC-H (aromatic)	υC-H (aliphatic)
7a	336.0 260.0	3150	1700	1300 1550	3050	2900
7b	318.0 253.0	3200	1700	1300 1520	3000	2900 2850
7c	325.0 279.0	3300	1720	1350 1500	3050	2950 2900
7d	310.0 215.0	3200	1690	1300 1500	3100	2920 2850
7e	315.0 257.0	3350	1710	1350 1500	3000	2950

Table -7: (C.H.N.) analysis for some of the synthesized compounds

Comp. No.	C.H.N. analysis % (Calculated)			C.H.N. analysis % (Found)		
	C %	H %	N %	C %	H %	N %
2a	67.49	5.03	17.49	67.02	5.32	17.30
2b	52.69	3.44	20.48	52.32	3.22	20.07
4a	62.18	6.14	17.06	62.73	6.01	16.88
7c	56.96	5.10	17.71	56.17	5.20	17.65

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Emission Beams Properties for (PSRB1, 13+16) Pulsar star

Sundus A. Abdullah and Hassanen H. Ali
Department of Astronomy, College of Science, University of Baghdad

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الخلاصة

النجوم النابضة تقسم إلى نوعين هي النجوم الاعتيادية و نجوم (اجزاء الثانية) اعتمادا على الفترات الزمنية للدوران . في هذا البحث وضحنا بعض مميزات حزم الانبعاث للنجوم النابضة. ومن اجل مقارنة صفات حزم الانبعاث مثل عرض النبضة وعامل التحزيم لتلك النجوم اعتمدنا موديل HCM حيث ان االمحور الدوراني لا ينطبق على المحور المغناطيسي بزاوية α . واعتمادا على زاوية الميل المداري حصلنا على عرض النبضة. وجدنا ان اغلب النبضات للنابض (PSRB1,13+16) سوف تختفي بعد فترة معينة من عمر النجم النابض وهذه تتفق تماما مع نتائج موديل WRT. كما اوضحت النتائج ان عرض البضة يعتمد بقوة على زاوية الميل بين محور الدوران والمحور المغناطيسي للنجم النابض.

ABSTRACT

Pulsar Stars divided into two types depending on the periods of rotation, normal pulsar and MSP (Millisecond pulsars) .In this research some characteristics of Emission Beam for pulsar stars are illustrated .In order to compare the emission properties (Pulse Width and beaming fraction) of these stars the HCM model (hollow cone model) are considered .The Misalignment angle between pulsar spin and orbital momentum is determined .Pulses width is then obtained using orbital inclination angle .It is found that pulsar (PSRB1,13+16) will not Beam toward Earth for its life time .In a good agreement with results by (WRT) model .Also it is indicated that pulse width depends strongly on the inclination angle between the rotation and the magnetic axis for pulsar star.

INTRODUCTION

A class of objects, which became known as pulsars, were discovered in 1960, they were rapidly pulsating radio sources and it was swiftly shown that only objects which could produce such behavior were spinning neutron stars. These spinning neutron stars behave in a similar way to lighthouses. Although lighthouses appear to flash on and off, it is an illusion produced by a rotating light. When a beam of light sweeps across out line of sight we see the light appear to flash on and then off again. In this same way, the beam of radiation is swept through space by a pulsar.As it crosses our line of sight from earth, we receive a pulse of radiation. The mechanism from producing this radiation is uncertain, at present. Also uncertain is the method for confining the radiation in such well-collimated beams [1].

Immediately after the discovery of pulsars the first attempts were appeared to interpret the pulsed nature of their emission that is poorly understood ,[2].Many theoretical models have been proposed ,but no single one is compelling , a single basic model probably can be applied to all pulsar .On the other hand ,the energy observed in pulsars is only a small of reaction of the total rotation energy dissipated .We can see some fundamental observational requirements for the pulsars emission mechanism there are:

1-1- The radiation must be emitted in relatively narrow beam, as shown in Fig.(1), [3]. Moreover, the beam shape and longitude must remain stable for many rotations.

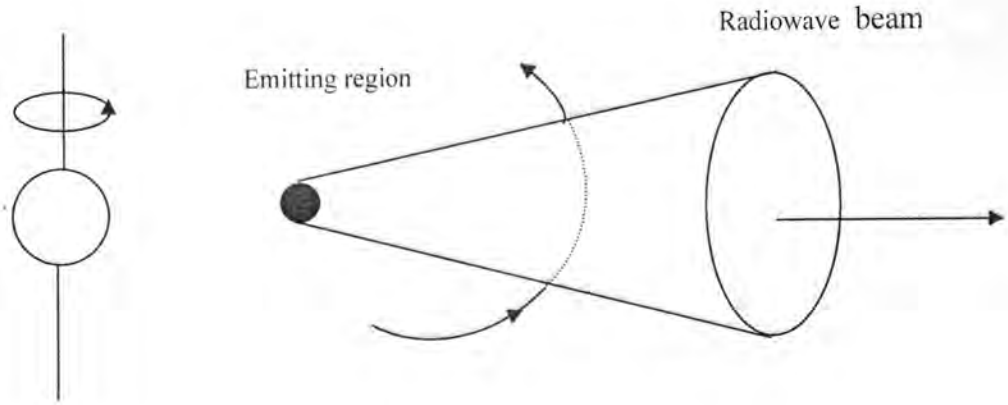

Fig.-1: Rotating neutron star mode with "Light-house" type emission. The active region rotates with an angular velocity corresponding to the interval between pulsar

The radiation mechanism must produce rather broad-band radiation at both radio and optical frequencies, the radio pulses have band widths about 100 MHZ, [3, 4].

The Pulses

Soon after the announcement of the discovery of pulsars by Hewish and Bell in the end of 1967,[1].,most of the radio telescopes around the world turned to pulsar observation,[2] .Many parameters of pulsars were established like the exact ,pulse shape ,the polarization and spectrum,[4].The studies of pulsars over the whole frequency range are of great importance because they are necessary for the elucidation of the mechanism that is responsible for the pulsar emission .The high polarization of pulsar radio emission at lower radio frequencies has supported the hypothesis of coherent emission mechanism , which is required to generate the high luminosity .Goldreich & Julian in1969 suggest that the radiation beam of MSPs (Millisecond Pulsars) , should be larger than that of

normal pulsars .There is number of models for the origin of pulsar signals but no consensus view has yet been reached,[1,2] .

Any processing model must explain why all the pulsars are observed at radio frequencies , but only the crab pulsar is observed in the optical and X-ray regions,[5].These models must also explain the limited rang of pulsar periods from milliseconds to seconds . When the star rotates the observer might see a light house-like pulsed signal as shown in Fig.(2), this model is called lighthouse effect .

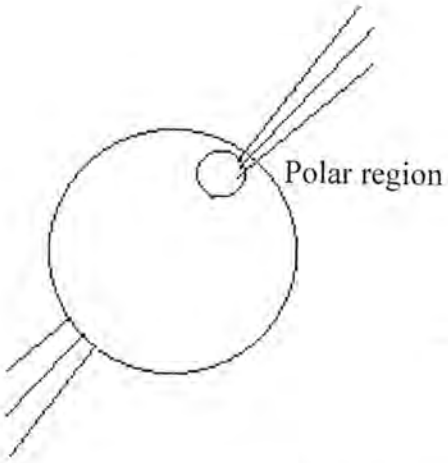

Fig -2: Radiation from the polar region of a rotation neutron star will produce a Lighthouse, like effect

1- Pulse Shapes:

The shapes of individual pulses are quite varied, ranging from very simple signal-peaked pulses to double and triple peaked pulse. In some pulsars with given pulsar there is a large variation in pulse shape from one pulse to another .However the mean pulse shape of a large number of pulses changes only very slightly over long time periods of the order of months,[4] . The pulsar-emitting region is less than 30 km in size, this .leads to the extremely high deduced brightness mentioned above and also is consistent only with size of a neutron star [5]

2 - Pulse Polarization.

In all radio polarization measurement the general rule is that the higher the observing frequency the higher polarization .Observations of polarized Galactic emission , polarization of radio sources(Super nova remnants , normal galaxies ,radio galaxies ,etc)follow this

general rule .Pulsar polarization at meter wave-length was known to be high ,some times up to 100 % (e.g Manchester 1971).It was also realized that the pulsar polarization falls (Manchester.1973) to higher frequency, but also exact depolarization evolution was not known due to lack of good high frequency , data ,[4].

MATHEMATICAL DERIVATION, CALCULATION AND RESULTS

1 - Solution regions

The evolution of the observed radio pulse profile of PSRB1,13+16, would be determined when the fiver parameters i ,α, ρ,λ, β and To, were specified for a given values, where ,[3,4]:

i: is the orbital inclination of the binary system . As shown in Fig.(3)

α: is the angle between the Magnetic and the spin axis

ρ: is the angular radius of the emission cone .

To= the epoch precession.

λ = the misalignment angle between pulsar spin and orbital momentum

β = the angle between pulsar spin and line of sight.

General relativity (GR) predicates a rate of precession Ω= 1.21 deg yr^{-1}, leading to a change in the pulse profile and polarization characteristics with time .Kramer first noticed a change in the components, [5]. This allows a solution region in parametric space with respects to GR and HCM. model

The inclination of the binary orbit with respect to the line of sight, i $\longrightarrow$ 180^{o} ,the possibilities are,[7] :

Case A, i =47.2^{o}

Case b : i =132.8^{o}

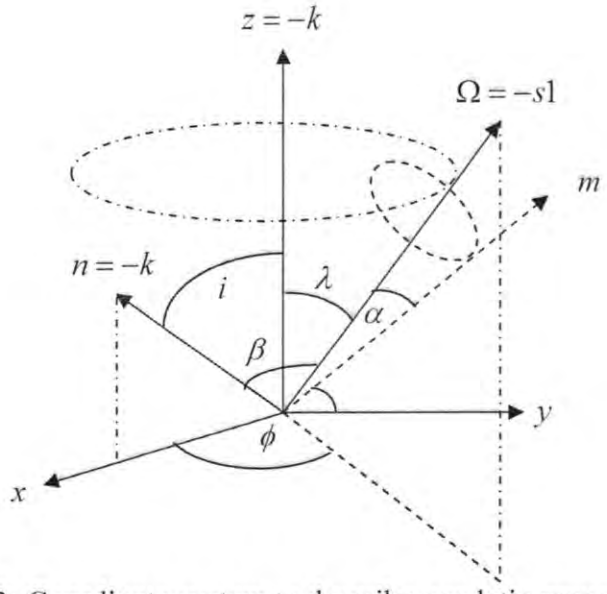

Fig -3: Coordinate system to describe geodetic precession.

2- Pulse Width with Best Model Solutions:

Weisbery Romani and Taylor (WRT), reported a change in the relative amplitude of the prominent leading and trailing components in the pulse of PSR1, 13+16, [7]. If the emission beam exhibits an over all hollow –cone shape , [3,7].One would also expect a change in the separation of two components , rather than only a change in relative intensity .As an interpretation . WRT argue that geodetic precession of the patchy emission beam structure , similar to that proposed by Lyne and Manchester , [3,5]. Two assumptions will be presented :

(1) General relativity is the correct theory of gravitation within the uncertainties of measurements.

(2)The emission beam exhibits an over all circular hollow – cone like shape.

The first assumption, given the excellent agreement of the measured orbital decay with prediction from a general relativity , [5,7]. While the assumption of an intensity dependence one magnetic longitude accounts for the component rotation change , the hollow – cone like shape follows the arguments given by (CWB) model, which can now be presented for slowly rotating pulsar , [8,9].

These information on beam structure indicate that the opening angle of the beam , ρ, follow a period relation as expected for a circular beam in a dipolar field structure . Recent results suggest that this is not true for very fast rotating pulsars ($p \leq 40$ ms) , but that it is still applicable to PSR B1,13+16 , [5]. Four equivalents Model solutions exist , which are listed in table 1 .

Table-1: The best model solutions.

Model	i (deg)	α (deg)	λ (deg)	ρ (deg)	To (yr)
1	47.2	27	22	9.0	1980
2	47.2	153	158	9.0	2128
3	132.8	153	22	9.0	2128
4	132.8	27	158	9.0	1980

Assumption (1) and the timing parameters presented by Taylor,[1992],imply an orbit inclination angle, $i=47.2^{o}$ or $i = 180^{o}-47.2 = 132.8^{o}$ and an expected precession rate of $\Omega = 1.21\ yr^{-1}$,[7]. Modeling the effects of precession, the same notation are used and coordinate system as introduced by (CWB Model but define the precession phase :

$$\Phi = \Omega \, . \, To \qquad ..(1)$$

Such that describes the closest approach of the pulsar spin axis , Ω , to the line of sight , n , as shown in Fig (3).

Note that the coordinate system which is earth –centered with the primary axis along the line of sight. The angle between pulsar spin and the line of sight, β, will change with time according to ,[5]:

$\cos\beta(t) = \cos(\lambda)\cos(i) + \sin(\lambda)\sin(i)\cos(\Phi)$ ---------- (2)

Affecting also the impact parameter:

$\sigma(t) = \beta(t) - \alpha$ ---------- (3)

The angle between the magnetic axis, m , and the line of sight at their closest approach .If the inclination angle between the magnetic axis, m, and pulsar spin axis is denoted by α, and emission beam exhibits an opening angle , ρ, the pulse width changed with time as , [5]:

$$W(t) = 4 \sin^{-1} \sqrt{\frac{\sin^2(\rho/2) - \sin^2(\alpha/2)}{\sin(\alpha)\sin(\beta)}}$$ ---------- (4)

The resulting mean values for the pulse width which may calculated by using eq.(4) ,with values adopted from models (no.1 with no.3),are presented in figures,(4,5).

As a results point out excellent agreement with the predication from the Weisberg , Romani,and Tylor,as shown in Fig.(6) .

Due to geodetic precession , the pulsar will not beam toward earth for significant fraction of its life time . In fact that our model (HCM) predicts that PSRBI,13+16 will not be observable after the year 2120 ,in a good agreement with results by WRT . Also the new obsaervations of PSRB1, 13+16 were made using the 305-m Arcibo telescopes, showing that the pulse width has weakened by about 40% since 1978 ,[9,10]. The gradual decrease in the pulses width caused by flux density variations due to interstellar scinnntillation.

3 - Determine The Beaming Fraction:

The normal pulsar and MSP apparently differ in the luminosity distribution and the intrinsic size of their emission beam ,[10]. The pulses of high –energy radiation from pulsar are due to a misalignment of the rotations axis and its magnetic axis ,[8,10].

Assuming a random distribution of the inclination angle α , the beaming fraction f , describing the fraction of the sky covered by the radiation beam , is given by ,[6,8]:

$f = (1-\cos\rho) + (\pi/2 - \rho)\sin\rho$ ..(5)

Due to the results if the beaming fraction is large , the chance of detecting a source is high , birthrate necessary compared to the case of a smaller beaming fraction .

For normal pulsars to fast-rotating pulsars, the beaming fraction should be very close to unity, $f = 1$ compared to the beaming fraction of $0.5 < f < 0.9$ represents the typical value for MSP.

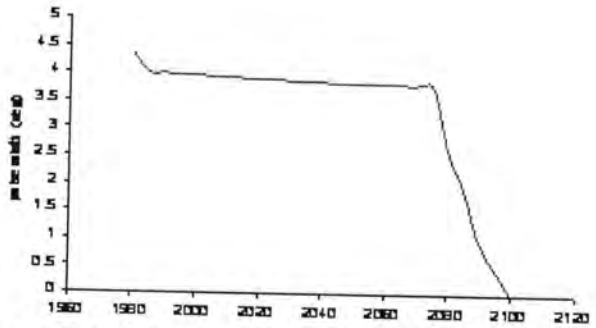

Fig.-4: The relation between pulse widths as a function of time according to the model no. 1

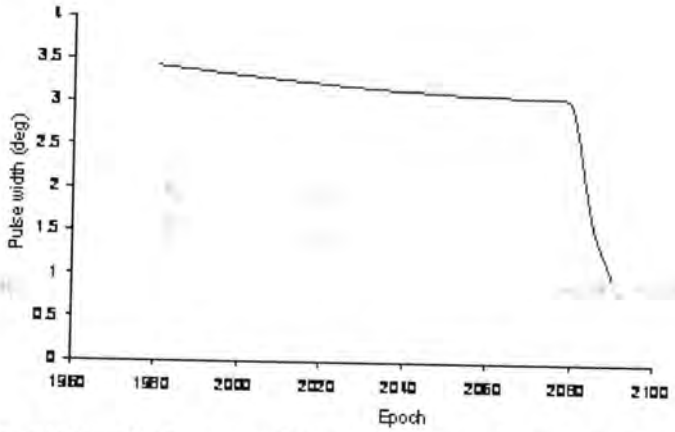

Fig.-5: The relation between pulse widths as a function of time according to the model no. 3

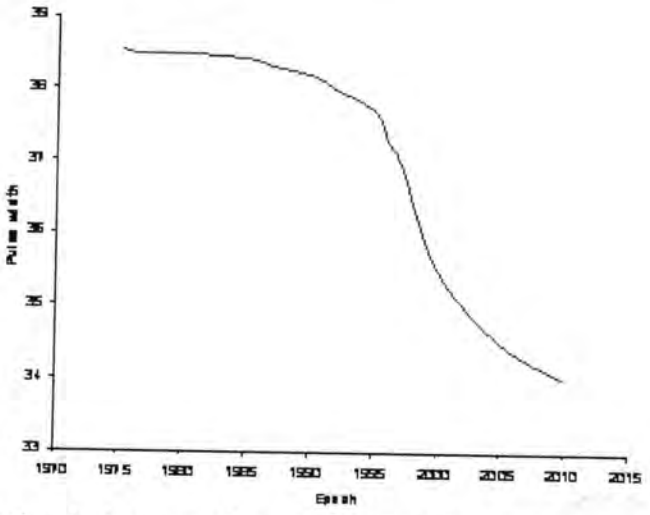

Fig.-6: The relation between pulse widths as a function of epoch according to WRT model

1) Due to geodetic precession with using models, (no.1 & no.3) the pulsar (PSR B13+16) will not be observable after year 2120.
2) The results are in good agreement with results by (WRT) model which using Model (no.4)
3) The beaming fraction for normal pulsars have value about = 1 , while Millisecond pulsar have value = $0.5 < f < 0.9$.
4) The pulse width depends strongly on the inclination angle between the rotation and the magnetic axis, and the impact parameter (β), which describes the close (angular) approach of our line of sight to magnetic axis .

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On Fourier Expansions of Integral Functionsof Two Complex Variables Having Zero Order

Mushtaq S. Al-Shaibani,
Department Of Mathematics, College Of Science, Al- Mustansiriyah University

E- mail: mushtdma@yahoo.com

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الخلاصة

ليكن α قياس بورل الموجب المنته على منطقة جوردن المتراصة $E \subset C^2$, لقد عرفنا فضاء هلبرت $L^2_{(\alpha)}$ للدوال ذات المتغيرين والممثلة بسلسلة القوى والتي تكون تحليلية في E مع الضرب الداخلي وذات الرتبة صفر بمثابة قياس سطحي كلي فوق E . لقد حصلنا على العلاقة التي تربط نمو الدالة الكلية $f(z_1,z_2) \in L^2_{(\alpha)}$ ذو المتغيرين z_1, z_2 والتي رتبتها صفر مع معاملات فورير بالنسبة الى المتتابعة المتعامدة لمتعددة الحدود في $L^2_{(\alpha)}$, وتم الحصول على الشروط الضرورية واللازمة بدلالة معاملات فورير للدالة $f(z_1,z_2) \in L^2_{(\alpha)}$ ذات الرتبة اللوغاريتمية والنوع اللوغاريتمي.

ABSTRACT

Let α be a finite positive Boral measure on a compact Jordan region $E \subset C^2$ and $L^2_{(\alpha)}$, the Hilbert space of functions of two complex variables represented by power series which is a holomorphic in E with inner product, having zero order is defined as a surface measure integral over E. The relations connection the growth of an integral function of two complex variables $f(z_1,z_2) \in L^2_{(\alpha)}$ having zero order with its Fourier Coefficients with respect to an orthonormal sequence of polynomials in $L^2_{(\alpha)}$, have been obtained . The necessary and sufficient conditions in terms of Fourier Coefficients have been obtained for $f(z_1,z_2) \in L^2_{(\alpha)}$ to be of logarithmic order and logarithmic type.

INTRODUCTION

Let $f(z_1,z_2) = \sum_{m,n=0}^{\infty} a_{mn}\, z_1^{\,m} z_2^{\,n}$, be a function of two complex variables z_1 and z_2, regular for $|z_i| \le r_i$, $i = 1,2$. If r_1 and r_1 are arbitrarily large, then $f(z_1,z_2)$ is an entire function of two complex variables.
Writing $z_1 = r_1 e^{i\theta_1}$ and $z_2 = r_2 e^{i\theta_2}$,

$f(z_1,z_2) = U(r_1, r_2, \theta_1, \theta_2) + i\, V(r_1, r_2, \theta_1, \theta_2)$, and $a_{mn} = \mu_{mn} + i\,\beta_{mn}$.

Bose and Sharma [2] defined order and type of entire function $f(z_1,z_2)$ and obtained necessary and sufficient conditions for the function to be of finite order , and also the same for functions of finite order and type. Many workers such as Gross [3], Kishka [4] , Krishna and Rao [5] , Opoola and Gbadeyan [7] and others obtained other coefficient characterizations of growth parameters associated with functions of several complex variables and have studied their properties. However, these studies fail when the order of $f(z_1,z_2)$ is zero. In this case no further classifications are possible. These functions may be called of slow growth. However, these functions also play an important role in the theory of entire function. The slow growth properties have been studied by H. S. Bahnam and G.S.Srivastava [1], they defined the logarithmic order and logarithmic type for these functions and they obtained their coefficients characterizations. We know that $M(r_1,r_2)=\max_{|z_i|\le r_i}|f(z_1,z_2)|$, $i=1,2$, is the maximum modulus of $f(z_1,z_2)$. The properties of $M(r_1,r_2)$ and the maximum term for entire function in series expansion of $f(z_1,z_2)$ were obtained by Bose and Sharma [2]. Let Γ denote the class of all integral functions of two complex variables $f(z_1,z_2)$, $|z_i|\le r_i$, $i=1,2$, represented by power series, having zero order. Suppose the order ρ defined in [2] is zero .Then we consider the quantity

$$\limsup_{r_1,r_2\to\infty}\frac{\log\log M(r_1,r_2)}{\log\log(r_1,r_2)}=\rho^*, \tag{1.1}$$

and call ρ^* as the logarithmic order of $f(z_1,z_2)$. It is easily seen that for any transcendental entire function , $1\le\rho^*\le\infty$. When $1<\rho^*<\infty$, we define the logarithmic type T^* of $f(z_1,z_2)$ as

$$\limsup_{r_1,r_2\to\infty}\frac{\log M(r_1,r_2)}{(\log r_1)^{\rho^*}+(\log r_2)^{\rho^*})}=T^*,\quad 0\le T^*\le\infty, \tag{1.2}$$

Bahnam and Srivistava defined the coefficient characterization of logarithmic order as the following theorem: [1]

Theorem 1.1. The entire function $f(z_1,z_2)$, $|z_i|\le r_i$, $i=1,2$ is of logarithmic order ρ^* if and only if

$$\limsup_{m,n\to\infty}\frac{\log(m+n)}{\log\log|a_{mn}|^{-1/(m+n)}}=\rho^*-1 \tag{1.3}$$

Bahnam and Srivistava [1] obtained the coefficient characterization for the logarithmic type of $f(z_1,z_2)$ defined by (1.2). They proved, the following theorem:

Theorem 1.2. Let the entire function $f(z_1,z_2)=\sum_{m,n=0}^{\infty} a_{mn}\, z_1^{\,m} z_2^{\,n}$, $|z_i|\le r_i$, $i=1,2$ be of logarithmic order ρ^* and logarithmic type T^*. Then

$$\limsup_{m,n\to\infty}\frac{(m+n)^{\rho^*}}{\left\{\log|a_{mn}|^{-1}\right\}^{(\rho^*-1)}}=\left(\frac{\rho^*}{\rho^*-1}\right)^{(\rho^*-1)}(2\rho^*T^*), \tag{1.4}$$

or

$$T^*=\left(\frac{\rho^*-1}{\rho^*}\right)^{(\rho^*-1)}\frac{v}{2\rho^*},$$

where

$$v=\limsup_{m,n\to\infty}\frac{(m+n)^{\rho^*}}{\left\{\log|a_{mn}|^{-1}\right\}^{(\rho^*-1)}}$$

Let α be a finite positive Boral measure on a compact Jordan region $E\subset C^2$ of transfinite diameter $d_i>0$, $i=1,2$ and $L^2_{(\alpha)}$, the Hilbert space of functions of two complex variables holomorphic in E with inner product

$$(f,g)=\int_E f(z_1,z_2)\overline{g(z_1,z_2)}\,d\alpha \qquad f,g\in L^2_{(\alpha)},$$

where

$$\|f\|_{L^2_{(\alpha)}}=\left(\int_E |f|^2\,d\alpha\right)^{1/2}<\infty.$$

We will assure that $E=\mathrm{supp}(\alpha)$ is not contained in any (proper) algebraic subset of C^2. This is equivalent to the following property of E: If $P_{m,n}(z_1,z_2)$ is an (analytic) polynomial then,

$$p_{m,n}(z_1,z_2)\big|_E\equiv 0\Rightarrow p_{m,n}(z_1,z_2)\equiv 0 \text{ on } C^2. \tag{1.5}$$

Sets with this property are said unisolvent. In this case of one complex variable, E satisfies (1.5) if and only if E contains infinitely many points, (see [8], p.2).

Proposition 1. Let α be a finite positive Boral measure with $E=\mathrm{supp}(\alpha)$ satisfying (1.5). Let $p_{m,n}(z_1,z_2)$ be an (analytic) polynomial such that

$\|p_{m,n}(z_1,z_2)\|_{L^2_{(\alpha)}}=0$. Then $p_{m,n}(z_1,z_2)\equiv 0$ on C^2.

Proof. We will show that if $p_{m,n}(z_1,z_2)\big|_E\neq 0$, then $\|p_{m,n}(z_1,z_2)\|_{L^2_{(\alpha)}}>0$. Suppose that $p_{m,n}(z_1,z_2)\big|_E\neq 0$ and let $z_{0_i}\in E=E_1\times E_2$, $i=1,2$, be such that $|p_{m,n}(z_1,z_2)|>0$. Then for some $z_i>0$, $|p_{m,n}(z_1,z_2)|\ge\left(|p_{m,n}|/2\right)$ for all $z_i\in\Delta(z_{0_i},r_i)$, where $\Delta(z_{0_i},r_i)$ denotes the closed balls of centre z_{0_i} and radius r_i. Since $z_{0_i}\in\mathrm{supp}(\alpha)$, we have $\alpha\left(\Delta(z_{0_i},z_i)\right)>0$.

Hence

$$\left\|p_{m,n}(z_1,z_2)\right\|^2_{L^2_{(\alpha)}} = \int_E \left|p_{m,n}(z_1,z_2)\right|^2 d\alpha$$

$$\geq \int_{E\cap\Delta(z_{0_i},r_i)} \left|p_{m,n}(z_1,z_2)\right|^2 d\alpha$$

$$\geq \left(\left|p_{m,n}(z_{0_1},z_{0_2})\right|/2\right)^2 \alpha\left(\Delta(z_{0_i},r_i)\right) > 0 .$$

Hence the proof is completed.

Here we consider the monomials $\{z_1^{\,m} z_2^{\,n}\}$ to be ordered lexicographically. By proposition 1, we apply the Gram-Schmidt orthogonalization procedure to the monomials and one obtains orthonormal polynomials denoted $p_{m,n}(z_1,z_2) \equiv p_{m,n}(z_1,z_2,\alpha)$ for each m and $n \cdot p_{m,n}(z_1,z_2,\alpha)$ denotes the orthonormal polynomial which is a linear combination of $z_1^{\,m} z_2^{\,n}$ and monomials of lower lexicographic order. Thus $A_{m,n}(E) \equiv \{p_{m-1,\,n-1}(z_1,z_2)\}_{m,n=1}^{\infty}$, $p_{m,n}(z_1,z_2)$ being a polynomial of degree $\leq m+n$, is a complete orthonormal sequence in $L^2_{(\alpha)}$.

The Fourier expansion of $f(z_1,z_2) \in L^2_{(\alpha)}$ is

$$f(z_1,z_2) = \sum_{m,n=0}^{\infty} b_{m,n}\, p_{m,n}(z_1,z_2) \text{ , where}$$

$$b_{m,n} = \int_E f(z_1,z_2)\,\overline{p_{m,n}(z_1,z_2)}\,d\alpha \qquad (1.6)$$

A question arises that " Do the relations (1.3) and (1.4) continue to hold if $a_{m,n}$ is replaced by Fourier Coefficient $b_{m,n}$ of $f(z_1,z_2) \in \Gamma \subset L^2_{(\alpha)}$ with respect to $L^2_{(\alpha)}$. In this paper we attempt to solve this question by using the logarithmic order and logarithmic type.

AUXILIARY RESULTS

In this section we prove some lemmas which are required in proving the main theorems.

Let E_{r_i} be the largest equipotential curve of $E = E_1 \times E_2$ such that $E_{r_i} = \{z_i \in C^2 : d_i \exp V_\alpha(z_i) = r_i\}$, $r_i/d_i > 1, i = 1,2$, and $V_\alpha(z_i)$ is the minimal Carrier-Green function of the measure α and $C^2/\hat{E}$ is simply connected [6], $\hat{E}$ denote the convex hull of E. Let D_{r_i} be the domain interior to E_{r_i}.

Lemma 2.1. If a polynomial $p_{m,n}(z_1,z_2)$ of degree $m+n$ satisfies the inequality

$|p_{m,n}(z_1,z_2)| \le L$, for $z_i \in E$, then we have

(2.1) $$|p_{m,n}(z_1,z_2)| \le L\, R_1^m\, R_2^n \text{ for } z_i \in E_{R_i}, R_i > 1, i = 1,2$$

Lemma 2.2. If $f(z_1,z_2)$ is analytic on E and we have

$$\int_E |p_{m,n}|^2 d\alpha \le L,$$

if E' is an arbitrary closed Jordan region interior to E, then we have

$$|p_{m,n}(z_1,z_2)| \le L\,L' \text{ for } z_i \in E',$$

where L' depends on E' but not on $p_{m,n}(z_1,z_2)$ nor on L.

These lemmas can be proved in the same way as in single complex variable (see [9]).

Lemma 2.3. If $p_{m,n}(z_1,z_2)$ forms a complete orthonormal sequence in $L^2_{(\alpha)}$, then for any $\varepsilon > 0$,

$$|p_{m,n}(z_1,z_2)| < M_\varepsilon \left(\frac{r_1}{d_1}\right)^m \left(\frac{r_2}{d_2}\right)^n (1+\varepsilon)^{m+n}, z_i \in E_{r_i},$$

where M_ε depends on ε but not on m,n.

Proof. Since we may assume $\int_E |p_{m,n}(z_1,z_2)|^2 d\alpha \le 1$ for all m,n.

By Lemma 2.2 , we have for any $E' \subset E$,

$$|p_{m,n}(z_1,z_2)| \le M_\varepsilon \text{ for } z_1 \in E',$$

where M_ε depends on E'. So for any $\varepsilon > 0$, applying Lemma 2 .1, we get

$$|p_{m,n}(z_1,z_2)| < M_\varepsilon (1+\varepsilon)^{m+n} \text{ for } z_i \in E'_{1+\varepsilon}$$

Now let $E'_{1+\varepsilon} \subset E$, so that

$|p_{m,n}(z_1,z_2)| < M_\varepsilon (1+\varepsilon)^{m+n}$ holds on E also .

Again applying Lemma 2.1, proof is completed.

Lemma 2.4. Let $f(z_1,z_2)$ be analytic in the domain D_{R_i} and have a singularity on E_{R_i}, then

(2.2) $$\limsup_{m,n\to\infty} |b_{m,n}|^{1/(m+n)} \le \frac{1}{R_i}, R_i > 1, i = 1,2.$$

Proof. Since $\|f(z_1,z_2)\|_{L^2_{(\alpha)}} \le 1$, we have

$$|b_{m,n}| < \int_E \overline{|p_{m,n}(z_1,z_2)|}\, d\alpha ,$$

using Cauchy -Schwarz inequality, we get

$$|b_{m,n}| \le (\alpha(E))^{1/2}$$

or

$$\limsup_{m,n\to\infty} |b_{m,n}|^{1/(m+n)} \le \frac{1}{R_i}, \quad R_i > 1. \tag{2.3}$$

However, strict inequality in (2.2) is equivalent to the analyticity of $f(z_1,z_2)$ in $D_{R_i'}$, for some R_i' with $R_i < R_i'$. Thus if $f(z_1,z_2)$ has a singularity on E_{R_i}, then equality holds in (2.3).

Lemma 2.5. Let $f(z_1,z_2) \in L^2_{(\alpha)}$ and $b_{m,n}$ satisfies (2.2) . Then $f(z_1,z_2)$ can be continued analytically to the domain D_{R_i}, $i = 1,2$.

Proof. To see that the series $\sum_{m,n=0}^{\infty} b_{m,n}\, p_{m,n}(z_1,z_2)$ converges uniformly on compact subsets of D_{R_i}, choosing a number R_i^*, $1 < R_i^* < R_i$. Let $\varepsilon > 0$, and $\varepsilon < \dfrac{R_i - R_i^*}{R_i^*}$, so that $R_i^*(1+\in) < R_i$. Let R_i^{**} be such that $R_i^*(1+\in) < R_i^{**} < R_i$. (2.2) gives that there exists $m = m_\circ(R_1^{**})$, $n = n_\circ(R_2^{**})$ such that

$$|b_{m,n}| < \frac{1}{\left(R_1^{**}\right)^m \left(R_2^{**}\right)^n} \quad \text{for } m \ge m_\circ,\ n \ge n_\circ \tag{2.4}$$

Applying Lemma (2.3), it gives

$$|p_{m,n}(z_1,z_2)| < M\left(\frac{R_1^*}{d_1}\right)^m \left(\frac{R_2^*}{d_2}\right)^n (1+\varepsilon)^{m+n} \quad \text{for } z_i \in E_{R_i^*}, i = 1,2. \tag{2.5}$$

Combining (2.4) and (2.5) implies that

$$|b_{m,n}\, p_{m,n}(z_1,z_2)| < M\left(\frac{R_1^*}{d_1 R_1^{**}}\right)^m \left(\frac{R_2^*}{d_2 R_2^{**}}\right)^n (1+\varepsilon)^{m+n}, \quad \text{for } z_i \in E_{R_i^*}.$$

Using above inequalities and Weirstrass M-test we conclude that $\sum_{m,n=0}^{\infty} b_{m,n}\, p_{m,n}(z_1,z_2) = 0$ converges uniformly on $E_{R_i^*}$. Since $R_i^* < R_i$ it implies that the series converges uniformly on compact subset of D_{R_i}. But

$$\int_E \left\{ f(z_1,z_2) - \sum_{m,n=0}^{\infty} b_{m,n}\, p_{m,n}(z_1,z_2) \right\} \overline{p_{m,n}(z_1,z_2)}\, d\alpha = 0 .$$

Since $p_{m,n}(z_1,z_2)$ forms a complete orthonormal sequence in $L^2_{(\alpha)}$, so

$$f(z_1,z_2)=\sum_{m,n=0}^{\infty} b_{m,n}\, p_{m,n}(z_1,z_2) \text{ on } E\subset C^2.$$

Hence $f(z_1,z_2)$ can be continued analytically on D_{R_i}.

Corollary. $f(z_1,z_2)\in L^2_{(\alpha)}$ is an integral function of two complex variables if and only if

$$\limsup_{m,n\to\infty}\left|b_{m,n}\right|^{1/(m+n)}=0$$

Lemma 2.6. Let $f(z_1,z_2)\in L^2_{(\alpha)}$. For any $\varepsilon>0$ there exists two integers $N_1(\varepsilon,E_1)$ and $N_2(\varepsilon,E_2)$ such that

$$\left|b_{m+1,n+1}\right|<K\,\overline{M}(r_1,r_2)\left(\frac{d_1\,e^{\varepsilon}}{r_1}\right)^m\left(\frac{d_2\,e^{\varepsilon}}{r_2}\right)^n,$$

for all $R_1>r_1\ge r_{1_0}(\varepsilon)$, $R_2>r_2\ge r_{2_0}(\varepsilon)$ and $m>N_1$, $n>N_2$.
Where $\overline{M}(r_1,r_2)=\max_{z_i\in E_{r_i}}\left|f(z_1,z_2)\right|$, K is independent of m,n and r_1,r_2

Proof. We construct a sequence $\{Q_{m,n}(z_1,z_2)\}_{m,n=0}^{\infty}$ of polynomials by induction such that

$$\left|f(z_1,z_2)-Q_{m,n}(z_1,z_2)\right|\le A\,\overline{M}(r_1,r_2)\left(\frac{d_1\,e^{\varepsilon}}{r_1}\right)^m\left(\frac{d_2\,e^{\varepsilon}}{r_2}\right)^n,$$

for $z_i\in E_{r_i}$, $m>N_{1_0}=N_{1_0}(\varepsilon,E_1)$, $n>N_{2_0}=N_{2_0}(\varepsilon,E_2)$ and for every r_1,r_2, $R_1>r_1>R_{1_0}=R_{1_0}(\varepsilon,E_1)$, $R_2>r_2>R_{2_0}=R_{2_0}(\varepsilon,E_2)$. Thus

$$\left(\int_E\left|f(z_1,z_2)-Q_{m,n}(z_1,z_2)\right|^2 d\alpha\right)^{1/2}\le K\,\overline{M}(r_1,r_2)\left(\frac{d_1\,e^{\varepsilon}}{r_1}\right)^m\left(\frac{d_2\,e^{\varepsilon}}{r_2}\right)^n.$$

Now by (1.6), we have

$$b_{m+1,n+1}=\int_E f(z_1,z_2)\,\overline{p_{m+1,n+1}(z_1,z_2)d\alpha}$$

$$=\int_E\left\{f(z_1,z_2)-\sum_{j_1,j_2}^{m,n}b_{j_1,j_2}p_{j_1,j_2}(z_1,z_2)\right\}\overline{p_{m+1,n+1}(z_1,z_2)d\alpha}$$

By Schwarz' a inequality, we have

$$\left|b_{m+1,n+1}\right|^2\le\left(\int_E\left|f(z_1,z_2)-\sum_{j_1,j_2=0}^{m,n}b_{j_1,j_2}p_{j_1,j_2}\right|^2 d\alpha\right)\left(\int_E\left|p_{j_1,j_2}(m+1,n+1)\right|^2 d\alpha\right)$$

$$=\int_E\left|f(z_1,z_2)-\sum_{j_1,j_2=0}^{m,n}b_{j_1,j_2}p_{j_1,j_2}(z_1,z_2)\right|^2 d\alpha$$

$$\leq \int_E \left| f(z_1, z_2) - Q_{m,n}(z_1, z_2) \right|^2 d\alpha ,$$

since Fourier sums give the best $L^2_{(\alpha)}$ approximations. So (2.6) gives

$$\left| b_{m+1,\, n+1} \right|^2 \leq K^2 \left[\overline{M}(r_1, r_2) \left(\frac{d_1 e^{\varepsilon}}{r_1} \right)^m \left(\frac{d_2 e^{\varepsilon}}{r_2} \right)^n \right]^2 ,$$ which gives required result.

