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Polyamide [1,3-Dicarboxymethoxybenzene and Ethylene Diamine] Complexation with Some Metal Ions

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ABSTRACT. Polyamide [1,3-dicarboxymethoxybenzene and ethylene diamine] complexes with Cd^{2+}, Fe^{3+} and UO_2^{2+} were prepared by melt condensation of bis-1,3-[DCMB] and [ED] and characterized by elemental and thermal analysis as well as different spectroscopic techniques. The data gathered showed that polyamide, ligand coordinates with metal ions in a bidentate manner through N,N donation. The metal ions are surrounded by coordinated water molecules and anions so as to establish the octahedral geometry.

KEYWORDS: Spectroscopic, [1,3-dicarboxymethoxybenzene (DCMB) and ethylene diamine (ED)], Thermal analysis TGA, DTA.

Introduction

Mononuclear and heterodi-trinuclear polymer complexes of nickel (II), Copper (II) and oxovanadium (IV) chloride with 2-acrylamido-1-phenyl-2-amino-thiourea (APATH) monomer derived from amidation of acryloyl chloride with 2-amino-1-phenyl thiourea have been prepared[1].

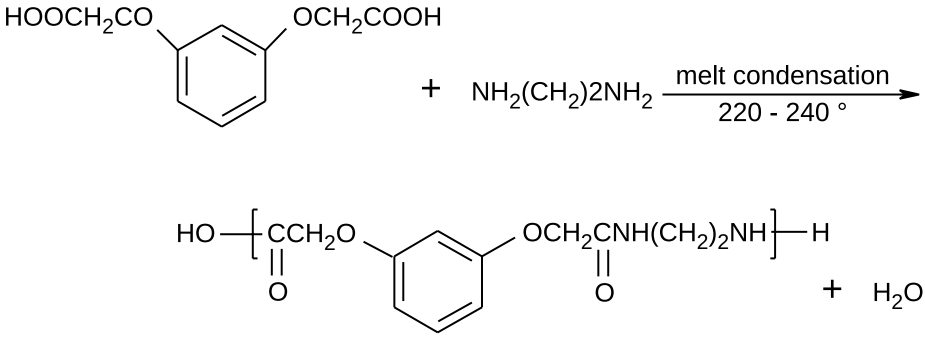
Some novel wholly aromatic polyamide-hydrazides containing various proportions of para and meta phenylene units were prepared and used as semi permeable membranes for water desalination by reverse osmosis separation performance[12]. Also metallized plastic films through transition metal complexation were synthesized charecteized[3-8].

Transition metal polymer complexes with mixed ligands have played a vital role in the development of coordination chemistry. The oxygen-bridged homo- and heterobinuclear complexes have attracted much attention due to their interesting spectral and magnetic properties and their use in biochemical processes and as industrial and homogeneous catalysts[9].

Recently several coordination polymers have been prepared which act as chelating groups in binding polyvalent metal ions[10]. Polyamine ligands such as ethylenediamine diethylenetriamine or triethelenetetramine were found to have excellent chelating properties[11]. The metal ion can be chelated in several ways, one of these is the use of a suitable number of functional groups (NH_2, OH, CO ... etc) by which coordination with metal ions causes polymer complexes[12]. Such polymer complexes exhibit a higher thermal stability than the parent polymer. In the present investigation, we report the complexation of polyamide derived from 1,3-dicarboxymethoxybenzene with some transition metal chlorides. The polymer complexes were characterized, their structures were elucidated and their thermal stabilities were studied.

Materials and Methods

1,3-dicarboxymethoxybenzene was prepared according to the previously mentioned method[13]. Polyamide was prepared by reaction of 1,3-dicarboxymethoxybenzene with ethylenediamine by melt condensation according to the following scheme:



The reaction was carried out in a three necked flask dipped in an oil bath (thermostatically controlled) provided with a mechanical stirrer and Dean-Stark trap to collect water produced. A pipette was inserted through a stopper down to the flask to introduce a slow dry deoxygenated nitrogen gas in order to facilitate the removal of the water produced. When the reaction was completed, the polyamide was dissolved in DMF then precipitated by adding a large amount of distilled water with vigorous stirring. The precipitate was then gathered by filtration and dried in a vacuum oven at 40°C. All other chemicals were supplied by (Aldrich or Merck chemicals) with a high degree of purity.

Solid complexes were prepared by refluxing equimolar quantities of polyamide (in DMF) and the metal chloride for about four hours. The mixture was allowed to cool and the solid complexes so formed were separated by adding a large amount of distilled water, filtered off, washed with water and dried in a vacuum oven at 40ºC for 3 days.

Characterization of Polymer Complexes

Elemental analysis (C, H and N) of polyamide and its complexes were carried out at the Microanalytical Centre, Cairo University, Giza, Egypt. Metal ion contents were determined by EDTA titration under appropriate conditions[14] while the percent of coordinated water molecules was determined by dehydration at ~130ºC. IR spectra were measured by the Perkin-Elmer 598 (4000-200 cm^{-1}) spectrophotometer as KBr discs. Electronic absorption spectra were recorded on the Perkin-Elmer λ_{3B} double beam spectrophotometer using the Nuiol-mull technique. Thermal analysis (TGA and DTA) were measured by the Shimadzu XD-30, Thermal Analyzer (Faculty of Science, Menoufia University). Samples were heated in platinum cell in dynamic nitrogen atmosphere with a heating rate 10ºC/min. ^{1}H-NMR spectra was recorded on a Varian analytical EM 390 spectrophotometer using d^6-DMSO as a solvent and trimethylsilene (TMS) as internal reference.

Results and Discussion

Elemental analysis (C, H and N) of the polyamide under study and its Cd^{2+}, Fe^{3+} and UO$_2^{2+}$ complexes show a satisfactory agreement between the proposed and measured values as illustrated in (Table 1). All the solid complexes are insoluble in common organic solvents and do not possess sharp melting points but decompose on heating above 300ºC. Thus measurements are expected due to their polymeric nature.

TABLE 1. Microanalytical analysis of polyamide and its complexes.

Complex	Elemental analysis (calc. / measured)				
	Colour	C %	H %	N %	M %
I	Brownish	53.71 / 53.9	6.0 / 6.4	10.4 / 0.2	–
IIa	Green	35.8 / 35.6	3.9 / 4.1	6.8 / 7.2	14.9 / 15.3
IIb	Green	37.1 / 36.8	3.8 / 4.2	6.9 / 7.1	14.4 / 14.2
IIc	Pink	35.8 / 36.2	3.4 / 4.1	7.2 / 7.1	14.2 / 14.6
IIIa	Green	41.9 / 42.1	4.6 / 4.5	8.2 / 8.1	9.3 / 9.3
IIIb	Green	42.6 / 42.3	4.7 / 4.5	7.9 / 8.1	8.7 / 8.6
IIIc	Pink	43.1 / 43.2	4.0 / 4.8	7.9 / 8.3	8.6 / 8.5

I – (polyamide), IIa →IIc (M:L) (1:1), IIIa →IIIc (M:L) (1:2)
a) Cd^{2+}, b) Fe^{2+} , c) UO$_2^{2+}$

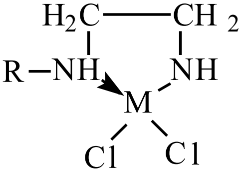
The μ_{eff}. values of the majority of solid complexes, measured at room temperature, show lower values than in case of many N,N donor complexes, the lower magnetic moments are due to antiferromagnetic interactions as a consequence of dimeric or polymeric structural arrangement[15]. The IR spectrum of polyamide ligand was studied and compared to those of its complexes, the important band frequencies are listed in Table (2). The IR spectrum of polyamide molecule shows broad and intense one at 3400 and 1160 cm^{-1} due to the stretching and bending (ν_{OH} and δ_{OH}) frequencies of the OH group respectively. The stretching vibrational band of NH group (ν_{NH}) appears at 3100 cm^{-1} while that of $\nu_{C=N}$ appears at 1650 cm^{-1}. The latter band may arise from the keto-enol tautomerism taking place in the free polyamide. The stretching vibrational frequency of the carbonyl carboxyl group ($\nu_{C\text{-}O}$) appears at 1720 cm^{-1}. On the other hand, the IR spectra of the metal complexes, show the absence of the stretching vibrational band of the C = N group, so it seems that coordination process precludes the keto-enol tautomerism as a result of delocalization of the lone pair of electrons on nitrogen atoms taking place in the complexation process. This is taken as an evidence for the contribution of this nitrogen atom to complex formation, which is supported by the shift of the band due to the NH group to lower frequency. On the other hand, the frequency of ($\nu_{C\text{-}O}$) remains nearly unaltered. A further support for the contribution of the NH groups of polyamide ligand to complex formation is the appearance of only one new band at 490-465 cm^{-1} due to $\nu_{M\text{-}S}$ stretching frequency.

TABLE 2. IR spectra data for polyamide and its complexes.

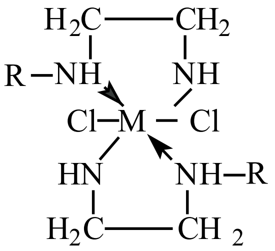
Complexes	IR cm^{-1}	Assignments
I Vc-o = 1710 cm^{-1}	3400 3100 2900 1720 1650	OH stretching NH stretching C-H stretching –CH_2- C = O Carbonyl C = N Stretching
(IIa, IIIa)	3400 2900 1700 470	OH Stretching NH Stretching C-O Carbony; M-N
(IIb, IIIb)	3380 2850 1700 470	OH Stretching NH Stretching C = O M-N
(IIc, IIIc)	3390 3000 1690 485	OH Stretching NH Stretching C = O M-N

I (Polyamide), IIa → IIc (M: L) (1:1), IIIa →IIIc (M:L) (1:2)
a) Cd^{2+}, b) Fe^{3+}, c) UO_2^{2+}

The ^1H NMR spectrum of polyamide is recorded in d^6-DMSO and compared to that of its UO_2^{2+} complex. For the free ligand, the singlet signal at $\delta = 3.3$ ppm (4 protons) is due the CH_2-CH_2- protons while the weak broad signal at 3.7 ppm is due to NH-proton. The other NH group (end groups) gave also a singlet band at 8.2 ppm. The later two signals are strongly affected on complexation with UO_2^{2+} ion indicating their participation in complex formation. So, the mode of bonding in this case can be represented as:



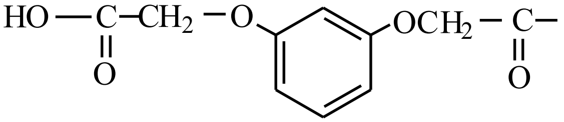
(1:1) (M:L)



(1:2) (M:L)

M = metal L = ligand

R =



The electronic absorption spectra of the polyamide derived from 1,3-dimethoxycarboxybenzene and its complexes, measured using the Nujol mull technique, show mainly the charge transfer band of the free molecule at ≅ 25974 cm^{-1} while Cd^{2+} complex shows a band at 15780 cm^{-1} due to $^4A2 \rightarrow {}^4T1$ (p) transition in tetrahedral field[16] whereas Fe^{3+} complex shows band at 14265 and 13675 cm^{-1} respectively due to the square planar configuration in both. These transitions are not observed in the spectrum of UO_2^{2+} complex but only the charge transfer band at 24096 cm^{-1}.

Thermogravimetric analysis of the polyamide ligand and its complexes (as represented in Fig. 1) show that each of them degrade in three steps.

In case of metal chelates, the first step in the decomposition sequence starts at 190ºC due to the evaporation of physically adsorbed water molecules, while the second step corresponding to the removal of chloride ion (in the form of HCl molecules) takes place at 250ºC. The final step is the degradation of the anhydrous complex which occurs at temperatures higher than 580ºC leading to be

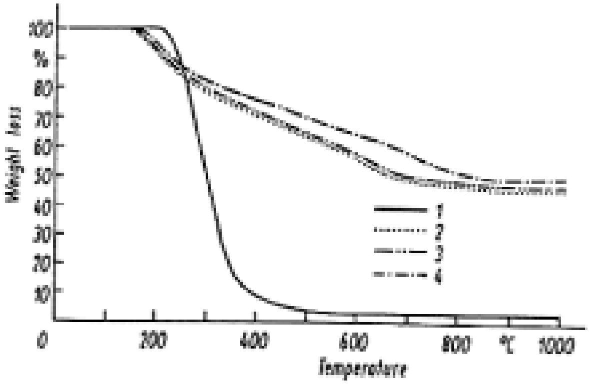
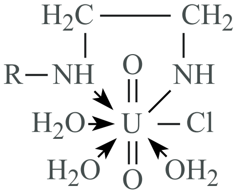


FIG. 1. TG curves of bis-1,3-[DCMB] and [ED] metal chloride polymer complexes. 1-bis-1,3-[DCMB] and [ED], 2-Cd^{2+} poly., 3-Fe^{3+} poly. and 4-UO_2^{2+} Polymer complexes.

more stable than their corresponding free polymer ligand which is in accordance with the results obtained previously[17-18] which is due to the formation of stable five member rings structures,



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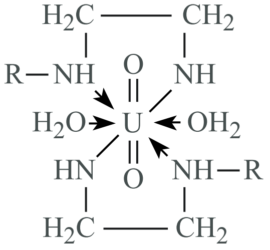

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متراكبات البولي أميد المحضرة من [١، ٣ ثنائي كربوكسي ميثوكسي البنزين و الإثيلين ثنائي الأمين] مع بعض الأيونات الفلزية

فوزية محمد النويصر
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المستخلص. يتناول هذه البحث تحضير متراكبات البولي أميد من [١، ٣ ثنائي كربوكسي ميثوكسي البنزين والإثيلين ثنائي الأمين] مع أيونات الكادميوم والحديد واليورانيوم بالصهر والتكثيف لمشتقات هذه التراكبات. وقد تم فحص وتحديد التركيب الجزئي للبوليمر والمتراكبات المشتقة من استخدام القياسات الطيفية المختلفة والتحليل العنصري والحراري للعناصر المكونة لها .

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Synthesis and Investigation of Some Polyesterurethanes Based on Hydroxy Terminated Polyesters

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ABSTRACT. Hydroxy terminated polyesters were synthesized by the reaction of tetrabromophthalic, phthalic, and maleic anhydrides with polyethylene glycol via melt condensation technique. They were characterized by hydroxyl number and intrinsic viscosity measurements. Also, the fire retardancy of polyesters was reacted with excess toluene-2, 4-diisocyanate to yield isocyanate terminated prepolymers which were subsequently reacted with 5,5-dihydroxymethyl-2-trichloromethyl-1,3-dioxane or ethylene diamine. These polymers were characterized by IR and ^{1}H NMR spectra, viscosity measurements, and thermogravimetric analysis. A change of the electrical conductance of the compounds with increasing temperature is observed for the solid samples.