Lemma 2.7. Let $f(z_1, z_2) \in \Gamma$ is of logarithmic order ρ^*, $(1 < \rho^* < \infty)$ and logarithmic type T^*. Then

(2.7) $$\rho^* = \limsup_{r_1, r_2 \to \infty} \frac{\log \log \overline{M}(r_1, r_2)}{\log \log (r_1, r_2)}$$

(2.8) $$T^* = \limsup_{r_1, r_2 \to \infty} \frac{\log \overline{M}(r_1, r_2)}{(\log r_1)^{\rho^*} + (\log r_2)^{\rho^*})}$$

Proof. Let (z_{1_0}, z_{2_0}) be a fixed point of the set E, and $r_1 > 1$, $r_2 > 1$. For any point $z_i \in E_{r_i}$ there exists a $z_i^* = z_i^*(z_i) \in E$, $i = 1,2$ such that

$$\left| z_i - z_i^* \right| = \operatorname{dist}(z_i, E) .$$

By the triangle inequality and by

$$\operatorname{dist}(z_i, E) \leq d_i(E) \exp V_\alpha(z_i) \leq \operatorname{dist}(z_i, E) + |E| \quad \text{for } z_i \in C^2/E .$$

We have

$$\left| z_i - z_{i_0} \right| \leq \left| z_i - z_i^* \right| + \left| z_i^* - z_{i_0} \right| \leq r_i + |E| \quad \text{for } z_i \in E_{r_i},\ r_i > 1 .$$

and

$$r_i - |E| \leq \left| z_i - z_i^* \right| , \qquad |E| \geq \left| z_i^* - z_{i_0} \right| .$$

We see that

$$r_i - 2|E| - \left| z_{i_0} \right| \leq \left| z_i \right| \leq r_i + |E| + \left| z_{i_0} \right| \quad \text{for } z_i \in E_{r_i}, r_i > 1 .$$

Let $R_i > 1$ be such that

$$r_i - 2|E| - \left| z_{i_0} \right| \geq \frac{r_i}{2} \text{ and } r_i + |E| - \left| z_{i_0} \right| \leq 2 r_i \text{ for } r_i > R_i$$

Hence for $r_i > R_i$ we have

$$\frac{\log \log M\left(\frac{r_1}{2}, \frac{r_2}{2} \right)}{\log \log (r_1 r_2)} \leq \frac{\log \log \overline{M}(r_1, r_2)}{\log \log (r_1, r_2)} < \frac{\log \log M(2r_1, 2r_2)}{\log \log (r_1, r_2)}$$

and if $1 < \rho^* < \infty$,

$$\frac{\log M(r_1 - a_1, r_2 - a_2)}{(\log r_1)^\rho + (\log r_2)^\rho} \leq \frac{\log \overline{M}(r_1, r_2)}{(\log r_1)^\rho + (\log r_2)^\rho} \leq \frac{\log M(r_1 + b_1, r_2 + b_2)}{(\log r_1)^\rho + (\log r_2)^\rho} ,$$

where

$a_1 = 2|E_1| + |z_{1_0}|$, $a_2 = 2|E_2| + |z_{2_0}|$, $b_1 = |E_1| + |z_{1_0}|$, $b_2 = |E_2| + |z_{2_0}|$, $E = E_1 \times E_2$.

Passing to limit superior the proof is completed.

MAIN RESULTS

Theorem 3.1. The integral function $f(z_1, z_2) \in L^2_{(\alpha)}$ is of logarithmic order ρ^* if and only if

$$\limsup_{m,n\to\infty} \frac{\log(m+n)}{\log\log\left|b_{m,n}\right|^{-1/(m+n)}} = \partial^* - 1 \tag{3.1}$$

and then $\partial^* = \rho^*$

Proof. Let $\partial^* < \infty$. Then for any $\varepsilon > 0$ exists $m_0 = m_0(\varepsilon)$, $n_0 = n_0(\varepsilon)$ such that

$$\frac{\log(m+n)}{\log\log\left|b_{m,n}\right|^{-1/(m+n)}} \le (\partial^* - 1) + \varepsilon \text{ , for } m > m_0,\ n > n_0$$

or $$\log\left|b_{m,n}\right|^{-1/(m+n)} \ge (m+n)^{\frac{1}{(\partial^*-1)+\varepsilon}},$$

or $$\left|b_{m,n}\right| \le \exp(m+n)^{\frac{-(m+n)}{(\partial^*-1)+\varepsilon}},$$

which implies that

$$\lim_{m,n\to\infty} \left|b_{m,n}\right|^{1/(m+n)} = 0, \tag{3.2}$$

By corollary of Lemma 2.5, $f(z_1, z_2) \in \Gamma$. Let its logarithmic order by ρ^*. Since the Fourier expansions of $f(z_1, z_2)$ in $L^2_{(\alpha)}$ is

$$f(z_1, z_2) = \sum_{m,n=0}^{\infty} b_{m,n}\, p_{m,n}(z_1, z_2) \text{ , and}$$

$$\left\|f(z_1, z_2)\right\|_{L^2_{(\alpha)}} \le 1, \qquad \left|b_{m,n}\right| \le (\alpha(E))^{1/2}.$$

Thus $|f(z_1, z_2)| \le (\alpha(E))^{1/2}\,(m+1)(n+1)\,M_0\left(\frac{r_1}{d_1}\right)^m \left(\frac{r_2}{d_2}\right)^n (1+\varepsilon)^{m+n}$ for $z_i \in E_{r_i}$.

So $$\overline{M}(r_1, r_2) \le M'_0\, g\left(\left\{\frac{r_1(1+\varepsilon)}{d_1}\right\}, \left\{\frac{r_2(1+\varepsilon)}{d_2}\right\}\right)$$

$$= M'_0\, M\left(\left\{\frac{r_1(1+\varepsilon)}{d_1}\right\}, \left\{\frac{r_2(1+\varepsilon)}{d_2}\right\}\right), \text{ where} \tag{3.3}$$

$$g(z_1, z_2) = \sum_{m,n=0}^{\infty} b_{m,n}\, z_1^{\,m} z_2^{\,n} \text{ , for } z_i \in E_{r_i},\ i = 1, 2, \tag{3.4}$$

and $$M(r_1, r_2) = \max_{|z_i| = r_i} |g(z_1, z_2)|.$$

Hence by (3.2), $g(z_1,z_2)\in\Gamma$ and (1.3) implies that it is of logarithmic order ρ^* and (3.3) gives.

$$\frac{\log\log\overline{M}(r_1,r_2)}{\log\log(r_1r_2)}\le\frac{\log\log M\left(\frac{r_1(1+\varepsilon)}{d_1},\frac{r_2(1+\varepsilon)}{d_2}\right)}{\log\log(r_1r_2)}+o(1),\ \text{for large } r_1 \text{ and } r_2.$$

So we get

(3.5) $\qquad \rho^*\le\partial^*,$

which show that $f(z_1,z_2)$ is of logarithmic order ρ^*. Now let $f(z_1,z_2)\in\Gamma$ of logarithmic order $\rho^*<\infty$. By (2.7), for any $\varepsilon>0$ there exists $r_{1_\circ}=r_{1_\circ}(\varepsilon)$, $r_{2_\circ}=r_{2_\circ}(\varepsilon)$ such that

$$\overline{M}(r_1,r_2)<\exp\left(\log r_1+\log r_2\right)^{((\rho^*-1)+\varepsilon)},\ \text{for } r_{1_\circ}>r_{1_\circ}(\varepsilon),\ r_{2_\circ}>r_{2_\circ}(\varepsilon),$$

using Lemma 2.6, we have

$$\left|b_{m,n}\right|\le K\frac{\exp\left(\log r_1+\log r_2\right)^{((\rho^*-1)+\varepsilon)}}{r_1^{m-1}r_2^{n-1}}d_1^{m-1}d_2^{n-1}e^{(m+n-2)\varepsilon},\ \text{for large } K \text{ and } r_1,r_2.$$

Choosing a sequences $r_m\to\infty, r_n\to\infty$ as $m,n\to\infty$ defined as

$$r_m=\left(\frac{m-1}{(\rho^*-1)+\varepsilon}\right)^{1/((\rho^*-1)+\varepsilon)},\ r_n=\left(\frac{n-1}{(\rho^*-1)+\varepsilon}\right)^{1/((\rho^*-1)+\varepsilon)}$$

in above expression, we get

$$\left|b_{m,n}\right|\le K\exp\left[\frac{1}{(\rho^*-1)+\varepsilon}\log\left(\frac{m-1}{(\rho^*-1)+\varepsilon}\right)+\frac{1}{(\rho^*-1)+\varepsilon}\log\left(\frac{n-1}{(\rho^*-1)+\varepsilon}\right)\right]^{(\rho^*-1)+\varepsilon}\times$$
$$\frac{d_1^{m-1}d_2^{n-1}e^{(m+n-2)\varepsilon}}{\left(\frac{m-1}{(\rho^*-1)+\varepsilon}\right)^{(m-1)/(\rho^*+\varepsilon)}\left(\frac{n-1}{(\rho^*-1)+\varepsilon}\right)^{(n-1)/(\rho^*+\varepsilon)}}$$

or

$$\frac{\log\log\left|b_{m,n}\right|^{-1}}{\log(m+n)}\ge\frac{\left(\frac{m-1}{(\rho^*-1)+\varepsilon}\right)\log\left(\frac{m-1}{(\rho^*-1)+\varepsilon}\right)+\left(\frac{n-1}{(\rho^*-1)+\varepsilon}\right)\log\left(\frac{n-1}{(\rho^*-1)+\varepsilon}\right)}{\log(m+n)}\cdot o(1)$$

as $m\to\infty$, $n\to\infty$

or

$$\liminf_{m,n\to\infty}\frac{\log\log\left|b_{m,n}\right|^{-1/(m+n)}}{\log(m+n)}\ge\frac{1}{(\rho^*-1)+\varepsilon},$$

or $\qquad \limsup_{m,n\to\infty}\frac{\log(m+n)}{\log\log\left|b_{m,n}\right|^{-1/(m+n)}}\le(\rho^*-1)+\varepsilon,$

which gives $\partial^* - 1 \le \rho^* - 1 + \varepsilon$. Since ε is arbitrary, so we get

(3.5) $\partial^* \le \rho^*$.

Which prove that 3.1 holds. taking (3.4) and (3.5) together in to account, we get

$\partial^* = \rho^*$.

Hence the proof is completed.

Theorem 3.2. Let $f(z_1, z_2) \in L^2_{(\alpha)}$ and for $0 < \rho^* < \infty$, then $f(z_1, z_2)$ can be extended to an integral function of logarithmic order ρ^* $(0 < \rho^* < \infty)$ and logarithmic type T^* $(0 < T^* < \infty)$ if and only if

$$(3.6) \qquad d^{\rho^*} e \rho^* T^* = \limsup_{m,n\to\infty} \left\{ \frac{(m+n)^{\rho^*}}{\left\{\log|a_{mn}|^{-1}\right\}^{(\rho^*-1)}} \right\} \left(\frac{\rho^* - 1}{\rho^*} \right)^{(\rho^*-1)} \frac{1}{(2\rho^*)},$$

Proof. Let (3.6) be holds, then we have to show that $f(z_1, z_2)$ can be extended to an entire function of logarithmic order ρ^* and logarithmic type T^*. By (3.6) it can be easily seen that

$$\limsup_{m,n\to\infty} \frac{\log(m+n)}{\log\log|b_{mn}|^{-1/(m+n)}} = \rho^* - 1.$$

Using theorem 3.1, we see that $f(z_1, z_2)$ is an integral function. Suppose $f(z_1, z_2)$ has logarithmic type T^*, then using Lemma 2.7,

$$\limsup_{r_1, r_2} \frac{\log \overline{M}(r_1, r_2)}{(\log r_1)^{\rho^*} + (\log r_1)^{\rho^*}} = T^*, \text{ when } 1 < \rho^* < \infty$$

Let $T^* < \infty$. For any $\varepsilon > 0$, there exists $r_1^\circ = r_1^\circ(\varepsilon)$, $r_2^\circ = r_2^\circ(\varepsilon)$ such that

$$\log \overline{M}(r_1, r_2) \le (T^* + \varepsilon)\left[(\log r_1)^{\rho^*} + (\log r_2)^{\rho^*}\right], \quad \text{for} \quad r_1^\circ > r_1^\circ,$$

$r_2^\circ > r_2^\circ$.

By Lemma 2.6, we obtain

$$(3.7) \qquad \log|b_{m,n}| \le (T^* + \varepsilon)\left[(\log r_1)^{\rho^*} + (\log r_2)^{\rho^*}\right] + (m+n-2)\varepsilon - (m-1)$$

$\log(r_1/d_1) - (n-1)\log(r_2/d_2) + \log K$,

for $r_1 > r_1^\circ$, $r_2 > r_2^\circ$ and $m > m^\circ(\varepsilon)$, $n > n^\circ(\varepsilon)$.

Choosing

$$r_m = \left(\frac{m}{\rho^*(T^* + \varepsilon)}\right)^{1/\rho^*}, \quad r_n = \left(\frac{n}{\rho^*(T^* + \varepsilon)}\right)^{1/\rho^*}, \text{ then for } r_1 = r_m,$$

$r_2 = r_n$, we get

$$\log|b_{m,n}| \le \frac{T^*+\varepsilon}{\rho^{*\rho^*}}\left\{\left(\log\frac{m}{\rho^*(T^*+\varepsilon)}\right)^{\rho^*}+\left(\log\frac{n}{\rho^*(T^*+\varepsilon)}\right)^{\rho^*}\right\}+(m+n-2)\varepsilon$$

$$-\left(\frac{m-1}{\rho^*}\right)\log\left(\frac{m}{d_1^{\rho^*}\ \rho^*(T^*+\varepsilon)}\right)-\left(\frac{n-1}{\rho^*}\right)\log\left(\frac{n}{d_2^{\rho^*}\ \rho^*(T^*+\varepsilon)}\right)+\log K$$

which gives

$$\limsup_{m,n\to\infty}\left\{\frac{(m+n)^{\rho^*}}{\left\{\log|a_{mn}|^{-1}\right\}^{(\rho^*-1)}}\right\}\left(\frac{\rho^*-1}{\rho^*}\right)^{(\rho^*-1)}\frac{1}{(2\rho^*)} \le e\rho^*(T^*+\varepsilon)d_1^{\rho^*}d_2^{\rho^*}e^{\rho^*\varepsilon},$$

since this is true for every $\varepsilon>0$, we have

$$(3.8)\qquad e\rho^* T^* d^{\rho^*} \ge \limsup_{m,n\to\infty}\left\{\frac{(m+n)^{\rho^*}}{\left\{\log|a_{mn}|^{-1}\right\}^{(\rho^*-1)}}\right\}\left(\frac{\rho^*-1}{\rho^*}\right)^{(\rho^*-1)}\frac{1}{(2\rho^*)}.$$

By (3.3), we obtain

$$\limsup_{r_1,r_2\to\infty}\frac{\log\overline{M}(r_1,r_2)}{(\log r_1)^{\rho^*}+(\log r_2)^{\rho^*}} \le \left(\frac{1+\varepsilon}{d_1}\right)^{\rho^*}\left(\frac{1+\varepsilon}{d_2}\right)^{\rho^*}$$ type of $g(z_1,z_2)$.

Using Lemma 2.7 and (1.4), leads to

$$(3.9)\qquad T^* e\rho^* d^{\rho^*} \le \limsup_{m,n\to\infty}\left\{\frac{(m+n)^{\rho^*}}{\left\{\log|a_{mn}|^{-1}\right\}^{(\rho^*-1)}}\right\}\left(\frac{\rho^*-1}{\rho^*}\right)^{(\rho^*-1)}\frac{1}{(2\rho^*)}$$

Combining (3.8) and (3.9), we get the required result.
The converse part is left to the reader.

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Strongly Purely Extending Modules

Saad A. Alsaadi
Department of Mathematics, College of Science, Al-Mustansiriya University

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الخلاصة

لتكن R حلقة و M مقاس معرفا على R. يقال للمقاس M بأنه توسع أذا كان كل مقاس جزئي من M يكون جوهري من مركبة جمع مباشر من M. تبعاً لفوكس و كلارك ، المقاس M يدعى توسع نقي أذا كان كل مقاس جزئي من M يكون جوهري من مقاس جزئي نقي من M. مقاسات التوسع النقية هي تعميم واسع لمقاسات التوسع لأن المقاسات الجزئية النقية هي خاصية أوسع بكثير من مفهوم مركبات الجمع المباشر. في هذا البحث، تم عرض و دراسة أصناف من المقاسات التي تكون على طرفي مقاسات التوسع النقية.

أولاً، كمفهوم أقوى فعلياً من مفهوم مقاسات التوسع النقية، نقول عن المقاس M أنه توسع نقي بشدة أذا كان كل مقاس جزئي من M يكون جوهري من مقاس جزئي نقي تام الاستقرار من M. تم أعطاء العديد من التشخيصات و الخواص لمقاسات التوسع النقية بشدة. تم التوضيح بمثال على أن الجمع المباشر المقاسات التوسع النقية بشدة ليس بالضرورة تكون مقاس توسع نقي بشدة. إضافة إلى ذلك، تم أعطاء شرط كافي و ضروري لجعل الجمع المباشر لأي مجموعة من مقاسات التوسع النقية بشدة تكون مقاس توسع نقي بشدة.

ثانياً، كتعميم فعلي لمقاسات التوسع النقية نقول عن المقاس M أنه توسع من النمط FI بنقاوة أذا كان كل مقاس جزئي تام الاستقرار من M يكون جوهري من مقاس جزئي نقي من M. تم أعطاء العديد من التشخيصات و الخواص لمقاسات التوسع من النمط FI بنقاوة. تم البرهنة على أن الجمع المباشر لأي مجموعة من مقاسات من النمط FI بنقاوة تكون مقاس توسع من النمط FI بنقاوة.

ABSTRACT

An R-module M is extending if every submodule of M is essential in a direct summand of M. Following Fuch an Clark, an R-module M is purely extending if every submodule of M is essential in a pure submodule of M. Purely extending modules is a wider generalization of extending modules because the gap between direct summand and pure submodules.

In this paper, we introduce and study classes of modules which are the extremists of purely extending modules. Firstly, as stronger properly than that of purely extending modules, we call an R-module M is strongly purely extending if every submodule of M is essential in a fully invariant pure submodule of M. Many characterizations and properties of strongly purely extending modules are given. It is explained by example that a direct sum of strongly purely extending modules need not be strongly purely extending. Moreover, we give a sufficient and necessary condition to make a direct sum of strongly purely extending modules is valid.

Secondly, as a proper generalization of purely extending modules, we call an R-module M is purely FI-extending if every fully invariant submodule of M is essential in a pure submodule of M. Numerous characterizations and properties of purely FI-extending modules are investigated. For example, it is shown that a direct sum of purely FI-extending modules is purely FI-extending.

INTRODUCTION

Throughout all rings have an identity and modules are unitary. Let R be a ring and M be a left R-module. A submodule N of M is essential if every non-zero submodule of M intersects N nontrivially. Also, a submodule N of M is closed in M, if it has no proper essential extensions in M [1]. By Zorn's lemma any submodule of M is contained in a maximal essential extension (a closed submodule) in M. Also, a submodule N of M is fully invariant if $f(N) \subseteq N$ for every endomorphism f of M [1].

Extending modules are defined as modules with the property that every submodule is essential in a direct summand, equivalently; every closed submodule is direct summand [1]. They have been intensively studied throughout the last two decades. In 1995 L. Fuchs [2], considered their generalization by replacing "direct summand" with "pure submodule" in the definition (recall that a submodule N of an R-module M is pure if $IM \cap N = IN$ for every finitely generated ideal I of R [3]). J.Clark [4] studied this concept under the name purely extending modules, that is, an R-module M is purely extending, if every submodule is essential in a pure submodule of M. Moreover, purely extending modules studied extensively in [5]. On other hand, recently a class of modules which is stronger properly than extending modules is given as follows: an R-module M is strongly extending every submodule is essential in a fully invariant direct summand of M [6].

Since purely extending modules is a wider generalization of extending modules because the gap between direct summands and pure submodules, so this motivates us to introduce the next class of modules which is intermediate the class of strongly extending modules and the class of purely extending modules as follows:

Definition (1.1): An R-module M is called strongly purely extending, if every submodule of M is essential in a fully invariant pure submodule of M.

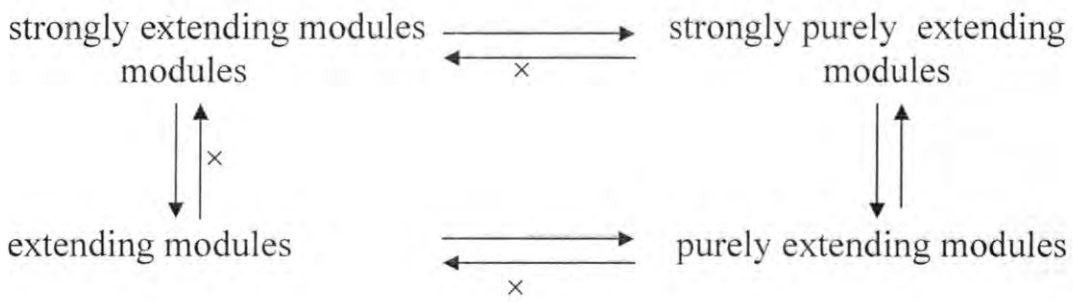
Remarks and Examples (1.2):

(1) Every strongly purely extending module is purely extending module, but the converse is not true in general (see (6)).

(2) Every strongly extending module is strongly purely extending module, but the converse is not true in general (we have no example yet).

(3) Every uniform module is strongly purely extending. In particular, Z_{p^∞} as Z-module is strongly purely extending (Recall that an R-module M is uniform if every submodule of M is essential in M [1]).

(4) The converse of (3) is not true in general. For example, Z_6 as Z-module is strongly purely extending which is not uniform.
(5) Recall that an R-module M is SS-module if every direct summand of M is fully invariant [6]. We can conclude that every strongly purely extending module is SS-module.
(6) Consider $M=Z_p^{\infty}\oplus Z_p^{\infty}$ as Z-module. By [5, Remarks and Examples (2.2.9)(2)], M is not SS-module and hence by using (5) $M=Z_p^{\infty}\oplus Z_p^{\infty}$ is not strongly purely extending Z-module, while $M=Z_p^{\infty}\oplus Z_p^{\infty}$ is purely extending (since M is extending) Z-module.
(7) Recall that an R-module M is pure-simple if *(0)* and M are the only pure submodules of M [7]. It is easy to check that, every strongly purely extending pure-simple is uniform.
(8) Recall that, a ring R is regular if for each x in R, there exists y in R such that x = xyx [8]. Easily, we can conclude that every commutative regular ring is strongly purely extending.
From all above remarks we get the following chart of implications:



The following result gives a characterization of strongly purely extending modules.

Theorem (1.3): An R-module M is strongly purely extending if and only if every closed submodule of M is a fully invariant pure in M .
Proof: ($\Rightarrow$). Suppose that M is strongly purely extending and let A be a closed submodule of M. Thus, by hypothesis, there exists a fully invariant pure submodule B of M such that A is essential in B. But A is closed in M, so $A = B$ (i.e.) A is fully invariant pure submodule of M.
($\Leftarrow$). Let A be a submodule of M. So, by Zorn's lemma, there exists a closed submodule K in M such that A is essential in K. Since K is closed submodule in M, hence (by our assumption) K is fully invariant pure submodule of M. Therefore, M is strongly purely extending. ◘

Recall that an R-module M is called duo if every submodule of M is fully invariant [8]. As a generalization of duo modules, we call an R-module M is cl-duo, if every closed submodule of M is fully invariant. This concept motivates us to get another useful

characterization of strongly purely extending modules (the proof is routine, so omitted).

Proposition (1.4): An R-module M is strongly purely extending if and only if M is cl-duo and M is purely extending. ◘

A natural question about any algebraic structure is whether the property is inherited by direct summands. The next proposition asserts that direct summands of strongly purely extending modules inherit property.

Proposition (1.5): A direct summand of a strongly purely extending is strongly purely extending.

Proof: Let K be a direct summand of a strongly purely extending module M. Let A be a closed submodule of K. But K is a direct summand of M and hence it is closed submodule of M [8]. Thus, A is a closed submodule of M [1]. So, since M is strongly purely extending, then A is a fully invariant pure submodule of M. Now, since $A \subseteq K \subseteq M$ and A is pure submodule of M, thus by [9] A is pure submodule of K. In other hand, we claim that A is fully invariant of K, to verify this, let f: $K \longrightarrow K$ be an endomorphism of K, then we have the following implications: $M \xrightarrow{\pi} K \xrightarrow{f} K \xrightarrow{i} M$, where π: $M \longrightarrow K$ and i:$K \longrightarrow M$ are the projection mapping and inclusion mapping respectively. Since A is fully invariant of M, then $(i \circ f \circ \pi)(A) \subseteq A$, but $f(A) = (i \circ f \circ \pi)(A) \subseteq A$, so A is a fully invariant of K. Thus, A is a fully invariant pure submodule of K. Hence, K is strongly purely extending. ◘

An R-module M is extending if and only if $A \cap M$ is a direct summand of M for each direct summand A of $E(M)$ [1]. This result motivates us to obtain another characterization of strongly purely extending modules as follows:

Theorem (1.6): The following statements are equivalent for an R-module M:

(1) M is strongly purely extending;
(2) Every closed submodule of M is fully invariant pure in M;
(3) If A is direct summand of the injective hull $E(M)$ of M, then $A \cap M$ is a fully invariant pure submodule of M.

Proof: (1) $\Rightarrow$(2). Form Theorem (1.3).
(2) $\Rightarrow$(3). Let A be a direct summand of the injective hull $E(M)$ of M. Thus, $E(M) = A \oplus B$, where B is a submodule of $E(M)$. Assume that $A \cap M$ is essential in a submodule H of M and let $h \in H$. So, $h=a+b$,$a \in A$ and $b \in B$. Suppose that $h \notin A$. Thus, $b \neq 0$. But M is essential in $E(M)$ and $0 \neq b \in B \subseteq E(M)$, therefore there exists $r \in R$ such that $0 \neq rb \in M$. Now, $rh = ra + rb$ and hence $ra = rb - rh \in A \cap M \subseteq H$. Thus, $rb = rh - ra \in B \cap H$. Since $A \cap M$ is essential in H, then $0 = (A \cap M) \cap B$ is essential in $B \cap H$ and hence $B \cap H = 0$. Thus, $rb = 0$ which is a contradiction. Thus, $A \cap M$ is closed submodule of M. So, by using (2) $A \cap M$ is fully invariant pure submodule of M.
(3) $\Rightarrow$(1). Let A be a submodule of M and let B a relative complement of A in M, then by [1] $A \oplus B$ is essential in M. But M is essential in $E(M)$, therefore, $A \oplus B$ is essential in $E(M)$. Thus, $E(A) \oplus E(B) = E(A \oplus B) = E(M)$ [8]. Since $E(A)$ is direct summand of $E(M)$, then $E(A) \cap M$ is fully invariant pure submodule of M. But A is essential in $E(A)$ and M is essential in M, so by [8], $A = A \cap M$ is essential in $E(A) \cap M$ which is fully invariant pure submodule of M. Thus, M is strongly purely extending. ◘

Recall that an R-module M is prime if $ann(x) = ann(y)$ for each non-zero elements x and y in M [8]. Firstly, we need the next lemma:
Lemma (1.7): [5] Let M be a prime R-module and let A be a pure submodule of an R-module E. If M is essential in E, then $A \cap M$ is closed in M. ◘

Proposition (1.8): Let M be a prime R-module. Then the following statements are equivalent:

(1) M is strongly purely extending;
(2) Every closed submodule of M is fully invariant pure in M;
(3) If A is a pure submodule of the injective hull $E(M)$ of M, then $A \cap M$ is fully invariant pure in M.

Proof: (1) $\Rightarrow$(2). Form Theorem (1.3).
(2) $\Rightarrow$(3). Let A be a pure submodule of $E(M)$ .Now since M is essential in $E(M)$, then by lemma (1.6), $A \cap M$ is closed in M and hence by hypothesis, $A \cap M$ is fully invariant pure submodule of M.
(3) $\Rightarrow$(1). Let A be a submodule of M and let B be a relative complement of A in M and hence by [8], $A \oplus B$ is essential in M. Thus, by using the same argument in Theorem (1.6) ((3) $\Rightarrow$(1)), $E(A)$ is a pure submodule of $E(M)$ and $E(A) \cap M$ is fully invariant pure submodule in M. Since A is essential in $E(A)$, then $A = A \cap M$ is essential in $E(A) \cap M$. So, M is strongly purely extending. ◘

We observed that every strongly purely extending module is purely extending, but the converse is not true in general (Remarks and Examples (1.2) (1)). In the following result, we give conditions which the converse is true. Firstly, Recall that an R-module M is multiplication if, each submodule of M is of the form IM for some ideal I of R [10].

Proposition (1.9): Every multiplication purely extending module is strongly purely extending.

Proof: Let M be a multiplication purely extending module and let N be a closed submodule of M. Since M is purely extending, thus N is a pure submodule of M. It is enough to show that N is a fully invariant of M. Let g: $M \longrightarrow M$ be any R-endomorphism of M. Since M is multiplication, thus $N=IM$ for some ideal I of R. Now, $g(N)=g(IM)=Ig(M)\subseteq IM=N$. Hence, by Proposition (1.3), M is strongly extending. ◘

Since every commutative ring is multiplication [10], so we have the next result:

Corollary (1.10): A commutative ring is strongly purely extending if and only if is purely extending. ◘

It is well-known that a direct sum of extending (resp., purely extending) modules need not be extending (resp., purely extending) [1] (resp., [5]). Likely, a direct sum of strongly purely extending modules need not be strongly purely extending, for example, consider $M=Z_p^{\infty}\oplus Z_p^{\infty}$ as Z-module is not strongly purely extending while the Z_p^{∞} is purely extending Z-module.

The following proposition gives a sufficient and necessary condition to make a direct sum of strongly purely extending modules is valid.

Proposition (1.11): Let $M=\bigoplus_{i\in I} M_i$ be an R-module, where each M_i is a submodule of M. Then, M is strongly purely extending if and only if M_i is strongly purely extending $\forall\, i\in I$ and each closed submodule of M is fully invariant.

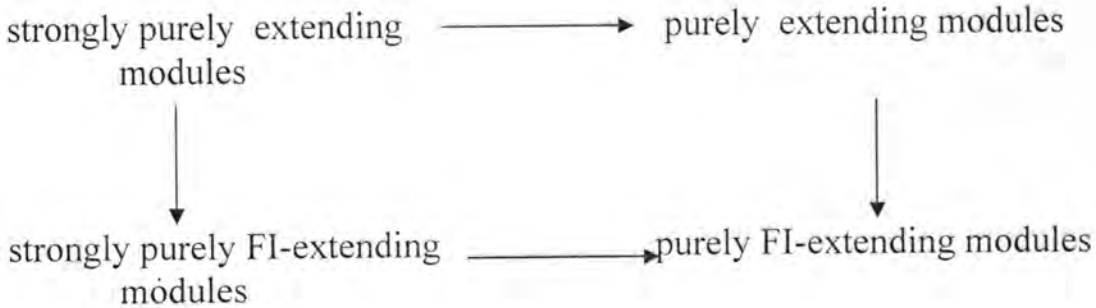
Proof: ($\Rightarrow$). By proposition (1.5) and Theorem (1.6).
($\Leftarrow$). Let A be a closed submodule of M and let π_i: $M \longrightarrow M_i$ be the natural projection on M_i for each $i \in I$. Let $x \in A$, then $x = \sum_{i \in I} m_i$ where $m_i \in M_i$ and hence $\pi_i(x) = m_i$. But A is closed in M, then (by our assumption) A is fully invariant and hence $\pi_i(A) \subseteq A \cap M_i$ for *each* $i \in I$. So, $\pi_i(x) = m_i \in A \cap M_i$. Thus, $x \in \bigoplus_{i \in I}(A \cap M_i)$ and hence $A \subseteq \bigoplus_{i \in I}(A \cap M_i)$. Since $\bigoplus_{i \in I}(A \cap M_i) \subseteq A$, then $A = \bigoplus_{i \in I}(A \cap M_i)$. Now since $A \cap M_i$ is a direct summand of A, so $A \cap M_i$ is closed submodule in M. But $A \cap M_i \subseteq M_i$, then $A \cap M_i$ is closed in M_i for each $i \in I$. By hypothesis, M_i is strongly purely extending module, thus $A \cap M_i$ is fully invariant pure submodule of M_i. By [7, proposition (4.2) ch.2], $A = \bigoplus_{i \in I}(A \cap M_i)$ is pure submodule of $M = \bigoplus_{i \in I} M_i$ and by hypotesis (since A is closed submodule of M), thus $A = \bigoplus_{i \in I}(A \cap M_i)$ is fully invariant submodule of $M = \bigoplus_{i \in I} M_i$. Hence, $M = \bigoplus_{i \in I} M_i$ is strongly purely extending. ◘

Recall that an R-module M is called FI-extending if, every fully invariant submodule of M is essential in a direct summand of M [11]. This concept motivates us to introduce the following concepts:

Definition (1.12): An R-module M is called purely FI-extending if, every fully invariant submodule of M is essential in a pure submodule of M.

Definition (1.13): An R-module M is called strongly purely FI-extending if, every fully invariant submodule of M is essential in a fully invariant pure submodule of M.

The following chart of implications unifies relationships among all concepts which considered in this paper:



It is known that a direct sum of purely extending modules need not be purely extending [5]. The following result investigates that a direct sum property valid on purely FI-extending modules.

Theorem (1.14): A direct sum of purely FI-extending modules is purely FI-extending module.

Proof: Let $M = \bigoplus_{\alpha\in\Lambda} M_\alpha$ where M_α is purely FI-extending modules for each $\alpha\in\Lambda$ and H be a fully invariant submodule of M. Since for each $\alpha\in\Lambda$, $\pi_\alpha: M \longrightarrow M_\alpha$ such that $\pi_\alpha(H)\neq 0$, $\pi_\alpha(H)$ is fully invariant submodule of M_α. But M_α is purely FI-extending, then there exists a pure submodule P_α of M_α such that $\pi_\alpha(H)$ is essential in P_α. By [11, lemma (1.1) (iii)], $H = \bigoplus_{\alpha\in\Lambda} \pi_\alpha(H)$ and so is essential in $\bigoplus_{\alpha\in\Lambda} P_\alpha$. Since P_α is pure submodule of M_α, then $\bigoplus_{\alpha\in\Lambda} P_\alpha$ is pure submodule of $M= \bigoplus_{\alpha\in\Lambda} M_\alpha$ [7]. Hence, M is purely FI-extending. ■

We observed that every purely extending module is purely FI-extending. Here we see the converse is not true in general, for example, consider the module $M = Z_8\oplus Z_2$ as Z-module. By using theorem (1.11) since Z_8 and Z_2 are purely FI-extending Z-module then $M = Z_8\oplus Z_2$ is purely FI-extending Z-module, while $M = Z_8\oplus Z_2$ is not purely extending since $A = (\bar{2},\bar{1})$ the submodule generated by $(\bar{2},\bar{1})$, it can be easily check that A is closed submodule of M, but A is not pure submodule of M since $(\bar{4},\bar{0}) = 4(\bar{1},\bar{0}) \in 4(Z_8\oplus Z_2)\cap A$ but $(\bar{4},\bar{0})\notin 4A = (\bar{0},\bar{0})$.

The next result gives a condition under which the concepts of purely extending modules and purely FI-extending modules are equivalent. Firstly, recall that for each submodule N of an R-module M define a submodule of M as follows: $Cl(N) = \{m\in M \mid [N:m]$ is an essential ideal in $R\}$. Clearly $Cl(N)$ is a submodule of M, and it is called the closure of N (in sense of Goldie) [12].

Proposition (1.15): Let M be a non-singular module such that the closure of any submodule of M is fully invariant. Then, M is purely extending if and only if M is purely FI-extending.

Proof: ($\Rightarrow$). It is obvious.
($\Leftarrow$). Let N be a submodule of M. by hypothesis, $Cl(N)$ is fully invariant of M and hence, by purely FI-extending property of M, $C(N)$ is essential

in a pure submodule P of M. Since each submodule of non-singular module is essential in its closure [8] (i.e) N is essential in $Cl(N)$. So, we have N is essential in a pure submodule P of M. Hence, M is purely extending.□

Proposition (1.16): Let M be a non-singular R-module. Then, the following statements are equivalent:

(1) M is purely FI-extending;
(2) Every closed fully invariant submodule of M is a pure submodule;
(3) M is strongly purely FI-extending.

Proof: (1)⇒(2). Assume that M is purely FI-extending module. Let N be a closed fully invariant submodule of M. Since M is purely FI-extending, then N is essential in a pure submodule P of M. But N is closed submodule of M, so $N = P$. Hence P is pure submodule of M.
(2)⇒(3). Let X be a fully invariant submodule of M. By non-singularity of M, there exists a closed submodule ($Cl(X)$) of M such that X is essential in $Cl(X)$. One can easily check that if N is fully invariant of M, then $Cl(X)$ is fully invariant of M. Hence, by hypothesis, $Cl(X)$ is a pure submodule of M (i.e) X is essential in a fully invariant pure submodule of M. Therefore, M is strongly purely FI-extending.
(3) ⇒(1). It is clear.□

It is known that every direct summand of purely extending module is purely extending [5]. In fact, we do not know whether purely FI-extending property is inherited by direct summands. The next result gives a condition under which this inheritance is valid. Firstly, recall that an R-module M has the pure intersection property (PIP) if the intersection of any two pure submodule of M is pure [7].

Proposition (1.17): Let M be a non-singular R-module with (PIP) property. If M is purely FI-extending, then every direct summand of M is purely FI-extending.

Proof: Let N be a direct summand of M and let X be a closed fully invariant submodule of N. Now, since M is non-singular thus by [8, p.259] there exists a closed submodule $Y = Cl(X)$ in M such that X is essential in Y. But N is essential in N, then $X = X \cap N$ is essential in $Y \cap N \subseteq N$. Since X is closed submodule of N, thus $X = Y \cap N$. But Y is closed fully invariant submodule of M, so by purely FI-extending property of M, Y is pure submodule of M. Also, N is direct summand of M, so in turn N is pure submodule of M.Thus. By (PIP) property of M, we have $X = Y \cap N$ is a pure submodule of M. But $Y \cap N \subseteq N$, then X is pure

submodule of N [7]. Also, since M is non-singular, then N so [8]. Thus, by proposition (1.6), N is purely FI-extending.□

By using the same argument in the proposition (1.17), we have the following result.

Proposition (1.18): Let M be an R-module with (PIP) property. Then, if M is strongly purely extending, then every fully invariant pure submodule of M is strongly purely extending.

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Locally Conformal Kahler Manifold of Class R_3

Habeeb M. Aboud and Haithem A. Rakees
College of Education, University of Basrah, Basrah-Iraq

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الخلاصة

في هذا البحث ندرس متعدد طيات كوهلر الكونفورمي المحلي وهو واحد من الأصناف الستة عشر لمتعدد الطيات الهرميتي التقريبي.نجد المعادلة التركيبية لمتعدد طيات كوهلر الكونفورمي المحلي ، مركبات تنسر الأنحناء الريماني، ومن ثم نجد الشرط الضروري والكافي الذي عنده يكون متعدد طيات كوهلرالكونفورمي المحلي هو متعدد الطيات من الصنف R_3 .

ABSTRACT

In this paper we study the locally conformal Kähler manifold, which is one of the sixteen classes of almost Hermitian manifold. We find the total structure equation of the locally conformal Kähler manifold, the components of the Riemannian curvature tensor and then we find the necessary and sufficient condition for which that the locally conformal Kähler manifold is the manifold of class R_3 .

INTRODUCTION

In this paper we will consider one of the important class of almost Hermitian manifold, namely "locally conformal Kähler manifold". The first study on this pattern appeared in 1955 by Libermann [1]. He thoroughly discussed this pattern. The real studies of this pattern locally conformal Kähler manifold appeared after the observation of the researcher Vaisman, which was that the classical example for Hermitian manifold is locally conformal Kähler manifold. He found out the rules by which locally conformal Kähler manifold will be a global conformal Kähler manifold. Vaisman put down some geometrical conditions for locally conformal Kähler manifold [2]. Vaisman [3] and Kashiwada [4] studied locally conformal Kähler manifold by the parallel rules of Lie form. The results of this study are summarized follows; the parallel rule of Riemannian connection form and Lie form makes the locally conformal Kähler manifold be as Kähler manifold. In 1982 Tricerri [5] published a study and mentioned so many different examples of locally conformal Kähler manifold.

It's worthy to say that the most studies or works about almost Hermitian manifold are presented and described by the assistance of Koshel's operator. At the same time, new studies started to exist about this subject by the help of the theory of G-structure space. V. F. Kirichenko found, in particular, the first group of structure equation of almost Hermitian manifold. He inserted the concept of (structure tensor) and (virtual tensor) [6]. The studies started to represent this method

which allows studies of the geometrical structural characteristics for each class of almost Hermitian manifold. In 1993, M.Banaru [7] succeeded to classify the 16 classes of almost Hermitian manifold using the two tensors of Kirichenko, which were named the Kirichenko's tensors [8].

In this study we consider the class of locally conformal Kähler manifold, using the method of G- structure space and Kirichenko's tensors.

ALMOST HERMITIAN MANIFOLD

We will consider an almost Hermitian manifold $\{M, J, g =<\cdot,\cdot>\}$, i.e. 2n-dimensional manifold M^{2n} with a Riemannian metric $g =<\cdot,\cdot>$ and an almost complex structure J. Moreover, the following condition must hold :

$g(JX, JY) = g(X, Y) \qquad \forall X, Y \in X(M)$

where $X(M)$ is the module of vector field on M.

Remark:

From [9], we conclude that the setting of an almost Hermitian structure is equivalent to setting of G-structure in principle fiber bundle of frames which it's elements are called the A-frames, where G is the unitary group $U(n)$. This group is called the adjoint G-structure .

Therefore, the matrices of the operators of the almost complex structure and the Riemannian metric can be written as the following:

1)
$$(J_j^i)=\begin{pmatrix} \sqrt{-1}I_n & 0 \\ 0 & -\sqrt{-1}I_n \end{pmatrix}$$
(2.1)

2)
$$(g_{ij})=\begin{pmatrix} 0 & I_n \\ I_n & 0 \end{pmatrix}$$
(2.2)

From [1], we have that given almost Hermitian structure on smooth manifold equivalent to the given Hermitian metric

$<< X, Y >> = < X, Y > + \sqrt{-1}\,\Omega(X, Y)$

where $\Omega(X, Y) =< X, JY >$ is 2-form which is called the fundamental (Kählerian) form of almost Hermatian manifold [10], [11].

By direct computing it is easy to obtain that in adjoint G-structure, the fundamental form matrix looks as follows:

$$(\Omega_{ij})=\begin{pmatrix} 0 & \sqrt{-1}I_n \\ -\sqrt{-1}I_n & 0 \end{pmatrix}$$
(2.3)

Where I_n is the identity matrix.

Definition 2.1:
An almost Hermitian manifold is said to be of J-invariant curvature tensor if $< R(X,Y)Z,W >=< R(JX,JY)JZ,JW >$
Such manifold, called also manifold of class R_3 [9].

THE STRUCTURE EQUATION OF LOCALLY CONFORMAL KAHLER MANIFOLD

Definition 3.1 [12]

Suppose that M is a Riemannian manifold and $f \in C^\infty(M)$, If given two Riemannian metrics g and $\widetilde{g}$ which are connected by $\widetilde{g} = e^{2f} g$, then we say that on M given a conformal transformation of the metric g into the metric $\widetilde{g}$.

Let M be almost Hermitian manifold with almost Hermitian structure $\{J, g =< \cdot, \cdot >\}$, if there exist a conformal transformation of the metric g into the metric $\widetilde{g}$, then $\{M, J, \widetilde{g} = e^{2f} g\}$ will be almost Hermitian manifold. In this case we say that on smooth manifold M given conformal transformation of almost Hermitian structure, denoted by $\widetilde{M}_f$.

Definition 3.2 [13]

An almost Hermitian manifold $\{M, J, g =< \cdot, \cdot >\}$ is called a locally conformal Kähler manifold, if for each point $m \in M$ there exist an open neighborhood U of this point and there exist $f \in C^\infty(U)$ such that $\widetilde{U}_f$ is Kähler manifold. We will denote the locally conformal Kähler manifold by *L.C.K.*.

Definition 3.3 [13]

Let M be an almost Hermitian manifold of dimension $2n$, then the form which is given by the relation $\omega = \frac{-1}{n-1} \delta\Omega \circ J$ is called Lie form, where δ represents the coderivative.
If Ω is r-form, then it's coderivative is r-1 –form $\delta\Omega$, and it's dual is vector which is called Lie vector.

Lemma 3.1 [13]

If M is *L.C.K.* manifold of dimension 2n, then $d\Omega = \omega \wedge \Omega$, and Lie form is closed which means that $d\omega = 0$.

Lemma 3.2 Let M be L.C.K. manifold, then the virtual tensor given by:

1) $B^{ab}{}_c = \alpha^{[a}\delta_c^{b]}$

2) $B_{ab}{}^c = \alpha_{[a}\delta_{b]}^c$

Proof:

According to Lemma (3.1.1) we have:

$d\Omega = \omega\Lambda\Omega$.

Suppose that $\{\alpha_i\}$ are the components of the Lie form in the dual basis $\{\omega^i\}$, then $\omega = \alpha_a\omega^a + \alpha^a\omega_a$

Consider the fundamental form Ω, from (2.2) we have $\Omega_{a\bar{b}} = -\Omega_{\bar{b}a}$ then we get:

$$\begin{aligned}\Omega &= \Omega_{ij}\omega^i\Lambda\omega^j = \Omega_{a\bar{a}}\omega^a\Lambda\omega^{\bar{a}} + \Omega_{\bar{a}a}\omega^{\bar{a}}\Lambda\omega^a \\ &= -\sqrt{-1}\omega^a\Lambda\omega_a - \sqrt{-1}\omega^a\Lambda\omega_a \\ &= -2\sqrt{-1}\omega^a\Lambda\omega_a\end{aligned}$$

Then:

$$\begin{aligned}d\Omega &= -2\sqrt{-1}(d\omega^a\Lambda\omega_a - \omega^a\Lambda d\omega_a) \\ &= -2\sqrt{-1}(B^{ab}{}_c\omega^c\Lambda\omega_b\Lambda\omega_a - B_{ab}{}^c\omega_c\Lambda\omega^b\Lambda\omega^a)\end{aligned}$$

(3.1)

But we have in general case $\Omega = -2\sqrt{-1}\delta_b^c\omega^b\Lambda\omega_c$, then

$$\begin{aligned}\omega\Lambda\Omega &= (\alpha_a\omega^a + \alpha^a\omega_a)\Lambda(-2\sqrt{-1}\delta_b^c\omega^b\Lambda\omega_c) \\ &= -2\sqrt{-1}(\alpha_{[a}\delta_{b]}^c\omega_c\Lambda\omega^b\Lambda\omega^a + \alpha^{[a}\delta_c^{b]}\omega^c\Lambda\omega_b\Lambda\omega_a)\end{aligned}$$

(3.2)

According to (3.1) and (3.2) we obtain:

$B^{ab}{}_c = \alpha^{[a}\delta_c^{b]}$ and $B_{ab}{}^c = \alpha_{[a}\delta_{b]}^c$

Lemma 3.3

The components of covariant differential of the Lie form of *L.C.K.* manifold satisfy the relation $\alpha_{ij} = \alpha_{ji}$.

Proof:

Suppose that $\{\alpha_{ij}\}$ are the components of covariant differential of Lie form, then we have:

1) $d\alpha_a + \alpha_b\omega_a^b = \alpha_{ab}\omega^b + \alpha_a{}^b\omega_b$

2) $d\alpha^a - \alpha^b\omega_b^a = \alpha^a{}_b\omega^b + \alpha^{ab}\omega_b$

(3.3)

From Lemma 3.1, we have the Lie form of *L.C.K* manifold is closed, then by differentiation $\omega = \alpha_a\omega^a + \alpha^a\omega_a$ we obtain:

$$d\alpha_a\Lambda\omega^a + \alpha_a(\omega_b^a\Lambda\omega^b + B^{ab}{}_c\omega^c\Lambda\omega_b) + d\alpha^a\Lambda\omega_a$$
$$+\alpha^a(-\omega_a^b\Lambda\omega_b + B_{ab}{}^c\omega_c\Lambda\omega^b) = 0$$

Substitute (3.3:1) and using (3.3:2) in above equation we get:

$$\alpha_{ab}\omega^b\Lambda\omega^a+\alpha_a{}^b\omega_b\Lambda\omega^a+\alpha^a{}_b\omega^b\Lambda\omega_a+\alpha^{ab}\omega_a\Lambda\omega_b$$
$$+\alpha_c B^{cb}{}_a\omega^a\Lambda\omega_b+\alpha^c B_{cb}{}^a\omega_a\Lambda\omega^b=0$$

According to linearly independent we get:

1) $\alpha_{[ab]}=0$,

2) $\alpha^{[ab]}=0$

(3.4)

3) $\alpha_a{}^b-\alpha^b{}_a-\alpha_c B^{cb}{}_a+\alpha^c B_{ca}{}^b=0$

By the Lemma 3.2:2 we get:

$$\alpha_c B^{cb}{}_a-\alpha^c B_{ca}{}^b=\frac{1}{2}\alpha_c(\alpha^c\delta_a^b-\alpha^b\delta_a^c)-\frac{1}{2}\alpha^c(\alpha_c\delta_a^b-\alpha_a\delta_c^b)$$
$$=\frac{1}{2}\alpha_c\alpha^c\delta_a^b-\alpha_a\alpha^b-\frac{1}{2}\alpha_c\alpha^c\delta_a^b+\alpha_a\alpha^b=0$$

Therefore, $\alpha_a{}^b=\alpha^b{}_a$.

Theorem 3.1

The structure equation of Locally conformal Kähler manifold in adjoint *G*-structure space has the following forms:

1) $d\omega^a=\omega_b^a\Lambda\omega^b+B^{ab}{}_c\,\omega^c\Lambda\omega_b$

2) $d\omega_a=-\omega_a^b\Lambda\omega_b+B_{ab}{}^c\,\omega_c\Lambda\omega^b$

3) $d\omega_b^a=\omega_c^a\Lambda\omega_b^c+A_{bc}^{ad}\,\omega^c\Lambda\omega_d+\{\frac{1}{2}\alpha^{a[c}\delta_b^{d]}+\frac{1}{4}\alpha^a\alpha^{[c}\delta_b^{d]}\}\omega_c\Lambda\omega_d$

Proof:

According to [13] we have that every *L.C.K.* manifold is Hermitian manifold and an almost Hermitian manifold is Hermitian manifold if and only if $B^{abc}=B_{abc}=0$, then the first group of the structure equation of L.C.K. manifold is given by:

1) $d\omega^a=\omega_b^a\Lambda\omega^b+B^{ab}{}_c\,\omega^c\Lambda\omega_b$

2) $d\omega_a=-\omega_a^b\Lambda\omega_b+B_{ab}{}^c\,\omega_c\Lambda\omega^b$ (3.5)

Differentiation (3.5:1) we get:

$$d\omega_b^a\Lambda\omega^b-\omega_b^a\Lambda d\omega^b+dB^{ab}{}_c\,\omega^c\Lambda\omega_b+B^{ab}{}_c(d\omega^c\Lambda\omega_b-\omega^c\Lambda d\omega_b)=0$$

Substitute (3.5:1) and (3.5:2) in above equation we obtain:

$$d\omega_b^a\Lambda\omega^b-\omega_b^a\Lambda(\omega_c^b\Lambda\omega^c+B^{bc}{}_r\,\omega^r\Lambda\omega_c)+dB^{ab}{}_c\,\omega^c\Lambda\omega_b$$
$$+B^{ab}{}_c(\omega_h^c\Lambda\omega^h+B^{cd}{}_r\,\omega^r\Lambda\omega_d)\Lambda\omega_b-B^{ab}{}_c\,\omega^c\Lambda(-\omega_b^h\Lambda\omega_h$$
$$+B_{bh}{}^r\,\omega_r\Lambda\omega^h)=0$$
$$d\omega_b^a\Lambda\omega^b-\omega_c^a\Lambda\omega_b^c\Lambda\omega^b+dB^{ab}{}_c\omega^c\Lambda\omega_b+B^{ab}{}_h\omega_c^h\Lambda\omega^c\Lambda\omega_b$$
$$-B^{hb}{}_c\omega_h^a\Lambda\omega^c\Lambda\omega_b-B^{ah}{}_c\omega_h^b\Lambda\omega^c\Lambda\omega_b+B^{ab}{}_cB^{cd}{}_r\omega^r\Lambda\omega_h\Lambda\omega_b \quad (3.6)$$
$$+B^{ab}{}_cB_{bh}{}^r\omega^c\Lambda\omega_r\Lambda\omega^h=0$$

Let $\Delta\omega_b^a = d\omega_b^a - \omega_c^a \Lambda \omega_b^c$

And $\Delta B^{ab}{}_c = dB^{ab}{}_c + B^{ab}{}_h \omega_c^h - B^{hb}{}_c \omega_h^a - B^{ah}{}_c \omega_h^b$

Note that every basis of *2*- form gives us the form $\omega_h^a \Lambda \omega_a^c$, $\omega_b^a \Lambda \omega^c$, $\omega_b^a \Lambda \omega_c$, $\omega^a \Lambda \omega^b$, $\omega_a \Lambda \omega_b$, $\omega^a \Lambda \omega_b$, and the basis of *1*-form give as ω_b^a, ω^a, ω_a.

Then from the above notation. We conclude that the form of $\Delta\omega_b^a$ and $\Delta B^{ab}{}_c$ will be written as the form:

$$\Delta\omega_b^a = A_{bch}^{adr}\ \omega_d^c \Lambda \omega_r^h + A_{bdr}^{ac}\ \omega_c^d \Lambda \omega^r + A_{bd}^{acr}\ \omega_c^d \Lambda \omega_r + A_{bcd}^{a}\ \omega^c \Lambda \omega^d + A_b^{acd}\ \omega_c \Lambda \omega_d + A_{bc}^{ad}\ \omega^c \Lambda \omega_d$$

$$\Delta B^{ab}{}_c = B^{ab}{}_{cd}{}^r\ \omega_r^d + B^{ab}{}_{cd}\ \omega^d + B^{ab}{}_c{}^d \omega_d .$$

Substitute $\Delta\omega_b^a$ and $\Delta B^{ab}{}_c$ in (3.6) we obtain:

$$A_{bch}^{adr}\ \omega_d^c \Lambda \omega_r^h \Lambda \omega^b + A_{bdr}^{ac}\ \omega_c^d \Lambda \omega^r \Lambda \omega^b + A_{bd}^{acr}\ \omega_c^d \Lambda \omega_r \Lambda \omega^b +$$
$$A_{bc}^{ad}\ \omega^c \Lambda \omega_d \Lambda \omega^b + A_{bcd}^{a}\ \omega^c \Lambda \omega^d \Lambda \omega^b + A_b^{acd}\ \omega_c \Lambda \omega_d \Lambda \omega^b +$$
$$B^{ab}{}_{cd}{}^r\ \omega_r^d \Lambda \omega^c \Lambda \omega_b + B^{ab}{}_{cd}\ \omega^d \Lambda \omega^c \Lambda \omega_b + B^{ab}{}_c{}^d \omega_d \Lambda \omega^c \Lambda \omega_b +$$
$$B^{ab}{}_c B^{cd}{}_r \omega^r \Lambda \omega_h \Lambda \omega_b - B^{ab}{}_c B_{bh}{}^r \omega^c \Lambda \omega_r \Lambda \omega^h = 0$$

According to property of the linearly independent we get:

1) $A_{bch}^{adr} = 0$

2) $A_{[b|d|r]}^{ac} = 0$

3) $A_{bc}^{adr} - B^{ar}{}_{bd}{}^c = 0$

4) $A_{[bcd]}^{a} = 0$

5) $A_{[bc]}^{ad} - B^{ad}{}_{[bc]} + B^{ah}{}_{[b} B_{|h|c]}{}^d = 0$ (3.7)

6) $A_b^{a[cd]} - B^{a[cd]}{}_b + B^{a[c}{}_h B^{|h|d]}{}_b = 0$.

By the same way we differentiate (3.5:2) and substitute (3.5:1) and (3.5:2) we obtain:

$$-d\omega_a^b \Lambda \omega_b - \omega_a^c \Lambda \omega_c^b \Lambda \omega_b + dB_{ab}{}^c \omega_c \Lambda \omega^b + B_{hb}{}^c \omega_a^h \Lambda \omega_c \Lambda \omega^b$$
$$+ B_{ah}{}^c \omega_b^h \Lambda \omega_c \Lambda \omega^b - B_{ab}{}^h \omega_h^c \Lambda \omega_c \Lambda \omega^b + B_{ab}{}^c B_{ch}{}^r \omega_r \Lambda \omega^h \Lambda \omega^b$$
$$- B_{ab}{}^c B^{bh}{}_r \omega_c \Lambda \omega^r \Lambda \omega_h = 0 \qquad (3.8)$$

Let $\Delta\omega_a^b = -d\omega_a^b - \omega_a^c \Lambda \omega_c^b$

And $\Delta B_{ab}{}^c = dB_{ab}{}^c + B_{hb}{}^c \omega_a^h + B_{ah}{}^c \omega_b^h - B_{ab}{}^h \omega_h^c$

According to the preceding note we have:

$$-\Delta\omega_a^b = A_{adr}^{bch}\ \omega_c^d \Lambda \omega_h^r + A_{adr}^{bc} \omega_c^d \Lambda \omega^r + A_{ad}^{bcr}\ \omega_c^d \Lambda \omega_r + A_{ad}^{bc}\ \omega_c \Lambda \omega^d + A_a^{bcd}\ \omega_c \Lambda \omega_d + A_{acd}^{b}\ \omega^c \Lambda \omega^d$$

And $\Delta B^{ab}{}_c = B_{ab}{}^{cd}{}_r \omega_d^r + B_{ab}{}^{cd} \omega_d + B_{ab}{}^c{}_d \omega^d$

Substitution of $-\Delta\omega_a^b$ and $\Delta B_{ab}{}^c$ into (3.8) we get:

1) $A^{bch}_{adr} = 0$

2) $A^{[h|c|r]}_{ad} = 0$

3) $A^{bc}_{adr} - B_{ar}{}^{bc}{}_{d} = 0$

4) $A^{[bcd]}_{a} = 0$ (3.9)

5) $A^{b}_{a[cd]} - B_{a[cd]}{}^{b} + B_{a[c}{}^{h} B_{|h|d]}{}^{b} = 0$

6) $A^{[bc]}_{ad} - B_{ad}{}^{[bc]} + B_{ah}{}^{[b} B^{|h|c]}{}_{d} = 0$

From (3.7:3) and (3.9:3) we have:

$A^{adr}_{bc} = B^{ar}{}_{bd}{}^{c} = 0$ and $A^{bc}_{adr} = B_{ar}{}^{bc}{}_{d} = 0$ then:

1) $\Delta\omega^{a}_{b} = A^{a}_{bcd}\,\omega^{c}\Lambda\omega^{d} + A^{ad}_{bc}\,\omega^{c}\Lambda\omega_{d} + A^{acd}_{b}\,\omega_{c}\Lambda\omega_{d}$

2) $\Delta B^{ab}{}_{c} = B^{ab}{}_{cd}\,\omega^{d} + B^{ab}{}_{c}{}^{d}\,\omega_{d}$

3) $\Delta B^{ab}{}_{c} = B_{ab}{}^{cd}\,\omega_{d} + B_{ab}{}^{c}{}_{d}\,\omega^{d}$.

Which implies that

1) $d\omega^{a} = \omega^{a}_{b}\Lambda\omega^{b} + B^{ab}{}_{c}\,\omega^{c}\Lambda\omega_{b}$

2) $d\omega_{a} = -\omega^{b}_{a}\Lambda\omega_{b} + B_{ab}{}^{c}\,\omega_{c}\Lambda\omega^{b}$ (3.10)

3) $d\omega^{a}_{b} = \omega^{a}_{c}\Lambda\omega^{c}_{b} + A^{ad}_{bc}\,\omega^{c}\Lambda\omega_{d} + A^{acd}_{b}\,\omega_{c}\Lambda\omega_{d}$

where A^{ad}_{bc} is the holomorphic sectional curvature tensor[9] .

By the Lemma 3.1.2 we have:

1) $B^{ab}{}_{cd} = \frac{1}{2}(\alpha^{a}{}_{d}\delta^{b}_{c} - \alpha^{b}{}_{d}\delta^{a}_{c})$

2) $B^{ab}{}_{c}{}^{d} = \frac{1}{2}(\alpha^{ad}\delta^{b}_{c} - \alpha^{bd}\delta^{a}_{c})$

3) $B_{ab}{}^{cd} = \frac{1}{2}(\alpha_{a}{}^{d}\delta^{c}_{b} - \alpha_{b}{}^{d}\delta^{c}_{a})$ (3.11)

4) $B_{ab}{}^{c}{}_{d} = \frac{1}{2}(\alpha_{ad}\delta^{c}_{b} - \alpha_{bd}\delta^{c}_{a})$

Consider $A^{a[cd]}_{b} + B^{a[c}{}_{h}{}^{d]} - B^{a[c}{}_{h}B^{|h|d]}{}_{b} = 0$, then

$$A^{a[cd]}_{b} = B^{a[c}{}_{h}B^{|h|d]}{}_{b} - B^{a[c}{}_{h}{}^{d]}$$

$$= \frac{1}{2}\{B^{ac}{}_{h}B^{hd}{}_{b} - B^{ad}{}_{h}B^{hc}{}_{b}\} - \frac{1}{2}\{B^{ac}{}_{b}{}^{d} - B^{ad}{}_{b}{}^{c}\}$$

According to the Lemma 3.1.2 and substitute equation(3.11:2) in the above equation, we get:

$$= \frac{1}{2}\{\alpha^{[a}\delta^{c]}_{h}\alpha^{[h}\delta^{d]}_{b} - \alpha^{[a}\delta^{d]}_{h}\alpha^{[h}\delta^{c]}_{b}\} -$$

$$\frac{1}{4}\{\alpha^{ad}\delta^{c}_{b} - \alpha^{cd}\delta^{a}_{b} - \alpha^{ac}\delta^{d}_{b} + \alpha^{dc}\delta^{a}_{b}\}$$

$$=\frac{1}{8}\{\alpha^a\alpha^h\delta^c_h\delta^d_b-\alpha^a\alpha^d\delta^c_h\delta^h_b-\alpha^c\alpha^h\delta^a_h\delta^c_b+\alpha^c\alpha^d\delta^a_h\delta^h_b-$$
$$\alpha^a\alpha^h\delta^d_h\delta^c_b+\alpha^a\alpha^c\delta^d_h\delta^h_b+\alpha^a\alpha^h\delta^a_h\delta^c_b-\alpha^d\alpha^c\delta^a_h\delta^h_b\}-$$
$$\frac{1}{4}\{\alpha^{ad}\delta^c_b-\alpha^{cd}\delta^a_b-\alpha^{ac}\delta^d_b+\alpha^{dc}\delta^a_b\}$$
$$=\frac{1}{4}\alpha^a\alpha^{[c}\delta^{d]}_b+\frac{1}{2}\alpha^{a[c}\delta^{d]}_b+\frac{1}{2}\alpha^{[ad]}\delta^a_b$$

According to the Theorem 3.1.1 we have $\alpha^{[ah]}=0$, then

$$A^{a[cd]}_b=\frac{1}{2}\alpha^{a[c}\delta^{d]}_b+\frac{1}{4}\alpha^a\alpha^{[c}\delta^{d]}_b$$

(3.12)

By the complex conjugate to (3.12) we get:

$$A^b_{a[cd]}=\frac{1}{2}\alpha_{a[c}\delta^b_{d]}+\frac{1}{4}\alpha_a\alpha_{[c}\delta^b_{d]}$$

(3.13)

Substitute the previous result (3.12) in (3.10:3) we obtain:

$$d\omega^a_b=\omega^a_c\Lambda\omega^c_b+A^{ad}_{bc}\,\omega^c\Lambda\omega_d+\{\frac{1}{2}\alpha^{a[c}\delta^{d]}_b+\frac{1}{4}\alpha^a\alpha^{[c}\delta^{d]}_b\}\omega_c\Lambda\omega_d\ .$$

RIEMANNIAN CURVATURE TENSOR OF LOCALLY CONFORMAL KAHLER MANIFOLD

Definition 1.4[14]

Suppose that $\{M,J,g=<\cdot,\cdot>\}$ is almost Hermitian manifold, let ∇ be the Riemannian connection of metric g.

A map $R:X(M)\times X(M)\times X(M)\to X(M)$ such that

$R(X,Y)Z=[\nabla_X,\nabla_Y]Z-\nabla_{[X,Y]}Z$ is called curvature operator.

Definition 2.4 [15]

The Riemannian curvature tensor of M, is covariant tensor field of order 4, its value at any point $p\in M$ is determined as

$R:T_p(M)\times T_p(M)\times T_p(M)\times T_p(M)\to R$ such that

$R(X_1,X_2,X_3,X_4)=g(R(X_3,X_4)X_2,X_1)$, $X_i\in T_p(M)$ $\quad i=1,2,3,4$

The Riemannian curvature tensor satisfies number of symmetry relations given by the following proposition.

Proposition 1.4 [15]

]

The Riemannian curvature tensor possesses the following properties

1) $R(X_1,X_2,X_3,X_4)=-R(X_2,X_1,X_3,X_4)$.

2) $R(X_1,X_2,X_3,X_4)=-R(X_1,X_2,X_4,X_3)$.

3) $R(X_1,X_2,X_3,X_4)+R(X_1,X_3,X_4,X_2)+R(X_1,X_4,X_2,X_3)=0$.

4) $R(X_1,X_2,X_3,X_4)=R(X_3,X_4,X_1,X_2)$.

By [14] we have in any coordinate neighborhood (U,φ) we have coordinate frames $E_1,...,E_{2n}$ and in A-frames we have $\varepsilon_1,...,\varepsilon_{2n}$, then the components $R^{\cdot}{}_{jkl}$ of the curvature operator are defined by:

$$R(X_k,X_l)X_j=\sum_i R^{i}{}_{jkl}X_i$$

Let $R^{i}{}_{jkl}$ and g_{ij} are the components of curvature tensor and Riemannian metric respectively, then the components R_{ijkl} of the Riemannian curvature tensor are given by:

$R_{ijkl}=\sum_h g_{ih}R^{h}{}_{jkl}$, and $R_{ijkl}=<R(\varepsilon_k,\varepsilon_l)\varepsilon_j,\varepsilon_i>$

Then the previous proposition can be formulated:

Corollary 1.4 [14]

For all $1\le i,j,k,l\le 2n$ we have:

1) $R_{ijkl}=-R_{jikl}$

2) $R_{ijkl}=-R_{ijlk}$

3) $R_{ijkl}+R_{iklj}+R_{iljk}=0$

4) $R_{ijkl}=R_{klij}$

Lemma 1.4 [6]

Suppose that a,b and c are at the range $1,...,n$; $\hat{a},\hat{b}$ and $\hat{c}$ are at the range $n+1,...,2n$; i,j,k are at the range $1,...,2n$. In the ajoint G-structure space we have:

1) $J^{a}_{b,k}=0$

2) $\omega^{\hat{a}}_{b}=\frac{\sqrt{-1}}{2}J^{\hat{a}}_{b,k}\omega^{k}$

3) $\omega^{a}_{\hat{b}}=-\frac{\sqrt{-1}}{2}J^{a}_{\hat{b},k}\omega^{k}$

4) $J^{\hat{a}}_{\hat{b},k}=0$

5) $B^{ab}{}_{c}=-\frac{\sqrt{-1}}{2}J^{a}_{\hat{b},c}$

6) $B^{abc}=\frac{\sqrt{-1}}{2}J^{a}_{[\hat{b},\hat{c}]}$

7) $B_{ab}{}^{c}=\frac{\sqrt{-1}}{2}J^{\hat{a}}_{b,\hat{c}}$

8) $B_{abc}=-\frac{\sqrt{-1}}{2}J^{\hat{a}}_{[b,c]}$

(4.1)

Theorem: 1.4

The components of the Riemannian curvature tensor of *L.C.K* manifold are given by:

1) $R^{a}{}_{bcd} = \alpha_{a[c}\delta^{h}_{d]} + \frac{1}{2}\alpha_{a}\alpha_{[c}\delta^{h}_{d]}$

2) $R^{a}{}_{b\hat{c}\hat{d}} = \alpha^{a[c}\delta^{d]}_{b} + \frac{1}{2}\alpha^{a}\alpha^{[c}\delta^{d]}_{b}$

3) $R^{a}{}_{bc\hat{d}} = A^{ad}_{bc} - \alpha^{[a}\delta^{h]}_{c}\alpha_{[h}\delta^{d}_{b]}$

4) $R^{\hat{a}}{}_{\hat{b}cd} = -\alpha_{a[c}\delta^{b}_{d]} - \frac{1}{2}\alpha_{a}\alpha_{[c}\delta^{b}_{d]}$

5) $R^{\hat{a}}{}_{\hat{b}\hat{c}\hat{d}} = -\alpha^{a[c}\delta^{d]}_{b} - \frac{1}{2}\alpha^{a}\alpha^{[c}\delta^{d]}_{b}$

6) $R^{\hat{a}}{}_{\hat{b}c\hat{d}} = -A^{bc}_{ad} + \alpha_{[a}\delta^{d}_{h]}\alpha^{[h}\delta^{h]}_{c}$

7) $R^{a}{}_{\hat{b}\hat{c}\hat{d}} = 0$

8) $R^{a}{}_{\hat{b}c\hat{d}} = \alpha^{[a}\delta^{h]}_{b}\alpha^{[h}\delta^{d]}_{c} - \alpha^{[a|d|}\delta^{h]}_{c}$

9) $R^{a}{}_{\hat{b}cd} = -2\alpha^{[a}_{[c}\delta^{b]}_{d]}$

10) $R^{\hat{a}}{}_{bcd} = 0$

11) $R^{\hat{a}}{}_{b\hat{c}\hat{d}} = 2\alpha^{[a}_{[c}\delta^{b]}_{d]}$

12) $R^{\hat{a}}{}_{bc\hat{d}} = \alpha_{[a|c|}\delta^{d}_{b]} - \alpha_{[a}\delta^{h}_{b]}\alpha_{[h}\delta^{d}_{c]}$

Proof:

Consider the second group of the structure equation of Riemannian manifold

$d\omega^{i}_{j} = \omega^{i}_{k}\Lambda\omega^{k}_{j} + \frac{1}{2}R^{i}{}_{jkl}\omega^{k}\Lambda\omega^{l}$.