KEYWORDS: Synthesis polyesterurethanes, IR, ^{1}H NMR, Viscosity, TGA, DTA and Electrical conductance.

Introduction

Polyurethanes form a class of industrially useful materials because of their excellent properties. The polyurethanes are used in a wide variety of applications but relatively few isocyanates are employed commercially in their manufacture. The most important are the toluene diisocyanates (TDI), although other types are now being developed and adopted industrially. The initial studies on polyurethane synthesis were based on simple diisocyanates and diols but the main importance of the reaction is now concerned with the use of intermediates which are often themselves polymeric in character (polyesters, polyethers) and carry terminal groups (usually –OH or NCO) capable of further reaction and thus of increasing the molecular size, often during the actual fabrication processing, by either chain extension, branching, or crosslinking.

One such method of preparing a polyurethane derivatives is first to prepare an isocyanate terminated prepolymer which is often reacted with diols[1]; diamines[2], and water[3]. Hydroxy terminated polyesters[4] are starting material for many of the urethane polymers. The polyesters were prepared by the melt condensation of glycols and dibasic acids of both aliphatic and aromatic type, or a mixture of both[5].

The electrical conductivity of solid organic compounds is a property which is covered by a very wide range of studies[6]. The enthusiasm for discovery and research of organic compounds which conduct the electric current owes to Mahmoud-El-Haty[7] who speculated about the conducting properties of proteins. This plays an important role in the life process. Recently, polyesters were shown to have semiconducting properties in an attempt for their use in solar energy storage[8]. In the present work some polyesterurethanes and polyesterurethaneureas were prepared by the reaction of isocyanate terminated prepolymers with 5,5-dihydroxymethyl-2-trichloro-methyl-1,3-dioxane and ethylene diamine respectively. In addition, the electrical conductance properties of the relevant compounds have been studied.

Experimental

Materials

Tetrabromophthalic anhydride (TBPA), phthalic anhydride (PA) maleic anhydride (MA) and polyethylene glycol (PEG) (Mwt., 400) were products of Aldrich Chemical Company. Toluene-2,4-diisocyanate (TDI) were used as supplied by British Drug Houses Chemicals, Ltd, England (BDH). 5,5-dihydroxymethyl-2-trichloromethyl-1,3-dioxane (HMCMD) was prepared according to the previous method[9]. All solvents used were of A.R. equivalent grade.

Preparation of Hydroxy Terminated Polyesters

A mixture of TBPA (0.04: 0.10 mol), PA (0.00: 0.10 mol), MA (0.00: 0.10 mol) and PEG (0.25 mol) was heated in the presence of oxygen-free nitrogen for 2h at 180ºC, for 2h at 200ºC, then for a further 3h at 220ºC to give a syrupy mass with an acid number less than one. The polyesters were purified twice by dissolving in chloroform and precipitating with light petroleum and then dried under reduced pressure.

Preparation of Polyesterurethanes and Polyesterurethane-Ureas

To a solution containing 0.1 equivalents of polyester in 40 ml dimethylformamide (DMF) and five drops of triethylamine as catalyst, 0.3 equivalents of TDI in 20 ml DMF were added at room temperature in N_2 atmosphere.

The reaction mixture was heated to 80ºC with stirring for 1hr, followed by addition of 0.2 equivalents of 5,5-dihydroxymethyl-2-trichloromethyl-1,3-dioxane or ethylene diamine in the cases of polyesterurethanes and polyesterurethane-ureas respectively. Reaction was done at 120ºC for 3h. The same reaction conditions were adopted for all polymerization to ensure the same amount of chain extension. The viscous solution was precipitated with water, filtered, washed with water, methanol and dried in a vacuum desiccator. The yield of polymers was 63-87 %.

Characterization of Polymers

The hydroxy and acid numbers of polyesters were determined by standard methods[10].

Densities were measured by means of a pycnometer using hexane at 30ºC. Viscosity measurements were carried out with an Ostwald viscometer using a 1% solution in dioxane and DMF for polyester resins and polyesterurethanes or polyesterurethane-ureas respectively.

Thermal Analysis

DTA was performed at a heating rate of 10º/min using a Shimadzu X-D-30 Thermal analyzer. TG Thermograms were obtained at a heating rate of 10º/min using a DT-30B. Thermal infrared spectra were recorded on a Shimadzu IR. 470 spectrophotometer in the range 4000-600 cm^{-1}.

The proton magnetic resonance spectra (in d6-dimethyl-sulfoxide as solvent and using TMS as zero reference) were obtained at room temperature with a Marian Gemini spectrometer operating at 200 MHz.

Preparation of Varnish Films

Plywood of dimensions 5" × 0.5" × 0.05" were varnished by dipping. The weight of the dried varnish film is equal to the weight of plywood strip. The strips are prepared for flammability test (ASTM D 635-56T, 1956).

Electrical Conductivity Measurements

These were carried out on some of the investigated polyesterurethane using a Super Megometer Electrometer Model RM 170. The samples had the form of discs of a diameter of 13 mm and a thickness 1 mm produced under a pressure of ~ 300 $kg.cm^2$. The cross section area of the pellets was covered with silver paste to eliminate as much as possible the contact resistance between the electrodes and the discs. The temperature was measured in air using a Ca-CuNi thermocouple placed close to the sample. Measurements were carried out from room temperature up to 460 K and then on cooling down to room temperature. The electrical conductivity control was accurate to ± 0.3 $\Omega^{-1}.\text{cm}^{-1}$.

Results and Discussion

In the present work hydroxy terminated polyesters (I-VII) were prepared from the reaction of TBPA, PA and MA with PEG (Mwt: 400) at different molar ratios as illustrated in Table 1.

Table 1. Moles of components.

Polyester	TBPA	PA	MA	PEG
I	0.06	–	0.08	0.21
II	0.07	0.01	0.07	0.22
III	0.04	0.03	0.08	0.20
IV	0.06	0.08	–	0.21
V	0.07	0.06	0.01	0.20
VI	0.04	0.07	0.03	0.21
VII	0.02	0.08	0.04	0.20

The prepared hydroxy terminated polyesters (I-VII) shown in Figure (1a) were brown or amber yellow, viscous materials soluble in various organic solvents except alcohol, n-hexane, and light petroleum. These linear polyesters showed greater resistance to gelation and remained soluble after long storage periods. The yield, hydroxyl number and intrinsic viscosity of the prepared polyesters are summarized in Table 2.

Table 2. Physical characteristics of the hydroxy terminated polyesters (I-VII).

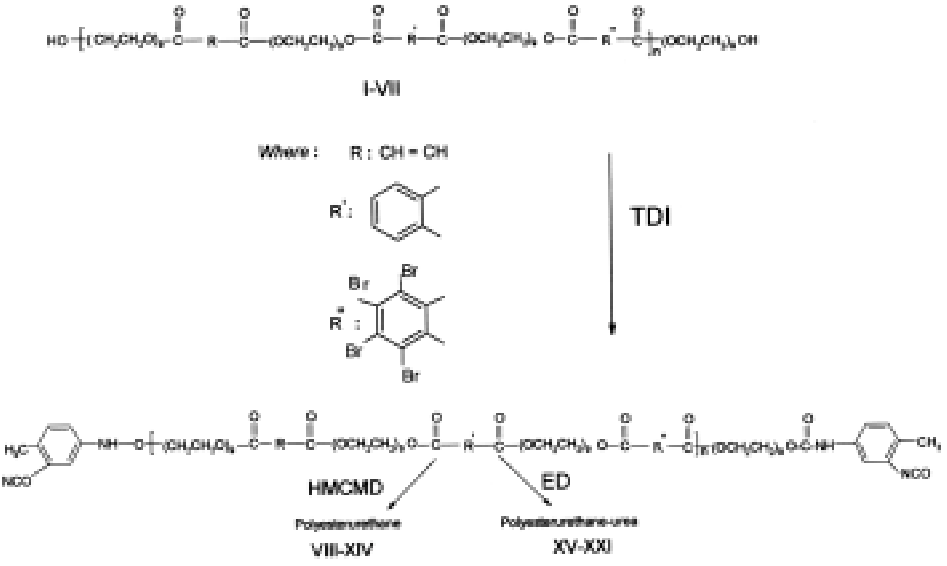
Polyester	Nature of polyester	Yield percentage	Hydroxyl value	η (dl/g)
I	Brown resin	93	67.28	0.019
II	Brown resin	81	57.97	0.003
III	Yellow resin	88	88.50	0.022
IV	Yellow resin	85	84.00	0.034
V	Yellow resin	90	74.21	0.029
VI	Yellow resin	87	80.00	0.048
VII	Yellow resin	88	68.00	0.013

Flamability test was used to evaluate the fire retardancy of polyesters (I-VII) as varnish films. Table 3 illustrates the time of burning of coated plywood strips. From Table 3, it is clear that the time of burning of coated plywood strips is greater than that of uncoated plywood strip. It is attributed to the presence of tetrabromophthalic moiety in polyester chain which act as fire retardant.

TABLE 3. Time of burning of polyesters (I-VII) as varnish films.

Polyester	Time/min
I	2.02
II	3.88
III	2.96
IV	2.57
V	3.57
VI	2.58
VII	1.89
Uncoated strip	0.57

The structures of polyesters (I-VII) were established by studying their IR and ^1H NMR spectra. The infrared spectra of the polymers showed characteristic absorption bands around 3400 cm^{-1} (ν_{OH}), 1720 cm^{-1} ($\nu_{C=O}$), 1630 cm^{-1} ($\nu_{C=C}$) and intense absorption at 1100 cm^{-1} (ν_{C-O}). Figure (1a) illustrates the IR spectra of polyester VI as example.



The ^1H NMR spectra of the hydroxy terminated polyesters showed bands at δ 7.2-8.0 due to the proton of phenyl and –CH=CH- groups; at δ 5.42 due to OH group; at δ 4.38 and δ 3.55 due to the protons of $-CH_2OCO-$ and $-CH_2OCH_2-$ groups respectively. Figure (1b) illustrates the ^1H NMR spectrum of polyester VI as example.

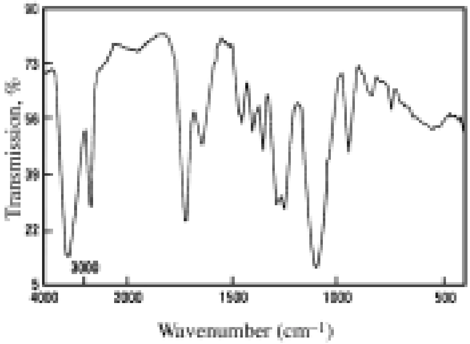


FIG. 1a. IR spectrum of polyester VI.

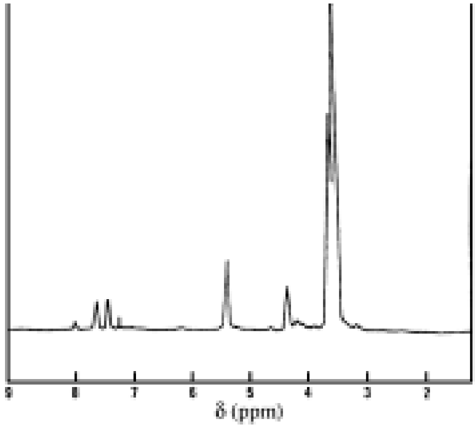


FIG. 1b. ^1H NMR spectrum of polyester VI.

The hydroxy terminated polyesters (I-VII) were used as starting materials for the preparation of some polyesterurethanes (VIII-XIV) and polyesterurethane-ureas (XV-XXI).

The structures of the prepared polyesterurethanes and polyesterurethaneureas were established by studying their IR and ^1H NMR spectra. The infrared spectrum of the polyesterurethane (XIII) (Fig. 2a) showed characteristic absorption bands around 3300 cm^{-1} (ν_{NH}) and an intense absorption band at 1100 cm^{-1} ($\nu_{C\text{-}O}$). The carbonyl absorption appeared as three strong bands at 1720, 1600, 1530 cm^{-1} for ester, amide I and amide II respectively.

The ^1H NMR spectra of the polyesterurethanes displayed bands at δ 6.9-9.2 due to protons of phenyl, CH=CH and NH groups; δ 4.2 due to protons of $-CH_2OCO-$ group; δ 3.5 due to protons of $-CH_2OCH_2-$ group; δ 2.2 due to

(IX) as example.

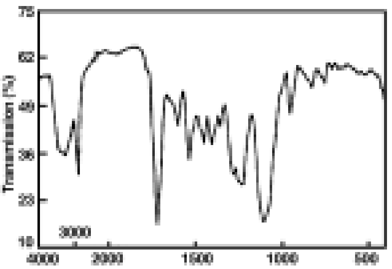


FIG. 2a. IR spectrum of polyesterurethane XIII.

protons of methyl group of TDI. Figure (2b) illustrates the 1H NMR spectrum of polyesterurethane (IX) as example.

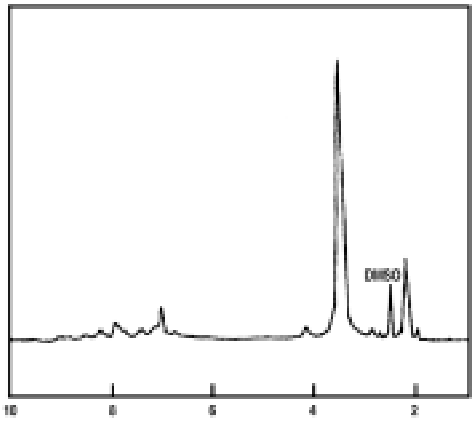


FIG. 2b. ^{1}H NMR spectrum of polyesterurethane IXI.

The intrinsic viscosities (η) of the polymers ranged from 0.0.089 to 0.344 dl/g when measured in DMF at 30ºC. The densities of the polymers were in the range 0.993-1.20g/cm^3. The values of yields, intrinsic viscosities, densities and some decomposition temperatures are given in Table 4.

Thermal analysis of some polyesterurethanes and polyesterurethane-ureas showed that the polymers were stable up to 300-349ºC. TG and DTA curves of polymer (XXI) respectively as example. These high thermal stability values obtained for the prepared polyesterurethanes and polyesterurethane-ureas are in agreement with those reported[11] for polyester based polyurethanes.