In adjoint *G*- structure space we have:

1) If $i = a$, $j = b$, then we get:

$$d\omega^{a}_{b} = \omega^{a}_{c}\Lambda\omega^{c}_{b} + \omega^{a}_{\hat{c}}\Lambda\omega^{\hat{c}}_{b} + \frac{1}{2}R^{a}{}_{bcd}\omega^{c}\Lambda\omega^{d} + \frac{1}{2}R^{a}{}_{b\hat{c}\hat{d}}\omega_{c}\Lambda\omega + R^{a}{}_{bc\hat{d}}\omega^{c}\Lambda\omega_{d}$$

From (2.8)) we have:

$$d\omega^{a}_{b} = \omega^{a}_{c}\Lambda\omega^{c}_{b} + B^{ac}{}_{d}B_{cb}{}^{h}\omega^{d}\Lambda\omega_{h} + \frac{1}{2}R^{a}{}_{bcd}\omega^{c}\Lambda\omega^{d} + \frac{1}{2}R^{a}{}_{b\hat{c}\hat{d}}\omega_{c}\Lambda\omega_{d} + R^{a}{}_{bc\hat{d}}\omega^{c}\Lambda\omega_{d}$$

But in other hand from (3.6) we have

$d\omega^{a}_{b} = \omega^{a}_{c}\Lambda\omega^{c}_{b} + A^{b}_{acd}\,\omega^{c}\Lambda\omega^{d} + A^{ad}_{bc}\,\omega^{c}\Lambda\omega_{d} + A^{acd}_{b}\,\omega_{c}\Lambda\omega_{d}$

Then we get:

i) $R^{a}{}_{bcd} = 2A^{b}_{acd}$

ii) $R^{a}{}_{b\hat{c}\hat{d}} = 2A^{acd}_{b}$

iii) $R^{a}{}_{bc\hat{d}} = 2A^{ad}_{bc} - B^{ah}{}_{c}B_{hb}{}^{d}$

2) If $i = \hat{a}$, $j = \hat{b}$, then we get:

$$d\omega_{\hat{b}}^{\hat{a}} = \omega_{c}^{\hat{a}}\Lambda\omega_{\hat{b}}^{c} + \omega_{\hat{c}}^{\hat{a}}\Lambda\omega_{\hat{b}}^{\hat{c}} + \frac{1}{2}R^{\hat{a}}{}_{\hat{b}cd}\omega^{c}\Lambda\omega^{d} + \frac{1}{2}R^{\hat{a}}{}_{\hat{b}\hat{c}\hat{d}}\omega_{c}\Lambda\omega_{d} + R^{\hat{a}}{}_{\hat{b}c\hat{d}}\omega^{c}\Lambda\omega_{d}$$

$$-d\omega_{a}^{b} = \omega_{a}^{c}\Lambda\omega_{c}^{b} + B_{ac}{}^{d}B^{bc}{}_{h}\omega_{d}\Lambda\omega^{h} + \frac{1}{2}R^{\hat{a}}{}_{\hat{b}cd}\omega^{c}\Lambda\omega^{d} + \frac{1}{2}R^{\hat{a}}{}_{\hat{b}\hat{c}\hat{d}}\omega_{c}\Lambda\omega_{d} + R^{\hat{a}}{}_{\hat{b}c\hat{d}}\omega^{c}\Lambda\omega_{d}$$

But in other hand we have:

$$d\omega_{a}^{b} = -\omega_{a}^{c}\Lambda\omega_{c}^{b} + A_{b}^{acd}\omega_{c}\Lambda\omega_{d} + A_{ad}^{bc}\omega_{c}\Lambda\omega^{d} + A_{acd}^{b}\omega^{c}\Lambda\omega^{d}$$

Then we get:

i) $R^{\hat{a}}{}_{\hat{b}cd} = -2A_{a}{}^{b}{}_{cd}$

ii) $R^{\hat{a}}{}_{\hat{b}\hat{c}\hat{d}} = -2A_{b}^{a\,cd}$

iii) $R^{\hat{a}}{}_{\hat{b}c\hat{d}} = -A_{ad}^{bc} + B_{ah}{}^{d}B^{bh}{}_{c}$

3) If $i = a$, $j = \hat{b}$, then we get:

$$d\omega_{\hat{b}}^{a} = \omega_{c}^{a}\Lambda\omega_{\hat{b}}^{c} + \omega_{\hat{c}}^{a}\Lambda\omega_{\hat{b}}^{\hat{c}} + \frac{1}{2}R^{a}{}_{\hat{b}cd}\omega^{c}\Lambda\omega^{d} + \frac{1}{2}R^{a}{}_{\hat{b}\hat{c}\hat{d}}\omega_{c}\Lambda\omega_{d} + R^{a}{}_{\hat{b}c\hat{d}}\omega^{c}\Lambda\omega_{d}$$

From (4.1) we have $\omega_{\hat{b}}^{a} = B^{ah}{}_{c}\omega^{c}$, and then we obtain:

$$d\omega_{\hat{b}}^{a} = dB^{ah}{}_{c}\omega^{c} = dB^{ah}{}_{c}\omega^{c} + B^{ah}{}_{c}d\omega^{c}$$

$$= B^{hh}{}_{c}\omega_{h}^{a}\Lambda\omega^{c} + B^{ah}{}_{c}\omega_{h}^{b}\Lambda\omega^{c} - B^{ab}{}_{h}\omega_{c}^{h}\Lambda\omega^{c} + B^{ab}{}_{c}{}^{d}\omega_{d}\Lambda\omega^{c} + B^{a\hat{b}}{}_{c}\omega_{d}^{c}\Lambda\omega^{d} + B^{ab}{}_{c}B_{h}{}^{cd}\omega^{h}\Lambda\omega_{d},$$

We get:

i) $R^{a}{}_{\hat{b}\hat{c}\hat{d}} = 0$

ii) $R^{a}{}_{\hat{b}cd} = B^{ab}{}_{h}B^{hd}{}_{c} - B^{ab}{}_{c}{}^{d}$

iii) $R^{a}{}_{\hat{b}cd} = 2B^{ab}{}_{[cd]}$

4) If $i = \hat{a}$, $j = b$, then we get:

$$d\omega_{b}^{\hat{a}} = \omega_{c}^{\hat{a}}\Lambda\omega_{b}^{c} + \omega_{\hat{c}}^{\hat{a}}\Lambda\omega_{b}^{\hat{c}} + \frac{1}{2}R^{\hat{a}}{}_{bcd}\omega^{c}\Lambda\omega^{d} + \frac{1}{2}R^{\hat{a}}{}_{b\hat{c}\hat{d}}\omega_{c}\Lambda\omega_{d} + R^{\hat{a}}{}_{bc\hat{d}}\omega^{c}\Lambda\omega_{d}$$

On other hand, we have:

$$d\omega_{b}^{\hat{a}} = -B_{hb}{}^{c}\omega_{a}^{h}\Lambda\omega_{c} - B_{ah}{}^{c}\omega_{b}^{h}\Lambda\omega_{c} + B_{ab}{}^{h}\omega_{h}^{c}\Lambda\omega_{c} + B_{ab}{}^{cd}\omega_{d}\Lambda\omega_{c} + B_{ab}{}^{c}\omega_{c}^{d}\Lambda\omega_{d} + B_{ab}{}^{c}B_{cd}{}^{h}\omega_{h}\Lambda\omega^{d}$$

We get:

i) $R^{\hat{a}}{}_{bcd} = 0$

ii) $R^{\hat{a}}{}_{b\hat{c}\hat{d}} = -2B_{ab}{}^{[cd]}$

iii) $R^{\hat{a}}{}_{bc\hat{d}} = B_{ab}{}^{d}{}_{c} - B_{ab}{}^{h}B_{hc}{}^{d}$

LOCALLY CONFORMAL KAHLER MANIFOLD OF CLASS R_3

Definition 1.5 [16]

From [16] A.Gray defined three special classes of almost Hermitian manifold, which can be characterized by the following equalities:

1) Class R_1 iff $< R(X,Y)Z,W >=< R(X,Y)JZ,JW >$

2) Class R_2 iff $< R(X,Y)Z,W >=< R(JX,JY)Z,JW > +$
$< R(JX,Y)JZ,W > +< R(JX,Y)Z,JW >$

3) Class R_3 iff $< R(X,Y)Z,W >=< R(JX,JY)JZ,JW >$

By [17], the class R_1 is called paraKähler manifold, the class R_3 is called *RK*- manifold[17].A.Gray in [16] proved that $R_1 \subset R_2 \subset R_3$.

Theorem 1.5

Let $\{M,J,g =< .,. >\}$ be *L.C.K* manifold then M is *RK*-manifold if and only if in the adjoint *G*-structure space, the components of Lie form and there covariant differential satisfies the equation $\alpha_{ac} = -\frac{1}{2}\alpha_a \alpha_c$.

Proof:

We know the tensor $R_{\hat{a}bcd}$ written as:

$< R(\varepsilon_c, \varepsilon_d)\varepsilon_b, \varepsilon_{\hat{a}} >$.

If $\{M,J,g =< .,. >\}$ is *RK*-manifold then we have:

$R_{\hat{a}bcd} =< R(\varepsilon_c, \varepsilon_d)\varepsilon_b, \varepsilon_{\hat{a}} >=< R(J\varepsilon_c, J\varepsilon_d)J\varepsilon_b, J\varepsilon_{\hat{a}} >$

According to *A*-frame basis we have:

$J\varepsilon_a = \sqrt{-1}\varepsilon_a$, $J\varepsilon_{\hat{a}} = -\sqrt{-1}\varepsilon_{\hat{a}}$

Then $< R(\varepsilon_c, \varepsilon_d)\varepsilon_b, \varepsilon_{\hat{a}} >= -< R(\varepsilon_c, \varepsilon_d)\varepsilon_b, \varepsilon_{\hat{a}} >$ then we get:

$R_{\hat{a}bcd} = 0$, $R_{ab\hat{c}\hat{d}} = 0$

By the symmetric properties of Riemannian curvature tensor we get:

1) $R_{\hat{a}bcd} = -R_{b\hat{a}cd} = -R_{cdb\hat{a}} = R_{cd\hat{a}b} = 0$

2) $R_{ab\hat{c}\hat{d}} = -R_{ba\hat{c}\hat{d}} = -R_{\hat{c}\hat{d}ba} = R_{\hat{c}\hat{d}a\hat{b}} = 0$ (5.1)

Then by theorem 3.2.1 and the relations (5.1) we get that, if M is *L.C.K.* manifold, then M is *RK*-manifold if and only if

$\alpha_{a[c}\delta^b_{d]} + \frac{1}{2}\alpha_a \alpha_{[c}\delta^b_{d]} = \alpha^{a[c}\delta^{d]}_b + \frac{1}{2}\alpha^a \alpha^{[c}\delta^{d]}_b = 0$

Since $\alpha_{a[c}\delta^b_{d]} + \frac{1}{2}\alpha_a \alpha_{[c}\delta^b_{d]} = 0$ then:

$$(\alpha_{ac}+\frac{1}{2}\alpha_a\alpha_c)\delta_d^b=(\alpha_{ad}+\frac{1}{2}\alpha_a\alpha_d)\delta_c^b$$

(5.2)

by folding (5.2) by the indexes b and d we get:

$(\alpha_{ac}+\frac{1}{2}\alpha_a\alpha_c)n=(\alpha_{ac}+\frac{1}{2}\alpha_a\alpha_c)$ Then

$$(\alpha_{ac}+\frac{1}{2}\alpha_a\alpha_c)(n-1)=0$$

if $n=1$ in this case we get that M is Kähler manifold.

Therefore $n>1$ and this means $n-1\neq 0$, then

$\alpha_{ac}=-\frac{1}{2}\alpha_a\alpha_c$.

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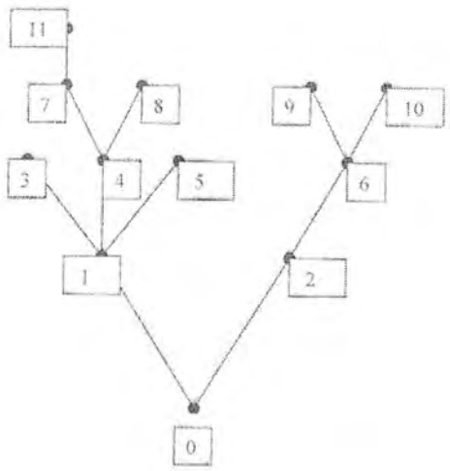
Some Calculations in a Tree of Partially Ordered Set

Hussain A.H. AL Juboury

Al- Mustansiriya J. Sci Vol. 19, No 4, 2008

Finally, we may illustrate combinatorially [9, 10, 11] that for any tree whether it is binary or closed, the statement of the main theorem is satisfied:

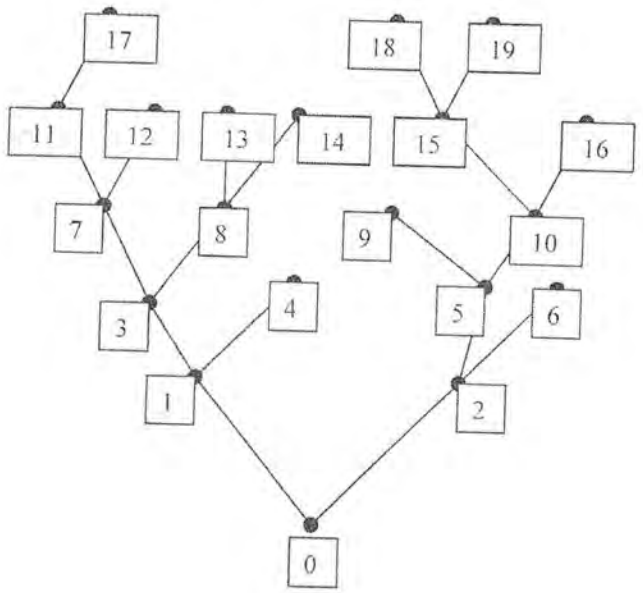
Example 1: Suppose we have chosen the maximal anti-chain $A=\{0,2,9\}$, (any other choice will work see fig. 3 above) obviously, the maximal level is $L_2=\{3, 4, 5, 6,\}$ or then it is clear that $|A|\leq|L|$.



P_5

Fig-3:

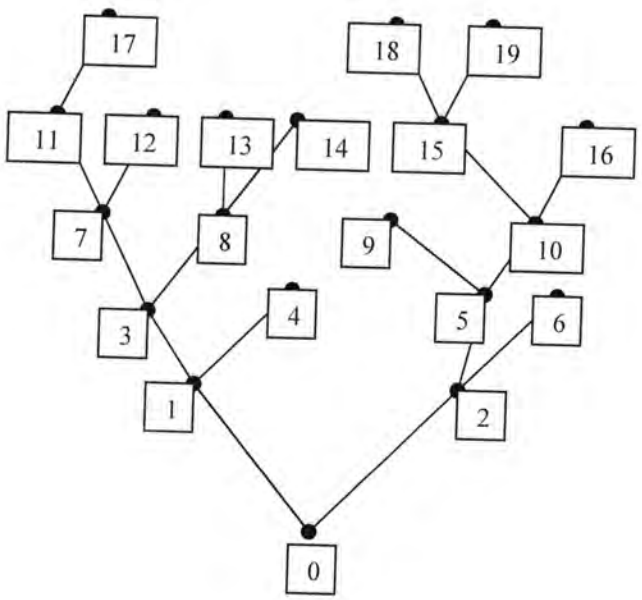
Example 2: In figure 4 any maximal anti-chain contains three nodes and the maximal level contains three nodes as well. Consequently, the statement of the main theorem is satisfied although condition (1) of the combinatorial lemma does not satisfied while condition (2) of this lemma is satisfied.



P_7

Fig- 4:

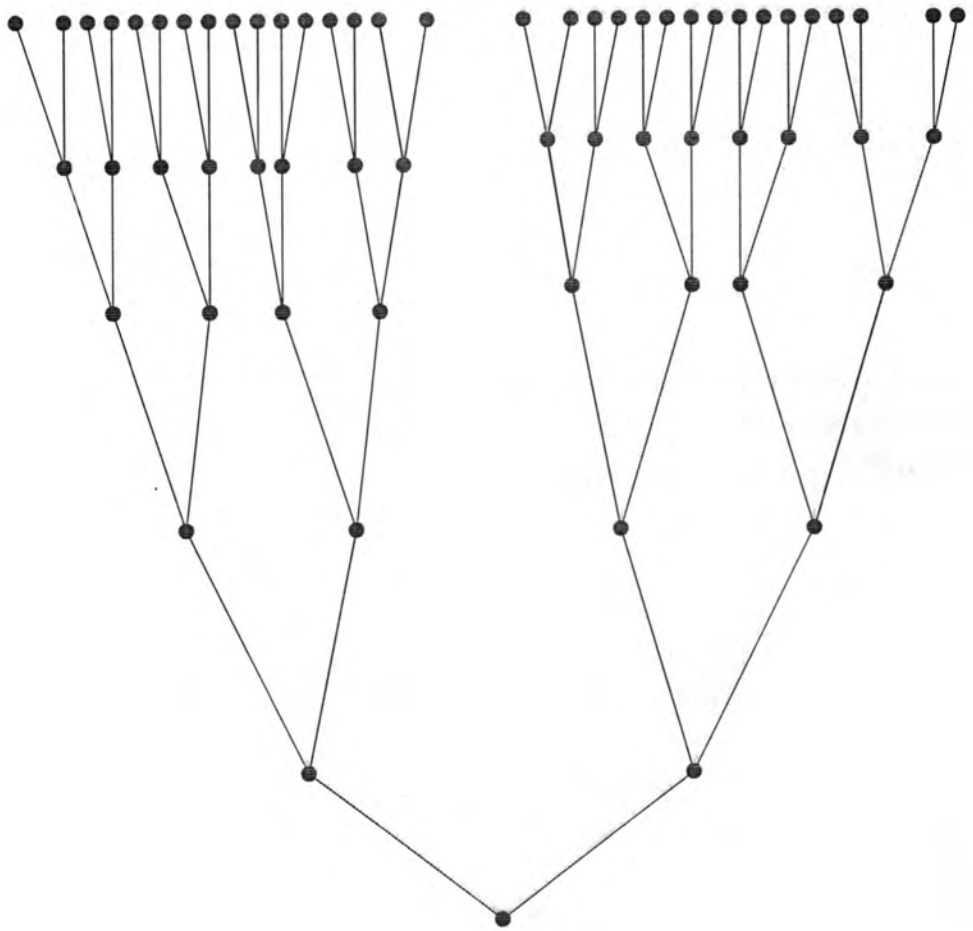
Example 3: If we take the maximal anti-chain $A=\{0, 4, 9, 14, 19\}$ and definitely the maximal level here is $L_4=\{11, 12, 13, 14, 15, 16\}$ (see fig.5). So $|A| \leq |L_4|$ the main theorem is satisfied once again.



P_7

Fig. 5

Finally, in appendix (figures 6 and 7) you may find a more general two examples for a binary tree and a diamond shape tree that satisfy the statement of the main theorem combinatorially i.e. $|A| \leq |L|$, for a maximal anti-chain A and a maximal level L.



φ

Fig.6

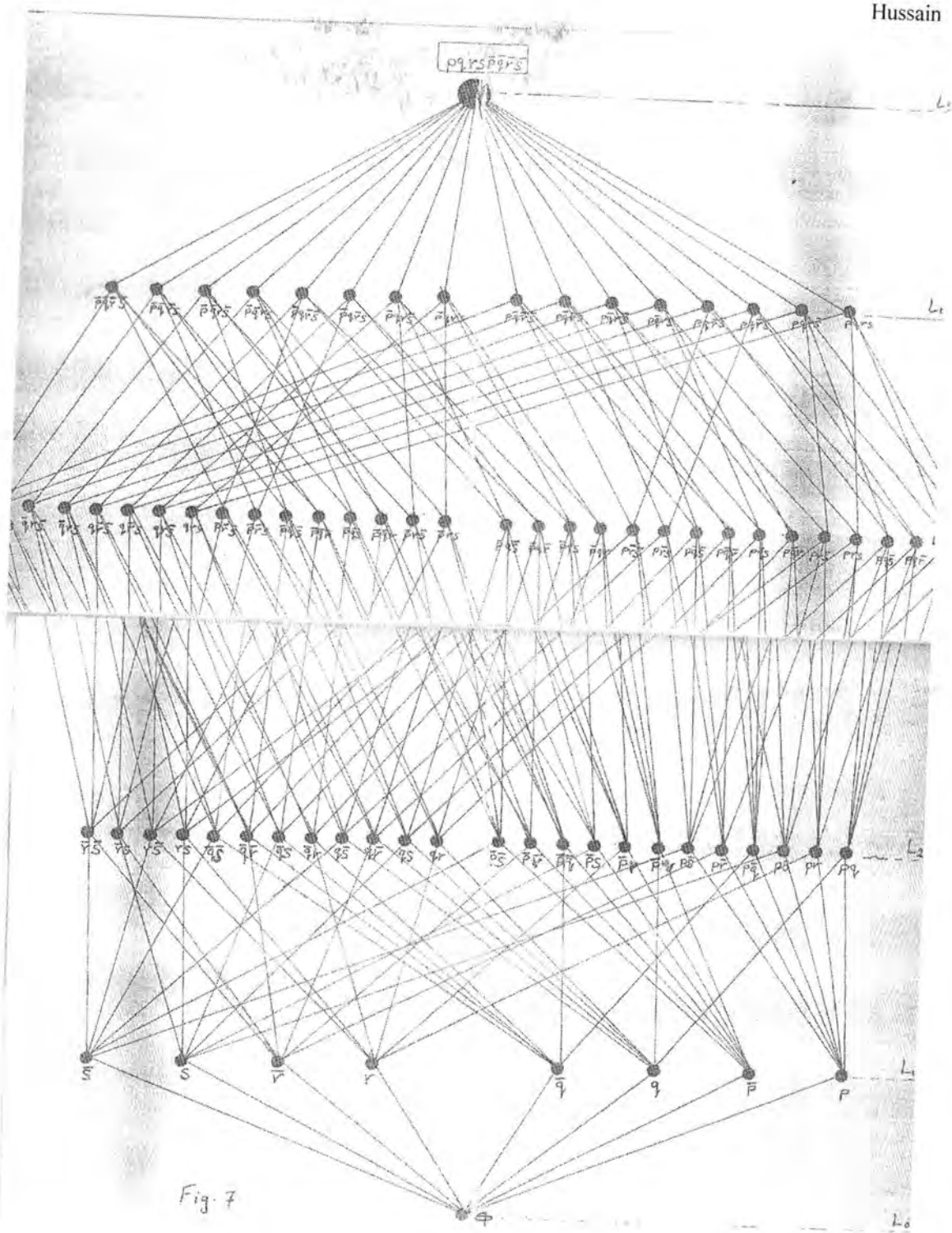


Fig. 7

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P-MODULES

Mehdi J. M. ALI[1] and Muna S. ABBAS [2]
[1]Department of Mathematics, College of Science, Al-Mustansirya Univ
[2]Department of Mathematics, College of Science for women, University of Baghdad

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الخلاصة

ليكن R حلقة تجميعية ذات عنصر محايد غير صفري و ليكن M مقاس أيمن أحادي على R المقاس M يكون أغماري- كاذب اذا كان كل تشاكل مقاسي متباين على R من مقاس جزئي من M إلى M يمكن توسيعه إلى M. في هذا البحث تم دراسة المقاسات التي كل مقاس جزئي منها هو مقاس أغماري- كاذب. تم تسمية هذه المقاسات بالمقاسات من النمط P حيث برهنا ان Mمقاس من النمط P اذا وفقط اذا كان M أغماري – كاذب و كل مقاس جزئي جوهري من M يكون مستقر- كاذب.

ABSTRACT

Let R be an associative ring with non-zero identity and let M be a unitary right R-module. An R-module M is pseudo-injective, if each R-monomorphism from a submodule of M into M can be extended to an R-endomorphism of M. In this paper we shall investigate and study modules in which each submodule is pseudo-injective. We call such modules P-modules. We prove that , an R-module M is P-module, if and only if M is pseudo-injective and each essential submodule of M is pseudo-stable.

INTRODUCTION

Throughout this work, unless otherwise stated, we assume that rings are associative rings with identity 1 ($\neq 0$) and modules are unitary right modules. An R-module M is called quasi-injectie if each R-homomorphism from a submodule of M into M can be extended to M [1]. S. K. Jain, S. H. Mohamed and S. Singh in [2] studied rings in which each right ideal is quasi-injective, such rings they called q-rings. H. K. Mohammeddi generalize the concept of q-rings to modules in [3]. As a natural generalization of quasi-injectivity S. Singh and S. K. Jain in [4] introduced the concept of pseudo-injectivity, an R-module M is pseudo-injective, if each R-monomorphism of a submodule of M into M is a restriction of some endomorphism of M. So it is natural to consider modules which provide pseudo-injectivity condition on their submodules. We call such modules P-modules it is proved, in particular, that an R-module M is P-module, if and only if each essential submodule of M is pseudo-stable. Also, if M is a P-module, then each submodule of M is of the form $\alpha(K)$ where K is a stable submodule of M and idempotent α in $End_R(M)$. The converse is also proved in case of uniform modules. Cohopfiaty property is considered for P-modules.

An R-module M is called P-module if each submodule of M is pseudo- injective. A ring R is called right (left) self P-ring, if each right (left) ideal is pseudo-injective R-module.

It is clear that every Q-module (modules in which every submodules is quasi-injective) is P-module, but the converse is not true in general. Also, every P-module is pseudo-injective module, in fact the injective envelop of non pseudo-injective module is pseudo-injective module which is not P-module.

A submodule N of an R-module M is called stable (pseudo-stable) if $\alpha(N) \subseteq N$ for each R-homomorphism (R-monomorphism) α from N to M. In case each submodule of an R-module M is stable (pseudo-stable), then M is called fully stable (fully pseudo-stable) module [5]. It is proved in [5] that uniform fully pseudo-stable module is fully stable.

Let M be an R-module and N be a submodule of M . Define:

$\underline{N} = < f(x) : x \in N$ and $f : N \to M$ is an R-monomorphism $>$

The submodule generated by all the images of elements of N under the R-monomorphisim from N into M. clearly $N \subseteq \underline{N}$. In fact M is fully pseudo-stable R-module , if and only if $N = \underline{N}$, this is equivalent to saying that $N = \sum \theta(N)$ for each submodule N of M where the sum is taken over all R-monomorphism θ from N into M.

Proposition (1):- Let N be a submodule of an R-module M. Then

(i) $\underline{N}$ is a pseudo-stable submodule of M

(ii) if M is pseudo-injective and N is essential submodule of M, then $\underline{N}$ is the smallest pseudo-stable submodule of M containing N.

Proof :- (i) Let $g: \underline{N} \to M$ be an R-monomorphism and $f(x) \in \underline{N}$. Then $g(f(x)) = (g \circ f)(x) \in \underline{N}$, and hence $\underline{N}$ is pseudo-stable.

(ii) Let K be a pseudo-stable submodule of M containing N and $f(x) \in \underline{N}$. Pseudo-injectivity of M implies that there is an R-homomorphism g : M $\to$ M which extends f. It is clear that $\ker(f) = \ker(g) \cap N$. Since N is essential in M, then g is monomorphism. Now $x \in N \subseteq K$, thus $f(x) = g(x) \in K$. Hence $\underline{N} \subseteq K$. □

Notice that, if N is an essential submodule of a pseudo-injective R-module, then $\underline{N}$ is the intersection of all pseudo-stable submodules of M containing N. We call $\underline{N}$ the pseudo-stable extension of N in M.

Let M be an R-module and E(M) be the injective envelop of M. We will consider M as a submodule (essential) of E(M). We denote PS(M) the pseudo-stable extension of M in E(M) and call it the pseudo-stable envelop of M. It is clear that PS(M) is an essential extension of M. On the other hand, in each injective envelop, the pseudo-stable envelop is unique, proposition (1). Since injective envelop is unique up to

isomorphism, then any two pseudo-stable envelops are isomorphic. Thus we have the following.

Theorem (1) :- Every module has pseudo-stable envelope, and any two envelops are isomorphic.

The following lemma is needed in our work.

Lemma (1) :- Every essential pseudo-stable submodule of pseudo-injective module is pseudo-injective.

Proof :- Suppose N is essential pseudo-stable submodule of pseudo-injective R-module M. Let K be a submodule of N and $\alpha : K \to N$ be an R-monomorphism. Then $i \circ \alpha : K \to M$ is monomorphism where i is the inclusion map of N into M. Pseudo-injectivity of M implies that there is $\beta : M \to M$ which extends $i \circ \alpha$. Essential property of N give that β is monomorphism so $\beta_1 = \beta|_N : N \to N$ is the extension of α. □

Proposition (2) :- For any R-module M, the pseudo-stable envelop PS(M) of M in E(M) is the pseudo-injective envelop of M.

Proof :- PS(M) is the smallest essential pseudo-stable submodule of E(M) containing M, proposition (1). Also lemma (1) asserts that PS(M) is pseudo-injective. Thus PS(M) is the smallest pseudo-injective module containing M, further it is essential extension of M. Hence PS(M) is the pseudo-injective envelope of M. □

Corollary (1) :- For any R-module M, the following are equivalent :

(1) M is essential pseudo-stable submodule of E(M);

(2) M is pseudo-injective.

Proof :- M is essential pseudo-stable submodule of E(M), if and only if M=PS(M). proposition (2) implies that PS(M) (and hence M) is the pseudo-injective envelope of M, if and only if M is Pseudo-injective. □

Theorem (2) :- Let M be an R-module. Then M is P-module, if and only if M is pseudo-injective and each essential submodule of M is pseudo-stable.

Proof :- $\Rightarrow$Let N be an essential submodule of M. Then N is pseudo-injective. Consider an R-monomorphism $g : N \to M$. set $N' = g^{-1}(N)$ clearly $g' = g|_{N'} : N' \to N$ is monomorphism. Pseudo-injectivity of N with the help of essential property of N implies that there is an R-monomorphism $f : N \to N$. Also, there exists an R-homomorphism $h : M \to M$ which extends f. We claim that (h-g)(N) = 0, if not, then $(h-g)(N) \cap N \neq 0$, and hence there are non-zero element x and y in N such that

$(h-g)(x) = y$, so $(f-g)(x) = y$ this implies $g(x) = f(x)-y \in N$ and hence $x \in N'$, thus $y = (h-g)(x) = 0$ which is a contradiction. Thus $(h-g)(N) = 0$ and hence $g(N) = h(N) = f(N) \subseteq N$.

$\Leftarrow$ Since each direct summand of pseudo-injective module is pseudo-injective [6] and hence $N \oplus N^c$ is essential submodule of M for every

submodule N of M, it is enough to show that every essential submodule of M is pseudo-injective. This follows from lemma (1). □

Recall that an R-module M is multiplication , if each submodule of M is of the form MA where A is an ideal of R [7].

Corollary (2) :- Every multiplication pseudo-injective module is P-module.

Proof :-Let M be a multiplication pseudo-injective R-module. By theorem (2), let N be essential submodule of M and $\alpha : N \longrightarrow M$ be an R-monomorphism. α can be extended to an R-endomorphism β of M. There is an ideal A of R such that N = MA. $\alpha(N) = \beta(N) = \beta(MA) = \beta(M)A \subseteq MA = N$. □

Corollary (3) :- Let R be a commutative ring. Then every cyclic pseudo-injective R-module is P-module. In particular a commutative ring R is self pseudo-injective ring, if and only if R is self P-ring.

Corollary (4) :- Every fully pseudo-stable pseudo-injective R-module is P-module.

Example (1) :-In [5] it is proved that. If R is a commutative Noetherian ring, then every fully pseudo-stable R-module has fully pseudo-stable injective envelope. So by corollary (2), the injective envelope of each every fully pseudo-injective module over commutative Noetherian ring is P-module, in particular the injective envelope of every fully pseudo-stable group is P-module. Furthermore, it is proved in [8] that fully pseudo-stable groups are abelian and a group is fully pseudo-stable, if and only if it is isomorphic to a subgroup of Q/Z . In particular Q/Z is P-module, also Z_P^{∞} as Z-module is P-module.

Proposition (3) :- If M is a pseudo-injective R-module in which each submodule is of the form $\alpha(K)$ where K is an essential stable submodule of M and idempotent α in $S = End_R(M)$, then M is P-module.

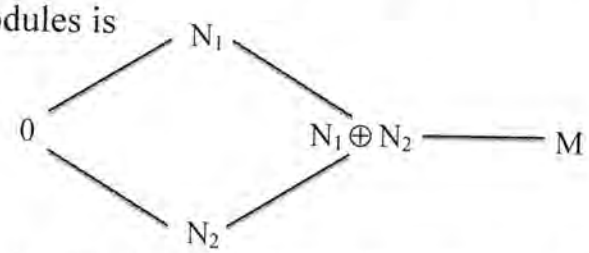
Proof :-Let N be a submodule of M. There exist a stable submodule K of M and idempotent α in S such that $N = \alpha(K)$. Lemma (1) implies that K is pseudo-injective module $M = \alpha(M) \oplus (1-\alpha)(M)$. Since K is stable submodule of M, then by ([5], proposition(1.4.5)), we have $K = K \cap M$

$= K \cap (\alpha(M) \oplus (1-\alpha)(M)) = ((K \cap \alpha(M)) \oplus (K \cap (1-\alpha)(M)) \subseteq \alpha(K) \oplus (1-\alpha)(K) = K$. Thus $K = \alpha(K) \oplus (1-\alpha)(K)$, so $\alpha(K)$ and hence N is pseudo-injective. Therefore M is P-module. □

Theorem (3) :- Let M be a uniform P-module. Then each submodule of M is of the form $\alpha(K)$ where K is a stable submodule of M and α is an idempotent in $S = End_R(M)$.

Proof :- Let N be a submodule of M. Then $W = N \oplus N^c$ is essential submodule of M. Theorem (2) implies that W is pseudo-stable of M. Essential property of W implies that $E(M) = E(W) = E(N) \oplus E(N^c)$. Let $f : E(M) \rightarrow E(N)$ be the natural projection of E(M) onto E(N). As M is pseudo-injective, then M is pseudo-stable submodule of E(M), corollary (1). Uniformity of M implies uniformity of E(M), hence M is a stable submodule of E(M), thus by ([5], proposition (1.4.5)) we have $M = (E(N) \cap M) \oplus (E(N^c) \cap M)$. Let ρ be a natural projection R-homomorphism and $\rho_1 = f|_M : M \rightarrow M$ is an idempotent, thus $\rho_2 = \rho_1|_W : W \rightarrow N$ and $\rho_2(W) = N$. □

Example (2) :- As we have mentioned that every Q-module is P-module, but the converse may not be true in general, let M be an R-module whose lattice of submodules is



Where N_1 is not isomorphic to N_2 and the endomorphism rings of N_i are isomorphic to $Z/2Z$, i = 1,2. The existence of such modules was shown by example of Hallet in [9]. It was showed in [10] that M is pseudo-injective module which is not quasi-injective. On the other hand in [5] proved that M is fully stable and hence fully pseudo-stable module, hence every essential submodule of M is pseudo-stable so theorem (2) implies that M is P-module and clearly M is not Q-module.

Next we consider conditions under which P-modules are Q-modules.

Proposition (4) :- Every uniform P-module is Q-module.

Proof :- Let M be a uniform P-module and N be a submodule of M. Then N is uniform pseudo-injective module. Let A be any submodule of N and $\alpha : A \rightarrow N$ be any R-homomorphism. It is an easy mater to see that $\ker(\alpha) \cap \ker(i-\alpha) = 0$, where i is the inclusion mapping of N into M, uniformity of N implies either $\ker(\alpha) = 0$ (and in this case we have nothing to prove) or $\ker(i-\alpha) = 0$. Then pseudo injectivity assumption, $(i-\alpha)$ can be extended to some $g : M \rightarrow M$. Now $I_M - g$ is obviously an extension of α, where I_M is the identity homomorphism of M. Thus N is quasi-injective and hence M is Q-module. □

Recall that an R-module M is extending, if and only if every submodule is essential in a direct summand of M [11].

Theorem (4) :- Let M be a module over a right Noetherian ring R in which each submodule of M is extending. Then M is P-module, if and only if it is Q-module.

Proof :- Let N be a submodule of M, then N is pseudo-injective extending module. By Okada result in [11] $N = \bigoplus_{\alpha\in\wedge} M_\alpha$ where M_α is uniform modules for each $\alpha \in \wedge$. In ([6], corollary (2.3)) it is proved that, if $\bigoplus_{\alpha\in\wedge} M_\alpha$ is pseudo-injective, then M_α is M_β-injective for all distinct $\alpha, \beta \in \wedge$. M_α is uniform pseudo-injective for each $\alpha \in \wedge$, hence by proposition (4) implies that M_α is quasi-injective for each $\alpha \in \wedge$. Now using ([12], proposition (1.18)) we get N is quasi-injective and this implies that M is Q-module. □

Theorem (5) :- Every P-module over a generalized uniserial ring is Q-module.

Proof :- Let N be a submodule of P-module M over a generalized uniserial ring R. Then N is a direct sum of uniserial module [13]. As uniserial modules are uniform, then $N = \bigoplus_{i\in I} W_i$ where W_i is uniform for

each $i \in I$. As in the proof theorem (4), W_i is W_j-injective for distinct $i, j \in I$ and each W_i is quasi-injective we get N is quasi-injective and hence M is Q-module. □

The proof of the following is almost on the same lines as those for quasi-injective modules in ([14], proposition (1)).

Lemma (2) :- let M be a non zero pseudo-injective R-module. Then M is non-cohopfain, if and only if for any positive integer n, $M = M_n \oplus (\overset{n}{\underset{i=1}{\oplus}} B_i)$ where $M_n \cong M$ and $B_i \neq 0$ for i =1, 2, .,n.

Corollary (5) :- Let M be a P-module. Then the following are equivalent for every non-zero submodule N

(1) N is non-cohopfian

(2) for each positive integer n, $N = N_n \oplus (\overset{n}{\underset{i=1}{\oplus}} W_i)$ where $N_n \cong N$ and $W_i \neq 0$, i=1,2, ,n.

Corollary (6):- Let M be a P-module and N be a submodule of M. If N is hopfian, then N is cohopfian

Proof :- Suppose that N is non-cohopfian, then by corollary (5), $N = N_1 \oplus W$ where $N_1 \cong N$ and $W \neq 0$. Let $w : N \rightarrow N_1$ be an isomorphism then $\rho \circ w : N \rightarrow N$ where ρ is the projection of N onto W, which is contradiction. □

Proposition (5) :- Let M be a P-module and N be a submodule of M. If either M has finite Goldie dimension or M has finite dual Goldie dimension, then for any positive integer $n \geq 1$, N^n is cohopfian.

Proof :- For any positive integer $n \geq 1$, N^n is pseudo-injective. By using the fact that $\dim(N^n) = n \dim(N) < \infty$, $\operatorname{codim}(N^n) = n \operatorname{codim}(N) < \infty$, hence it is enough to show that N is cohopfian. Let $\alpha : N \rightarrow N$ be an R-monomorphism. Pseudo-injectivity of N implies that α splits and hence $N = \alpha(N) \oplus L$ for some submodule L of N. As $\alpha(N) \cong N$, then $\dim(N) =$

dim(N) + dim(L) and codim(N) = codim(N) + codim(L), hence dim(L) = 0 = codim(L). Thus implies that L = 0 and hence α is an R-epimorphism. □

Theorem (6) :- Let M be a pseudo-injective R-module and N be an essential pseudo-stable submodule of M. Then M is cohpfian, if and only if N is cohopfian.

Proof :- Assume that N is cohopfian and $\varphi : M \to M$ be an R-monomorphism. Since $\varphi(N) \subseteq N$, there exists an R-monomorphism $\bar{\varphi} : N \to N$, cohopfiaty of N implies that $\bar{\varphi}$ is an isomorphism. Let $K = Im(\varphi)$. From the relation $i \circ \bar{\varphi} = \varphi \circ i$ where i is the inclusion map of N into M we have $N \subseteq K$ and hence K is essential in M. pseudo-injectivity implies that there is $\psi : M \to M$ such that $\psi \circ \varphi = I_M$, where I is the identity map of M to M and hence $M = \ker(\psi) \oplus K$, so K is a direct summand of M. Thus K = M and hence φ is isomorphism. Conversely, if M is cohopfian and $f : N \to N$ is an R-monomorphism, then there is an R-monomorphism $g : M \to M$ Thus g is isomorphism and $Im(f) = Im(g) \cap N = N$. So N is cohopfian. □

Corollary (7):- Let M be a P-module. M is cohopfian, if and only if every submodule of M is cohopfian.

Proof :- Let N be a submodule of M. Then $W = N \oplus N^c$ is essential in M. Theorem (2) implies that W is essential pseudo-stable submodule of M, then W is cohopfian, theorem (6), hence N is cohopfian. □

Corollary (8) :- Let M be a P-module. Then N is cohopfian, if and only if E(N) is cohopfian for any submodule N of M.

Proof :- Since N is pseudo-injective, then corollary (1) implies that N is essential pseudo-stable of E(N). Now the conclusion follows from theorem (6). □

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Web System for Registering Images by visible Watermarking

Isra'a A. Abdul Jabbar
University of Technology, Computer Science Department
Israabdulameer @ yahoo.com

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الخلاصة

في الطرق التقليدية نجد ان مالك الصورة يلجأ لحماية صوره عن طريق اضافة العلامة المائية الرقمية المرئية ومن الامثلة على هذه الطرق هي طريقة البت الاقل تأثير او طريقة تحويل الجيب تمام المتقطع وغيرها من الطرق بعدها يمكن للمالك ان يَنْشرَ هذه الصور على الشبكة لكن هذه الطرق لا تُزوّدَ حماية كافية لأن الصورة ما زالتْ تُعاني مِنْ مختلفِ انواعُ الهجوم وتَتطلبُ تقنياتَ أكثرَ للسَيْطرَة والمراقبة.

العمل يقترح تسجيل الصور المنشورة على الشبكة عن طريق تصميم "خادم العلامة المائية " الذي يسمح للناشر ومالك المعلومات من تأشير وتمييز موادهم المحفوظة الحقوق خلال الشبكة الانترنت العالمية (WWW). بتقديم خدمة العلامة المائية يمكن لمالك حق النشر حماية عمله خلال وسائط الشبكة دون الحاجة الى برامج العلامة المائية كما ويمكنه اثبات ملكيته عن طريق هذا الخادم.ان فكرة خادم العلامة المائية تدعم اداء العلامة المائية عن طريق توفيرها طرق امنية افضل ضد الهجوم وذلك عن طريق تسجيل الصورة في قاعدة بيانات الخادم التي تستعملُ عنوان الصورة الرسمي الفريد (URL) مَع الاحتفاظ بالصورة الحاوية على العلامة المائية في القرص الصلب للخادم.

ABSTRACT

Traditionally, the Copyright Owner (CO) protect their images by adding a digital watermark visibly or invisibly to image using conventional watermarking method such as Least Significant Bit and Discrete Cosine Transform, etc , then the owner can publish these images on the web , but this way not provide enough protection because the image still suffer from different types of attack and require more techniques for controlling and monitoring.

The propose system suggest registering the images published on the web by " Digital Watermarking Server" which allows the publisher and information provider to mark and identify their copyrighted materials through the World Wide Web (WWW). By producing watermarking services the CO can protect his work through network media without having watermarking software and the CO can proof his ownership by the server. The idea of producing watermarking server instead of conventionally watermarking system is to support the performance of the watermark against attackers and provide more security, since the image registered at server database using its Unique Uniform Resource Locator (URL) address with visibly watermarked image stored at server hard disk.

INTRODUCTION

The wide use of digitally formatted audio, video and printed information in network environment has been slowed by the lack of adequate protection on them. Developers and publishers hesitate to distribute their sensitive or valuable materials because of the easiness of illicit copying and dissemination. Compared to ordinary paper from

information, digitized multimedia of information (image, text, audio, and video) provides many advantages such as easy and inexpensive duplication and reuse, less expensive and more flexible either electronically (through the Internet) or physically media (as CD-ROM), further, transferring such information electrically through network is faster and needs less efforts than physical paper copying, distribution and update [1, 2].

However, these advantages have increased the potential for misuse and theft of such information and significantly increase the problems associated with enforcing copyrights on multimedia [3].

The major solution is basically divided into two technical approaches [4]: *First* is the usage control requires some hardware or software that is able to control the usage of the protected material. More physically, it means that any usage of the protected material, such as viewing, playing, or printing must be controlled by authorized rendering hardware or software. *Second* digital watermarking techniques embed digital marks into protected material to designate copyright-related information, such as origin, owner, content or recipient.

RELATED WORK

The Fraunhofer center for research in computer graphics developed many projects to protect multimedia through network means:

- ***J.Zhao [5,6]:*** presented watermarking server called *SYSCOP* "System for Copyright Protection" This system, started in 1996 , operating on a demonstration server available for public use ,and is available for commercial licensing. To try out the SYSCOP server, users can go to the web site and enter type of data (either still images or MPEG-1 video), a label and the secret key. Once submitted, the SYSCOP server retrieves the content from the URL where it was located, encodes it, and returns a link on which the user can click to retrieve the marked content.

- ***Wolfgang Funk [6]:*** produced project called *TALISMAN* "Tracing Author's right by Labeling Image Service and Monitoring Access Network" started in 1995 and completed in 1998.This project provide European community service provider with a standard copyright mechanism to protect digital products against privacy and illegal copying.

- ***Boucqueau J.,M., Lacroxi S., Marchal B [6]:*** produced a project called *OCTALIS* " Offer of Content through Trusted Access LInkS

"started in 1997 , the main purpose is realization of important mechanism for securing multimedia information access over network through broadcasting technology. The OCTALIS project combines both techniques equitable conditional access and watermarking to offer a good balance of security and flexibility. "OCTALIS" uses equitable conditional access to restrict access to an object. Once the object has been accessed in environment, labeling or watermarking technologies are used to protect author rights.

- In 21 century More studies and researches was produced that used the watermark as protection tool in Internet and other communication media such as satellite, radio, audience and advertising..

The proposed system

The proposed system consist of two stages the first one explain the design with some details and the second will display the implementation of the proposed design.

The Design of the System

This system is a three tier architectures, the first tier is the client computer with the tools needed to perform the interaction with server computer, and the second tier is the server computer with the tools needed to provide the service to client computer, and the third is the SQL Database The block diagram of the system is shown in Figure (1).

Client Tier

Client tier component represented by web Browser which is Internet explorer. The client request the system in URL ,then the system sent the home page which represents the interface of the system that allows the client to deal with the system.

Server Tier

This tier contains the design of the watermarking service which is consist of watermark embedding and extracting operations which take client information that entered by Active Server Page (ASP) using Active Data Object (ADO) from SQL database (SQL DB), the system operates invisibly to client and its result return to client using ASP with the release of Internet Information Service (IIS).

Database Tier

The third tier of the system is the database system, The ASP's primary interface to relational SQL database and deal with it using

ADO and ODBC. Where **ADO,** mean Active Data Objects provides an object oriented programming interface for accessing data sources such as Microsoft SQL server and ADO directly in ASP to access data source. In this work the ADO using directly in ASP to access data source. And **ODBC**, mean Open Database Connectivity is developed by Microsoft to simplify the development of applications that need to be independent of database platforms[7,8].

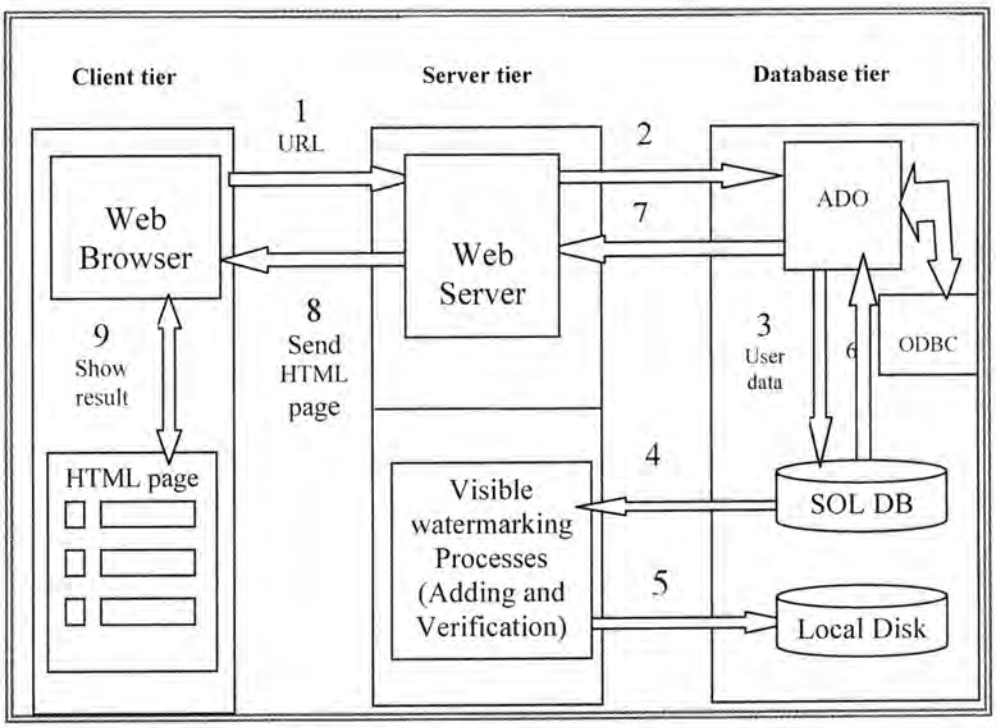

Figure-1: the proposed system design

The Automatic System Work

The work of this system can be briefly described by the mechanisms that allow the client to interact with the server, how the client request for embedding and extracting operations, and how the server response to these requests using server watermarking application. The system is worked automatically without interfere of client and the client does not see the entire work of the system.

Client Request for Embedding Operation

The watermark embedding gateway program accomplishes a watermarking request in the following four steps as shown in algorithm (1):

Algorithm (1) client request for embedding operation

Input: URL, The watermark and a secret key **Output:** HTML page.
Step1: The server gets the request from the information provided by the client using the ASP, including URL of the image; the watermark is to be embedded in the image and a secret key. **Step2:** The server gets the image data to be watermarked according to its complete URL address. **Step3:** Add visible watermark to image by Calling Watermark embedding application. **Step4:** Create an HTML page which will be shown on the requester's web browser, this page reports the status of the watermark embedding process.

Client Request for Extracting Operation

This operation can be done by the following steps as shown in algorithm (2):

Algorithm (2) client request for extracting operation

Input: URL, secret key **Output:** The watermark
Step1: The server gets the request from the information provided by the client using the ASP, Including the complete URL of the watermarked image and a secret key. **Step2:** The server gets the watermarked data according to its URL address. **Step3:** Call watermark extraction application. **Step4:** Create an HTML page, and show it on requester's web browser using ASP, this page displays the extracted watermark and shows the verification result.

Server Embedding Application

This application work automatically, once the user request the system service and deal with system interface to fill the image's

ownership information (Image URL, Watermark to be embed, and the Secret key) and sending this page to server to store it in its database, the embedding application consist of timer work on database to pick the information, load the image from that URL, Add the watermark visibly to image, then store it on server hard disk.

Server Extracting Application

Once an image has been watermarked, the client can verify the presence of the watermark and to prove that the watermark that added to his image is the same one stored in server Database.

The proposed verification operation which depends on the server uses the original watermark in its database. The verification process can be done by a server automatically and it consists of three steps [1]:

- Retrieve the embedded watermark using from the image to be verified.
- Retrieve the watermark from the server database according to the unique image identification (URL).
- Compare the two watermarks that are retrieved from the image and the database, respectively if the matching occurs the server send "The Watermark " to the client, otherwise the server send "not proved image" to client.

The implementation of the System

The proposed system consist of two applications which are web application (server website application) and windows application (Watermark Embedding and Extracting application).The windows application run automatically and it has no interface with the user.

The web applications have two main web pages that represent the user interface of search engine. These pages are:

A- Embedding form page.

B- Retrieval form page.

These entire pages will be displayed and explained in the next subsections with example to show the watermarking operation of image which located at URL "http://www.yahoo_com/canel%20flower203 " and this image is shown in figure (2) as an example to implement the system.

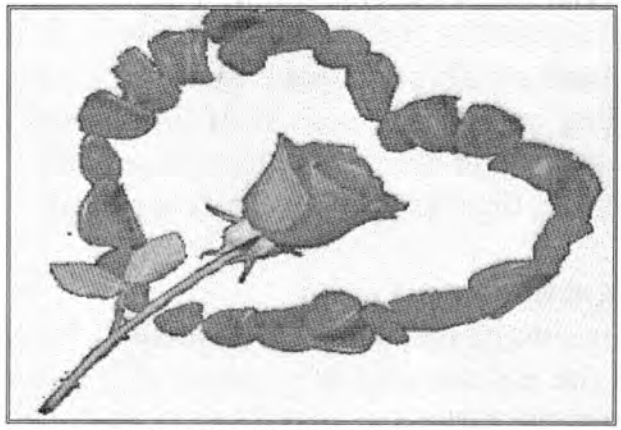

Figure -2: original image

The client should fill all fields in the HTML form appeared on its browser with image information (URL, the watermark and the secret key) and click on the submit button as shown in Figure (3).After submitting, the client should download the image to a specific file ,then all client information are stored in the server database and become the parameters that activate the embedding application that added the watermark to image as shown in Figure (4) and return timer to SQL database to activate the ASP to return page result appear at browser.

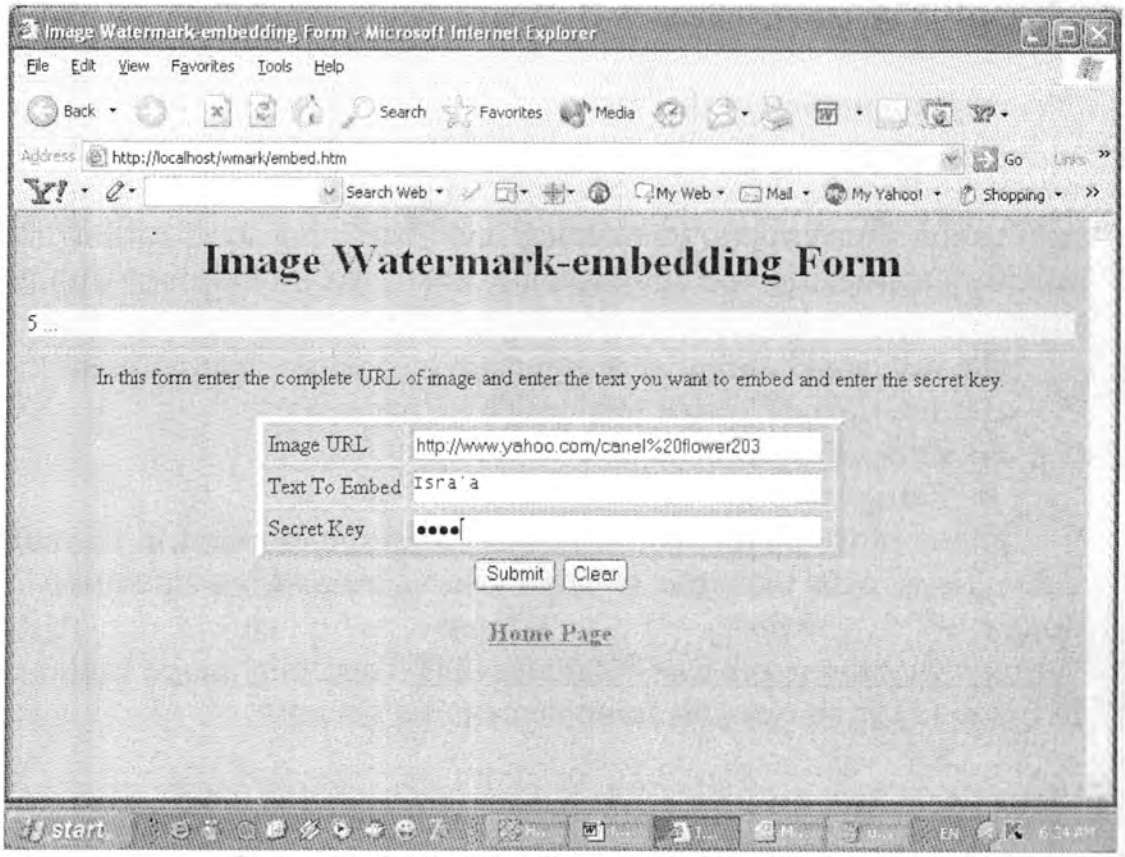

Figure -3: Embedding Form with Client Information

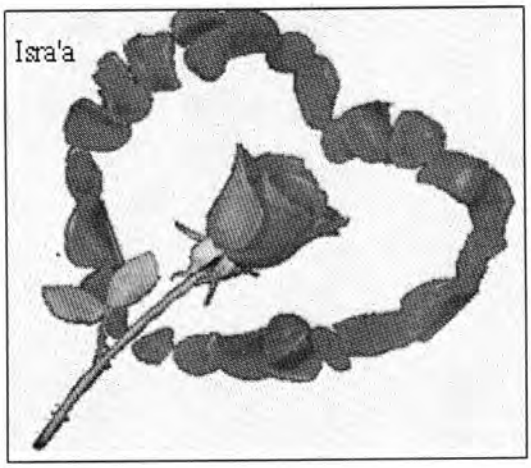

Figure -4: watermarked image stored at server

For extracting choice the client can click on extracting button, and then the Extracting Form page will appear to the user as shown in Figure (5), the client should fill the field with his image URL and his secret key, then click on the submit button, Then, verification result will be done automatically by the server and the watermark send to client in a new HTML page in order to prove the ownership

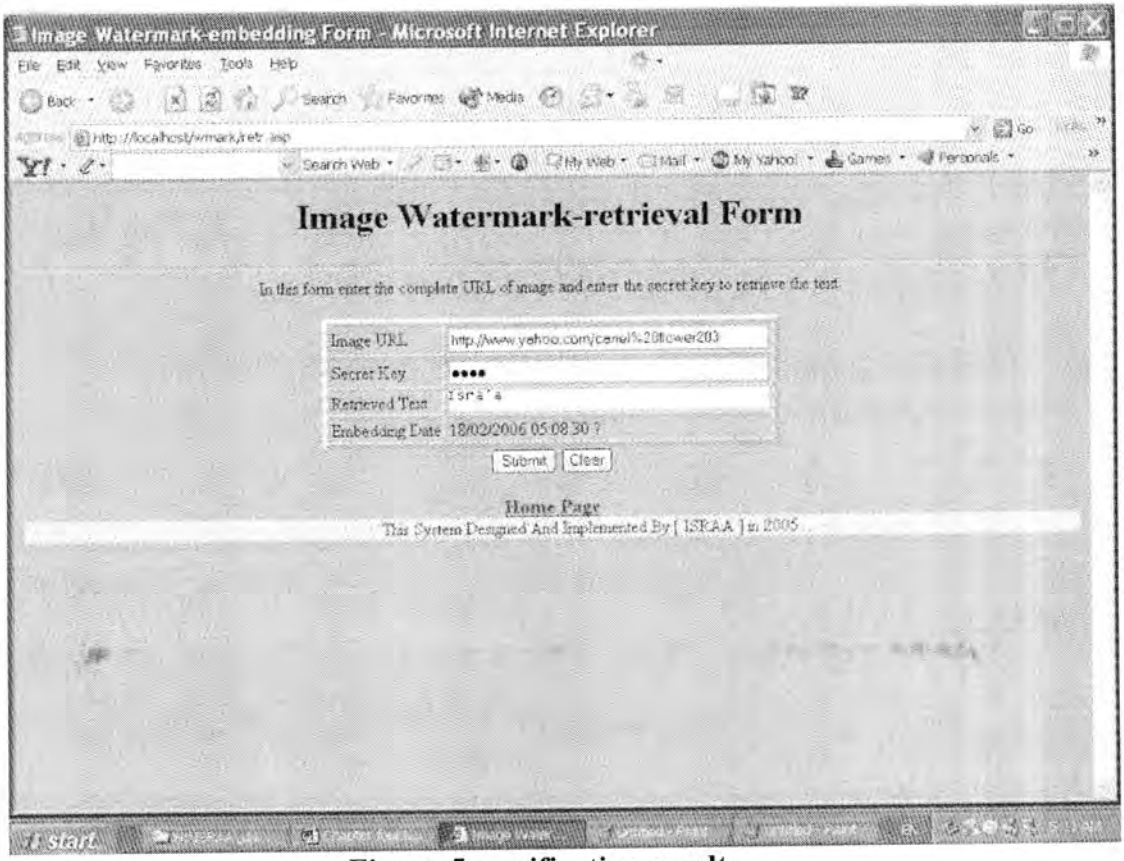

Figure-5: verification result

The present work has reached to the following conclusions:

1. The security of the system depends in the inability of the intrusion to access to server or tamper with the information on the server database. In addition, SQL server 2000 provides three levels of protection automatically: authentication, monitoring and administration, these levels prevent any access to the server database.

2. Design of server that producing registration service by visible watermarking gives the users ability to verify the presence of the watermark using the system that can be implemented in two ways: automatically and locally so the users have many ways to watermark their images:
- sending the image to the server for watermarking and registration.
- watermarking and register the image locally.

3. Unique Image Identification is assigned to each image using its URL, This means that the watermark is added to the image only once, so there is no way to the thief to register the same image at server by this way if two image have same watermark, the server certificate provides evidence to be used to solve disputes, so this server works as an electronic court.

RECOMMENDATIONS FOR FUTURE WORK

The following can be recommended for future work:

1. The present work can be developed to protect the other formats of multimedia such as audio, video and web pages.

2. Digital signature can be used instead of visible watermark to recognize the right of the original owner to the image registered at the server.

3. Using threshold to compare the original image with tampered one to study the robustness of watermark provided by the web system.

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Propose and Implement Firewall Strategy Using Multi Agent System

Soukaena H. Hashem
University of Technology, Computer Science Department
Soukaena_hassan@yahoo.com

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الخلاصة

الانترنيت هو شبكة شبكات , الانترنيت يمتلك عدد هائل من المواقع. هذه المواقع غالبا ماتحتوي على بيانات حساسة تتم حمايتها من انواع التطفل بواسطة انظمة حماية قوية. ادارة امنية البيانات تهدف الى الحفاظ على التكاملية والموثوقية وكل خدمات انظمة الحماية.

هذا البحث يركز على ناحية محددة تتعلق بحالة نمو الشبكة مما يجعلها اكثر تعقيدا هذا يجعل الشبكة عرضة لانواع متعددة من الهجوم. لذلك هذا البحث يقترح جدار ناري قادر على التعامل مع كل متطلبات امنية الشبكات, من خلال استخدام النظام المتعدد الايجينت لدعم اثنين من اهم الفعاليات: هذا من خلال بناء معمارية امنية قادرة على حماية الشبكة من جراء القدرة على تحديد الهجوم وبعدها عند تحديد الهجوم المعمارية الامنية سوف تتعامل مع هذا الهجوم حسب المقايس الامنية المحددة ضمن الجدار الامني.

ABSTRACT

Internet is network of networks; the Internet has numerous numbers of Internet sites. Many of these sites are sensitive and protected against the intentional hostile intrusion by strong protection systems. Network security management system aim to maintain the integrity, confidentially and availability of systems and services.

This research concentrate on one particular aspect: where the networks become more complex, making them more vulnerable to various kinds of complex security attacks. Therefore the research suggest a proposed firewall to deal with all security networking requirements, by using multi-agent system (MAS) to provide two important activities: that by build security architecture be able to protect networks by detecting attack; and then when attacks are detected the security architecture deals with these attacks in real time by taking security measures determined by the proposed firewall.

INTRODUCTION

An intelligent agent is an encapsulated computer system that is situated in some environment, and that is capable of flexible, autonomous action in that environment in order to meet its design objectives [1, 2].

There are a number of points about this definition that require further explanation. Agents are:

(i) clearly identifiable problem solving entities with well-defined boundaries and interfaces;

(ii) situated (embedded) in a particular environmentthey receive inputs related to the state of that environment through their sensors and they act on the environment through their effectors;

(iii) designed to fulfill a specific role - they have particular objectives to achieve, that can either be explicitly or implicitly represented within the agents;

(iv) autonomousthey have control both over their internal state and over their own behavior;

(v) Capable of exhibiting flexible (context dependent) problem solving behaviorthey need to be reactive (able to respond in a timely fashion to changes that occur in their environment in order to satisfy their design objectives) and proactive (able to opportunistically adopt new goals and take the initiative in order to satisfy their design objectives).

Today applications are more and more complex and a possible solution to deal with this complexity is the use of multi-agent based systems. Usually this kind of systems considers an environmental where all is predicable. The multi agent system community generally considers the MAS as being adaptive because agents are autonomous, situated, pro-active; social ... where the condition for the system adapts is to be composed of autonomous agents [1, 2, 10].

Firewall technology in TCP/IP internetworking provides a mechanism to help enforce access policies on communication traffic entering and leaving networks. Now we declare firewall types to give clear picture on the proposed work **Firewall mechanisms:** The common types of the firewalls according to the levels of TCP/IP and OSI stacks are: **Network Level Firewall (Packet Filtering Firewall):** A packet filtering is an access control mechanism for network traffic. Instead of processing or forwarding all packets that leave and arrive on the node's network adapters, the packet filters consults its access control rules before handling each packet. A filter is a program that, in general examines the IP addresses (source and destination addresses), ports numbers, protocol type , and service type fields of every incoming specified access control mechanism. **Application Level Firewall (Application Proxy):** These firewalls work a bit differently from packet filtering firewalls. Application gateway firewalls are software-based when a remote user from the void contacts a network running an application gateway, the gateway blocks the remote connection. Instead of passing the connection along, the

gateway examines various fields in the request, if these meet a set of predefined rules, the gateway create abridge between the remote host and the internal host (in common called proxy). **Circuit Level Firewall (Circuit Proxy):** A circuit level gateway firewall is a generic proxy that does not know the specifies of the application but performs a more generic set of capabilities. Circuit level gateways work at transport layer of TCPIP stack and OSI stack in same principle. The circuit level firewalls monitor TCP three handshaking in the TCP connection (session) between packets to determine whether a requested session is legitimate. **Stateful Multilayer Inspection Firewall:** Stateful firewall combines the aspects of the other three types of firewalls. They filter packets at the network layer, determine whether session packets are legitimate and evaluate contents of packets at the application layer. So, this firewall examines all TCP/IP layers and OSI layers in same principle to either accept or reject the requested communication [3, 4, 5, 9].

REQUIRMENT OF DETECTING ATTACKS

The following important requirements for detecting intrusion efficiently [6, 7, 8, 9, 10]:

- *Distribution*: many network attacks are characterized by abnormal behavior at different network elements. Detecting them by a single system, running on a single component, is too complicated. So it is easier to distribute monitoring and processing tasks among a number of entities at different points.
- *Autonomy*: excessive data traffic between distributed entities can cause network congestion problem. So, it is more judicious to let the entity monitoring a network element perform local analysis and detect intrusive behaviors.
- *Delegation*: the high level of dynamics in networks requires modifying, at any time, security management functions to adapt them to changes occurring in the monitored network. The model of delegation among various management entities allows fulfilling this requirement.
- *Communication and Cooperation*: coordinated attacks cannot be detected easily by an individual entity, which has a restricted view of the network. It is therefore necessary to correlate various analysis made by the autonomous entities. So communications and cooperation between entities are needed to detect coordinated intrusive behaviors.
- *Reactivity:* the aim of efficient intrusion detection is to react against an attack before serious damages can be caused.

- *Adaptability and Flexibility*: when a new security policy is added or modified, intrusion detection and monitoring tasks must be adapted.

THE PROPOSED SYSTEM

From the previous section, the research will consider the introduced features as main requirements for detecting attacks efficiently. The a proposed Firewall present the *Multi-Agents Systems (MAS)* is suitable solution, since multi-agent system properties (distribution, cooperation, .) and agent properties (adaptability, autonomy, pro-activity,) match the whole requirements. The general algorithm of the proposed system is as in the following steps:

Input: entering network packet's to the proposed firewall.
Output: determine if these packets are authorized or not.
Process:

1. *entering the packets to the proposed firewall system which consist of two levels they are:*
   - *1.1the external level which make the proposed firewall deal with the structure of MAS. This level represent the following agents each one has it is specified rule for management only:*
     - *1.1.1- security policy monitoring (consider as high layer).*
     - *1.1.2- external monitoring (consider as high layer).*
     - *1.1.3- lan monitoring (consider as high layer).*
     - *1.1.4- local monitoring (consider as low layer).*
   - *1.2- the internal level which make the proposed firewall deal with the structure of security agent. This level represent the following agent each has it is specified rule for security functions only:*
     - *1.2.1- discovering agent function*
     - *1.2.2- interfacing agent function*
     - *1.2.3 discussion agent function*

   2- the results of the security function will determine if the entered packets are authorized or not.
   3- end.

EXTERNAL LEVEL

This level define the MAS structure, which be defined by set of roles and relations between them, according the ***monitoring tasks***. These roles are:

- ***Security policy monitoring***: manages the security polices and communicates with the security officer.
- ***External monitoring***: describes the security management functions of distributed network. This functions concern the detection of complex attacks happening in a high level. Thus, an agent having this role will have a global view of the network and will detect coordinated attacks. It also will specify monitoring and detection tasks to the low level agents. This role manages the security of the distributed network with external networks and between LANs of the distributed network.
- ***LAN monitoring***: manages the security of LAN constituted of several domains. It concerns activities monitoring and detection of coordinated attacks within LAN and between it is various domains.
- ***Local monitoring***: that defines the local monitoring functions. It concerns the detection of attacks, which are local to domain.

So the proposed firewall consists of several agents structured hierarchically. Agents, which have various roles, re located at specific network entities and distributed at different points of the network. The hierarchical structure of agents enables local as well as global intrusion analysis and detection. Each agent has it is own perception of the network, which limited by the domain to monitor. According the agent role there are two layers: ***high layer and low layer:***

- ***High layer***: manages the global security of a network. In this layer the firewall identify three levels of manager agents: a security policy manager agent, an external manager agent and several LAN manager agents. The external manager agent controls LAN manager agent, which report pertinent analysis. It performs then another analysis to confirm the detection of an attack. It can also ask for more data processing and delegate new monitoring tasks to LAN manager agent. The external manage agent is also responsible for distributing a set of local agent to each LAN manager agent. The LAN manager agent controls local agents and analyses the monitored events reported by these agent.
- ***Low layer***: manages the security of a domain. It is composed of a group of local agent, which has specific monitoring roles.

INTERNAL LEVEL

To build good universal firewall by MAS, agent must have knowledge base of firewall rules to reason about complex attacks and stimulus-response to react rapidly to the environments changes.

AGENT FUNCTION

So agent has three functions, see figure (1):

1. ***Discovering function***: those discovering security events. This done by filtering process, this research suggest the filtering to be at all the layers of tcp/ip: this mean check both source and destination IP address, port, sequence no., and acknowledge no..
2. ***Interfacing function***: that manages its interactions with its environment and other agents. For example: the security policy agent give the results of monitoring to all the external agents and so on.
3. ***Discussion function***: that enables it to analyze new data and detect attacks.

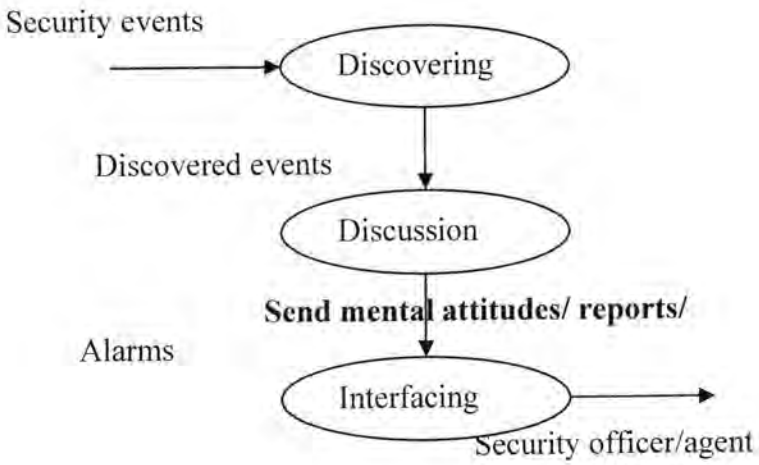

Figure-1: Agent functions

EVENT DISCOVERING FUNCTION

A security event is characterized by its type, its observation point, a temporal attribute (representing the event occurring moment), and a set of non-temporal attributes. According to the event type and its observation point, this research identifies various event classes. Such as network connection events, ICMP events, UDP events, TCP events and file events. The event discovering function filters security events produced in the network, according to event classes specified in detection goal. Indeed, the events occurring in network are not all collected. In fact, when a detection goal is sent to an agent, a set of event classes to observe is specified to it. Thus when an event occurs in

the network, the agent tests if it matches the event classes specified in the goal. If it matches, it is collected. The discovered events are then stored waiting to be treated by the discussion function.

INTERFACING FUNCTION

This function describes interactions between the above-described agents. It allows them to communicate their analysis and knowledge and mental attitudes (belief, suspicion,). In fact, manager agent interacts with local agents by:

- ***Sending goals***, derived from security policies.
- ***Delegating*** specific functions of monitoring/detection and specifying the various domains to monitors.
- ***Asking particular information***: the suspicion level of a specific user, the list of events generated by a user, etc.,
- ***Receiving*** the relevant reports or analysis results and alarms.

Interfacing function also permits interactions between the security officer and security policy manager agent/external manager agent. It ensures the reception of specifications and requests from the security officer such as security policies to apply. It allows the delivery of security reports and alarms when an attack is detected.

DISCUSSION FUNCTION

As it has been outlined, security management must deals with significant network characteristics such as:

- Its continuous variation, particularly in terms o user and offered services;
- And variation of its security problems such as new vulnerabilities and increasingly complex attacks.

In this function the agent is ale to reason and extrapolate by relying on its mental attitudes, built knowledge and experience in rational way, to find the adapted answers. The agent uses its beliefs resulting from filtered events and beliefs of the neighboring agents for reaching its specified goals. When a goal is reached (an attack is detected), it executes appropriate actions.

IMPLEMENTATION

To display the idea of this research in more clearly by present the real implementation of that system as follow:

Since the security policy agent responsible to monitor and mange over the entire network and all it is components and other agents,

so the implementation of that agent will be such as network explorer see figure (2).

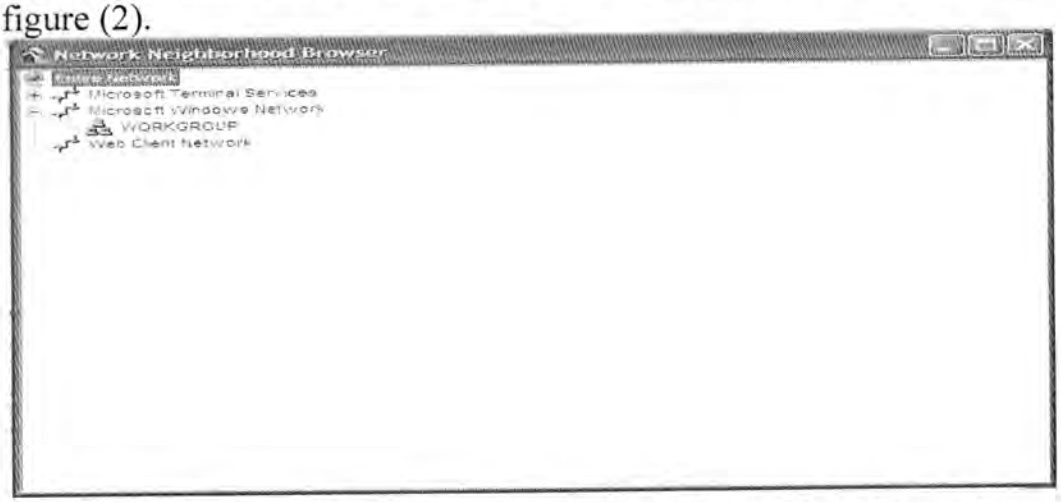

Figure -2: the proposed security policy agent implementation (network explorer).

Since the external agent responsible to monitor and mange the security over all the LAN agents in the universal network, so the implementation of that agent will be such as packet capturing see figure (3). The last will collect the log in/out information and submit this information to firewall application program, see figure (4) to detect the intrusion on the LANs.

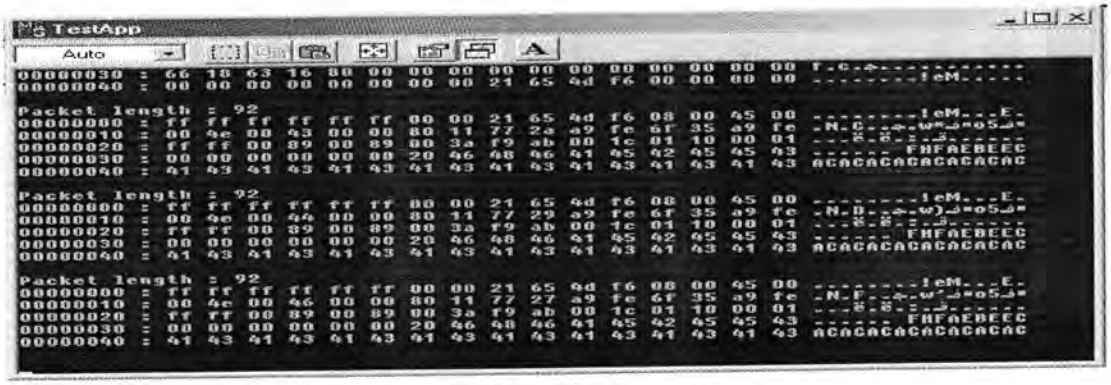

Figure -3: packet capture software

The external agent implementation (firewall application program) is responsible to take the hexadecimal values of local address, local port, remote address, remote port, state, time-stamp, and protocol type from the packet. And then this information would show in understandable information for the administration.