TABLE 4. Physical properties of polyesterurethanes and polyesterurethaneureas.

Polyester	Yield percentage	η (dl/g)	Density g/cm^3	Polymer decomposition temperature
VIII	80	0.321	1.150	–
IX	76	0.263	1.174	–
X	70	0.257	1.180	–
XI	61	0.296	1.050	300.25ºC
XII	63	0.329	1.080	–
XIII	68	0.344	1.150	315.85ºC
XIV	63	0.312	1.120	–
XV	83	0.268	1.172	–
XVI	80	0.287	1.085	–
XVII	85	0.254	0.993	–
XVIII	71	0.089	1.200	320.65ºC
XIX	79	0.257	1.200	–
XX	68	0.298	1.159	–
XXI	82	0.288	1.120	348.96ºC

Electrical Conductivity Measurements

The electrical conductivity was measured over a relatively moderate temperature range to avoid melting of the materials. Figures (3a,b) represent the variation of the electrical conductivity (log σ) as a function of temperature ($1000/TK^{-1}$) for some of the polyester under investigation. The following relation is applicable:

$$\sigma = \sigma_o \cdot \exp(-\Delta E/KT) \qquad (1)$$

The parameters have their usual meanings. The plot of the electrical conductivity as a function of reciprocal absolute temperature. Figs. 3a and 3b show two inflections for compounds I, II, VII and IX. This denotes that the mode of conduction changes during the conductivity measurements. A linear behavior is observed for compounds VIII and V.

The values of the transition temperature and activation energies on heating and cooling rates were calculated according to equation 1 and are listed in Table 5.

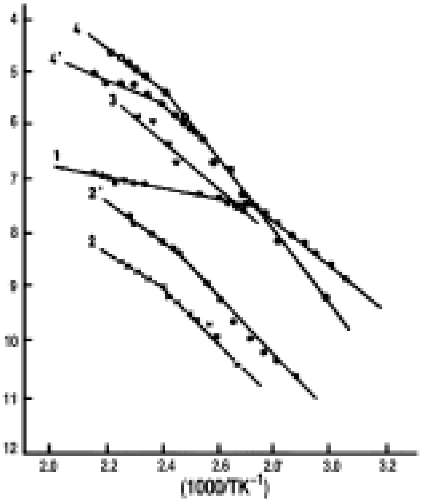


FIG. 3a. Variation of electrical conductivity (log σ, Ω^{-1}, cm^{-1}) as a function of reciprocal absolute temperature for some solid polyester.

1,1' (V), 2,2' (IX) and 3,3' (VII) where 1,1': heating and cooling respectively.

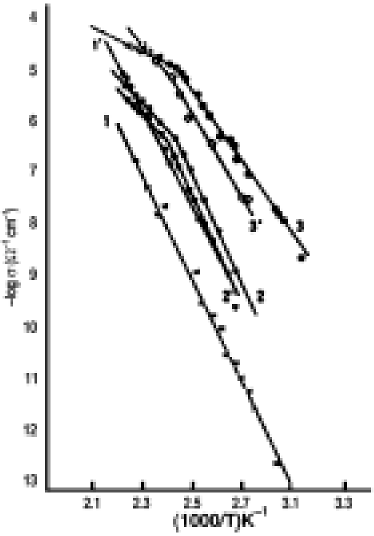


FIG. 3b. Variation of electrical conductivity (log σ, Ω^{-1}, cm^{-1}) as a function of reciprocal absolute temperature for some solid polyester.

1,1' (V), 2,2' (IX) and 3,3' (VII) where 1,1': heating and cooling respectively.

TABLE 5. Values of activation energy for the conduction (eV) and transition temperature (K) for some of the investigated polyester.

Compd.	Heating activation energy			Cooling activation energy		
	ΔE_1	ΔE_2	Transition temperature	ΔE_1	ΔE_2	Transition temperature
I	0.742	0.260	353.36	–	–	–
II	1.025	0.715	436.68	1.206	0.693	429.18
V	2.121	–	–	2.199	–	–
VII	1.230	0.990	413.22	1.240	0.778	411.52
VIII	1.732	–	–	–	–	–
IX	2.249	1.164	409.84	2.224	1.109	414.94
X	1.320	0.469	399.20	1.237	0.616	402.41

The activation energy of the polyester decreases in the order I < II < VII < X < VIII. Consequently, the electrical conductivity increases in a reverse order. This is probably explained on the basis of increased electron density and polarization of the molecule as a function of the substitution inductive effect, facilitating the electron delocalization in the molecule. A justification for the above conclusion stems from the linear relationship observed between the activation energies under and above the transition temperature with σ^+ values of substitution. The electrical conductivity values for compounds of the same type of substituent, at different positions, (*e.g.* VIII and IV) increase in the order p > m position, due to the mesomeric effect of the substituent[12].

The difference in the position of the heating and cooling curves has no essential effect on the specific conductivity level and causes only slight changes of the activation energy (Table 5). The activation energies below and above the transition temperature are large. This can be attributed to the following[13,14]:

1 – As the conjugation is increased through the molecule, the π-electrons are not delocalized over a corresponding greater distance, and the activation energy (ΔE) for generation of the carriers no longer falls linearly with the conjugation chain length;

2– The triazole and the phenyl rings are actually not coplaner. Consequently, the rotation of the two molecules against each other in a twisting motion is considered which breaks the conjugation between them; hence, the atomic p-orbital can no longer overlap.

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تخليق وفحص بعض البولييوريسان معتمدا على الهيدروكسي بولي استرات

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المستخلص. فى هذا البحث تم تخليق وفحص بعض الهيدروكسي بولي استر اليوريسان بتفاعل بين رباعي برومو حمض الفيثاليك والفيثاليك والماليك مع البولى إثيلين جيليكون بطريقة الاندماج الانصهاري. تتميز هذه المركبات بعدد الهيدروكسي وقياسات اللزوجة وأيضًا مضادات للنار من البولي إسترات. أيضًا تم تفاعلها مع زيادة من الثيوسيانيت والأيزوثيوسيانيت لزيادة خواصها المضادة للنار.

لقد تم فحص ووصف التركيب الجزيئي للبوليمرات باستخدام أجهزة الطيف المختلفة (الأشعة تحت الحمراء)، والرنين المغناطيسي ، وقياسات اللزوجة ، والتحليل الوزني الحراري ، وأيضًا تمت دراسة تغيرات في التوصيل الكهربي للعينات الصلبة باستخدام معدل زيادة درجة الحرارة .

وتبين أن هذه المركبات – قيد الدراسة – لها توصيلاً كهربيًا مميزًا ، مما يعمم استخدامها كأشباة موصلات ومضادات للاستخدامات النارية .

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Aromatic Constituents of *Stachys* sp. aff. *schimperi*

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Abstract. *Stachys* sp. aff. *schimperi* (family Labiatae) is a widespread species in the south west of the Kingdom of Saudi Arabia. This plant species has not been investigated previously for its chemical constituents. Chromatographic separation of its extract afforded β-sitosterol and stigmasterol. Additionally, some fatty acids, 2-hydroxy-4-phenylbutanoic acid, syringic acid, vanillic acid, isoferulic acid and *p*-coumaric acid were identified by GC/MS technique. In addition to two flavonoids; 4',5-dihydroxy-6,7,8-trimethoxyflavone and 4',5-dihydroxy-3,6,7,8-tetramethoxyflavone, were identified by the proton NMR and the MS spectra.

Introduction

The genus *Stachys* of the family Labiatae comprises many medicinal plants. *S. baicalensis* is prescribed in the USSR for the treatment of hypertension, *S. lavandulifolia* is used in Jordan for indigestion and *S. officinalis* is used in Ukrainea for treating heart disorders. Also, in Ukrainea compresses made with *S. recta* boiled in milk are applied for rheumatism[1].

Typical phytochemical constituents of the genus *Stachys* are essential oils[2-5], C_9-iridoidal glycosides[6,7], labdane[8,9] and neo-clerodane[9,10] diterpenoids, flavonoids[11-13], megastagmane glycosides[14], phenylpropanoids[7,15,16], and phenylethanoids[17].

Stachys sp. aff. *schimperi* is an aromatic species, commonly distributed in the south west of Saudi Arabia, was not investigated previously for chemical constituents. In this article, we report the isolation of many aromatic constituents from this species.

Experimental

General

GC/MS spectra were taken on a QP-7000 Shimadzu, with fused silica capillary column (30 m × 0.25 mm ID), film (5% phenyl, 95% methylsilicon) thickness 0.25 μ, and the output of an IBM computer with software Class 500 and NIST library for comparison; NMR spectra were recorded on Bruker FT-400 MHz.

Plant Material

Stachys sp. aff. *schimperi* was collected in January 2001 from Taief-Baha road at Mayssan about 100 km south of Taif, Saudi Arabia and identified by Prof. Dr. A. Faied, Botany Dept., Faculty of Science, King Abdulaziz University. A specimen was deposited in the Herbarium of Botany Dept., Faculty of Science, King Abdulaziz University.

Processing of Plant Material

The air-dried, whole plant, (680 g) was cut into small pieces and extracted at room temperature by soaking in a mixture of methanol/ether/pet. ether 40-60° (1:1:1) for 24 hours. The crude extract (31.7 g) was defatted by dissolving in cold MeOH (150 ml) and standing in the fridge freezer for overnight, then, quick filtration and evaporation gave the defatted extract (20.8 g).

Separation of Compounds

The defatted extract was fractionated over silica gel (160 g) CC (100 cm length × 4 cm inner diameter) using stepwise elution into three main fractions.

The second fraction (Ss2, 6.2 g, eluted by pet.ether/ether 1:1) was rich in chemical constituents. It was reseparated on sephadex LH-20 CC into 13 fractions (Ss21-Ss29, Ss210, Ss211, Ss212, Ss213). Fraction Ss24 (540 mg, eluted by pet. ether/CH_2Cl_2 1:4) afforded a mixture of β-sitosterol, stigmasterol, flavonoid **6** and flavonoid **7** (4:1:3:4). Fraction Ss26 (93 mg, eluted by pet. ether/ CH_2Cl_2 1:4) contained flavonoid **7**.

Fraction Ss210 (1.2 g, eluted by CH_2Cl_2/acetone 4:1) gave by GC/MS the hydroxyacid **1** (at R_t 8.00 min., 37.5%), syringic acid **2** (at R_t 10.12 min., 6.3%), palmitic acid (at R_t 11.58 min., 15.6%), linoleic acid (at R_t 13.27 min., 6.2%), and oleic acid (at R_t 13.33 min., 7.5%).

Fraction Ss211 (820 mg, eluted by CH_2Cl_2/acetone 3:2) afforded by GC/MS vanillic acid **3** (at R_t 7.30 min., 11.7%), the hydroxyacid **1** (at R_t 8.00 min., 5.0%), nonandioic acid (at R_t 8.23 min., 18.3%), isoferulic acid **4** (at R_t 9.46

min., 3.3%), syringic acid **2** (at R_t 10.12 min., 7.3%), palmitic acid (at R_t 11.58 min., 16.7%), oleic acid (at R_t 13.35 min., 13.3%) and stearic acid (at R_t 13.58 min., 4.7%).

Fraction Ss212 (750 mg, eluted by acetone) gave by GC/MS vanillic acid **3** (at R_t 7.32 min., 7.4%), nonandioic acid (at R_t 8.23 min., 29.6%), palmitic acid (at R_t 11.57 min., 11.1%), linoleic acid (at R_t 13.28 min., 30.4%) and stearic acid (at R_t 13.59 min., 3.0%).

Fraction Ss213 (660 mg, eluted by acetone) afforded by GC/MS *p*-coumaric acid **5** (at R_t 9.86 min., 9.1%), palmitic acid (at R_t 11.57 min., 18.3%), linoleic acid (at R_t 13.28 min., 13.6%), oleic acid (at R_t 13.35 min., 20.0%) and stearic acid (at R_t 13.58 min., 6.4%).

Results and Discussion

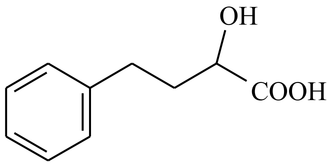
The extract of *Stachys* sp. aff. *schimperi* was separated firstly by silica gel CC. The main fraction was reseparated on sephadex LH-20, followed by GC/MS, in case of some fractions, to give two phytosterols, two flavonoids, five fatty acids and five aromatic acids.

The separated compounds were identified from their ^{1}H NMR and MS spectra and were confirmed by comparing with authentic spectra or literature data.

The phytosterols were β-sitosterol[18] and stigmasterol[18]. The fatty acids were palmitic[18], linoleic[18], oleic[18], stearic[18] and azelaic (nonandioic)[19]. The aromatic acids were 2-hydroxy-4-phenylbutanoic acid **1**[20], syringic acid **2**[21], vanillic acid **3**[21], isoferulic acid **4**[21] and *p*-coumaric acid **5**[22].

A spot of flavone **6** on a chromatographic plate was yellow in colour, brown under the UV light and turned flourescent blue when fumed by ammonia and viewed under UV. Structure of flavone **6** was followed from ^{1}H NMR spectrum (in $CDCl_3$), which gave a singlet in the downfield at δ 12.5 ppm (C-5 OH), an AA'BB' system at δ 6.97 and 7.82 with coupling of 8.6 Hz due to ring B (4'-oxygenated), in addition to three methoxyl group singlets at δ 4.12, 3.98, 3.96 ppm and a 1H-singlet at δ 6.60, which was in agreement with H-3. Thus **6** was found by comparison with authentic spectra to be 4',5-dihydroxy-6,7,8-trimethoxyflavone, isolated previously from *S. aegyptiaca*[12]. The structure was supported also by the MS spectrum.

A spot of flavone **7** on a chromatographic plate was yellow in colour, brown under the UV light and turned flourescent blue when fumed by ammonia and viewed under UV. ^{1}H NMR spectrum of 7 (in $CDCl_3$) was approximately similar to that of **6**. But the singlet of H-3 disappeared, the methoxyl group singlets became four (at δ 4.11, 3.96, 3.95, 3.86) and the downfield component of the AA'BB' system moved from 7.82 to 8.10 ppm, in agreement with additional C-3 OCH_3 group. Thus **7** was identified as 4',5-dihydroxy-3,6,7,8-tetramethoxyflavone, which was isolated previously from *S. aegyptiaca*[23]. The structure was supported also by the MS spectrum.