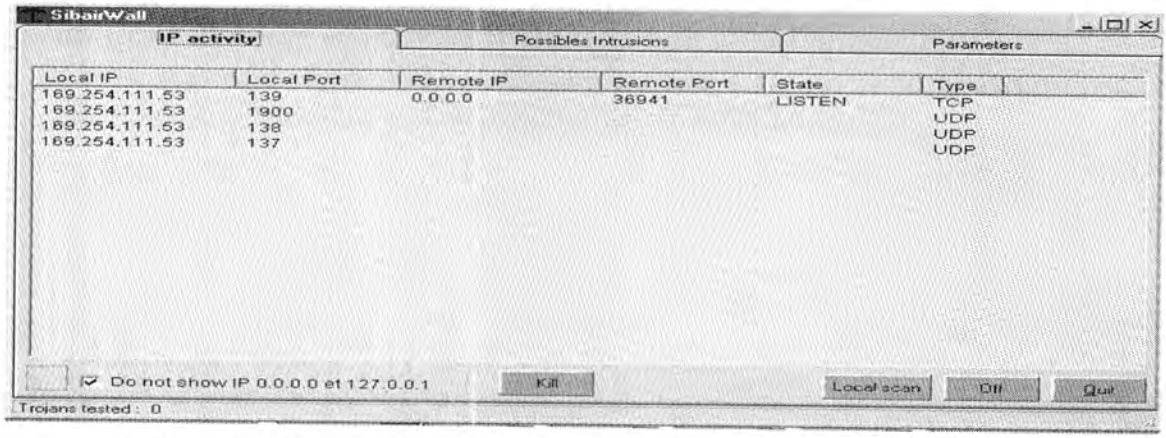

Figure -4: the proposed implementation of external agent (firewall application program).

Since the LAN agent responsible to monitor and mange the security over the entire LAN network in the universal network, so the implementation of that agent will be such as LAN firewall customized according the prosperities of each LAN architecture see figure (5).

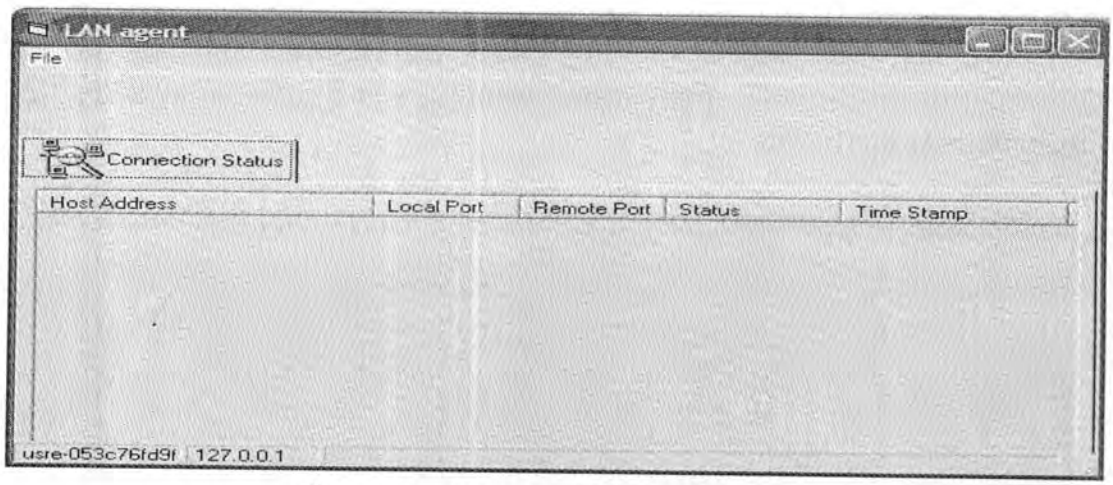

Figure -5: the firewall of LAN agent.

Since the low layer manages the security of a domain. It is composed of a group of local agent, which has specific monitoring roles, so the implementation of these agents will be such as specified firewall customized according the prosperities of each local PC architecture see figure (6).

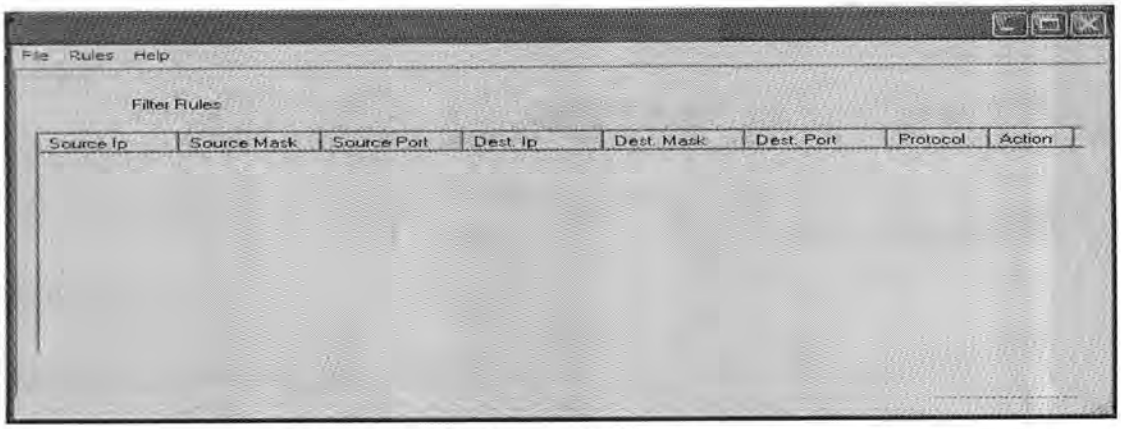

Figure -6: the firewall of local agents.

This research, presented the MAS as a multi level firewall in a complex network, since it provide suitable solution. All known and good MAS methodology applied and we conclude these methodologies are good for online systems. Applying the three functions in the agent working making the proposed firewall faster and has high precision. But the adaptation and flexibility features are not provided by the proposed multilevel systems, which can not be upgraded easily and cannot easily adapt their intrusion detection tasks to changes in networks and user behaviors. In addition, they do not have the ability to learn new attacks. So we suggest for future work in the proposed firewall by agent-based system using the new theory of adaptive multi-agent system (AMAS).

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مجلة
علوم المستنصرية

الهيئة الاستشارية

بسم الله الرحمن الرحيم

تعليمات النشر لمجلة علوم المستنصرية

1. تقوم المجلة بنشر البحوث الرصينة التي لم يسبق نشرها في مكان آخر بعد إخضاعها للتقويم العلمي من قبل مختصين وبأي من اللغتين العربية او الانكليزية .
2. يقدم الباحث طلبا تحريريا لنشر البحث في المجلة على أن يكون مرفقا بأربع نسخ من البحث مطبوعة على الحاسوب ومسحوب بطابعة ليزرية وعلى ورق ابيض قياس (A4) مع قرص مرن (Disk) محمل بأصل البحث ويكون عدد صفحات البحث **10** صفحات وبضمنها الاشكال والجداول على ان لايكون الحرف اصغر من قياس **12** .
3. يطبع عنوان البحث واسماء الباحثين (كاملة) وعناوينهم باللغتين العربية والانكليزية على ورقة منفصلة شرط ان لاتكتب اسماء الباحثين وعناوينهم في أي مكان اخر من البحث ، وتعاد كتابة عنوان البحث فقط على الصفحة الاولى من البحث .
4. تكتب اسماء الباحثين كاملة بحروف كبيرة وفي حالة استخدام اللغة الانكليزية وكذلك الحروف الاولى فقط من الكلمات (عدا حروف الجر والاضافة) المكونة لعنوان البحث ، وتكتب عناوين الباحثين بحروف اعتيادية صغيرة .
5. تقدم خلاصتان وافيتان لكل بحث ، احداهما بالعربية والاخرى بالانكليزية وتطبع على ورقتين منفصلتين بما لايزيد على (**250**) كلمة لكل خلاصة.
6. يشار الى المصدر برقم يوضع بين قوسين بمستوى السطر نفسه بعد الجملة مباشرة وتطبع المصادر على ورقة منفصلة ، ويستخدم الاسلوب الدولي المتعارف عليه عند ذكر مختصرات اسماء المجلات.
7. يفضل قدر الامكان تسلسل البحث ليتضمن العناوين الرئيسة الاتية : المقدمة ، طرائق العمل ،النتائج والمناقشة و الاستنتاجات ، المصادر، وتوضع هذه العناوين دون ترقيم في وسط الصفحة ولا يوضع تحتها خط وتكتب بحروف كبيرة عندما تكون بالانكليزية .
8. يتبع الاسلوب الاتي عند كتابة المصادر على الصفحة الخاصة بالمصادر: ترقيم المصادر حسب تسلسل ورودها في البحث ، يكتب الاسم الاخير (اللقب) للباحث او الباحثين ثم مختصر الاسمين الاولين

فعنـوان البحـث ، مختصـر اسـم المجلـة ، المجلـد او الحجـم ، العـدد ، الصـفحات ، (السـنة) . وفـي حالـة كـون المصـدر كتابـا يكتـب بعـد اسـم المؤلـف او المـؤلفين عنـوان الكتـاب ، الطبعـة ، الصـفحات ، (السـنة) الشركة الناشرة ، مكان الطبع .

10. بخصـوص اجـور النشـر يـتم دفـع مبلـغ (**25000**) خمسـة وعشـرون الـف دينـار عنـد تقـديم البحـث للنشـر وهـي غيـر قابلـة للـرد ومـن ثـم يـدفع الباحث (**25000**) خمسة وعشرون الف دينـار اخـرى عنـد قبـول البحـث للنشر وبهذا يصبح المبلغ الكلي للنشرخمسون الف دينار .

المـــحتـــويـــــــات

دراسة تأثير مستخلص نبات الزعتر *Thymbra spicata* على طفيلي الابواغ الخبيئة *Cryptosporidium parvum* في الفئران

سبأ طاهر محمد
الجامعة المستنصرية /كلية العلوم /قسم علوم الحياة

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ABSTRACT

This study includes isolation and purification of *cryptosporidium parvum* oocysts from calves suffering from sever diarrhea . This oocysts used to occur experimental infection for study if can used the watery extract of *Thymbra spicata* as a treatment for the parasite and to compare with spiramycin drug . This study showed high efficacy in treating *Thymbra spicata* extract with0.1 ml dose 3 times a day , which led to suspend shedding oocysts in the (9^{th}) day with treatment efficiency (90.3 %) compared with spiramycin drug at the dose of (0.001 gm) of drug , that the mice maintain shedding oocysts till the (20^{th}) days of treatment in efficacy of(91. 5%) . Also this study includes to test the effect of the watery extract of *Thymbra spicata* on average of oocyst excystation compared by HBSS , found significant effect for *Thymbra* on the average of oocyst parasite excystation reach (40 %) compared with HBSS was (80 %) .

الخلاصة

تضمنت هذه الدراسة عزل وتنقية أكياس بيض الطفيلي *Cryptosporidium parvum* من براز عجول مصابة بالإسهال ، ثم استخدمت أكياس البيض لأحداث أصابة تجريبية في الفئران لدراسة أمكانية كعلاج للطفيلي ومقارنته بعقار *Thymbra spicata* استعمال المستخلص المائي لنبات الزعتر نوع السبايرامايسن ،أظهرت هذه الدراسة الكفاءة العلاجية العالية لمستخلص نبات الزعتر وبالجرعة العلاجية 0.1 أدى إلى توقف الفئران عن طرح أكياس البيض في اليوم التاسع بعد العلاج وبمعدل ثلاث مرات في اليوم مل %مقارنة مع عقار السبايرامايسن بجرعة علاجية0.001غم آذ استمرت الفئران 90.3وبكفاءة علاجية بلغت %. كما شملت الدراسة على 91.5بطرح أكياس البيض إلى اليوم العشرين بعد العلاج وبكفاءة علاجية بلغت اختبار تأثير المستخلص المائي للزعتر على معدل تبويغ أكياس البيض ومقارنته مع محلول هانكس الملحي هنالك تأثيرا ملحوظا للزعتر على معدل تبويغ أكياس بيض الطفيلي آذ بلغ 40%مقارنة مع المتوازن اذ لوحظ محلول هانكس الملحي المتوازن الذي بلغ 80%.

المقدمة

يعد مرض الابواغ الخبيئة Cryptosporidiosis من الأمراض الطفيلية المشتركة بين الإنسان والحيوان، يسببه احد الاوالي الاكرية التابعة لجنس *Cryptosporidium* ،وهو احد الاوالي المعوية الإجبارية الواسعة الانتشار في العالم يتطفل على الحافة الفرشاتية للخلايا الطلائية للأمعاء وكذلك في مضائف مختلفة مسببا إسهالاً مائياً شديداً خصوصاً عند الأطفال دون السنة الخامسة (1) . تستكمل دورة حياة الطفيلي في مضيف واحد وليس للطفيلي مضيف متخصص ، وهو عادة مرتبط بمناعة المضيف إذ وجد الطفيلي في الإنسان مصاحباً لحالات النقص المناعي (2) . وتكون دورة حياة الطفيلي مشابه لدورة حياة الاكريات الأخرى مع بعض الاختلافات، ويحدث الخمج عن طريق تناول الماء والغذاء الملوثين بأكياس البيض الطفيلي oocysts المطروحة مع براز المضائف المخمجة بالمرض (3) . وأن البحوث مازالت جارية لإيجاد العلاج المؤثر إذ انه على الرغم من استعمال أنواع مختلفة من

سبا

المضادات الحياتية فقد جرب استعمال أكثر من 95 مركباً مضاداً للمرض لكنها لم تعطي نتائج ايجابية في العلاج (4) . حديثاً اتجهت البحوث العلمية لإيجاد علاجات تكون اقل سمية من المركبات الكيميائية المستعملة ولهذا فلقد توجهت البحوث نحو المركبات الطبيعية مثل ألاعشاب فمثلاً استعملت بذور فاكهة ألسندي و أوراق الزيتون و الثوم والحبة السوداءوالزعتر في علاج العديد من الطفيليات (5) . ولذلك فقد تولدت فكرة استعمال نبات مثل الزعتر لعلاج الخمج بهذا الطفيلي . فكما هو معروف فأن نبات الزعتر ينتمي إلى العائلة الشفوية (labiate) , وينتمي إلى جنس *Thymbra* والاسم الشائع هو Thyme وهي عبارة عن شجيرات صغيرة يتراوح ارتفاعها من 100 – 500 ملم (6) . تكون أوراقه شريطية رمحيه الشكل تحتوي على ما لا يقل عن (1 – 2 %) من وزنها زيوتاً طيارة وعلى مواد راتنجية ودباغيه وصمغية , ويحتوي على صابونيات متعادلة وحامضية وعلى مواد مرة وفلافونات , كما يحتوي زيت الزعتر على مواد فينولية أهمها الثايمول والكارفاكرول (7) . وله استخدامات منها داخلية وخارجية , وتعود أهميته الطبية إلى احتوائه على الزيوت الطيارة , فهو يستعمل في صناعة معاجين الأسنان ومستحضرات غرغرة الفم والحلقوم ولعلاج حالات التهاب اللثة والأسنان واللوزتين (8) . ويستخدم كمثبط لنمو البكتريا فضلاً عن تأثيره المثبط لأنواع من الفطريات الجلدية (9) . كما يعمل كطارد للطفيليات الداخلية وخاصة الديدان المسطحة (10) .

وقد جاءت هذه الدراسة لتوضيح تأثير نبات الزعتر على طفيلي الابواغ الخبيئة في الفئران المختبرية المضعفة مناعياً وإمكانية استخدامه كعلاج للإسهال المتسبب عن هذا الطفيلي .

المواد و طرائق العمل

جمع عينات البراز

تم جمع 300 عينة براز من عجول تتراوح أعمارها من (3 – 30)يوماً ولكلا الجنسين , كانت قد ظهرت عليها علامات سريريه متمثلة بالإسهال المائي الشديد ذات اللون الأصفر أو الأخضر مع هزال وارتفاع طفيف في درجات الحرارة. وكانت العجول تابعة إلى محطة الاسحاقي في الدجيل , وقد جمعت عينات البراز من مستقيم الحيوان مباشرة مع مراعاة لبس الكفوف الطبية لمنع التلوث ووضعت العينات في حافظات بلاستيكية نظيفة ومحكمة الغلق ونقلت في حافظات مبردة لإجراء الفحوصات المختبرية عليها في المختبر .

الفحص ألمختبري للبراز

أجري الفحص ألمختبري للتحري عن وجود أكياس بيض الطفيلي ،اذ تم فحص النماذج بعمل شرائح زجاجية صبغت باستعمال صبغة الزيل نيلسن الباردة المحورة modified cold zeihl neelsen stain وحسب طريقةBeaver and Jung (11) . ثم فحصت الشرائح تحت المجهر باستعمال العدسة الزيتية .

عزل وتنقية أكياس البيض

بموجب نتائج صبغة الزيل نيلسن فقد تم استخدام العينات الموجبة في عزل وتنقية أكياس البيض وذلك باستعمال طريقة المحلول الملحي المشبع saturated salt solution وحسب الطريقة المتبعة من قبل **Ungar *et al*** (12) . ثم حفظت أكياس البيض النقية في قناني زجاجية تحتوي على ثنائي كرومات البوتاسيوم بتركيز 2.5% وفي درجة 4 م لحين الاستعمال .

تحضير عالق أكياس البيض

1 . أخذ حوالي 20 مل من عالق أكياس البيض النقية والمحفوظة في محلول ثنائي كرومات البوتاسيوم والتي تم عزلها وتنقيتها سابقاً , ووضعت في أنابيب اختبار نظيفة ومعقمة .

2 . غسلت أكياس البيض عدة مرات بالماء المقطر وبسرعة انباذ (700 دورة / دقيقة) للتخلص من محلول ثنائي كرومات البوتاسيوم .

3 . باستعمال شريحة العد Hemocytometer حظر عالق من أكياس البيض وبتركيز (10^4 x 1) كيس بيض / مل لغرض تجريع حيوانات التجربة وإحداث الخمج .

تحضير المستخلص المائي الحار لنبات الزعتر

أستخدم نبات الزعتر المحلي ***Thymbra spicata*** والذي تم الحصول عليه من احد المعاشب في بغداد وحضر المستخلص حسب طريقة Anesini and Perez (13) .

حيوانات التجربة

تم الحصول على (18) فأراً من الفئران السويسرية البيضاء ذكور وبمعدل عمر يتراوح بين (12-14) أسبوع وبوزن (22-25) غم ولقد تم الحصول عليها من معهد الأجنة وأبحاث العقم التابع إلى جامعة بغداد . وضعت الفئران في أقفاص بلاستيكية تم تطهيرها بمادة السبتول بتركيز 10 % كما زودت بصورة مستمرة بمياه الشرب المعقم بواسطة قناني خاصة بذلك وعلف معقم تم الحصول عليه من المعهد نفسه مع توفير درجة حرارة وتهوية مناسبتين . تم فحص براز الفئران قبل بدأ التجربة للتأكد من خلوها من الإصابات المعوية الطفيلية , وذلك بوضع كمية قليلة من البراز على شريحة زجاجية ومزجها بالقليل من الأيودين ثم غطيت بغطاء الشريحة وتم فحصها تحت المجهر.

تصميم التجربة

1 . ثبطت مناعة [18] فأراً وفقاً للطريقة المقترحة من قبل Regh (14) وذلك باستعمال عقار الدكساميثازون Dexamethasone إذ حقن بمقدار (0.1 مل) بالعضلة بجرعة (0.10 ملغم / فأر/ يوم) وطيلة فترة أجراء التجربة .

2 . بعد 5 أيام جرعت الحيوانات بـ (0.1) مل من العالق الحاوي على (10^4 x 1) كيس بيض عن طريق الفم وباستعمال الأنبوب المعدي (Stomach tube) من العينة المنتقاة سابقاً .

3 . فحص براز الفئران المجرعة أبتداءاً من اليوم الثاني بعد إعطاء جرع الخمج إلى حين ظهور أكياس البيض في البراز , أذ حددت الفترة قبل البائنة (prepatent period) .

4 . وبعد ظهور أكياس البيض في البراز اختيرت الفئران التي كانت الفترة قبل البائنة متشابهه وقسمت إلى 3 مجاميع وبمعدل 6 فأر لكل مجموعة , ثم جرعت كل مجموعة عن طريق الفم وباستخدام الأنبوبة المعدية وكالاتي :-

- **المجموعة الأولى :-** جرعت بـ (0.1 مل) من المستخلص المائي للزعتر (المحضر سابقاً) وبمعدل ثلاث جرع يومياً .
- **المجموعة الثانية :-** جرعت حيوانات هذه المجموعة بالمضاد الحيوي السبايرامايسين Spiramycin المصنع في مختبرات أسيا للصناعات الدوائية / سوريا . وبجرعة (0.01 غرام) من المضاد أذيب بـ (0.1) مل من الماء المقطر عن طريق الفم يومياً وطيلة فترة التجربة .
- **المجموعة الثالثة :-** جرعت حيوانات هذه المجموعة بـ 0.1 مل من محلول الملح الفسلجي PBS وعدت كمجموعة سيطرة .عزلت الفئران بشكل منفرد لكل المجاميع

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ثم جمع وفحص برازها كل 24 ساعة ، ابتداءا من اليوم التالي من إعطاءها الجرعة حتى نهاية التجربة .

بعدها تم قياس المعايير التالية للمجاميع العلاجية وكالاتي :

1. مراقبة الحيوانات وتسجيل أي علامات سريريه واضحة .
2. حساب الفترة قبل البائنة للخمج .
3. فحص البراز وحساب أعداد أكياس البيض لكل غرام من البراز وذلك بتطبيق المعادلة الآتية التي أستعملها Ryan (15):

$$N = S / (Vol \times Wt)$$

حيث ان:

N : عدد أكياس البيض في غرام من البراز.

S: عدد أكياس البيض المحسوبة في الشريحة.

Vol: حجم العينة المحسوبة بـ(0.01مل).

Wt: وزن عينة البراز المأخوذة (1 غم).

4 . قياس الكفاءة العلاجية للزعتر ومقارنتها مع عقار السبايرامايسين وذلك بتطبيق المعادلة التي أستعملها Xiao (16) .

$$\text{كفاءة العلاج المستعمل \%} = \frac{\text{معدل أعداد أكياس بيض الطفيلي في 1 غم من البراز لمجموعة السيطرة} - \text{معدل أعداد أكياس بيض الطفيلي في 1 غم من البراز للمجموعة العلاجية}}{\text{(معدل أعداد أكياس بيض الطفيلي في 1 غم من البراز لمجموعة السيطرة)}} \times 100$$

تأثير مستخلص الزعتر على تبويغ أكياس البيض

لدراسة تأثير المستخلص المائي للزعتر على تبويغ أكياس البيض فلقد تم استعمال محلول هانكس الملحي المتوازن وهو محلول معتمد يستخدم لغرض تبويغ أكياس بيض الطفيلي وبنسبة عالية لغرض مقارنته مع المستخلص المائي للزعتر ولقد أتبعت الطريقة المتبعة من قبلRiggs (17) . مع الأخذ بنظر الاعتبار أن التجربة للمحلولين قد أجريت في نفس الظروف ، وأستعمل عالق أكياس البيض بتركيز (1×10^8 كيس بيض / مل) .

وفي نهاية التجربة أخذت قطرة من وسط الاختبار ووضعت على شريحة زجاجية نظيفة ، ثم تركت لتجف وصبغت بصبغة الزيل نلسن المحورة ، ثم وضعت تحت المجهر لحساب النسبة المئوية للتبويغ ، إذ عدت أكياس البيض ذات جدار رقيق ومعتم وداخلها شفاف ولا تحتوي على أية حبيبات أو تحتوي من [1 – 2] حبيبات فقط في داخلها ، عدة هذه الأكياس مبوغة وأحياناً لوحظ وجود بقايا الكيس على شكل نصف دائرة أو شكل هلالي فأنها عدة مبوغة أيضاً ، ولاستخراج النسبة المئوية للتبويغ ، فلقد تم حساب أول[50] كيس بيض يشاهد على الشريحة الزجاجية ثم أستخرج المعدل لثلاث مكررات .

التحليل الإحصائي

حللت النتائج إحصائيا باستعمال الفرق المعنوي الأصغر Least significant differences عند مستوى ($p<0.05$) ولقد ثبتت النتائج على شكل المعدل الحسابي ± الانحراف المعياري Standard deviation .

النتائج والمناقشة

لم تظهر فئران التجربة المخمجة والمعالجة أي علامات سريريه واضحة أو تغيرات مرضية ، كما سجلت الفترة قبل البائنة في الفئران المخمجة وقد تراوحت بين (3-4) أيام لجميع المجاميع العلاجية.

وبين الفحص المجهري للشريحة المحضرة من البراز الحاوي على أكياس البيض بعد تصبيغها بصبغة الزيل نلسن المحورة الباردة والمفحوصة بالعدسة الزيتية ، بأنها أجسام كروية الشكل حمراء براقة ،وتظهر في داخلها أربعة حبيبات وأحياناً بقعة واحدة كبيرة الحجم ذات لون أسود تمثل البويغات (شكل 1) .ولقد جرعت الفئران بـ (1000) كيس بيض لغرض أحداث الخمج التجريبي في الفئران وأن هذه الجرعة تعد أنسب جرعة لإحداث خمج تجريبي .

أظهرت نتائج الدراسة الحالية وكما مبين في الجدول (1) ، بأن معدلات أعداد أكياس البيض عند ظهور الخمج كانت متقاربة في المجموعتين العلاجية واختلفت قليلاً مع مجموعة السيطرة ، إذ بلغت (1750.6) و (1733.3) كيس بيض / غرام . من البراز لمجموعتي الزعتر والسبايرامايسين على التوالي بينما بلغت في مجموعة السيطرة (183.33) كيس بيض /غرام . ثم بدأت معدلات أعداد أكياس البيض بالانخفاض تدريجياً منذ اليوم الثاني بعد العلاج وأستمر ليصل المعدل صفراً في اليوم التاسع في المجموعة المعالجة بالمستخلص المائي للزعتر .

أما المجموعتين الأولى والثالثة (مجموعة السيطرة ، ومجموعة المعالجة بالسبايرامايسين) فلقد أستمر معدل طرح أكياس البيض ليصل إلى (1700.0) و (20.00) كيس بيض / غرام من البراز في اليوم العشرين بعد التجريع على التوالي وبعد متابعة التجربة تبين أن مجموعة السيطرة استمرت بطرح أكياس البيض إلى اليوم (52) . بينما استمرت مجموعة السبارامايسين إلى اليوم (25) ، ولم يتم تسجيل ذلك رقمياً ولكن لوحظ ذلك ودون مع الملاحظات .

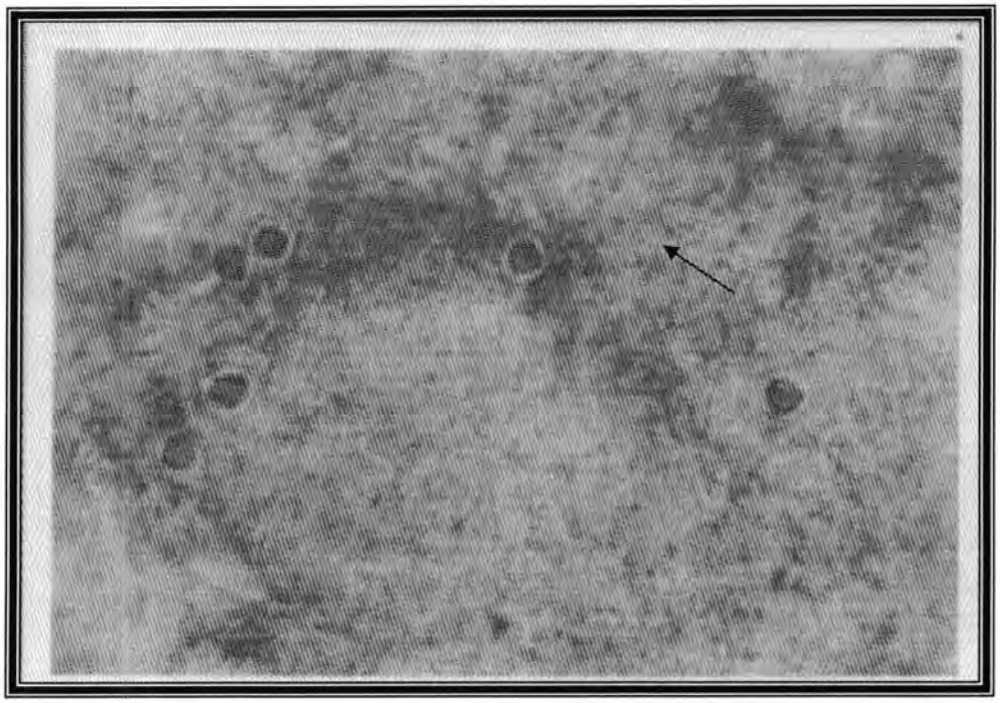
وعند تحليل النتائج إحصائيا تبين أن هناك فرق معنوي بين مجموعة السيطرة وبين المجاميع العلاجية الأخرى وهناك فرق معنوي بين المجاميع العلاجية نفسها وبمستوى ($p<0.05$) .وعند تطبيق المعادلة الخاصة بقياس الكفاءة العلاجية كما ورد في الجدول (2) ، تبين أن عقار السبارامايسين وبجرعة (0.001) غم ، ولمدة (20) يوم كان ذا كفاءة علاجية عالية بلغت (91.5 %) ، أما المستخلص المائي للزعتر وبجرعة (0.1) مل وبمعدل ثلاث جرع في اليوم فلقد كانت (90.3 %) .

علماً بأن قياس الكفاءة العلاجية اعتمدت على معدل طرح أكياس البيض خلال مدة العلاج ، ولم تأخذ بنظر الاعتبار مدة العلاج أي الوقت الذي استغرقته المادة المستخدمة في العلاج لتوقف طرح أكياس البيض بصورة نهائية ، إذ نلاحظ من الجدول (1) بأن المستخلص المائي للزعتر قد أستغرق وقت أقصر بقليل من عقار السبايرامايسين إذ تطلب (9) أيام فقط لتوقف طرح أكياس البيض وحصول العلاج التام ، كما أن الكفاءة العلاجية له كانت متقاربة مع الكفاءة العلاجية لعقار السبايرامايسين. وقد أظهرت نتائج دراسة تأثير المستخلص المائي للزعتر على معدل تبويغ أكياس البيض مقارنة مع محلول هانكس الملحي المتوازن وهو محلول معتمد في الدراسات التجريبية لتبويغ أكياس وكما موضحة في الجدول (3) ، أن المستخلص المائي قد أظهر تأثيرا واضحاً على تبويغ أكياس البيض فلقد بلغت النسبة المئوية للتبويغ (40 %) فقط ، مقارنة مع محلول هانكس الملحي المتوازن فلقد بلغت نسبة التبويغ (80 %) ولقد أجريت الطريقتين في درجة حرارة (37 م°) .

ولم تتوفر العدة اللازمة لاختبار تأثير المستخلص على حيوية الابواغ الناتجة فقد تكون الابواغ الناتجة هي ميتة ولا يمكنها أحداث خمج .

جدول -: 1:أعداد أكياس البيض في المجاميع العلاجية ومجموعة السيطرة خلال (20) يوم ± الانحراف المعياري

المجموعة / يوم بعد التجريع العلاجي	مجموعة السيطرة	مجموعة الزعتر	مجموعة سبارامايسين
1	75.27 ± 183.33	81.54±1750.6	30.10±1733.33
2	109.54±500.000	150.30±1430	151.65± 1350.00
3	150.55 ± 666.66	85.24±850.2	343.02±833.33
4	250.33±2133.33	21.00±502.00	120.06± 791.66
5	122.47±2450.00	54.26±155.50	125.16±733.33
6	89.44±3500.00	5.66±94.15	103.27±1033.33
7	285.77±4083.33	7.52±45.00	121.12±733.33
8	517.68±4600.00	7.52±20.16	91.74±491.66
9	558.56±6900.00	-	37.77±333.33
10	715.54±8600.00		38.83±230.00
11	465.95±9693.33		8.01±170.83
12	223.64±14800.0		8.01±139.16
13	236.64±16300		18.70±95.00
14	114.30±13083.33		11.6±41.66
15	103.14±9566.66		10.48±55.00
16	403.31±6050.00		7.52 ±38.33
17	248.32±3216.66		10.48±40.00
18	194.07±2216.66		7.52 ±31.66
19	135±1833.33		8.16 ±26.66
20	200.00±1700.00		20.000



شكل- 1: أكياس بيض طفيلي الابواغ الخبيئة المعزولة من عجول تعاني من إسهال مائي والمصبوغة بصبغة الزيل نلسن المحورة (1000 X) .

جدول -2 : الكفاءة العلاجية لجرع المستخلص المائي لنبات الزعتر مقارنه مع عقار السبايراميسين

نوع العلاج	الجرعة المستخدمة	الكفاءة العلاجية
السبارامايسين	0.001 غم	% 91.5
المستخلص المائي للزعتر	0.1 مليلتر	% 90.3

جدول- 3 : تأثير المستخلص المائي للزعتر على النسبة المئوية لتبويغ أكياس بيض طفيلي الابواغ الخبيئة

المحلول	النسبة المئوية للتبويغ %
محلول هانكس	80
المستخلص المائي للزعتر	40

وجود فرق معنوي بمستوى ($p < 0.05$) .

أظهرت نتائج الدراسة الحالية كفاءة عالية لنبات الزعتر في علاج الفئران المخمجة بطفيلي *cryptosporidium prvum* ، إذ أستطاع طرد الطفيلي بعد تسعة يوم وبكفاءة علاجية بلغت (90.3 %) وهذه النتائج جاءت متفقة مع ما توصلت أليه البحوث الحديثة والتي أكدت بأن نبات الزعتر بدأ يستخدم في معالجة الإسهال ويفضل استعماله ، وقد يعود ذلك لعدت أسباب منها لعدم ملاحظة حدوث تأثيرات جانبية سمية عند استعماله فهو يستخدم كماده غذائية معروفة في العديد من الدول كذلك لم تسجل له أي تأثيرات جانبية ضارة عند اختباره على الفئران المختبرية (18) . كما أن احتوائه على مادة التاينين يمنحه تأثيراً مثبطاً لنمو الجراثيم وهذا يفسر استخدامه في علاج حالات الإصابة بالإسهال والتهاب الأمعاء ، إضافة إلى وجود مادة الثايمول الموجودة بكثرة في نبات الزعتر والتي تساعد في طرد بعض أنواع الديدان المعوية وتطهير الأمعاء من الطفيليات (19) .كما أن الزعتر يستخدم في علاج الكثير من الطفيليات وهو يستعمل في مساعدة الجهاز المناعي (يحفز الجهاز المناعي) في قتل ومحاربة العديد من الفطريات (20) ،وربما هذا يفسر قدرته على طرد طفيلي الابواغ الخبيئة *cryptosporidium prvum* أذ أن الطفيلي يعد من الطفيليات التي تصيب الأشخاص الذين يعانون من خلل في الجهاز المناعي .

وهناك دواء جديد عبارة عن حبوب(Tablet) تحتوي على زيت الزعتر من نوع *Thyme vulgaris* و تستعمل حالياً في علاج العديد من الطفيليات وأثبتت فعاليتها (21) .

أما تأثير النبات على تبويغ أكياس البيض فلقد أظهرت النتائج أن المستخلص المائي للزعتر يقلل من تبويغ أكياس البيض ويعود سبب ذلك أن الأس الهيدروجيني لمستخلص نبات الزعتر كان pH 6 بينما لمحلول هانكس الملحي المتوازن هو pH 7.2. وبما أن عملية التبويغ تحتاج إلى شروط محيطة خاصة منها درجات الحرارة ،المدة الزمنية ، والأس الهيدروجيني فلقد لوحظ أن أنسب أس هيدروجيني للتبويغ هو (pH 7.6) وفي درجة 37 مْ بينما تقل عملية التبويغ عند الأس الهيدروجيني (pH 6) وعند نفس درجة الحرارة (22) .

أما النتائج التي تم الحصول عليها فيما يخص عقار السبارامايسين فلقد اتفقت مع ما سجلاه (23) و (24) في أن عقار السبارامايسين يستعمل لعلاج الإسهال المتسبب عن طفيلي الابواغ الخبيئة كما أنه يقلل من طرح أكياس بيض الطفيلي . ولم نلاحظ حدوث شفاء ذاتي للفئران المخمجة طيلة مدة التجربة ، وقد يعود سبب ذلك إلى مناعة المضيف فضلاً عن حدوث الخمج الذاتي (Autoinfection) والذي يلعب دوراً هاماً في استمرارية الخمج وزيادة أعداد أكياس البيض المطروحة .

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التأثير المثبط للراشح والمستخلص البكتيري *Pseudomonas fluorescens* في بعض الفطريات المرضية

خليل مصطفى خماس[1] و أمل حسين موسى[2] و راند خماس عبد الكريم[3]
[2,1] قسم علوم الحياة/كلية العلوم/الجامعة المستنصرية
[3] وزارة الصحة/دائرة صحة بغداد/الرصافة

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ABSTRACT

This study was performed to isolate and identify the *Pseudomonas fluorescens* from rhizospher of plants root (maize) and study the antifungal activity of the filtrate of there isolate against some pathogenic fungi :
Candida albicans ,Trichophyton sp, Alternaria sp ,Cryptococcus neoformans, Then selected the isolate which showed higher inhibitory effects for extraction of some active metabolites produced by it, and evaluate the activity in vitro, via inhibition the growth of the fungi using different concentration of extracted (10µL/ml 50µL/ml, 100µL/ml) , The results showed that the ultraviolet scan of the extracted and the infrared scan revealed the presence of several peaks at (256, 295, 280 nm) which is related to 2,4 diacetylphloroglucinol and phenazine.

The filtrate of the isolate *P. fluorescens* hase inhibition effect against pathogenic fungi ,the inhibition percentage was 20% - 68% against *Trichophyton sp, Alternaria sp*, and the inhibition zone was 10-15 mm against *Candida albicans, Cryptococcus neoformans* . While the extracted that contain active metabolite showed higher inhibition effect against the pathogenic fungi ,and The concentrate 100µL/ml was the beast in the inhibition effect by obtained inhibition percentage 100% against *Trichophyton sp, Alternaria sp*, the inhibition zone was 22 mm against *Candida albicans, Cryptococcus neoformans*.

الخلاصة

شملت الدرسة عزل وتشخيص بكتريا *P. fluorescens* من مناطق رايزوسفيرية لنبات الذرة . وتم التحري عن الفعالية التثبيطية للراشح والمستخلص البكتري ضد عدد من الفطريات المرضية شملت :-
Candida albicans, Trichophyton sp, Alternaria sp, Cryptococcus neoformans
وانتخبت العزلة ذات الكفاءة الأعلى في التثبيط من اجل الحصول علىالمستخلص البكتيري الذي يحتوي عدد من المركبات الفعالة المنتجة من هذه البكتريا. حيث أظهرت مفرسة الاشعة فوق البنفسجية ومفرسة الاشعة تحت الحمراء وجود عدد من القمم(256, 272, 380) نانوميتر والحزم والتي تعود الى مركبات 4 2, ثنائي استيل فلورو كلوسينول والفينازين . ودرست الفعالية التثبيطية للمستخلص ضد الفطريات أعلاه وباستخدام تراكيز مختلفة (10 ، 50 ، 100) مايكروليتر/ مل .
حيث أظهرت النتائج أن رواشح عزلات *P. fluorescens* لها فعالية تثبيطية جيدة ضد الاعفان والخمائر المرضية وتراوحت نسبة التثبيط المئوية للراشح ضد اعفان *(Alternaria sp , Trichophyton sp)* بين (20% - 68%) وضد خمائر *(Cryptococcus neoforman, Candida albicans)* بلغ قطر مناطق التثبيط (10-15) ملم . فيما كان للمستخلص فعالية تثبيطية اعلى من الراشح ضد الاعفان والخمائر وكان تركيز (100) ماكروليتر/ مل هو الافضل لحصوله على أعلى نسبة تثبيط بلغت 100% ضد الاعفان وقطر منطقة تثبيط بلغت 22 ملم ضد الخمائر.

المقدمة

تعد ميثارـــج*P. fluorescens* من أهم الانواع المستخدمة في المكافحة البيولوجية لقابليتها الكبيرة في السيطرة على الممرضات بميكانيكيات متعددة متضمنة انتاج عدد من نواتج الايض الثانوي(Secondary metabolites) وهي مركبات ذات اوزان جزيئية واطنة تنتج في مراحل متأخرة من طور نمو الخلية الجرثومية السريع ومراحل متقدمة من طور نموها المستقر(Exponential & Stationary Phase) . (1)
يختلف انتاج وتصنيع هذه المركبات باختلاف سلالات *P. fluorescens* والظروف الخاصة بالتنمية والاستخلاص . (2)
تشمل هذه المركبات الفعالة عدد من المضادات الحياتيةAntibiotic مثال عليها 2,4) Diacetylphloroglucinol) ومركبات الفينازين والمشتقات العديدة له اضافة الى انتاج مركبات (Siderophore) HCN, سيانيد الهدروجين (3), (4), (5), (6)
ان عملية الكشف عن وجود هذه المركبات واستخلاصها بصورة نقية والتعرف على تركيبها الكيمياوي الدقيق عملية معقدة ونحتاج الى اجهزة وتقنيات متقدمة مثال جهاز الاستشراب السائل الرفيع الانجاز(HPLC) ومقياس الطيف الكتلوي(MS) والرنين المغناطسي النووي (NMR) . (7)
ان كثير من الابحاث ركزت على دراسة تأثير هذه المركبات الفعاله المختلفة المنتجة من قبل *P. fluorescens* في مكافحة الممرضات النباتية(4),(7) ، الا ان فعالية هذه المركبات ضد المسببات المرضية التي تصيب الانسان كانت محددة جدا لذا جاءت هذه الدراسه لتهدف الى تقيم فعالية راشح ومستخلص عزلات *P. fluorescens* في تثبيط نمو مسببات مرضية فطرية معزولة من الجلد .

المواد و طرائق العمل

العزلات البكترية والفطرية:
جمعت (12) عينة ترابية من مناطق رايزوسفيرية لنبات الذرة وتم الحصول على (6) عزلات تعود*P. fluorescens* واجريت الاختبارات الخاصة بالعزل والتشخيص وكما ذكر في (8), (10),(9)
نمت العزلات البكتريا في وسط المرق المغذي بحرارة (22م°) لمدة (24) ساعة وتم الحصول علىعزلات فطرية من مختبرات الصحه المركزي/ بغداد شملت كل من خمائر واعفان *Cryptococcus neoformans, Alternaria sp , Trichophyton sp)* , *(Candida albicans*
نميت عزلات الخمائر والاعفان في وسط Sabouraud dextrose broth بدرجة (30 م°) لمدة (24) ساعة لعزلات الخمائر فيما نميت عزلات الاعفان في درجة (30 م°) لمدة 5 ايام (11)

تقدير الفعاليـة التثبيطيـة *P. fluorescens*:
تحضير الراشح للبكتريا*P. fluorescens*
نميت عزلات*P. fluorescens* في وسط(King's B) وحضنت بدرجة (20م°) لمدة (5) ايام في حاضنة هزازة بسرعة (150) دورة/دقيقة ويعد هذا الوسط انتاجيا لعدد من المركبات الفعالة التى تنتجها البكتريا ثم نبذ العالق مركزيا اهمل الراسب ومرر الراشح عبر مرشحات Millipore بقطر (0.22) مايكرومتر للحصول على الراشح (7) .

تحضير المستخلص:
نميت عزلات *P. fluorescens* في وسط(King's B) وبعد انتهاء فترة الحضانة بنفس الظروف السابقة تمت عملية الاستخلاص بالطريقة التى ذكرت في (12) حيث جعل الوسط حامضيا pH=2 باستعمال TFA ثم عومل المزيج بخلات الاثيل وعزل الطور العضوي من عملية الاستخلاص وتعاد العملية باستخلاصه بخلات الاثيل لحين الحصول على مستخلص نقي ومركز.
عملت مفرسة شدة امتصاصية بالاشعة تحت الحمراء(Fourier transforming infrared) للمستخلص بواسطة جهاز بمفرسة مداها (4000- 5000) عدد موجات/سم ومفرسة شدة امتصاصية بالاشعة فوق البنفسجية بواسطة طيف الضوئي للاشعة فوق البنفسجية والمرئية بواسطة جهاز(Uv.visible spectrophotometer) وضمن مدى (200-600) نانوميتر

تقدير الفعالية التثبطية للراشح والمستخلص:

أ- الفعالية التثبطية للراشح ضد الخمائر.
للتحري عن الفعالية التثبطية لراشح *P. fluorescens* ضد الخمائر قيد الدراسة استعملت طريقة الانتشار في الحفر Well method الموصوفة من قبل (13) وذلك بتحضير عالق الخمائر بتركيز (2×10^6)خلية/مل وباستعمال شريحة عد الخلايا Haemocytometer (11) وحضنت الاطباق بدرجة (37°م) لمدة(24) ساعة وقدرت الفعالية التثبطية للراشح بقياس قطر منطقة التثبيط بالملميتر.

ب - الفعالية التثبطية للمستخلص ضد الخمائر.

تم اختبار الفعالية التثبطية للمستخلص ضد الخمائر كما ذكر في (أ) مع استبدال راشح البكتريا ب (50) مايكروليتر من المستخلص وبتراكيز تضمنت (10 ,50 ،100) مايكرولتير/ مل .

ج - الفعالية التثبطية للراشح ضد الاعفان(*Alternaria sp, Trichophyton sp*)

تم التحري عن الفعالية التثبطية للراشح ضد الاعفان باستعمال طريقة الخلط مع الوسط الزرعي وذلك باضافة الراشح الى الوسط المعقم بواقع (1) مل من الراشح لكل طبق (13) وحضنت الاطباق بدرجة (30°م) لمدة (7) ايام .
وقيست الاقطار المتعامدة لمستعمرات الفطر النامية في الاطباق الحاوية على الراشح ومقارنتها بمستعمرات الفطر النامية في اطباق السيطرة الخالية من الراشح (14) .وحسبت النسبة المؤية للتثبيط بتطبيق المعادلة التالية :

$$\text{النسبة المئوية للتثبيط } \% = \frac{\text{معدل النمو الفطري في معاملة السيطرة- معدل النمو الفطري في معاملة الراشح}}{\text{معدل النمو الفطري في معاملة السيطرة}}$$

د - الفعالية التثبطية للمستخلص ضد الاعفان.

تم اختبار الفعالية التثبطية للمستخلص ضد الاعفان كما ذكر في الفقرة (ج) مع استبدال راشح البكتريا بالمستخلص بتركيز (10 ,50 ,100) مايكروليتر/مل وذلك باضافة (0.5)مل و (1) مل و(2)مل من الستخلص في كل طبق وعلى التوالي للحصول على التراكيز اعلاه .

النتائج والمناقشة

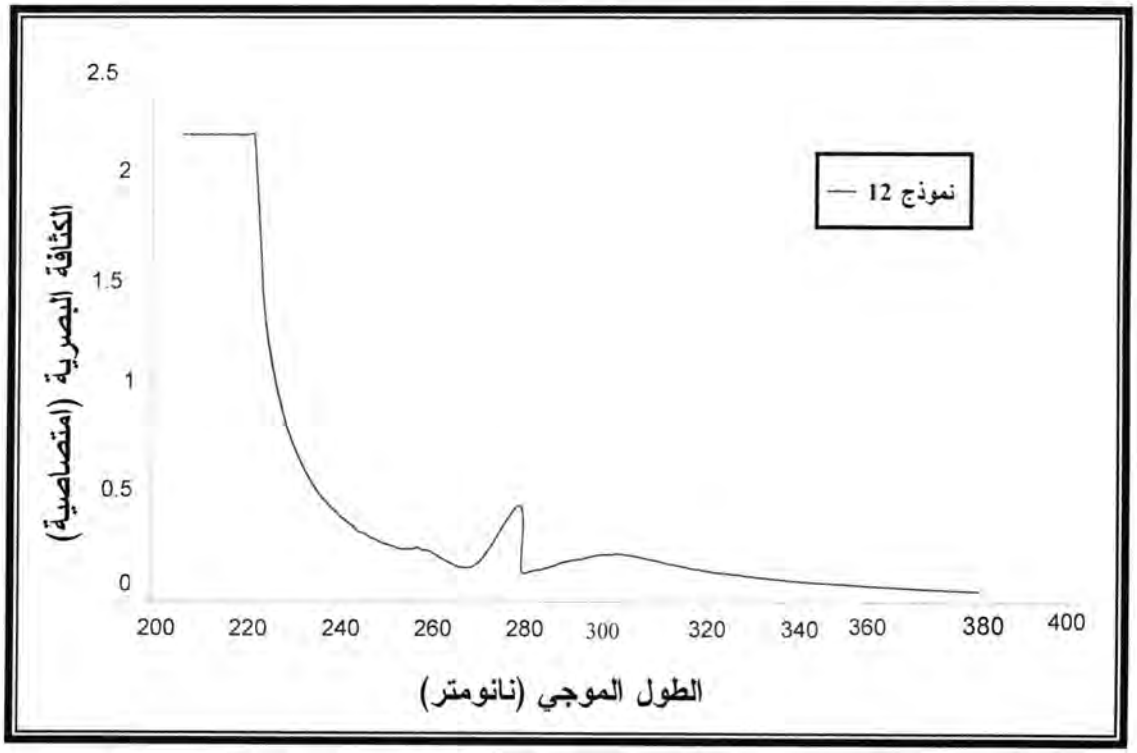
تم الحصول على (6) عزلات تعود لل*P. fluorescens* من اصل (12) عينة ترابية مأخوذة من مناطق رايزوسفيرية لنبات الذرة وتم تأكيد التشخيص اعتماد على نتائج الاختبارات المورفولوجية والزرعية وقابلية نموها في الاوساط الزرعية الخاصة والاختبارات البيوكيمياوية وكما ذكر (15), (16) حيث اظهرت الفحص العيني للمستعمرات كونها صغيرة ، ملساء ، محدبة، ترتفع قليلا عن سطح الوسط الزرعي واظهر الفحص المجهري كونها عصيات مفرد مستقيمة او منحنية قليلا سالبة لصبغة كرام غير مكونة للسبورات او المحفظة نمت جميع العزلات في درجة (4 °م)ولم تنمو في (42 °م) وكما تنمو في وسط يحوي كلوريد الصوديوم (6%) وهذه الصفة تميزها عن باقي الانواع . (15) (جدول رقم 1)

جدول -1: نتائج الاختبارات التأكيدية في تشخيص*P. fluorescens* المعزولة من عينات ترابية

ألاختبارات	النتيجة
• صبغة غرام	سالبة
• اختبارات كيموحيوية (انزيمية)	
اختبار اكسيداز	موجبة
اختبار كاتلاز	موجبة
اختبار جيلاتيناز	موجبة
اختبار ليستين	موجبة
• اختبارات بيوكيميائية (تفاعلية)	
استهلاك سترات	موجبة
استهلاك سكر طرهالُوز	موجبة
اكسدة سكر الكلكوز	موجبة
اختبار اندول	سالبة
اختبار حمرة المثيل	سالبة
اختبار قوكس بروسكار	سالبة
• اختبارات فسيولوجية	
طور نمو الحركة	موجبة
• انتاج الصبغات	
صبغة بايوسيانين	سالبة
صبغة فلوروسين(المتألقة)	موجبة
• نموها في الوسط الزرعي	
عند درجة حرارة 4 °م	موجبة
عند درجة حرارة 22 °م	موجبة
عند درجة حرارة 42 °م	سالبة
باضافة كلوريد الصوديوم (6%)	موجبة

استخلاص وتقيم المواد الفعالة المنتجة من البكتريا *P. fluorescens*

اتبعت الطريقة المذكورة في(12) لاستخلاص المادة الفعالة 4,2 ثنائي استيل فلورو كلوسينول وعملت لها مفرسة الاشعاع فوق البنفسجية باستخدام المذيب ايثانول في اذابة المركب قبل اخضاعه الى المفرسة وكانت نتائج المفرسة (شكل 1) حيث تم الحصول على اطوال موجية هي 256,295,280 نانوميتر ويلاحظ وجود اكثر من قمة واحدة في مفرسة الاشعة فوق البنفسجية دلالة على وجود مركبات فعالة اخرى . تشير الدراسات ان امتصاصية المركب4,2 ثنائي استيل فلورو كلوسينول تحصل في عدة اطوال موجية منها 260 نانوميتر و323نانوميتر والتي تعطي انطباع عن وجود الحلقة الاروماتية وكذلك Carbonyl Chromophores.

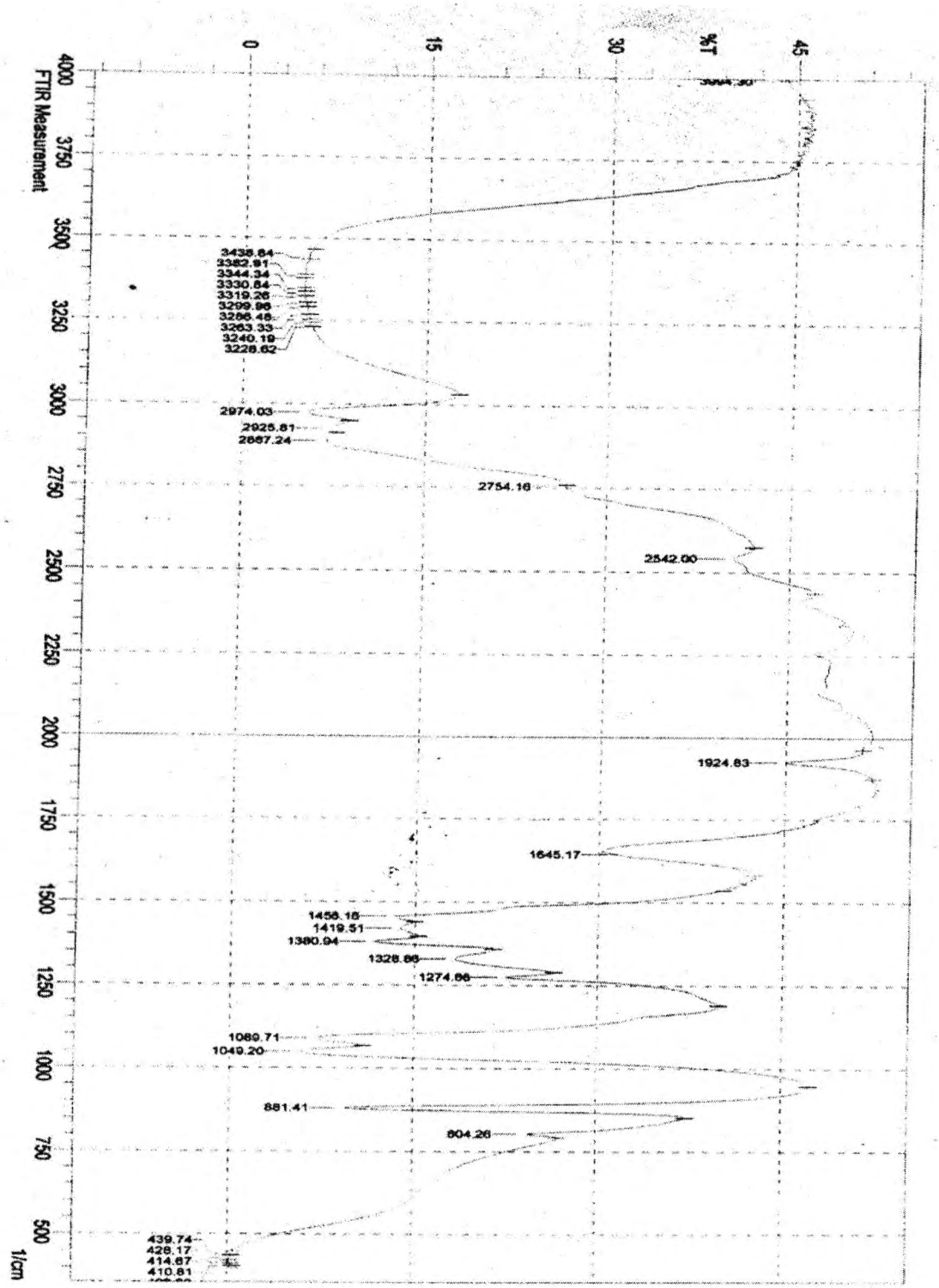


شكل -1: مفرسة مقياس الطيف الضوئي للأشعة فوق البنفسجية

فضلا عن الاطوال الموجية (254,350) نانوميتر وهذا يعتمد على المذيب الذي يتم اذابة المستخلص فية (12 و 17)

وتشير الدراسات ذاتها ان طريقه الاستخلاص هذه طريقة نموذجية لاستخلص المركبات الفعالة الاتية:- مضاد الجراثيم phenazine-1-Carboxylic acid ومشتقه Hydroxy phenazine, Pyrrolnitrin, pyoluteorin, 2-4 diacetyl phoroglucinol

وللتحقق من وجود مركبات فعالة في هذا المستخلص وباستخدام الكحول الاثيلي كمذيب, فقد اجريت مفرسة الاشعة تحت الحمراء وبواسطة مقياس طيف الاشعة تحت الحمراء نوع Fourier Transforming infrared(FTIR) وكانت النتيجة على النحو الاتي (شكل2) :



شكل -2: مفرسة الاشعة تحت الحمراء للمستخلص البكتيري *P. fluorescens*

حزمة عريضة بمدى (3228.8 – 3438.84) مشدودة تدل على وجود مجموع هيدروكسيل في فينول فينازين.حزمة عريضة مشدودة بمدى (2542 – 2974)تعود الى مجموعة هيدروكسيل العائدة الى حمض الكربوكسيلك.حزمة مشدودة عريضة غير متناظرة (1942) الدالة على وجود C=C تشير الى وجود حلقة فينول ، والحزمة المشدودة (1645,17) الدالة على وجودC=C تشير الى مجموعة

Infared (KBr) V_{max}/cm^{-1} : 3 broad (a bounded OH stretching,1924W C=C a symmetrical stretching),1645.17m(C=C stretching) 141.051 1089.715,1049.20 [C=S Thio carbonyl,881.415.804.26 w[s-OR, 1328.8 43,-94 1274.865(O=C,Carboxylic acid derivative) enter], ,410.8 ,428.17 ,414.67

الفعالية التثبيطية للراشح والمستخلص:

تمت دراسة الفعالية التثبيطية للراشح والمستخلص ضد بعض الفطريات المرضية. حيث اظهر الراشح فعالية تثبطية ضد الاعفان بطريقة الخلط مع الوسط الزرعي بنسبة بلغت 20% الى 68% كما مبين في جدول (2).

جدول-2: النسبة المئوية لتثبطالاعفان *Alternaria sp, Trichophyton sp* بتأثير راشح عزلات *P. fluorescens* بطريقة الخلط مع الوسط الزرعي .

رقم العزلة *P. fluorescens*	النسبة المئوية لتثبيط *Trichophyton sp*	النسبة المئوية لتثبيط *Alternaria sp*
1	20	42
2	34	58
3	60	40
4	47	60
5	55	68
6	42	50

حيث بلغت أعلى نسبة للتثبيط بفعل الراشح لل60% *Trichophyton sp* فيما كان اعلى نسبة تثبيط لل*Alternaria sp* 68% , فيما أظهر الراشح تأثير مثبط لل *Candida albicans, Cryptococcus neoformans* بطريقة الحفر حيث بلغ قطر مناطق التثبيط لكل منهما (10-15)ملم جدول(3) . وكان للمستخلص فعالية تثبيطية أعلى من الراشح ضد الاعفان وبأستعمال طريقة الخلط مع الوسط الزرعي حيث بلغت نسبة التثبيط 100% بأستعمال تركيز 100مايكروليتر/ مل من المستخلص لكلا الفطرين , فيما كانت أقل نسبة للتثبيط هي 5% بأستعمال تركيز 10 مايكروليتر/ مل جدول رقم (4) .أما فيما يتعلق بالخمائر فكانت أعلى نسبة للتثبيط هي(20-22) ملم عند التركيز 100 مايكروليتر/ مل , وأقل نسبة هي 14,15 ملم بتركيز 10 مايكروليتر/ مل لكل من *Candida albicans, Cryptococcus neoformans*على التوالي جدول(5) .

أظهرت هذه الدراسة فعالية كبيرة للراشح والمستخلص في تثبيط الفطريات وتدل هذه النتائج على فعالية أعلى للمستخلص وتعزى هذه الفعالية الى وجود المركبات الفعالة التى تم الكشف عن وجودها مثل (Pyoluteorin, phenazine,2-4 diacetyl phoroglucinol)

جدول -3: تأثير راشح عزلات *P. fluorescens* في نمو الخمائر *Candida albicans, Cryptococcus neoformans* باستخدام طريقة الحفر.

رقم العزلة*P. fluorescens*	قطر منطقة التثبيط بالملم *Candida albicans*	قطر منطقة التثبيط بالملم *Cryptococcus neoformans*
1	15	15
2	14	12
3	12	13
4	10	10
5	16	16
6	15	15

جدول -4: النسبة المئوية لتأثير المستخلص الفعال من*P. fluorescens* في نمو الفطريات بطريقة الخلط مع الوسط الزرعي .

الفطر الممرض	تركيز المستخلص*P.f* في 10 مايكروليتر/ مل	تركيز المستخلص*P.f* في 50 مايكروليتر/ مل	تركيز المستخلص*P.f* في 100 مايكروليتر/ مل
Trichophyton sp	5%	63%	100%
Alternaria sp	3.5%	48.5%	100%

جدول -5: تأثير مستخلص*P. fluorescens* في نمو الخمائر *Candida albicans, Cryptococcus neoformans* بقياس منطقة التثبيط (ملم) بطريقة الحفر في الوسط الزرعي.

الفطر الممرض	تركيز المستخلص*P.f*في 10 مايكروليتر/ مل	تركيز المستخلص*P.f*في 50 مايكروليتر/ مل	تركيز المستخلص*P.f*في 100 مايكروليتر/ مل
Candida albicans	15	18	22
Cryptococcus neoformans	14	18	20

والكثير من الدراسات أكدت الفعل المثبط لهذه المركبات ضد عدد من الجراثيم والفطريات مثل (Mucor, Rhizobium, Bacillus, Trichoderma, Penicillium) (7) (18).
أن مركب 4,2 ثنائي استيل فلورو كلوسينول هو مركب فينولي له طيف واسع في تضاده للفطريات والجراثيم والديدان فضلا عن فعاليتة السامة في النبات (18) أما الية عمله كمضاد حيوي فما زالت غير معروفه الا ان تثبيط أمراض النبات يتم عن طريق تداخل الجراثيم المصاحبة لجذور النبات مع المسببات المرضية كما لها القابلية على انتاج Phytotoxin (19)

أما الفينازين ومشتقاته المختلفة فهو مركب ذو وزن جزيئي واطئ يحوي في تركيبه الحلقي ذرة ناتروجين وله فعالية مضادة لبعض الفطريات المرضية . أن ألية عمل الفينازين تعود الى تداخله في عملية الاكسدة والاختزال التي تحدث في الخلية محررا جذور حرة مثل سوبر اوكسيد (Superoxoide Radical) وبيروكسيد الهدروجين التي تتراكم في خلايا الفطريات المرضية مؤديا الى موتها, وقد تعود الفعالية التضادية لهذه المركبات الى الفعل السام للجذور الحرة . (20)

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دراسه سريريه في نسبة حدوث أحتباس المشيمه والمشاكل التناسليه في أبقارالحليب

عبدالكريم محمد جعفر محمد مهدي
كليه الطب البيطري/ جامعه القادسيه

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ABSTRACT

The study was conducted on (125) newly born fresian cows aged (3-6) years.Fifteen (12%) case of retained placenta was recorded. Uterine complications such as (septic and puerperal metritis) were (100%) of the (15) case also were observed.Ten cases (8%) uterine infections without retained placenta , nine cases(7.2%) from different causes like (fetal over size , abnormal fetal presentation and birth canal narrow) , two cases (1.6%) of twins and one case(0.8%) of fetal death were recordal also. one cow was slaughtered due to traumatic reticulo pericaditis (T.R.P.) .

We concluded that , these problems lead to large economic losses in the animal production and medicines used for these complications.

We recomonded to put programs to decrease incidence of retained placenta , dystocia and the in effects and controlling them. The benefit is to high economic income and to reduce medicals besides maintenance of animal fertility. To reduce dystocia and retained placenta through studing the best selections by using artificial insemination for reducing them.

الخلاصه

أجريت الدراسه على (125) بقره فريزيان حديثة الولاده وبأعمار (3-6) سنوات وقد سجلت (15) حالة أحتباس مشيمه وبنسبة (12%) وتبعت هذه الحالات مضاعفات وألتهابات رحميه مثل (ألتهاب الرحم الأنتاني وألتهاب الرحم النفاسي) في جميعها وقد كانت نسبة المضاعفات (100%) .

أيضا سجلت (10) حاله من ألتهابات رحميه وبدون الأصابه بأحتباس مشيمه وبنسبة (8%) . وسجلت (9) حاله من عسر الولاده لأسباب مختلفه (كبر حجم الجنين , حضورغيرطبيعي للجنين وضيق القناة التناسليه) وبنسبة (7.2%) وحالتي توام بنسبة (1.6%) وحالة هلاك جنين واحده بنسبة (0.8%) . ذبحت بقره واحده نتيجه أصابتها بألتهاب التامور الشبكي الكلومي.

نستنج من ذلك أن هناك مشاكل تؤدي الى خسائر كبيره في الأقتصاد نتيجه أنخفاض أنتاجية الحيوان من الحليب والمواليد وأستعمال العلاجات بسبب مضاعفات هذه المشاكل لذا توصي هذه الدراسه بوضع برامج تؤدي الى تقليل نسب حدوث الأحتباس ومضاعفاتها والسيطره عليها لما له أثر كبير في المردود الأقتصادي على مستوى تقليل العلاجات والمحافظه على خصوبه الحيوان . أن تقليل حالات عسر الولاده وأحتباس المشيمه من خلال دراسة أفضل الخيارات في التلقيح الأصطناعي لتقليل مشاكلها .

المقدمه

تعتبر حالات أحتباس المشيمه من أهم المشاكل التي يتبعها مضاعفات (ألتهابات رحميه) وأنخفاض في النتاجية الحيوان من الحليب والمواليد مما يسبب خسائر أقتصاديه لذا يجب الأهتمام بهذه الحالات من خلال تحسين الأداره والتغذيه والنسل (2,1). حيث أن لها تأثير على أرتداد الرحم وقلة الخصوبه (5,4,3,1) .وقد أستخدم الكثير من العلاجات مثل هرموني البروستاكلاندين والأوكسي توسين لمنع حدوثها (6,4). وبما أن أحتباس المشيمه من الحالات المرضيه ولها تأثير على التكاثر والخصوبه (2) .

ونتيجة لما تقدم فأن أهداف بحثنا تهدف الى ما يلي :

1.معرفة نسب حدوث أحتباس المشيمه والمشاكل التي تنتج عنها.

2.دراسة نسب المشاكل الولاديه ليتسنى وضع خطه لتقليلها والسيطره على مضاعفاتها لما له من مردود أقتصادي في تقليل الخسائر في العلاج.
3.دراسة نسب حدوث عسر الولاده والتي تعتبر من الحالات التي تسبب في أغلبها أحتباس المشيمه وما يتبعها من التهابات رحميه وتأثير ذلك على مستوى الكفاءه التناسليه للحيوان حيث يراعى تحسين النسل من خلال الأختيار الصحيح للصفه الوراثيه عند التلقيح الاصطناعي وأستخدام عملية نقل الأجنه (Embryo transfer) في البلدان الزراعيه المتقدمه.

المواد وطرائق العمل

أجريت هذه الدراسه على (125) بقره فريزيان حديثة الولاده بعمر (3-6) سنوات قسمت الى مجاميع وحسب الحاله المرضيه وعلى النحو التالي .
1.مجموعة أبقار ذات أحتباس مشيمه بعد الولاده وكانت بعدد (15) حاله وبنسبة (12%) والتي صاحبها مضاعفات رحميه بعد الأحتباس وبنسبة (100%).
2.*مجموعه أبقار ذات مشاكل بعد الولاده (ألتهابات رحميه) وبدون أن تصاب بأحتباس المشيمه فكانت بعدد (10) وبنسبة (8%).
3.مجموعة أبقار ذات مشاكل أخرى (هلاك جنين,**عسر ولاده لأسباب مختلفه ,توائم) وكانت بعدد كلي (12) حاله وقسمت الى (2,9,1) حاله وحسب ترتيب المشاكل أعلاه وعلى التوالي وبنسبه عامه (9.6%) وبنسب منفرده حسب ترتيب المشاكل أعلاه (0.8%,7.2% و1.6%) على التوالي.
ولقد تم أستخدام العلاجات المختلفه في السيطره على المشاكل التناسليه بعد الولاده والتي شملت حقن الهرمونات والمضادات الحياتيه. هلكت بقره واحده نتيجة الأصابه بألتهاب التامور الشبكي الكلومي.

النتائج

يوضح الجدول رقم (1) أن هناك (15) حالة أحتباس مشيمه وبنسبة (12%) أصيبت جميعها بمضاعفات رحميه (ألتهاب الرحم الأنتاني وألتهاب الرحم النفاسي) وكانت نسبة الأصابه (100%). كما أن هناك (10) حاله وبنسبة (8%) أصيبت بألتهابات رحميه دون الأصابه بأحتباس المشيمه وسجلت مشاكل أخرى (هلاك جنين ,عسر ولاده لأسباب مختلفه , توائم) وكان مجموعها (12) حاله وبنسبه عامه (9.6%) قسمت الى (2,9,1) وبنسبه منفرده (0.8%,7.2% و1.6%) على التوالي وكما موضح في الجدول. حصل هلاك بقره واحده بعد الولاده نتيجه أصابتها بألتهاب التامور الشبكي الكلومي (صفه تشرحيه).

*ألتهابات رحميه حدثت نتيجة تدخل خاطىء (سحب الجنين عند الولاده, العمل بظروف غير صحيه وملامسه و ضعف الحاله الصحيه العامه للأم). وتميزت الألتهابات بأفرازات ذات رائحه كريه وأفرازات قيحيه.
**عسر الولاده ناتج من أوضاع الجنين الغير طبيعيه أو ضيق القناة التناسليه وعدم توافق حجم الجنين.

جدول – 1: يوضح أعداد الأبقار المصابه بأحتباس المشيمه ومضاعفات الاصابه والأبقار ذات المشاكل الأخرى والأبقار المصابه بألتهابات رحميه دون أحتباس مشيمه.

العدد الكلي	الأبقار ذات احتباس المشيمه بعد الولاده والتي صاحبها مضاعفات رحميه	أبقار ذات المضاعفات بدون أحتباس المشيمه**	أبقار ذات مشاكل أخرى		الهلاكات
			هلاك جنين	عسر ولاده لأسباب مختلفه***	توائم
125	15	10	1	9	2
النسبه المئويه من المجموع الكلي	%12 * نسبة المضاعفات الرحميه لنفس المجموعه(15) بعد الاحتباس(100%)	%8	%0.8	%7.2	%1.6

بقره واحده بسبب أصابتها بألتهاب التامور الشبكي الكلومي

*النسب المئويه من المجموع العام للأبقار ما عدا (نسبة 100% فهي تعود للأبقار المصابه بألتهابات رحميه كمضاعفات بعد الأصابه بأحتباس المشيمه وأعتبرت الحاله محتبسه بعد 12 من الولاده).

**حدثت المشاكل (مضاعفات) رحميه نتيجة تدخل خاطىء مثل (سحب الجنين عند الولاده ,العمل بظروف غير صحيه و ضعف الحاله العامه للبقره).

***عسر الولاده لأسباب مختلفه مثل (ضيق القناة التناسليه وعدم توافق حجم الجنين ,أوضاع الجنين الغير طبيعيه).

المناقشه

يلاحظ من الجدول رقم (1) أن نسبة أحتباس المشيمه (15%) وهذه النسبه تعتبر منخفضه مقارنه مع مصادر أخرى مثل (4,3,2) اللذين أشاروا أن نسبة حدوثها ما بين (30-40)% في العراق وبما أنه أجريت هذه الدراسه في حقول ذات أداره وتغذيه جيده فأن هذا الأنخفاض في النسبه قد يعود الى هذه الأسباب وهذا ما أتفق مع (7,5,1) اللذين أكدوا على ضرورة تحسين الأداره والتغذيه والصفه الوراثيه لمنع وتقليل نسب الأصابه بأحتباس المشيه التي تسبب مشاكل تؤثر على الأداء التناسلي كالألتهابات الرحميه مسببه خسائر أقتصاديه ويوضح الجدول رقم (1) هذه المشاكل بنسبة (100%) كألتهابات رحميه بعد الأصابه بأحتباس المشيمه أستدعى ذلك للتدخل العلاجي للسيطره عليها وهذا له أثر كبير في الخسائر الأقتصاديه أضافه الى قله الكفاءه التناسليه. هذا ما أشار اليه الباحثون (8,7,6) وأتفق ذلك معهم.

يلاحظ أيضا أن هناك أصابات رحميه حدثت بعد الولادة وبدون الأصابه بعسر الولاده أو أحتباس المشيمه وقد يكون ذلك بسبب التدخل الخاطىء (كسحب الجنين عند الولاده أو العمل بظروف غير صحيه أو سوء الحاله العامه للأم أو العمر) وهذا ما أتفق مع (9,5) اللذين أشاروا الى أن الولاده تحتاج الى عوامل مناسبه كأداره جيده وظروف صحيه وبيئيه جيده.

أيضا يوضح الجدول رقم (1) وجود حالات عسر ولاده لأسباب مختلفه (منها ما يعود للأم أو الجنين أو كليهما) لذا من الضروري تحسين الصفه الوراثيه من خلال أجراء عملية نقل الاجنه أضافة الى التلقيح الأصطناعي أوالطبيعي للسيطره على هذه المشكله أتفق ذلك مع الباحثون (13,12,11,10) اللذين أشاروا الى ضرورة تحسين الصفه الوراثيه للأم والجنين لتقليل مشاكل العسر والأحتباس.

نستنتج من ذلك ولتقليل نسب المشاكل الولاديه والتناسليه وأحتباس المشيمه و مشاكلها التأكيد على ضرورة تحسين الصفه الوراثيه للأم والجنين وتحسين ظروف أدارة عملية التلقيح الطبيعي أو الاصطناعي وذلك بأختيار ثور مناسب لتلقيح البقره أو الأبقار الشبقه (الصارف) وبحجم مناسب يكون له أثر كبير في تقليل نسبة حدوث عسر الولاده والمشاكل التناسليه التي

تتبعها وتوفير التغذيه الجيده ومتابعه الحالات المرضيه المصابه لتقليل الخسائر الناجمه عنها خلال الفترة ما بعد الولاده.أن هدف وضع مثل هكذا دراسه هو لتقليل نسب الأصابات والأبتعاد عنها ومعرفة علاقة ذلكبالمستوى الأنتاجي والأقتصادي.