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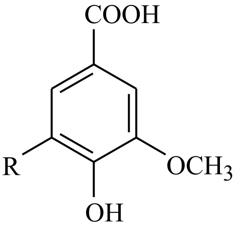
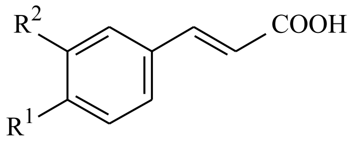
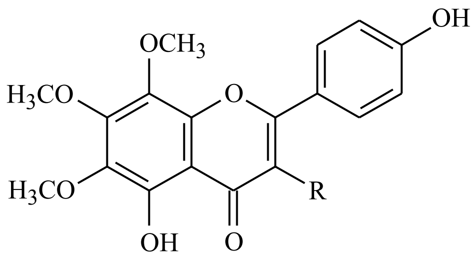


2; R = OCH_3
3; R = H



4; $R^1 = OCH_3$, $R^2 = OH$
5; $R^1 = OH$, $R^2 = H$



6; R = H
7; R = OCH_3

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المكونات العطرية لنوع استاكس شبيه شمبري

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المستخلص. ينتشر نوع استاكس شبيه شمبري (الفصيلة الشفوية) انتشارًا كبيرًا في جنوب غرب المملكة العربية السعودية. لم يتم فحص هذا النوع مسبقًا لمعرفة محتواه من المكونات الكيميائية. في هذا البحث أدى الفصل الكروماتوجرافي لخلاصة هذا النبات إلى فصل المكونات التالية: بيتاسيتواستيرول ، و استجما استيرول ، كما تم التعرف على بعض الأحماض الدهنية ، حمض ٢-هيدروكسي-٤-فينايل بيوتانويك ، حمض سيرنجك ، حمض فانيليك ، حمض أيزوفيريوليك ، حمض باراكوماريك ، وذلك باستخدام التحليل الكروماتوجرافي الغازي المقترن بطيف الكتلة ، بالإضافة إلى اثنين من الفلافونويدات ، وهما ٤ '،٥-داي هيدروكسي -٦،٧،٨-تراي ميثوكسي فلافون و٤َ،٥-داي هيدروكسي -٣،٦،٧،٨-تترا ميثوكسي فلافون ، تم التعرف على بنائهما باستخدام طيف الرنين النووي للبروتون بالإضافة إلى طيف الكتلة.

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Dissipation of Fenitrothion Residues in Some Fruits and Vegetables Using High-Performance Liquid Chromatography Method

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Abstract. High performance liquid chromatographic method was described for the determination of the dissipation of fenitrothion residues in some fruits and vegetables. Crops were sprayed with very dilute solution of fenitrothion, and collected daily one day after spraying for 7 to 13 days, and then extracted with acetonitrile and partitioning in normal hexane. Solid phase florisil cartridges were used for clean up. The analysis was carried out by reversed-phase high performance liquid chromatography (HPLC) with methanol-water (90:10) as a mobile phase. Detection limit is 0.01 mg/kg. The percentage of losses are 89.55, 85.71, 76.01, 93.39, 98.75, and 99.24 for rocket, parsley, lettuce, fig, grape and guava, respectively.

Introduction

Organophosphorus pesticide came into general use in early 1960s. The growth in use of these compounds as a result of the resistance of insects toward chlorinated pesticides. Fenitrothion (o,o-dimethyl 4-nitro-3-methyl-phenylphosphonothionate) [$C_9H_{12}NO_5PS$] is an organophosphorus insecticide. It is used almost worldwide for such crops as rice, fruits, vegetables, cotton, cereals and soybeans. It is also used in public health, principally as residual spray in houses for control of mosquitoes. It has low toxicity to mammals[1].The toxicity is much lower than many similar insecticides. LD_{50} the amount or concentration of a toxicant required to kill 50% of the test animal population under a standard set of conditions is 800 mg/kg[2]. Maximum Residue Limits (MRL's) permitted by Food Agriculture Organization (FAO) is 0.5 ppm[3]. Gas chromatography (GC) is the basic technique for analysis of several multiresidue pesticides in plants[4-6]. (HPLC) is the most important alternative to GC for pesticide residue analysis[7-10]. Liquid-liquid partitioning and adsorption chromatography have been traditionally applied forclean-up[11,12]. Head space solid-phase microextraction was used in strawberries and cherries[13]. Fast supercritical fluid extraction and high-resolution gas chromatography with electron-capture and flame photometric detection was used for multiresidue screening of organochlorine and organophosphorus pesticides in Brazil's medicinal plants[14]. Supercritical fluid extraction was also used for removal of organophosphate pesticides from waste water by supercritical carbon dioxide extraction[15]. This paper describes the dissipation of fenitrothionin six crops, which are rocket, parsley, lettuce, fig, grape and guava over a period of time. Florisil cartridges were used for clean-up prior to analysis by High-Performance Liquid Chromatography (HPLC).

Experimental

The study was carried out at the Agricultural Research Center, King Abdulaziz University, Faculty of Meteorology, Environment, and Arid Land Agriculture, at Hada Alsham region. The study included spraying the pesticide on three types of fruits (fig, grape, and guava) and three types of vegetables (lettuce, rocket, and parsley).

Pesticide Spraying

Pure or undiluted pesticides are highly toxic to both animals and plants, so they must be diluted before spraying. According to a procedure used in the farm where 4.5 g of fenitrothion dissolved in 5 liters of water to form liquid emulsion, then placed in the sprayer (Honda Electronic Ignition GX 270). Five basins of vegetables and three trees of fruits were sprayed with the emulsion (one of each remains without spray as blank).

Crops Sampling

Twenty-four hours after spraying, the first batch was collected from each plant and transferred to the laboratory, this process was followed regularly to the end of the period (7-13 days).

Extraction and Clean-up Procedures

The sample extraction was based on the method described by Sastry and Vijaya[10]. A 25 g sample of each of lettuce, rocket, parsley, fig, grape, and guava was homogenised with acetonitrile (50 ml) in a blender. The extract was filtered through a Buchner funnel by suction and washed twice with 10 ml of acetonitrile. The combined filtrate was used for partitioning in a separatory funnel with 50 ml n-hexane with strong shaking for 5 minutes. Then 50 ml deionized water and 5 ml saturated sodium chloride solution were added and the contents were shaken slowly in a horizontal direction for one minute. The lower aqueous layer was discarded and the upper organic layer containing the pesticides was collected and washed twice with 25 ml deionized water. The extract was dried using a minimum amount of anhydrous sodium sulphate, and filtered. Then, the filtrate was concentrated to 5 ml with rotary evaporator under vacuum at 40ºC. The organic extracts were cleaned up prior to HPLC analysis using florisil cartridges, which were rinsed with 20 ml of n-hexane for conditioning. The sample was applied to the cartridge by syringe. Finally the analyte was eluted from the sorbent using 10 ml of a mixture of n-hexane and acetone in the ratio of 80:20.

Reagent and Standard

HPLC-grade acetonitrile, methanol, n-hexane, acetone and analytical grade sodiun sulfate and sodium chloride were obtained from BDH, (England). Water purified using Milli-Q Plus Sytem (Millipore, Bedford, MA, USA) was used for solution preparation. Fenitrothion pesticide standard was obtained from Allied Signal, (Riedle-deHaen, Germany).

HPLC Instrumentation

A Beckman HPLC system consisting of 114 multisolvent delivery system, programmable 165 variable wavelength detector, 7725i Rheodyne injector fitted with 20 µl-sample loop. The column was Ultraspere C-18, 5 µm, 250 × 4.6 mm, Beckman. The column effluent was monitored at 254 nm and 0.01 absorbency unit full scale. The mobile phase was composed of methanol-water (90:10) and the flow-rate was 1.0 ml/minute. The solvent used was of HPLC grade and filtered through 0.45 and 0.5 µm Millpore filter paper and degassed with Ultrasonic (Brasonic 2210 R- DTH) before using.

Results and Discussion

The dissipation of fenitrothion from the six plants is shown in Table 1. The initial concentration in the first day after spraying in ppm for fenitrothion on rocket, parsley, lettuce, fig, grape and guava are 2.017, 3.397, 0.4581, 0.7575, 2.303 and 19.40, respectively. Then decrease gradually reaching 0.2108 ppm after 12 days in rocket the percentage of losses being 89.55%. For parsley the final concentration is 0.4854 to reach 85.71% after 13 days. In lettuce the period of experiment is only 7 days that gives 76.01% of residue losses. On the other hand for the fruits the initial concentration in figs is 0.7575 ppm and the final concentration after 12 days is 0.0500 ppm and percentage losses is 93.39%. For grape the initial concentration is 2.3030 and the final concentration is 0.0287 ppm after 11 days and the pecentage losses is 98.75. Finally the guava has the highest initial concentration in the first day 19.40 ppm, while in the final day the concentration was 0.1474 ppm. Figure 1 shows the dissipation of fenitrothion in the six crops used in this study.

TABLE 1. The dissipation of fenitrothion from the six plants in ppm.

Day	Rocket	Parsley	Lettuce	Fig	Grape	Guava
1	2.017	3.397	0.4581	0.7575	2.303	19.40
2	1.635	3.231	0.4154	0.5666	0.8589	3.145
3	1.041	2.864	0.3995	0.4936	0.8209	2.226
4	1.019	2.233	0.2190	0.4687	0.6582	0.6754
5	0.849	1.926	0.1767	0.4414	0.6569	0.6782
6	0.844	1.319	0.1586	0.3539	0.4425	0.4140
7	0.6880	1.270	0.1099	0.3375	0.4184	0.0372
8	0.6875	1.254	–	0.3066	0.3916	0.3446
9	0.5975	1.154	–	0.2505	0.3265	0.2642
10	0.5281	0.794	–	0.2218	0.2590	0.1638
11	0.2787	0.788	–	0.0952	0.0287	0.1602
12	0.2108	0.7444	–	0.0500	–	0.1474
13	–	0.4854	–	–	–	–
% of loss	89.55%	85.71%	76.01%	93.39 %	98.75 %	99.24 %

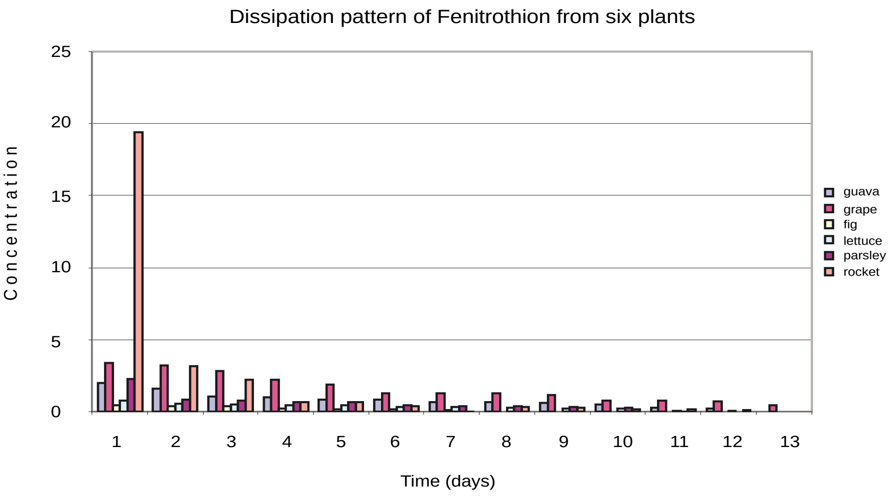

FIG. 1. Dissipation of fenitrothion residues in the six crops used in this study.

Solid-phase extraction reduced the analysis time and solvent consumption compared with traditional methods such as liquid-liquid extraction. The present data indicate that solid-phase extraction using florisil cartridges is capable of effecting rapid clean-up of fenitrothion from hexane extracts of vegetables and fruits. The peak areas of the monitoring fenitrothion on the chromatograms were measured, and the concentration of pesticide residue was determined from the calibration curve.

Conclusion

Periodic analysis of the treated vegetables and fruits over 7-13 days showed progressive dissipation especially in the first days. Sep-Pack solid-phase florisil cartridges were used for clean-up. Reversed-phase high performance liquid chromatography at wavelengh of 254 nm was used for the determination. The detection limit is 0.01 ppm. The period of study was suitable for dissipation of pesticide from crops to reach less than maximum residue limit permitted by Food Agriculture Organization (FAO) and World Health Organization(WHO)[16].

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تبدد بقايا الفينثرون في بعض الفواكه والخضراوات باستخدام الكروماتوجرافي السائل عالي الكفاءة

صالح عمر سعيد باحفي ، و فاتن محمد زيني ، و عبد الغني حمزه
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المستخلص. تم في هذ البحث وصف طريقة لتقدير تبدد بقايا مبيد الفينثرون في بعض الفواكه والخضراوات باستخدام جهاز الكرماتوجرافي السائل عالي الكفاءة. حيث ترش المحاصيل بمحلول مخفف من مبيد الفينثرون ثم تقطف جزئيا بعد يوم واحد من بداية الرش، وتستمر عملية القطف لمدة تتراوح من ٧ إلى ١٣ يوم. يستخلص المحصول بمذيب الأسيتونيتريل ، ويتم توزيع المبيد بمذيب الهكسان العادي ، ثم يمرر الهكسان على أنابيب صغيرة تحتوي على الفلورسيل الصلب ، وذلك لتنقيتها من الشوائب. تجرى عملية التحليل باستخدام جهاز الكروماتوجرافي السائل عالي الكفاءة باستخدام تقنية الطور العكسي ، حيث يتكون وسطه المتحرك من٩٠٪ ميثانول :١٠٪ ماء . وقد وجد أن حد الكشف للجهاز ٠,٠١ مليجرام / كجم. ووجد أن نسبة الفقد للمبيد في الفواكه والخضراوات هي ٨٩,٥٥ ، و٨٥,٧١ ، و٧٦,٠١ ، و٩٣,٣٩ ، و ٩٨,٧٥ ، و ٩٩,٢٤ في الجرجير و البقدونس والخس والتين والعنب والجوافة على التوالي .