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أستخلاص الموليبدنيوم بالكاشف 2 – مركبتوبنزوثايازول

جميل موسى ضباب ، احسان احمد عبد الباري و زمان صاحب مهدي
الجامعة المستنصرية – كلية العلوم – قسم الكيمياء

تاريخ تقديم البحث 2007/9/17 - تاريخ قبول البحث 2008/5/5

ABSTRACT

This study include solvent extraction for molybdenum (VI) by reagent 2-mercptobenzothiazole that refers (HMBT) . Many various factors which influence in the value distribution ratio (D) and percentage extraction (E%) has been study . The best medium to extraction Mo(vi) by reagent HMBT from an aqueous phase with concentration acid (5N) HCl .The results showed the ideal solvent of extraction process of Mo (vi) was 1,2 dichloromethan and best provides for equilibrium process was (2) minutes .To study the influence of temperature degree found the value of (D) increase with increasing of temperature degree . Proving the ionic property of the complex for measuring electric conductivity was 10.5 $ohm^{-1} . cm^2 . mole^{-1}$. and determination of melting point of solid complex was $230C^o$ Study of stiochoiometry of complex using two methods and the result showed the mole ratio of Mo(vi) to the reagent was (1:2) . The effect of divers ion on the extraction was studied.

الخلاصة

تناول البحث استخلاص الموليبدنيوم بواسطة 2- مركبتوبنزوثايازول ودرست العوامل التي تؤثر في قيمة نسبة التوزيع (D) والنسبة المئوية للاستخلاص (E%) ، وتبين ان الوسط الحامضي عند التركيز 5NHCl افضل وسط للاستخلاص ، وكان المذيب العضوي 1 و 2 – ثنائي كلورواثان افضل مذيب لاستخلاصه .

بينت الدراسة ان افضل مدة للاتزان في عملية الاستخلاص هي دقيقتين ونسبة التوزيع تزداد بزيادة درجة الحرارة . وقيست نسبة التوصيل المولاري للمعقد المستخلص وكانت تساوي ($10.5\ ohm^{-1}.cm^2.mol^{-1}$.)، وعينت درجة انصهار المعقد المستخلص وكانت $230C^o$. درست جزيئية المعقد وكانت نسبة العنصر الى الكاشف (2:1) ، و كذلك تأثير المتداخلات على عملية الاستخلاص .

المقدمـــة

يعد المركب 2- مركبتوبنزوثايزول احد مركبات الثايوامايد (Thiomid) لاحتوائه على مجموعة الثايوامايد (-N-C = S-)[1] .

واستخدم هذا الكاشف في التقدير الطيفي لعدد من العناصر مثل Cu[2] ، كما طورت طريقة لتقدير كميات نزرة لنفس العنصر بواسطة الكاشف مذاباً في رابع كلوريد الكاربون[3] .

اما عنصر الموليبدنيوم فيعد من الفلزات الثقيلة القليلة التي تمتلك مقاومة للحوامض[4] ويعتبر ثاني كبريتيد الموليبدنيوم المادة الاساسية لتحضير اوكسيد الموليبدنيوم [5] . تم تقدير الموليبدنيوم ومركباته في نماذج من البروتين بطريقة طيفية باستخدام كاشف خاص [6] . كما استخلصت كميات نزرة من Mo(VI) بواسطة الكاشف -N- Tetramethyl benzidine propane sulfonic acid [7] وفي دراسة اخرى قام بها Trujillo تم استخدام عدة كواشف لاستخلاص Mo(VI) منها 8-hydroxyl quinolin [8] .

استخدم الباحث Sharma وجماعته [9] المركب CHMFC في استخلاص Mo(VI) على هيئة معقد اصفر باستخدام مذيب عضوي ، وفي دراسة اخرى لنفس الباحث واخرون [10] استخدم فيها عدة كواشف منها 3-Hydroxy-2-2(2-thionyl)4-H-Chromene4-one لاستخلاص الموليبدنيوم السداسي ، واقترنت عملية الاستخلاص بالمذيب للموليبدنيوم السداسي

بطرق تفلورية وكهربائية تسحيحية [15 - 11] . اما الهدف من هذه الدراسة هو ايجاد طريقة سريعة وموثوقة لاستخلاص Mo(VI) من بيئة تحليلية معينة .

المواد و طرائق العمل

الأجهزة

أ- مطياف الاشعة المرئية – فوق البنفسجية نوع
Shimadzu UV- visible spectrophotometer recording 160 A

ب- مطياف الاشعة تحت الحمراء نوع
Shimadzu Fourier trans form infra – red (FT-IR 8000)

ج- ميزان حساس نوع Mettler semimicro balance model HL 52

د- جهاز قياس التوصيلية الكهربائية نوع Conductimeter type CD 810 (TA cussel)

هـ- جهاز قياس درجة الانصهار نوع Melting point measuring apparatus (English model) .

المواد الكيميائية :

جميع المواد المستخدمة ذات درجة عالية من النقاوة من نوع Analytical grade

تحضير المحاليل القياسية :

أ- حضر المحلول القياسي للموليبدنيوم السداسي (1000ppm) وذلك بأذابة 1.8401 g من $(NH_4)_6Mo_7O_{24}.4H_2O$ في لتر واحد من الماء المقطر .

ب- تحضير محلول (HMBT)

حضر محلول (0.6%) HMBT من اذابة 0.6 gm منه في 100 ml من الايثانول .

تحضير المنحني القياسي لتحضيرالموليبدنيوم بهيئة $Mo^{+6} – NCS^{-1}$:

تم اعتماد الطريقة الطيفية [14] لقياس الامتصاصية لتراكيز مختلفة للموليبدنيوم السداسي تراوحت (0.1-22 ppm) عند طول موجي 458nm .

استخلاص معقد الموليبدنيوم السداسي مع الكاشف HMBT :

اجرى استخلاص ايون الموليبدنيوم السداسي بتركيز 35ppm بأخذ 5ml منه مع 3.5ml من 0.6% محلول HMBT المذاب في الايثانول ضمن وسط حامضي (5N) من حامض الهيدروكلوريك ويوضع في حمام مائي بدرجة 50°C لمدة 15 دقيقة ويترك ليبرد بدرجة حرارة الغرفة ثم يوضع في قمع فصل ويضاف اليه 10ml من محلول الطور العضوي . يرج الطورين لمدة دقيقتين ويفصل الطور العضوي المحتوي على الايون .

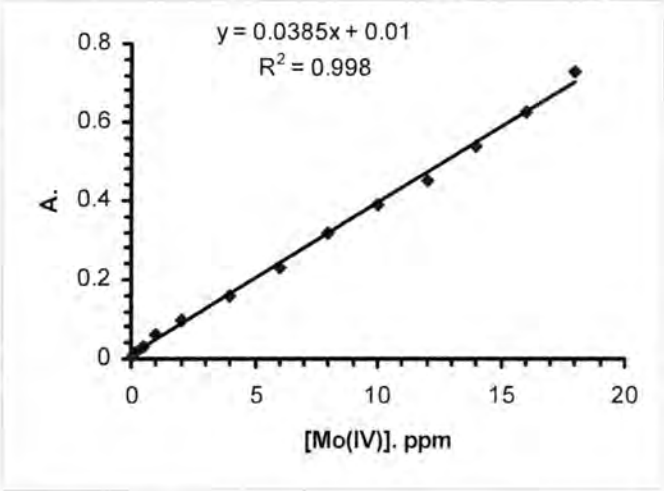
تقدير الموليبدنيوم السداسي في الطور المائي :

تم ايجاد تركيز الموليبدنيوم المتبقي في الطور المائي بعد اجراء الاستخلاص باستخدام الطريقة الطيفية حيث تقاس امتصاصية المعقد المائي Mo-NCS عند الطول الموجي الاعظم .

النتائج والمناقشة

المنحني القياسي لتقدير الموليبدنيوم

يبن الجدول (3-1) قيم امتصاص معقد الموليبدنيوم مع الكاشف SCN^{-1}– عند طول موجي 438 نانوميتر والشكل (3-1) يوضح المنحني القياسي لتقدير الموليبدنيوم السداسي المتبقي في الطور المائي بهيئة معقد مع الثايوسيانات .



الشكل -1: مدى استجابة المنحني القياسي لتقدير الموليبدنيوم بالطريقة اللونية.

دراسة الظروف المثلى لاستخلاص معقد الموليبدنيوم السداسي مع الكاشف HMBT :

أ- تأثير تركيز الموليبدنيوم السداسي في الاستخلاص : استخلصت ايونات الموليبدنيوم السداسي من محاليلها المائية المحتوية على كميات متزايدة من الايون من ppm(5-45) والجدول (1) يبين ذلك حيث وجد ان 35ppm هو افضل تركيز .

جدول -1: قيم logD لتأثير تركيز الموليبدنيوم في الاستخلاص.

[Mo] ppm	$[Mo]x10^{-4}$	Log[Mo]	Log[Mo]+10	D	logD
.005	0.521	-4.283	5.717	4.15	0.61
10.0	1.042	-3.981	6.019	7.13	0.85
15.0	1.563	-3.805	6.195	9.63	0.98
20.0	2.084	-3.68	6.32	13.28	1.12
25.0	2.605	-3.584	6.416	13.7	1.13
30.0	3.126	-3.504	6.496	20.42	1.31
35.0	3.648	-3.437	6.563	28.16	1.44
40.0	4.169	-3.379	6.621	25.33	1.40
45.0	4.69	-3.328	6.672	25.12	1.40

ب- تأثير تركيز الوسط الحامضي في الاستخلاص : حسبت قيم نسب التوزيع لاستخلاص تركيز ثابت من Mo وبأوساط حامضية مختلفة من HCl حيث وجد ان حامضية 5N من 5NHCl هو افضل تركيز والجدول (2) يوضح ذلك .

جدول -2: تأثير الدالة الحامضية على استخلاص Mo(VI).

[HCl] N	D	%E
0.5	3.93	79.7
1.0	6.46	86.5
2.0	12.72	92.7
2.5	17.42	94.5
3.0	20.21	95.2
3.5	25.51	96.2
4.0	28.61	96.6
4.5	28.65	96.6
5.0	28.66	96.6
6.0	28.63	96.6

ج- تأثير زمن التفاعل : درس تأثير زمن التفاعل بعد اخذ فترات زمنية تراوحت بين (20,0) دقيقة حيث وجد انه 15 دقيقة هي افضل زمن للتفاعل والجدول (2) يبين ذلك.

جدول -3: تأثير زمن التفاعل في تكوين المعقد

Time (min.)	D	%E
0	0.89	47.0
4	5.6	84.8
6	12.45	92.5
8	22.96	95.8
10	428.6	96.6
12	29.82	96.7
15	30.81	96.8
20	30.81	96.8

د- تأثير كمية الكاشف في الاستخلاص : اخذت 5ml من ايون Mo بتركيز 35ppm مع حجوم مختلفة من الكاشف بتركيز (0.6%) المذاب في الايثانول وبوسط حامضي (5N) فوجد ان افضل كمية الكاشف هي 3.5ml تركيز (0.6%)هي المناسبة والجدول (4) يبين ذلك .

جدول -4: تأثير كمية الكاشف HMBT (0.6%) في الاستخلاص.

0.6%HMBT solution /ml	D	%E
1.0	10.29	91.1
1.5	14.66	93.6
2.0	18.2	94.7
2.5	23.96	95.9
3.0	30.77	96.8
3.5	31.14	96.8
4.0	29.81	96.7
5.0	26.34	96.3

هـ- تأثير زمن الرج في الاستخلاص : درس تأثير زمن الرج وكان دقيقتان هو الافضل والجدول (5) يوضح ذلك .

جدول -5: تاثير الرج في استخلاص المولبيدنيوم السداسي.

Time (min.)	D	%E
0.5	17.65	94.6
1.0	27.00	96.4
2.0	31.25	96.8
3.0	31.14	96.8
4.0	31.11	96.8
5.0	30.25	96.8

و- تأثير تقنية الاستخلاص بالدفعات : لمعرفة تأثير استخدام تقنية الدفعات الصغيرة في عملية الاستخلاص عوضاً عن استخدام دفعه واحدة من الطور العضوي وجد ان النتائج متقاربة في كلتا التقنيتين كما مبين في الجدول (6) مما يؤكد الكفاءة العالية للاستخلاص.

جدول -6: نتائج الاستخلاص الخاصة بالموليبدينوم السداسي بالكاشف HMBT

%E	D	نوع الاستخلاص
96.8	31.25	استخلاص بدفعة واحدة
96.9	31.33	استخلاص بدفعات صغيرة

ز- تأثير المذيبات العضوية المستخدمة في الاستخلاص : حسبت قيم نسب التوزيع لاستخلاص الموليبدنيوم السداسي من محلوله المائي باستخدام مذيبات عضوية تتباين في ثابت العزل الكهربائي كطور عضوي .

لوحظ ان مذيب 2,1- ثنائي كلورو ايثان افضل من غيره في عملية الاستخلاص كما موضح في الجدول (7) .

جدول -7 : تأثير قطبية المذيب العضوي في استخلاص الوليبدينوم السداسي

نوع المذيب	ثابت العزل ε	1/ε	D	%E
Nitrobenzene	35.74	0.02798	4.25	80.98
1-Butanol	17.10	0.05848	7.33	87.99
1,2-Dichloroethane	10.65	0.09389	31.25	96.89
Benzyl chloride	3.32	0.3012	34.71	97.19
Chlorobenzene	5.70	0.17543	28.34	96.59
Chloroform	4.90	0.20408	30.81	96.85
Diethyl ether	4.19	0.23866	6.52	86.7
Toluene	2.40	0.41666	28.57	96.61
Carbon tetrachloride	2.20	0.45454	21.29	95.51
Trichloroethylene	-----	-----	Nill	----

ح- تأثير اضافة العوامل المؤكسدة والمختزلة : وجد ان اضافة العامل المؤكسد H_2O_2 والمختزل $SnCl_2$ قد يؤثر سلباً على عملية الاستخلاص وكما مبين في الجدول (8) وقد يعزى السبب الى حصول تغيرات في تركيب الكاشف او الايون المستخلص .

جدول -8: تأثير بيروكسيد الهيدروجين وكلوريد القصديروز المائي في استخلاص الموليبدنيوم السداسي.

Oxidizimyt & Reducing species	D	%E
-----	31.25	96.9
H_2O_2	1.73	63.3
$SnCl_2.2H_2O$	27.18	96.4

ط- تأثير درجة الحرارة : حسبت قيم نسب التوزيع كدالة لدرجة الحرارة في استخلاص ايون الموليبدنيوم السداسي بواسطة الكاشف HMBT بدرجات حرارية مختلفة فلوحظ ان $50C^{o}$ هي الافضل والجدول (9) يوضح ذلك .

جدول -9: قيم نسب التوزيع لاستخلاص الموليبدنيوم السداسي عند درجات حرارية مختلفة .

T (^{o}C)	T (k^{o})	1/T x10^{4} K^{-1}	D	Log D
20	293	34.129	22.53	1.352
30	303	33.003	32.23	1.508
40	313	31.948	43.86	1.642
50	323	30.959	55.91	1.684

ي- تأثير المتداخلات : درست اضافة كل من الايونات الموجبة والسالبة وكانت لها تأثير واضح في زيادة او نقصان قيم D والجدولين (10) و(11) يبينان ذلك مما تؤخذ الاجراءات التحليلية الاولية قبل عملية الاستخلاص .

جدول-10: تأثير بعض الايونات السالبة في استخلاص 175µg/ml من الموليبدينوم وحسب الظروف المثلى .

الايونات السالبة	الكمية المضافة (µg)	D	%E
-----	-----	31.25	96.9
Cl^-	500	29.32	96.7
	250	31.09	96.88
	175	31.05	96.87
Br^-	500	29.38	96.75
	250	30.29	96.8
	175	30.61	96.83
NO_3^-	500	24.24	96.03
	250	24.55	96.08
	175	27.98	96.54
I^-	500	27.5	96.49
	250	28.21	96.57
	175	30.66	96.84
CrO_4^{-2}	500	26.35	96.34
	250	28.5	96.61
	175	30.14	96.78
SO_4^{-2}	500	25.23	96.18
	250	27.13	96.44
	175	29.92	96.76
MnO_4^-	500	20.87	95.29
	250	26.33	96.34
	175	21.03	96.87
thiourea	500	1.72	63.23
	250	7.74	88.55
	175	10.92	91.61

جدول-11: تأثير بعض الايونات الموجبة في استخلاص 175µg من الموليبدنيوم وحسب الظروف المثلى .

الايونات الموجبة µg	D	%E
-	31.25	96.9
Fe(III)	10.22	91.0
Co(II)	21.42	95.5
Cu(II)	7.05	87.5
Ni(II)	18.75	94.9
Al(III)	13.06	92.8
V(V)	28.87	96.6
Cr(III)	21.69	95.5
Cd(II)	15.87	94.0
Ag(I)	9.28	90.2
Bi(III)	8.43	89.3
Pb(II)	11.25	91.8
Ru(III)	12.5	92.5
Hg(II)	7.83	88.6

المعطيات التحليلية الاحصائية :

يبين الجدولان (12) قيم كل من مديات التركيز ومعامل الامتصاصية المولارية وحساسية ساندل ومعادلة الخط المستقيم ومعامل الارتباط لتقدير الموليبدنيوم السداسي بالطريقة الطيفية عند طول موجي 458 نانوميتر وكذلك حساب قيم , Er% , RSD% E% لاستخلاص الموليبدنيوم السداسي مع الكاشف HMBT .

جدول -12: مديات التراكيز الامتصاصية المولارية وحساسية ساندل ومعادلة الخط المستقيم ومعامل الارتباط

Linearity ppm	ε $L.mole^{-1}.cm^{-1}$	S $\mu g.cm^{-2}$	Regre.Eq Y=Bx+A	Corr. Coef. (r)
0.1-18	$4.57x10^4$	0.027	0.0385x+0.01	0.9989

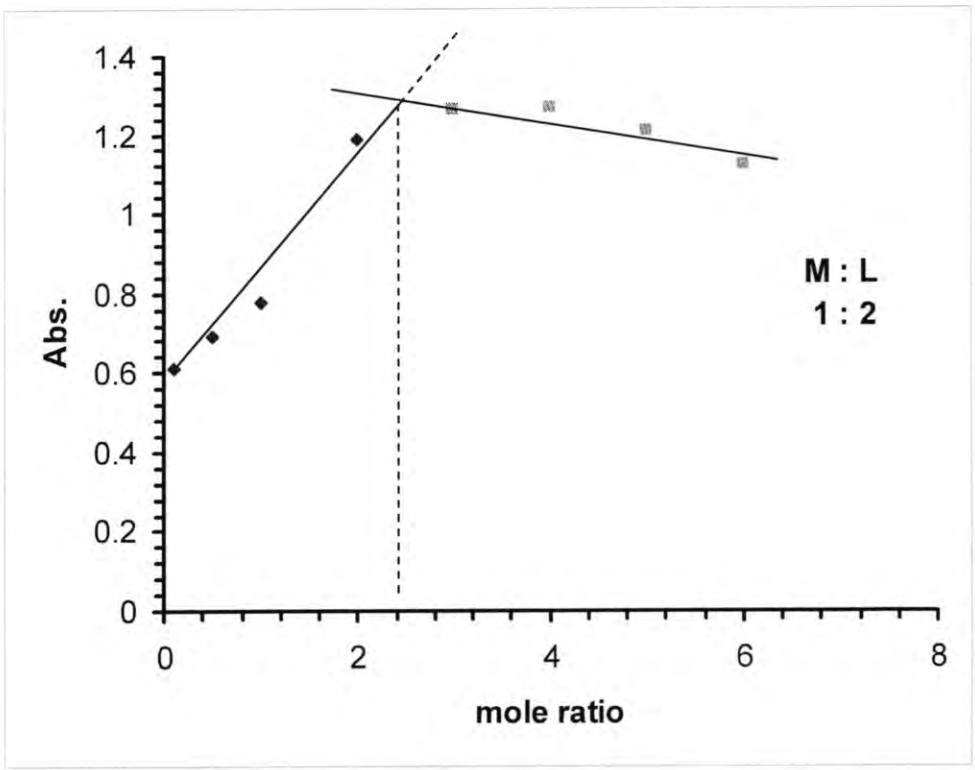
جدول -13: قيم RSD% و .Erel% و E% لاستخلاص الموليبدنيوم

Conc. (ppm)	%R	Er%*	%RDS*
15	95.14	-3.81	2.77
25	96.504	-----	3.942
35	96.899	-----	5.32

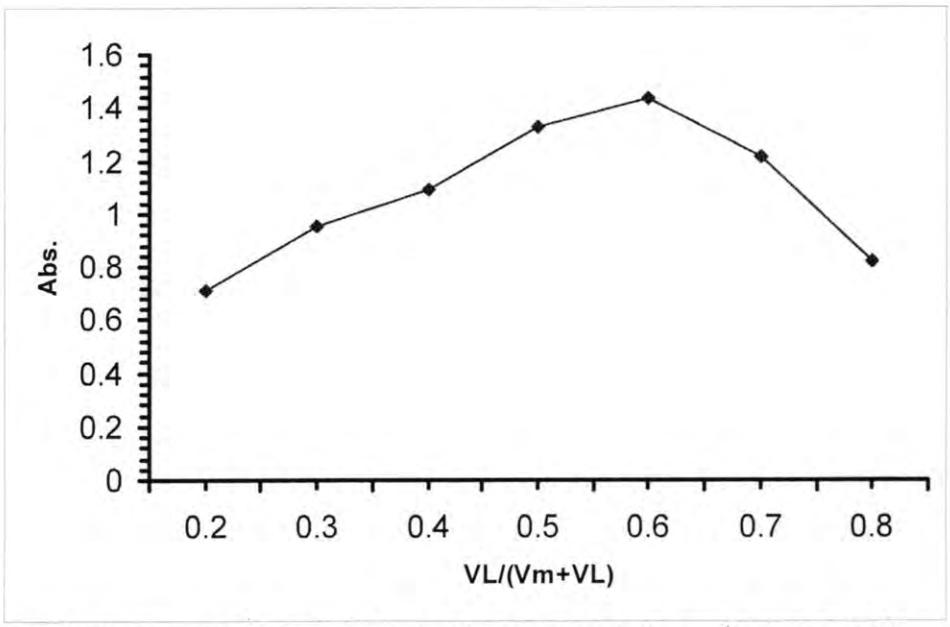
* معدل لخمس قراءات

دراسة النسبة المولية للمعقد المستخلص

استخدمت طريقة النسبة المولية وطريقة التغييرات المستمرة لايجاد نسبة الفلز الى الكاشف في المعقد فوجدت النسبة هي 2:1 كما موضح في الشكلين (2) و(3) .



الشكل -2: طريقة النسب المولية لمعقد الموليبدينوم السداسي مع HMBT



الشكل -3: طريقة جوب للتغيرات المستمرة لمعقد المولبيدنيوم السداسي مع HMBT
.(λmax=376nm)

حساب ثابت الاستقرارية للمعقد المستخلص :-

حسبت قيمة ثابت الاستقرار للمعقد (K) والمحسوب وفق معادلة خاصة فكانت قيمته 1.012×10 .وكما يلي:-

$$_mM + nL \Leftrightarrow M_mL_n$$

$0 \quad 0 \quad C$

$\alpha C \quad n\alpha \; C \quad C(1-\alpha)$

$$k = \frac{[M_mL_n]}{[M]^m[L]^n} \text{.....(1)}$$

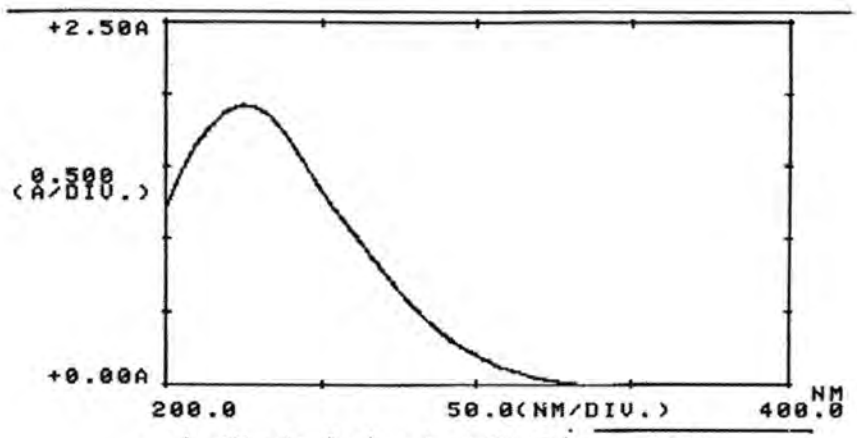
$$k = \frac{(1-\alpha)C}{(\alpha C)(2\alpha C)^2} \text{.....(2)}$$

$$k = \frac{(1-\alpha)C}{\alpha C(4\alpha^2C^2)} \text{.....(3)}$$

$$k = \frac{1-\alpha}{4\alpha^3C^2} \text{.....(4)}$$

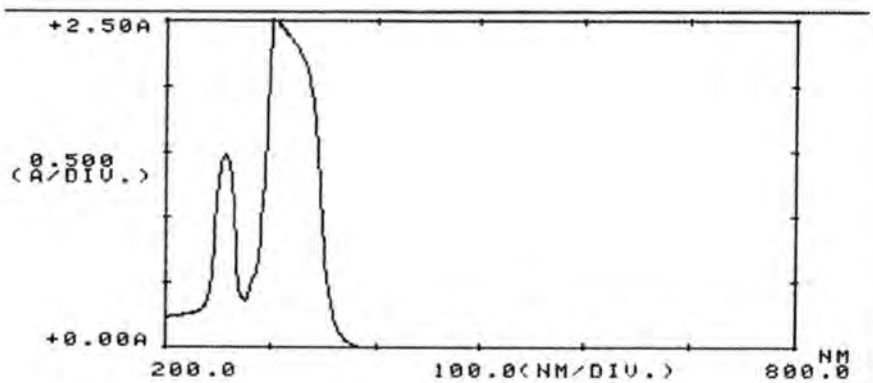
القياسات الطيفية للمعقد المستخلص : -

يوضح الشكل (4) طيف امتصاص لمولبيدات الامونيوم .



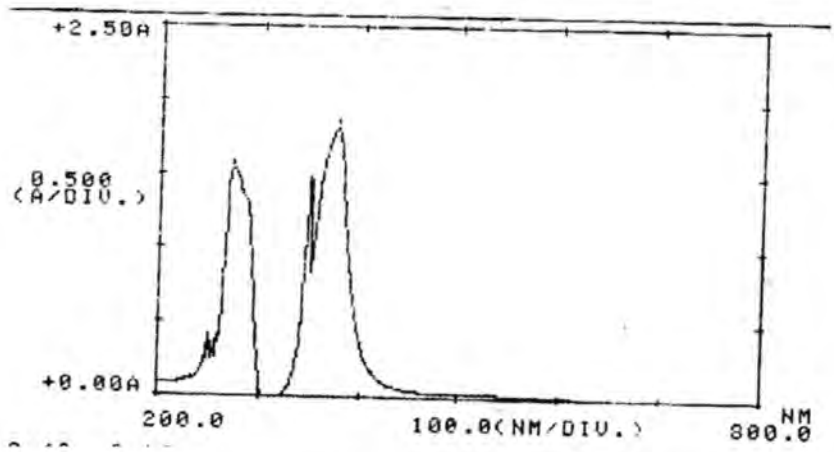
الشكل -4: طيف الامتصاص لمولبيدات الامونيوم

يوضح الشكل (5) طيف الكاشف 2-مركبتوبنزوثايزول حيث يلاحظ ظهور قمتين امتصاص .



الشكل -5: طيف الامتصاص الكاشف HMBT .

يوضح الشكل (6) طيف امتصاص المعقد HMBT Mo(VI) الطول الموجي ازيح الى 376 nm وحدوث ازاحة من نوع (red shift) مما يشير الى حصول تغير في التركيب الجزيئي الى كل من Mo والكاشف .



الشكل -6: طيف امتصاص الموليبدينيوم المعقد مع الكاشف HMBT.

كما تم قياس التوصيلة المولارية للمعقد المستخلص وكانت قيمها 10.5 $ohm^{-1}.cm^2.mole^{-1}$.

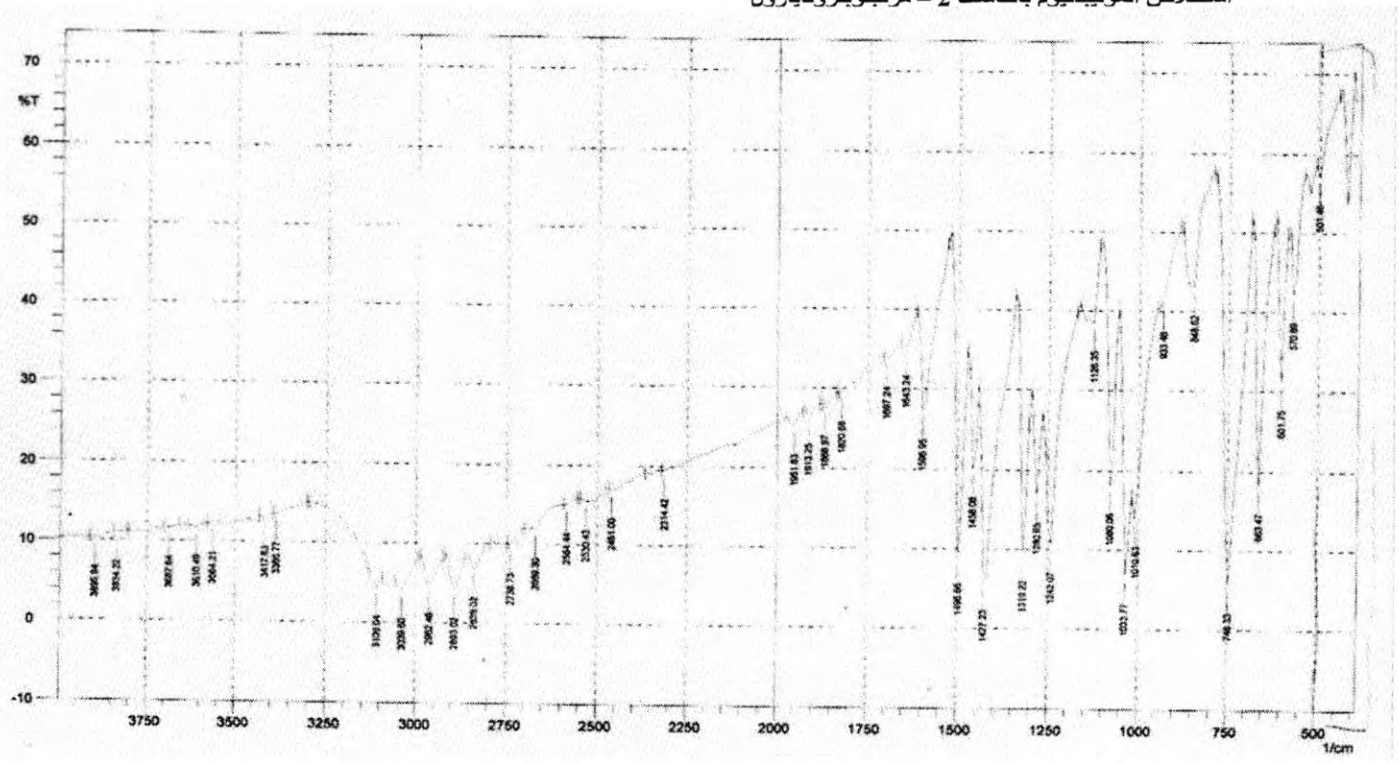
تم استخدام اطياف الاشعة تحت الحمراء (FT-IR) لغرض التحليل الوصفي للمعقد المستخلص . أوضحت هذه الدراسة بأن الكاشف 2-مركبتوبنزوثايازول له حزم فعالة جيدة التآصر مع الفلز فقد اظهر الطيف حزمة متوسطة عند العدد الموجي $1596cm^{-1}$ والتي تعود الى تردد امتطاط الاصرة (C=N) وانحلال الاصرة (N–H) في المركب (HN-C ≡ S) والكاشف للنظام الحلقي غير المتجانس والشكل (7) يوضح الجدولين (14) و (15) المجاميع الفعالة ونوع الارتباط وكما يظهر في الشكلين (7) و (8) .

جدول -14: يوضح قيم تردد امتطاط الاواصر للمجاميع الاخرى .

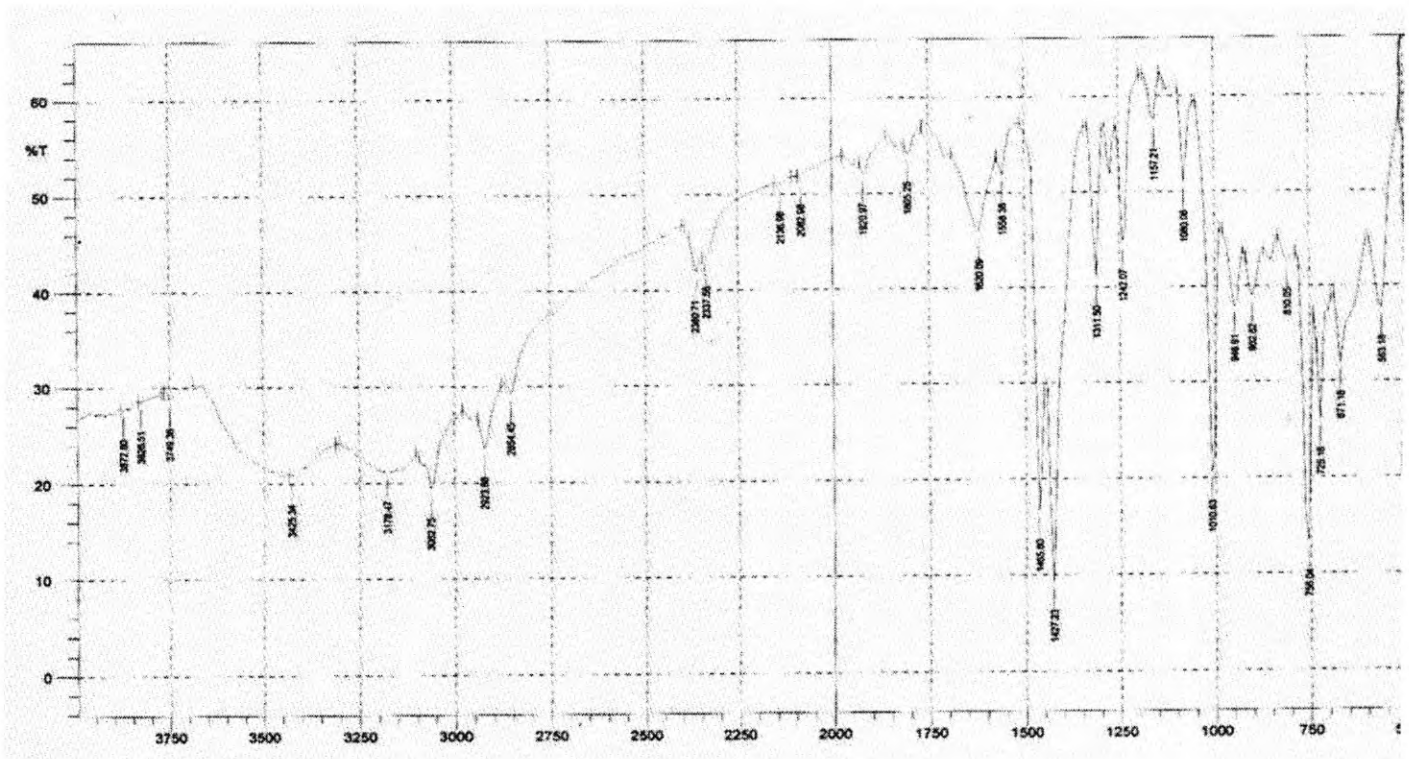
Band type	ν (cm^{-1})
(C-H) aro	3039
(C-N)	1280
(C-S-C)	748

الجدول -5 :يوضح العدد الموجي للمجاميع الفعالة لمعقد MBT : Mo^{+6}

Functional group	υ(cm^{-1})
(Mo-S)w	362
(Mo-N)w	447
(Mo=O)M	902



شكل -7 : يوضح طيف FT- IR للكاشف HMBT

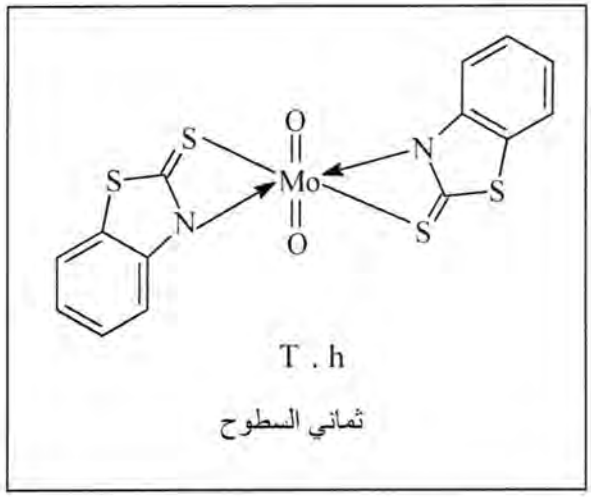


شكل -8 : يوضح طيف FT- IR للمعقد المستخلص

الاستنتاجات

1- امكانية استخلاص الموليبدنيوم السداسي بواسطة الكاشف HMBT من وسط حامضي .

2- اقترحت صيغة جزيئية وتركيبه للمعقد المستخلص من خلال الدراسة كالاتي :



T . h

ثماني السطوح

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