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Synthesis of 4-Pyrazolylmethylidene-2-Oxazoline and -2-Imidazoline Derivatives

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ABSTRACT. 4-Formyl-2-pyrazolin-5-ones **(1a,b)** is condensed with hippuric acid derivatives **(2a,b)** to give the corresponding pyrazolylmethylidene azalactones **(3a-d)**. Aminolysis of oxazolones **(3)** with aromatic amines in boiling acetic acid afforded imidazolones **(4a-l)**. Treatment of oxazolones **(3)** with benzene in the presence of $AlCl_3$ afforded α-benzamidoacetophenone **(5)**. Structural assignments of the new products were based on elemental analysis and IR, ^1H NMR spectral data.

Introduction

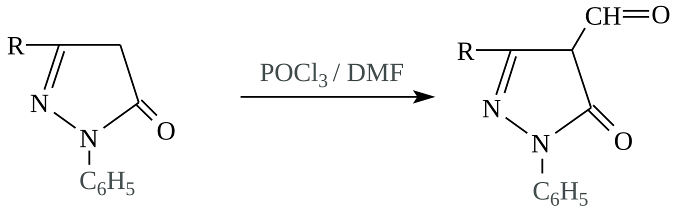
It was reported that pyrazolone derivatives are used as biologically active compounds such as drugs, agrochemicals, antibacterial[1], antifungal[2] microbicides and herbicides[3] in addition to the well-known antipyretic and anti-inflammatory effects.

The synthesis and reactions of some new pyrazolylmethylidene oxazolones **(3)** is reported here with the hope that they may add some new biological activity to the reported ones[1-3].

Results and Discussion

Vilsmeyer formylation of 3-substituted-1-phenyl-2-pyrazolin-5-ones with $POCl_3$/DMF mixture yielded the corresponding 4-formyl-2-pyrazolin-5-one derivatives **(1a,b)**[4-6], which are condensed with N-(4-substituted) benzoylglycines **(2a,b)** in hot acetic anhydride- sodium acetate mixture[7] to give the corresponding 2-aryl-4-(5-hydroxy-1-phenyl-3-substituted-pyrazol-4-yl) methylidene-2-oxazolin-5-ones **(3a-d)**.

The IR spectra of azalactones **(3)** displayed an absorption bands in the regions 3430 – 3410 cm^{-1} (ν_{OH} broad enolic OH of pyrazolones), 1815 – 1775 cm^{-1} ($\nu_{C=O}$ of 5-oxazolones), 1665 – 1645 cm^{-1} ($\nu_{C=O}$ of 5-pyrazolones) and 1605 – 1595 cm^{-1} ($\nu_{C=C}$ or $\nu_{C=N}$). which confirmed their existence in keto-enol tautomeric mixture.



(1)

1 R = CH_3 or C_6H_5

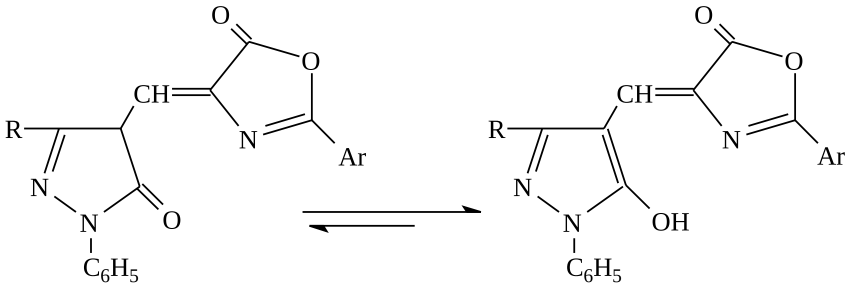
a) R = CH_3 ; **b)** R = C_6H_5

$$\mathbf{1(a,b)} + \begin{array}{l} CH_2\text{—}COOH \\ | \\ NHCOAr \end{array} \xrightarrow[CH_3COONa]{Ac_2O}$$

(2)

a) Ar = $C_6H_4OCH_3$ -4

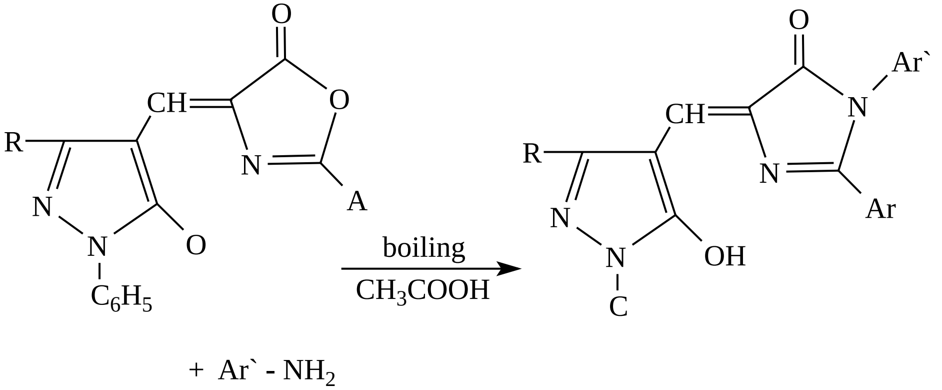
b) Ar = C_2H_4Cl -4



(3)

	R	Ar
a)	CH_3	$C_6H_4OCH_3$-4
b)	C_6H_5	$C_6H_4OCH_3$-4
c)	CH_3	C_6H_4Cl-4
d)	C_6H_5	C_6H_4Cl-4

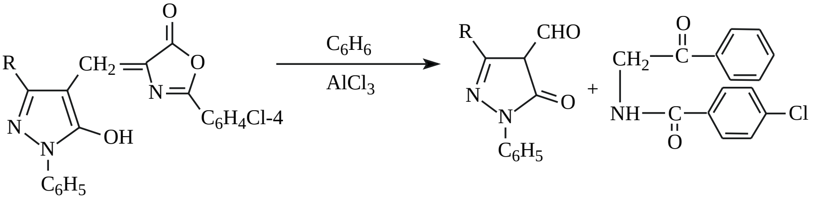
Aminolysis of **(3)** with primary aromatic amines, namely, aniline, p-anisidine, and p-chloroaniline in boiling acetic acid yielded 1,2-diaryl-4-(5-hydroxy-1-phenyl-3-substituted-pyrazol-4-yl) methylidene-2-imidazoline-5-ones **(4a-l)** respectively. The infrared spectra of imidazolones **(4)** showed absorption bands in the regions 3430-3425 cm^{-1} (ν_{OH} broad enolic OH), 1730 – 1710 cm^{-1} ($\nu_{C=O}$ of imidazolones), 1670 – 1645 cm^{-1} ($\nu_{C=O}$ of 5- pyrazolones) and 1610 – 1590 cm^{-1} ($\nu_{C=C}$ or $\nu_{C=N}$).



(3) **(4)**

	R	Ar	Ar`
a)	CH_3	$C_6H_4OCH_3$-4	C_6H_5
b)	CH_3	$C_6H_4OCH_3$-4	$C_6H_4OCH_3$-4
c)	CH_3	$C_6H_4OCH_3$-4	C_6H_4Cl-4
d)	CH_3	C_6H_4Cl-4	C_6H_5
e)	CH_3	C_6H_4Cl-4	$C_6H_4OCH_3$-4
f)	CH_3	C_6H_4Cl-4	C_6H_4Cl-4
g)	C_6H_5	$C_6H_4OCH_3$-4	C_6H_5
h)	C_6H_5	$C_6H_4OCH_3$-4	$C_6H_4OCH_3$-4
i)	C_6H_5	$C_6H_4OCH_3$-4	C_6H_4Cl-4
j)	C_6H_5	C_6H_4Cl-4	C_6H_5
k)	C_6H_5	C_6H_4Cl-4	$C_6H_4OCH_3$-4
l)	C_6H_5	C_6H_4Cl-4	$C6H_4Cl$-4

Friedel-Crafts reaction of oxazolones **(3c,d)** with benzene in the presence of anhydrous $AlCl_3$ proceeds via depyrazolation and ring opening of oxazolone ring to give a mixture of 4-formyl-2-pyrazolin-5-ones **(1a,b)** and α-(4-chloro) benzamidoacetophenone **(5)**. The infrared spectrum of acetophenone derivatives **(5)** displayed bands at 3360 cm^{-1} (ν_{NH}), 3060 – 2970 cm^{-1} (ν_{CH} aliphatic) 1705 cm^{-1} ($\nu_{C=O}$ ketone) and 1660 cm^{-1} ($\nu_{C=O}$ amide).



(3) **(1)** **(5)**

Experimental

All melting points are not corrected. The IR absorption spectra were measured on a Nicolet Magna 520 FT IR spectrophotometer using KBr Water technique. ^{1}H-NMR were recorded in δ (ppm) on a Brucker DPX 400 MHz spectrometer using TMS as internal standard. The micro-elemental analyses were carried out using a Perkin Elmer 240 B analyzer.

2-Aryl-4-(5-Hydroxy-1-Phenyl-3-Substituted Pyrazol-4-yl)Methylidene-2-Oxazolin-5-Ones (3a-d)

An equimolar mixture of 4-formy-1-phenyl-3-substituted-2-pyrazoliin-5-one (**1a,b**; 0.01 mol), finely powdered N-(4-substituted)benzoylglycine (**2a,b**; 0.01 mol) and anhydrous sodium acetate (0.05 mol) in acetic anhydride (20 ml) was heated on steam-bath for 3 h, cooled and ethanol (20 ml) was added. The mixture was kept 12 h at room temperature.

The solid product which separated was filtered, washed successively with water (3 × 50 ml), dried and recrystallized from acetic acid to give the corresponding azalactones **(3)** as yellow crystals. The results are listed in Table 1.

TABLE 1. The physical data of oxazolones **(3a-d)**.

Compound	m.p °C	Yield % %	Mol. formula (m. wt)	Analysis % calculated/found		
				C	H	N
3a*	241	83	$C_{21}H_{17}N_3O_4$	67.20	4.53	11.20
			(375)	67.06	4.47	11.03
3b	249	80	$C_{26}H_{19}N_3O_4$	73.39	4.35	9.61
			(437)	71.21	4.29	9.48
3c	232	79	$C_{20}H_{14}N_3O_3Cl$	63.24	3.69	11.07
			(379.5)	63.07	3.73	10.91
3d**	254	81	$C_{25}H_{16}N_3O_3Cl$	67.95	3.62	9.51
			(441.5)	67.74	3.55	9.28

*PMR ($CDCl_3$); δ (ppm): 1.48 (s, 1H, enolic OH), 2.67 (s, 3H, CH_3), 3.76 (s, 3H, OCH_3), 7.03 (s, 1H, C_4-CH=), 7.13-7.38 (m, 9H, Ar-H).

**PMR ($CDCl_3$); δ (ppm): 1.53 (s, 1H, enolic OH), 6.87(s, 1H, C_4-CH=), 7.18-7.43 (m, 14H, Ar-H).

1,2-Diaryl-4-(5-Hydroxy-1-Phenyl-3-Substituted Pyrazol-4-yl)Methylidene-2-Imidazolin-5-Ones (4a-l).

A solution of oxazolones (**3,** 0.01 mol) and primary aromatic amines, namely, aniline, p-anisidine or p-chloroaniline (0.01 mol) in glacial acetic acid (50 ml) was refluxed for 5 h. The solid which separated after concentration and cooling was filtered and recrystallized from acetic acid to give the corresponding pyrazolylmethylideneimidazolones **(4a-l)** as yellow crystals. The results are listed in Table 2.

TABLE 2. The physical data of benzamidoacrylamides (4a-l)

Compound	m.p °C	Yield % %	Mol. formula (m. wt)	Analysis % calculated/found C	H	N
4a*	212	63	$C_{27}H_{22}N_4O_3$	72.00	4.88	12.44
			(450)	71.85	4.79	12.37
4b	209	65	$C_{28}H_{24}N_4O_4$	70.00	5.00	11.66
			(480)	69.86	4.94	11.57
4c	215	61	$C_{27}H_{21}ClN_4O_3$	66.87	4.33	11.55
			(484.5)	66.75	4.27	11.40
4d***	218	68	$C_{26}H_{19}ClN_4O_2$	68.64	4.18	12.32
			(484.5)	68.53	4.08	12.19
4e	222	64	$C_{27}H_{21}ClN_4O_3$	66.87	4.33	11.55
			(484.5)	66.81	4.28	11.47
4f	226	68	$C_{26}H_{18}Cl_2N_4O_2$	63.93	3.68	11.47
			(489)	63.82	3.61	11.33
4g	235	58	$C_{32}H_{24}N_4O_3$	75.00	4.68	10.93
			(512)	74.87	4.62	10.78
4h***	231	61	$C_{33}H_{26}N_4O_4$	73.06	4.79	10.33
			(542)	73.38	4.71	10.26
4I	241	57	$C_{32}H_{23}ClN_4O_3$	70.26	4.20	10.24
			(546.5)	70.11	4.17	10.13
4j	232	63	$C_{31}H_{21}ClN_4O_2$	72.02	4.06	10.86
			(516.5)	71.88	4.00	10.73
4k+*	219	66	$C_{32}H_{23}ClN_4O_3$	70.26	4.20	10.24
			(546.5)	70.11	4.13	10.05
4l	225	68	$C_{31}H_{20}Cl_2N_4O_2$	67.51	3.63	10.18
			(551)	67.38	3.55	10.03

*PMR ($CDCl_3$); δ(ppm): 1.46 (s, 1H, enolic OH). 2.50 (s, 3H, CH_3), 3.65 (s, 3H, OCH_3), 6.58 (s, 1H, CH =), 7.18-7.57 (m, 14H, Ar-H).

**PMR (DMSO); δ (ppm): 1.53 (s, 1H, enolic OH), 2.67 (s, 3H, CH_3), 6.43 (s, 1H, CH =), 7.21-7.53 (m, 14H, Ar-H).

***PMR (DMSO); δ (ppm): 1.47 (s, 1H, enolic OH), 3.68 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 6.42 (s, 1H, CH =), 7.13-7.48 (m, 18H, Ar-H).

+*PMR (DMSO); δ(ppm): 1.58 (s, 1H, enolic OH). 3.72 (s, 3H, OCH_3), 6.37 (s, 1H, CH =), 7.18-7.47 (m, 18H, Ar-H).

α-(4-Chloro)Benzamidoacetophenone (5)

A solution of azlactones (**3c,d,** 1.0 g), anhydrous $AlCl_3$ (3 g) in dry benzene (50 ml) was stirred at room temperature for 1 h. Then under reflux for 3 h and left overnight at room temperature. The solution was poured onto ice (100 g) containing Conc. HCl (2.0 ml). The organic layer was separated, washed with water (3 × 50 ml), and dried over anhydrous Na_2SO_4. The oil residue which separated after evaporation of benzene was triturated with hot petroleum ether (60-80ºC) to give benzamidoacetophenone **(5)** as colourless crystals, while the left residue was recrystallized from ethanol to give 4-formyl pyrazolone **(1a,b)**[4-6]. α-(4-Chloro)benzamidoacetophenone **(5)**, m.p 156ºC, $C_{15}H_{12}ClNO_2$ (273.5); calculated, C,65.81; H, 4.39; N, 5.12; found; C, 65.70; H, 4.30; N, 5.01. ^1H NMR ($CDCl_3$); δ (ppm): 2.72 (s, 1H, N<u>H</u>), 4.72 (s, 2H, CH2) and 7.14-7.42 (m, 9H, Ar-<u>H</u>).

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تحضير مشتقات ٤-بيرازولايل ميثيليدين -٢-أوكسازولين و-٢-إيميدازولين

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جدة - المملكة العربية السعودية

المستخلص. تم في هذا البحث تكاثف مركبات ٤-فورمايل-٢-بيرازولين-٥-أون (1a,b) مع مشتقات حمض الهيبيوريك (2a,b) لتعطي مركبات بيرازولايل ميثيليدين أزا لاكتون (3a-d). التحلل الأميني لمركبات الآزا لاكتون (٣) مع أمينات عطرية في حمض الخل عند الغليان أدى إلى تكوين مركبات ايميدازولون (4a-l) ، كما أدت معالجة مركبات الآزا لاكتون (٣) بالبنزين في وجود كلوريد الألمنيوم الجاف إلى تكون مركبات ألفا بنزاميدو أسيتوفينون (٥). تم التعرف على تركيب النواتج الجديدة من خلال تحليل العناصر، وأطياف الأشعة تحت الحمراء والرنين النووي المغناطيسي للبروتون.

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2-Pentyne Complexes of Molybdenum (II) and Tungsten (II)

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ABSTRACT. Treatment of $[MI_2(CO)_3(NCMe)_2]$(M = Mo, W) with two equivalents of EtC_2Me in CH_2Cl_2 at 0C° yields the bis (2-Pentyne) complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$ (1 and 2). complexes. 1 and 2 react with two equivalents of PPh_3 in CH_2Cl_2 to give the complexes $[MI_2 (CO) (PPh_3)_2 (\eta^2\text{-}EtC_2Me)]$ (3 and 4).

Reaction of 1 and 2 with an equimolar amount of $Ph_2P (CH_2)_n PPh_2$ to give $[MI_2(CO)\{(Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}EtC_2Me)]$ (for M = MO, W; n = 1-4) (5-12).

Introduction

The ability of alkyne ligands to act as four-electron donor ligands to transition-metal centers has been well illustrated in the alkyne complexes of molybdenum (II) and tungsten (II)[1,2]. Although a number of 2-butyne, methyl propyne, phenylacetylene and related alkyne complexes of molybdenum (II) and tungsten (II) have been prepared[3-20].

Recently, many 3-hexyne derivatives have been reported[21-26] these include the dimeric tungsten complex $[\{W(\mu\text{-}Br)Br(CO) (\eta^2\text{-}EtC_2Et)_2\}_2]$[21]; molybdenum dichloro and dibromophosphine complexes $[MoX_2 (CO) L_2(\eta^2\text{-}EtC_2Et)]$ (X = Cl, L = PPh_3, X = Br, L = PEt_3, PPh_3, X = Cl, Br, L_2 = dppe)[22] and the bis (dially dithiocarbamate) complexes $[Mo(CO) (S_2CNEt_2)_2(\eta^2\text{-}EtC_2\text{-}Et)]$[23] and $[Mo(\eta^2\text{-}PhC_2H) (\eta^2\text{-}EtC_2Et) (S_2CNMe_2)_2]$[24].

In 1988, Baker and others reported the synthesis and x-ray crystal structures of the tungsten bis (alkyne) complexes $[WI_2(CO) (NCMe) (\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph), and also described the synthesis and crystal structures of the related molybdenum complexes $[MoI_2 (CO) (NCMe) (\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph)[25]. The chemistry of $[MI_2(CO) (NCMe) (\eta^2\text{-}RC_2R)_2]$ (M = Mo, W; R = Me, Ph) with both neutral and anionic ligands has been studied in details[27].

In 1999, crystal structures of $[WI_2(CO) (PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ and $[WI_2(CO) \{Ph_2P(CH_2)_3PPh_2\} (\eta^2\text{-}EtC_2Et)]$ was determined and investigated[28].

In 2000, Mutlaq and others synthesized many derivatives of 3-hexyne complexes including phosphines and phosphates groups with some crystal structures[29-31]. P.K. Baker *et. al* prepared the nitrile exchanged products, $[WI (CO)L\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)] [BPh_4]$ from reaction of $[WI(CO) (NCMe)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)] [BPh_4]$ and L{L = Net, NC^iPr, NC^tBu, NCPh, $NCCH_2Ph$, 1,2-$C_6H_4(NCCH_2)_2$, $NCCH_2(C_4H_3S\text{-}3)$}; and the complexes for L = NC^iPr, NC^tBu, $NCCH_2Ph$, 1,2-C_6H_4 $(NCCH_2)_2$ have all been crystallographically characterized[32].

In 2003, Oktay and others, reacted pentacarbonyl (η^2-bis(trimethylsilyl) ethyne) tungsten(0), $[W(CO)_5(\eta^2\text{-btmse})]$ with tricycle hexylphosphine PCy_3 to yield two stable endoproducts which could be isolated and fully characterized by using the single crystal x-ray diffractometry[33].

In this paper we described the first 2-Pentyne diiodo complexes $[MI_2 (CO) (NCMe) (\eta^2\text{-}EtC_2Me)_2]$ (M = Mo, W) and their reactions with phosphine groups.

Experimental

Physical Measurements and Instruments

Elemental analysis (C, H and N) were determined by department of chemistry, King Abdulaziz University of Jeddah. Using a Carlo Erba Elemental Analysis MOD 1108 (Using helium as carrier gas). Infrared spectra were obtained by $CHCl_3$ films between NaCl plates and recorded on a Perkin-Elmer 1430 ratio recording IR spectrophotometer.

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC 500 MH_z NMR spectrometer. ^1H and ^{13}C NMR spectra were referenced to $SiMe_4$, whereas ^{31}P NMR spectra were referenced to 85% H_3PO_4.

Reagents and Materials

All reactions and purifications were carried out under an atmosphere of dry nitrogen using standard vacuum/chlenk line techniques. The complexes $[MI_2 (CO)_3 (NCMe)_2]$ (M = Mo,W), were prepared by the published method[27]. All solvents and chemicals used were of reagents grade quality and were purchased from commercial sources. The solvents used were dried and distilled before use.

Preparation of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$ (1)

To a stirred solution of $[MoI_2(CO)_3 (NCMe)_2]$ (0.5 g, 0.96 mmol) in 25 ml of CH_2Cl_2 at 0ºC 2-Pentyne (0.13 g, 0.20 ml, 1.9 mmol) was added. The solution was stirred at room temperature for 24 h. Filtration and removal of the solvent in vacuum gave crystalline powder which was recrystallized from dichloromethane and diethyl ether giving pure $[MoI_2(CO) (NCMe)(\eta^2\text{-}EtC_2Me)_2]$ (Yield = 0.35 g, 0.66%).

In a similar reaction of $[WI_2(CO)_3(NCMe)_2]$ with two equivalents of 2-Pentyne in CH_2Cl_2 at 0ºC gave the bis(2-Pentyne) complex $[WI_2(CO) (NCMe) (\eta^2\text{-}EtC_2Me)_2]$ (2). See Table 1 for physical and analytical data .

TABLE 1. Physical and analytical data[a] for 2-Pentyne complexes. 1-12.

Compound no.	Colour	Yield %	Analytical data found (calcd)		
			C	H	N
$[MoI_2(CO) (NCMe) (\eta^2\text{-}EtC_2Me)_2]$ (1)	Brown	66	27.9 (28.1)	3.2 (3.4)	2.1 (2.5)
$[WI_2(CO) (NCMe) (\eta^2\text{-}EtC_2Me)_2]$ (2)	Yellow	72	24.6 (24.3)	3.1 (2.9)	2.4 (2.2)
$[MoI_2(CO) (PPh_3)_2 (\eta^2\text{-}EtC_2Me)]$ (3)	Green	66	51.2 (51.6)	4.3 (4.5)	
$[WI_2(CO) (PPh_3)\ 2(\eta^2\text{-}EtC_2Me)]$ (4)	Green	72	47.1 (47.3)	3.9 (4.1)	
$[MoI_2(CO) \{Ph_2P(CH_2)PPh_2\} (\eta^2\text{-}EtC_2Me)]$ (5)	Green	55	47.8 (48.1)	4.2 (4.4)	
$[WI_2(CO) \{Ph_2P(CH_2)PPh_2\} (\eta^2\text{-}EtC_2Me)]$ (6)	Green	48	43.3 (43.0)	4.1 (3.9)	
$[MoI_2(CO) \{Ph_2P(CH_2)_2PPh_2\} (\eta^2\text{-}EtC_2Me)]$ (7)	Green	57	48.6 (48.8)	4.1 (4.5)	
$[WI_2(CO) \{Ph_2P(CH_2)_2PPh_2\} (\eta^2\text{-}EtC_2Me)]$ (8)	Green	43	44.1 (43.9)	4.3 (4.1)	
$[MoI_2(CO) \{Ph_2P(CH_2)_3PPh_2\} (\eta^2\text{-}EtC_2Me)]$ (9)	Green	61	49.7 (49.5)	4.9 (4.7)	
$[WI_2(CO) \{Ph_2P(CH_2)_3PPh_2\} (\eta^2\text{-}EtC_2Me)]$ (10)	Green	36	44.8 (44.6)	4.3 (4.2)	
$[MoI_2(CO) \{Ph_2P(CH_2)_4PPh_2\} (\eta^2\text{-}EtC_2Me)]$ (11)	Green	52	49.8 (50.1)	4.6 (4.9)	
$[WI_2(CO) Ph_2P(CH_2)_4PPh_2\} (\eta^2\text{-}EtC_2Me)]$ (12)	Green	39	45.4 (45.2)	4.7 (4.4)	

[a] Calculated values in parentheses.

Preparation of [MoI$_2$(CO)(PPh$_3$)2(η^2-EtC$_2$Me)] (3)

To a stirred solution of [MoI$_2$(CO) (NCMe) (η^2-EtC$_2$Me)$_2$] (0.2 g, 0.36 mmol) in CH$_2$Cl$_2$ (20 cm^3) PPh$_3$ (0.19 g, 0.7 mmol) was added for 48 h, then filtration and removal of solvent in vacuum yielded a brown crystalline powder which was recrystallised from CH$_2$Cl$_2$/Et$_2$O to give pure [MoI$_2$(CO) (PPh$_3$)$_2$(η^2-EtC$_2$Me)](3); (yield = 0.23 g, 66%). A similar reaction of (WI$_2$(CO)(NCMe) (η^2-EtC$_2$Me)$_2$] with two equivalents of PPh$_3$ in CH$_2$Cl$_2$ at room temperature gave the complex [WI$_2$(CO) (PPh$_3$)$_2$(η^2-EtC$_2$Me)] (4). See table 1 for physical and analytical data.

Preparation of [MoI$_2$(CO){Ph$_2$P(CH$_2$)PPh$_2$}(η^2-EtC$_2$Me)] (5)

To a stirred solution of [MoI$_2$(CO) (NCMe) (η^2-EtC$_2$Me)$_2$] (0.2 g, 0.36 mmol) in CH$_2$Cl$_2$ (15 cm^3) Ph$_2$P(CH$_2$)PPh$_2$. (0.14 g, 0.36 mmol) was added. After 24 h filtration and removal of solvent in vacuum gave a crystalline powder of [MI$_2$(CO){Ph$_2$P(CH$_2$)PPh$_2$}(η^2-EtC$_2$Me)] (5) (yield = 0.15 g, 55%).

Similar reactions of equimolar quantities of [MI$_2$(CO)(NCMe)(η^2-EtC$_2$Me)$_2$] and Ph$_2$P(CH$_2$)$_n$PPh$_2$ in CH$_2$Cl$_2$ at room temperature gave the complexes (M = Mo, n = 2-4; M = W, n = 1-4) (6-12). See table 1 for physical and analytical data (6-12).

Results and Discussion

The starting materials used in this research [MI$_2$(CO)$_3$(NCMe)$_2$] (M = Mo,W) were prepared by treating the zero-valent complexes *fac*-[M(CO)$_3$(NCMe)$_3$] (prepared *in situ*) with one equivalent of I$_2$ at 0ºC[27]. Reaction of [MI$_2$(CO)$_3$ (NCMe)$_2$] (M = Mo,W) with two equivalents of EtC$_2$Me in CH$_2$Cl$_2$ at room temperature gave good yields of the bis (2-Pentyne) complexes [MI$_2$(CO) (NCMe)(η^2-EtC$_2$Me)$_2$] (1 and 2).

Both complexes 1 and 2 were characterized by elemental analysis (C, H and N) (Table 1), I R (Table 2) and ^{1}HNMR spectroscopy (Table 3).

Both complexes are air-sensitive in solution, but can be stored under nitrogen or argon in the solid state for an indefinite period. The complexes are very soluble in polar organic solvents such as CH$_2$Cl$_2$ and CHCl$_3$, but only slightly soluble in diethyl ether.

The IR spectra for 1 and 2 show carbonyl stretching bands at ν(C $\equiv$ O) = 2053 and 2057 cm^{-1} respectively. These are in very similar positions to their related 3-Hexyne derivatives [MI$_2$(CO) (NCMe) (η^2-EtC$_2$Et)$_2$] {ν(C $\equiv$ O) = 2059 and 2056 cm^{-1} for M = Mo and W respectively}[28] and also similar to 2-butyne derivatives $[MI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ {$\nu(C \equiv O) = 2061\ cm^{-1}$ and 2050 cm^{-1} for M = Mo and W respectively}[2,25].

The nitrile bands $\nu(C \equiv N)$ at 2289 and 2256 cm^{-1} respectively, where the an acetonitrile is acting as a σ-donor ligand[34], and the weak alkyne stretching bands at 1609 and 1629 cm^{-1} for 1 and 2 are lower than for the uncoordinated alkyne which is expected since there is back-donation of electron density from filled metal d-orbitals to empty π*-orbitals on the 2-pentyne ligands. The structure of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$ is very likely the structure as shown in Fig. (1).

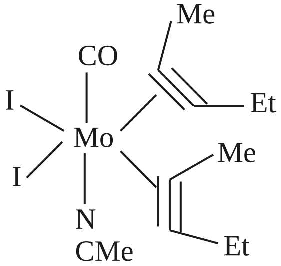

FIG. 1. Proposed structures of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$ (1and 2).

Since the spectroscopic properties are closely related to the previously reported bis (alkyne) complexes of molybdenum (II) and tungsten (II)[1,2,25,35,36]. The ^{1}HNMR spectra of 1 and 2 show two different sets of CH_2 groups, which confirmed the structure shown in Fig. 1. At room temperature ^{13}CNMR spectra of 1 and 2 show alkyne carbon contact resonance at $\delta = 175.12$ and 167.35 (for 1) and 161.30 and 172.45 (for 2) .

The resonances observed for complexes 1 and 2 are in accord with two alkynes donating a total of four electrons to the metal centre, which also enables the complexes to obey the effective atomic number rule .

Treatment of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Me)_2]$ (M = Mo, W) with two equivalents of PPh_3 in CH_2Cl_2 at room temperature gives the complexes $[MI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Me)]$ (3 and 4).

Complexes 3 and 4 have also been characterized by elemental analysis (Table 1); IR (Table 2), ^{1}HNMR (Table 3) and ^{31}P.NMR spectroscopy (Table 4).

Complexes 3 and 4 are more stable in solution, but very much less soluble than bis (2-Pentyne) complexes (1 and 2). They are slightly soluble in CH_2Cl_2 and $CHCl_3$. Hence, it was difficult to obtain the ^{13}CNMR spectra.

TABLE 2. Infrared data[a] for 2-Pentyne complexes 1-12.

Compound no.	$\nu(C \equiv O)$ cm^{-1}	$\nu(C \equiv N)$ cm^{-1}	$\nu(C \equiv C)$ cm^{-1}
(1)	2053(s)	2289(w)	1609(w)
(2)	2057(s)	2256(w)	1629(w)
(3)	1951(s)	1951(s)	1665(2)
(4)	1940(s)	–	1656(w)
(5)	1943(s)	–	1659(w)
(6)	1932(s)	–	1607(w)
(7)	1933(s)	–	1653(w)
(8)	1942(s)	–	1655(w)
(9)	1935(s)	–	1640(w)
(10)	1935(s)	–	1637(w)
(11)	1936(s)	–	1656(w)
(12)	1929(s)	–	1653(w)

[a]spectra recorded in CHCl3 as thin films between NaCl plates;
S = strong, W = weak.

TABLE 3. ^1H NMR data for selected 2-Pentyne complexes.

Complex no.	^1H NMR (δ) ppm
(1)	3.2-3.4 (m, 2H, $C \equiv C\ CH_2$; 2.8-3.1 (br, m, 2H, CH_2); 2.70 (S, 3H, $NC\ CH_3$); 2.5 (S, 3H, $CH_3\text{-}C \equiv C$); 1.1- 1.3(t, 6H, $CH_3\ CH_2$).
(2)	3.1-3.4 (m, 2H, CH_2); 2.9-3.15 (m, 2H, CH_2); 2.8(S, 3H, $NCCH_3$); 2.5 (S, 6H, $CH_3\text{-}C \equiv C$); 1.3 (t, 6H, CH_3CH_2).
(3)	7.0-7.65 (br, m, 30H, Ph); 2.6-3.4 (br, m, 2H, CH_2); 1.6-2.5 (S, 3H, CH_3); 0.8-1.3 (t, 3H, CH_2CH_3).
(4)	7.1-7.6 (br, m, 30H, Ph); 2.5-3.4 (br, m, 2H, CH_2); 1.5-2.5 (S, 3H, CH_3); 0.7-1.2 (t, 3H, CH_2CH_3).
(5)	6.9-7.3 (br, m, 20H, Ph); 4.5-4.8 (q, 2H, $Ph.P\text{-}CH_2$); 3.6-3.6 (q, 2H, CH_2); 2.9-3.1 (S, 3H, CH_3); 1.0-1.25 (t, 3H, CH_3CH_2).
(6)	6.8-7.2 (br, m, 20H, Ph); 4.4-4.7 (q, 2H, $PhP\text{-}CH_2$); 3.4-3.7 (q, 2H, CH_2); 2.9-3.2 (S, 3H, CH_3); 1.1-1.2 (t, 3H, CH_3CH_2).
(7)	6.9-7.3 (br, m, 20H, Ph); 4.4-4.6 (br, m, 4H, Ph.P, CH_2CH_2); 3.3-3.7 (q, 2H, CH_2); 2.8-3.2 (S, 3H, CH_3); 1.2-1.3(t, 3H, CH_3CH_2).
(8)	7.1-7.8 (br, m, 20H, Ph); 4.3-4.5 (br, m, 4H, PhP, $CH_2\ \underline{CH_2}$); 3.2-3.6 (q, 2H, CH_2); 2.5-3.1 (S, 3H, CH_3); 1.3-1.4 (t, 3H, CH_3CH_2).
(9)	7.3-7.9 (m, 20H, Ph); 3.4-3.6 (q, 2H, $C \equiv C\ CH_2$); 3.4 (br, m, 4H, Ph_2PCH_2); 2.6 (S, 3H, $C \equiv C\ CH_3$); 1.2 (t, 3H, CH_3); 0.9-1.1 (br, m, 2H, $Ph_2PCH_2\ \underline{CH_2}$).

TABLE 3. Contd.

Complex no.	^1H NMR (δ) ppm
(10)	7.4-8.0 (m, 20H, Ph); 3.5-3.7 (q, 2H, $C \equiv C\ CH_2$); 3.1-3.3 (br, m, 4H, Ph_2PCH_2); 2.7 (S, 3H, $C \equiv C\ CH_3$); 1.3 (t, 3H, CH_3); 0.8-1.1 (br, m, 2H, $Ph_2PCH_2\ \underline{CH_2}$).
(11)	7.1-7.8 (br, m, 20H, Ph); 3.3-3.5 (m, 2H, Ph_2PCH_2); 3.2 (q, 2H, $C \equiv C\ CH_2$) 2.6-2.9 (br, m, 4H, $Ph_2PCH_2\ \underline{CH_2}$); 2.4 (S, 3H, $C \equiv C\text{-}CH_3$); 1.0-1.3 (t, 3H, $C \equiv C\text{-}CH_2\ CH_3$).
(12)	7.2-8.0 (br, m, 20H, Ph); 3.2-3.5 (m, 4H, $PhPCH_2$); 3.3 (q, 2H, $C \equiv C\ \underline{CH_2}$); 2.7-3.0 (br, m, 4H, $Ph_2PCH_2\ \underline{CH_2}$); 2.3 (S, 3H, $C \equiv C\text{-}\underline{CH_3}$); 1.1-1.35 (t, 3H, $C \equiv C\ CH_2\ \underline{CH_3}$).

^{a}spectra recorded in $CDCl^3$ (25°C) and referenced to $SiMe_4$;
S = Singlet; br = broad; d = doublet; m = multiplet; t = triplet; q = quartet.

TABLE 4. ^{13}C NMR data^a (δ) for selected 2-Pentyne complexes.

Complex no.	^{13}C NMR (δ) ppm
(1)	6.65 S, CH_3, CN); 12.36, 12.80, 13.4, 14.23, 14.57, (S, $CH_2\underline{CH_3}$); 16.7, 17.53, 17.85 (S, $\underline{CH_3}$. $C \equiv C$); 24.60, 27.32 (S, CH_2); 129.85 (S, $C \equiv N$); 165.36, 173.2 (S, $C \equiv C$); 216.08 (S, $C \equiv O$).
(2)	5.7 (S, CH_3, CN); 12.6, 12.76, 13.06, 13.9, 14.2 (S, $CH_2\ \underline{CH_3}$); 16.3, 16.7, 17.02 (S, CH_3. $C \equiv C$); 25.3, 26.7 (S, CH_2); 128.50 (S, $C \equiv N$); 163.62, 172.15 (S, $C \equiv C$); 210.03 (S, $C \equiv O$).

^{A}spectra recorded in $CDCl_3$ (25°C) and referenced to $SiMe_4$.
S = Singlet.

The IR and ^{1}HNMR spectral properties of 3 and 4 are similar to their 3-hexyne and 2-butyne tungsten and molybdenum analogue, $[MI_2(CO)\ (PPh_3)_2\ (\eta^2\text{-}MeC_2Me)]$[35] and $[MI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$[28]; which have a carbonyl stretching band at 1951 and 1940 cm^{-1} in the same solvent for (M = Mo and W) respectively.

The ^{31}PNMR spectra for 3 and 4 have single resonances at $\delta = -2.56$ and -13.36 respectively; similar to complexes of 3-hexyne which exhibit resonances at $\delta = -2.89$ and -15.93 respectively. This suggests a trans arrangement of PPh_3 ligands[28].

Equimolar quantities of $[MI_2(CO)\ (NCMe)\ (\eta^2\text{-}EtC_2Me)_2]$ (M = Mo, W) and $Ph_2P(CH_2)_nPPh_2$; (n = 1-4) react in CH_2Cl_2 at room temperature to yield the mono (2-Pentyne) complexes $[MI_2 (CO) Ph_2P(CH_2)_nPPh_2\} (\eta^2\text{-}EtC_2Me)]$ (5-12) were fully characterized (See Tables 1 to 4).

They are intermediate in solubility between 1,2 and 3,4 and similar in sensitive to air as the previous complexes .

The colours and spectroscopic properties resemble that to 3-hexyne complexes $[MI_2 (CO)\{Ph_2P(CH_2)_nPPh_2\} (\eta^2\text{-}EtC_2Et)]$[28] as well as for 2-butyne $[MI_2 (CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}MeC_2Me)]$[37].

The ^{31}PNMR spectra of $[MI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}EtC_2Me)]$ (n = 1-4) have two resonances (Table 5) expected for a single isomer from crystal structure of $[WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\} (\eta^2\text{-}EtC_2Et)]$[28].

TABLE 5. ^{31}P NMR data[a] (δ) for selected 2-Pentyne complexes.

Complex no.	^{31}P NMR (δ) ppm
(3)	δ (P) = – 2.56
(4)	δ (P) = –13.36
(6)	$\delta (P_A) = -24.36$; $\delta (P_B) = -35.27$
(9)	$\delta (P_A) = -27.72$; $\delta (P_B) = -36.75$
(10)	$\delta (P_A) = -22.85$; $\delta (P_B) = -31.24$
(11)	$\delta(P_A) = -24.13$; $\delta (P_B) = -29.72$

[a] spectra recorded in $CDCl_3$ (25°C) and referenced to H_3PO_4.

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مركبات تناسقية من 2-Pentyne مع المولبيدنوم (II) والتنجستن (II)

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المستخلص. إن التفاعل الكيميائي بين المركبات التناسقية مع المركبات العضوية التي تحمل الرابطة الثلاثية هي محل اهتمام اصطناع عضو فلزي ، ومن هذه المعقدات تفاعل $[MI_2(CO)_3(NCMe)_2]$ (M=Mo, W) مع (2-Pentyne) لتعطي $[MI_2(CO)(NCMe)$ (1 and 2) $(\eta^2\text{-}EtC_2Me)_2]$ ثم يتم تفاعل المركبان ١ و ٢ مع متصلات أخرى مثل : PPh_3 أو $Ph_2P(CH_2)_nPPh_2$ لتعطي على التوالي:
$[MI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Me)]$ (3 and 4) & $[MI_2(CO)\{Ph_2P(CH_2)_n PPh_2\}(\eta^2\text{-}EtC_2Me)]$ (for M=Mo, W, n=1-4) (5-12) .

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Stereoselective Crossed-Aldol Condensation of Some Active Methylene Compounds with Aromatic Aldehydes in Aqueous Medium. Synthesis of (2E)-1,3-Disubstituted Propenones

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ABSTRACT. Aldol condensation of cyclopropylmethyl ketone, 4-methoxyacetophenone and cyclohexanone with different aromatic aldehydes were carried out in water in heterogeneous phases in the presence of cetyltrimethylammonium bromide as a cationic surfactant at room temperature. All the reactions occur in a relatively short time with excellent yields of stereoselective propenones in water as an environmental friendly solvent. The structures of the resulting products were determined by spectral and elemental analysis.

Introduction

The U.S. Environmental Protection Agency (EPA) has recommended a drastic reduction in the use of more than ten of hazardous common organic solvents in the industrial production of chemicals. We are dealing in this paper with a clean and safe production of high yield of stereoselective chalcones, known as an important biologically active compounds, in water as a cheap solvent as well as an environmental friendly reaction medium.

Chalcones are α,β-unsaturated ketones and they have great abundance in the plant kingdom. It is well known that most of natural and synthetic chalcones are highly biologically active with a great pharmaceutical and medicinal applications[1]. Recently they are used as anti-AIDS[2], cytotoxic with antiangiogenic activity[3,4], antimalarial[5,6], anti-inflammatory[7,8] and antitumor[9,10] agents.

Recently, water has been considered as an attractive medium for many organic reactions[11]. The important advantages of aqueous media with respect to organic solvents are less expensive, healthy, safe and environmentally friendly. Also, it allows the pH control and the use of surfactants as micro aggregates[12].

The hydrophobic effect and the large cohesive energy of water[12] are considered to be the main factors responsible for increasing reactivity and selectivity of the reactions[13].

Mixed or crossed aldol condensation is a base-catalyzed addition of different aldehydes and ketones, one of them must contain at least one α-hydrogen to give an aldol or ketol which are then dehydrated to give α,β-unsaturated aldehydes or ketones.

The classical reaction conditions of aldol condensation are sodium hydroxide solution in a hydroalcoholic medium which are, often, yielded a mixture of (*E*) and (*Z*) chalcones[14,15]. Recently, aldol reaction can also be catalyzed in an aqueous medium by a surfactants to increase molecular aggregations and stereoselectivity[16-18]. It is considered cleaner conditions for the production of some known and unknown chalcones.

Experimental

All melting points reported are uncorrected. IR spectra were recorded using a Perkin Elmer's Spectrum RXIFT-IR spectrophotometer (υ in cm^{-1}). The NMR spectra were recorded on a Bruker Avance DPX400 spectrometer, using $CDCl_3$ as a solvent and TMS as an internal standard (chemical shifts (δ) values in ppm, *J* in Hz). Elemental analyses were preformed on a Perkin Elmer 2400, series II microanalyzer.

General Procedure

a) Methyl ketone (**1**, **3**, 100 mmol), aromatic aldehyde (100 mmol) and cetyltrimethylammoium bromide (CTABr) (5.46 g, 15 mmol) were added to an aqueous solution of NaOH (200 ml, 0.5 M). The mixture was vigorously stirred at 20°C for the time reported in Tables 1 and 2. The reaction was monitored by TLC of dissolving sample of the reaction mixture in CH_2Cl_2 during the reaction period. After the completion of the reaction, the solid product was filtered off, washed with water (3 × 25 ml), dried and crystallized from the proper solvent. The yields of the purified products are listed in Tables 1 and 2.

b) Cyclohexanone (**5**, 100 mmol), aromatic aldehyde (200 mmol) and cetyltrimethylammoium bromide (CTABr) (5.46 g, 15 mmol) were added to an aqueous solution of NaOH (200 ml, 0.5 M). The mixture was vigorously stirred at 20°C for the time reported in Table 3. The reaction was monitored by TLC of dissolving sample of the reaction mixture in CH_2Cl_2 during the reaction period. After the completion of the reaction, the solid product was filtered off, washed with water (3 × 25 ml), dried and crystallized from the proper solvent. The yields of the purified products are listed in Table 3.

(2*E*)-3-(4`-Tolyl)-1-cyclopropylprop-2-en-1-one (2a): Pale yellow crystals from methanol; m.p. 73-74°C; IR: 1601 (C = C), 1671 (C = O), 2866, 2921, 3013 (CH); ^{1}H-NMR: 0.96 (m, 2H), 1.15 (m, 2H), 2.24 (m, 1H), 2.37 (s, 3H), 6.84 (d, 1H, C_2-H, *J* = 16.0), 7.19-7.47 (dd, 4H, *J* = 7.5), 7.60 (d, 1H, C_3-*H*, *J* = 16.0); Anal. Calcd for $C_{13}H1_4O$ (186.10): C, 83.83; H, 7.58; Found: C, 83.71; H, 7.49.

(2*E*)-3-(4`-Chlorophenyl)-1-cyclopropylprop-2-en-1-one (2b): Pale yellow crystals from ethanol; m.p. 54-56°C; IR: 1596 (C = C), 1670 (C = O), 2920, 3022 (CH); ^{1}H-NMR: 0.97 (m, 2H), 1.15 (m, 2H), 2.21 (m, 1H), 6.83 (d, 1H, C_2-H, *J* = 15.8), 7.34-7.47 (dd, 4H, J=8.3), 7.54 (d, 1H, C_3-H, *J* = 15.8); Anal. Calcd for $C_{12}H_{11}ClO$ (206.54): C, 69.72; H, 5.37; Found: C, 69.64; H, 5.31.

(2*E*)-3-(4`-Bromophenyl)-1-cyclopropylprop-2-en-1-one (2c): Pale yellow crystals from dimethylformamide; m.p. 69-71°C; IR: 1563 (C = C), 1672 (C = O), 2921, 3020 (CH); ^{1}H-NMR: 0.99 (m, 2H), 1.21 (m, 2H), 2.22 (m, 1H), 6.86 (d, 1H, C_2-H, *J* = 16.0), 7.41-7.51 (dd, 4H, *J* = 8.2), 7.53 (d, 1H, C_3-H, *J* = 15.9); Anal. Calcd for $C_{12}H_{11}BrO$ (250.99): C, 57.37; H, 4.42; Found: C, 57.26; H, 4.37.

(2*E*)-3-(2`-Bromophenyl)-1-cyclopropylprop-2-en-1-one (2d): Pale yellow crystals from ethanol; m.p. 78-80°C; IR: 1598 (C = C), 1672 (C = O), 2893, 3020 (CH); ^{1}H-NMR: 0.99 (m, 2H), 1.17 (m, 2H), 2.23 (m, 1H), 6.86 (d, 1H, C_2-H, *J* = 16.0), 7.42-7.52 (dd, 4H, *J* = 8.3), 7.54 (d, 1H, C_3-H, *J* = 15.9); Anal. Calcd for $C_{12}H_{11}BrO$ (250.99): C, 57.37; H, 4.42; Found: C, 57.28; H, 4.36.

(2*E*)-3-(4`-Methoxyphenyl)-1-cyclopropylprop-2-en-1-one (2e): Pale yellow crystals from ethanol; m.p. 57-59°C; IR: 1584 (C = C), 1669 (C = O), 2840, 2985, 3014 (CH); ^{1}H-NMR: 0.95 (m, 2H), 1.14 (m, 2H), 2.23 (m, 1H), 3.84 (s, 3H), 6.76 (d, 1H, C_2-H, *J* = 16.1), 6.90-7.53 (dd, 4H, *J* = 8.4), 7.58 (d, 1H, C_3-H, *J* = 16.1); Anal. Calcd for $C_{13}H_{14}O_2$ (202.10): C, 77.19; H, 6.98; Found: C, 77.08; H, 6.91.

(2*E*)-3-(3`,4`-Methylenedioxyphenyl)-1-cyclopropylprop-2-en-1-one (2f): Pale yellow crystals from ethanol; m.p. 82-84°C; IR: 1588 (C = C), 1671 (C = O), 2918, 3006, 3047 (CH); ^{1}H-NMR: 0.96 (m, 2H), 1.14 (m, 2H), 2.20 (m, 1H), 6.01 (s, 2H), 6.71 (d, 1H, C_2-*H*, *J* = 16.0), 6.81-7.26 (m, 3H), 7.53 (d, 1H, C_3-H, *J* = 16.0); Anal. Calcd for $C_{13}H_{12}O_3$ (216.09): C, 72.19; H, 6.00; Found: C, 72.10; H, 5.93.

(2*E*)-3-Phenyl-1-(4`-methoxyphenyl)prop-2-en-1-one (4a): Pale yellow crystals from ethanol; m.p. 119-121ºC; IR: 1598 (C = C), 1655 (C = O), 2933, 3058 (CH); ^{1}H-NMR: 3.87 (s, 3H), 6.99 (d, 2H, *J* = 7.6), 7.42 (m, 3H), 7.56 (d, 1H, C_2-H, *J* = 15.7), 7.64 (d, 2H, *J* = 5.7), 7.98 (d, 1H, C_3-H, *J* = 15.7), 8.05 (d, 2H, *J* = 7.6); Anal. Calcd for $C_{16}H_{14}O_2$ (238.11): C, 80.64; H, 5.93; Found: C, 80.56; H, 5.88.

(2*E*)-3-(4`-Chlorophenyl)-1-(4`-methoxyphenyl)prop-2-en-1-one (4b): Pale yellow crystals from methanol; m.p. 120-122ºC; IR: 1601 (C = C), 1656 (C = O), 2922, 3014 (CH); ^{1}H-NMR: 3.90 (s, 3H), 6.99 (d, 2H, *J* = 8.6), 7.39 (d, 2H, *J* = 8.3), 7.52 (d, 1H, C_2-H, *J* = 15.7), 7.57 (d, 2H, *J* = 8.3), 7.75 (d, 1H, C_3-H, *J* = 15.7), 8.04 (d, 2H, *J* = 8.6); Anal. Calcd for $C_{16}H_{13}ClO_2$ (272.56): C, 70.44; H, 4.81; Found: C, 70.37; H, 4.75.

(2*E*)-1,3-bis-(4`-Methoxyphenyl)prop-2-en-1-one (4c): Pale yellow crystals from methanol; m.p. 89-91ºC; IR: 1596 (C = C), 1655 (C = O), 2962, 3015, 3069 (CH); ^{1}H-NMR: 3.85 (s, 3H), 3.88 (s, 3H), 6.92-6.99 (dd, 4H, *J* = 8.3), 7.44 (d, 1H, C_2-H, *J* = 15.5), 7.60 (d, 2H, *J* = 8.4), 7.78 (d, 1H, C_3-H, *J* = 15.6), 8.04 (d, 2H, *J* = 8.4); Anal. Calcd for $C_{17}H_{16}O_3$ (268.13): C, 76.08; H, 6.01; Found: C, 76.01; H, 5.95.

(2*E*)-3-(3`,4`-Methylenedioxyphenyl)-1-(4`-methoxyphenyl)prop-2-en-1-one (4d): Pale yellow crystals from pet. ether 60-80; m.p. 124-126ºC; IR: 1586 (C = C), 1657 (C = O), 2919, 3030 (CH); ^{1}H-NMR: 3.89 (s, 3H), 6.02 (s, 2H), 6.83 (d, 1H, *J* = 8.0), 6.97 (d, 2H, *J* = 8.6), 7.16 (m, 2H), 7.38 (d, 1H, C_2-H, *J* = 15.4), 7.73 (d, 1H, C_3-H, *J* = 15.4), 8.02 (d, 2H, *J* = 8.6); Anal. Calcd for $C_{17}H_{14}O_4$ (282.11): C, 72.31; H, 5.00; Found: C, 72.26; H, 4.95.

2,6-Dibenzylidene cyclohexanone (6a): Yellow crystals from acetic acid; m.p. 104-106ºC; IR: 1575 (C = C), 1661 (C = O), 2932, 3070 (CH); ^{1}H-NMR: 1.79 (m, 2H), 2.87 (m, 4H), 7.25-7.37 (m, 10H), 7.72 (s, 2H, 2 CH olefinic); ^{13}C-NMR: 22.73 (CH_2), 28.32 ($2 \times CH_2$), 127.78 (2 × Cquat Ar), 129.48 (4 × CH Ar), 130.75 (2xCH Ar), 132.37 (4 × CH Ar), 134.98 (2 × Cquat), 136.52 (C_2-H, C_3-H), 189.77 (C = O); Anal. Calcd for $C_{20}H_{18}O$ (274.14): C, 87.55; H, 6.62; Found: C, 87.49; H, 6.57.

2,6-bis(4`-Tolylidene) cyclohexanone (6b): Yellow crystals from acetic acid; m.p. 159-161ºC; IR: 1565 (C = C), 1661 (C = O), 2937, 3055 (CH); ^{1}H-NMR: 1.79 (m, 2H), 2.38 (s, 6H), 2.93 (m, 4H), 7.20-7.39 (m, 8H), 7.78 (s, 2H, 2 CH olefinic); Anal. Calcd for $C_{22}H_{22}O$ (302.17): C, 87.36; H, 7.34; Found: C, 87.25; H, 7.29.

2,6-bis(4`-Chlorobenzylidene) cyclohexanone (6c): Yellow crystals from acetic acid; m.p. 104-106ºC; IR: 1577 (C = C), 1666 (C = O), 2973, 3059 (CH);

^{1}H-NMR: 1.78 (m, 2H), 2.86 (m, 4H), 7.26-7.53 (m, 8H), 7.69 (s, 2H, 2 CH olefinic); ^{13}C-NMR: 24.50 (CH_2), 30.15 (2 × CH2), 124.67 (2 × Cquat Ar), 132.49 (4 ×CH Ar), 133.97 (4 ×CH Ar), 136.35 (2 ×C-Cl Ar), 136.78 (2 ×Cquat), 138.32 (C_2-H, C_3-H), 191.42 (C = O); Anal. Calcd for $C_{20}H_{16}Cl_2O$ (343.04): C, 69.96; H, 4.70; Found: C, 69.87; H, 4.64.

2,6-bis(4`-Bromobenzylidene) cyclohexanone (6d): Brown crystals from acetic acid; m.p. 149-151ºC; IR: 1574 (C = C), 1664 (C = O), 2937, 3028 (CH); ^{1}H-NMR: 1.79 (m, 2H), 2.94 (m, 4H), 7.26-7.48 (m, 8H), 7.81 (s, 2H, 2 CH olefinic); Anal. Calcd for $C_{20}H_{16}Br_2O$ (431.95): C, 55.56; H, 3.73; Found: C, 55.45; H, 3.69.

2,6-bis(4`-Methoxybenzylidene) cyclohexanone (6e): Yellow crystals from acetic acid; m.p. 154-156ºC; IR: 1592 (C = C), 1659 (C = O), 2941, 3059 (CH); ^{1}H-NMR: 1.80 (m, 2H), 2.91 (m, 4H), 3.84 (s, 6H), 6.92-7.46 (m, 8H), 7.76 (s, 2H, 2 CH olefinic); ^{13}C-NMR: 21.41 (CH_2), 26.92 (2 × CH_2), 54.42 (2× CH_3), 113.07 (4 ×CH Ar), 127.10 (2 ×Cquat Ar), 131.45 (4 ×CH Ar), 134.16 (2×Cquat), 135.70 (C_2-H, C_3-H), 158.28 (2×C-O Ar), 188.53 (C = O); Anal. Calcd for $C_{22}H_{22}O_3$ (334.17): C, 79.00; H, 6.64; Found: C, 78.91; H, 6.59.

2,6-bis(3`,4`-Methylenedioxybenzylidene) cyclohexanone (6f): Yellow crystals from acetic acid; m.p. 154-155ºC; IR: 1589 (C = C), 1665 (C = O), 2925, 3061 (CH); ^{1}H-NMR: 1.79 (m, 2H), 2.89 (m, 4H), 5.99 (s, 4H), 6.84-7.01 (m, 6H), 7.70 (s, 2H, 2 CH olefinic); Anal. Calcd for $C_{22}H_{18}O_5$ (362.14): C, 72.90; H, 5.01; Found: C, 72.81; H, 4.96.

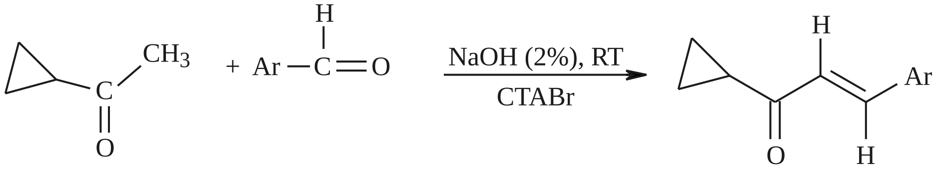
Results and Discussion

We extended the previous investigations[16-18] to carbon-carbon bond formation and we focus in this paper on the aldol condensation of some active methylene compounds with a variety of different aromatic aldehydes in water at room temperature and in the presence of cetyltrimethylammoium bromide (CTABr) as the proper cationic surfactant for the synthesis of (2*E*)-1,3-disubstituted propenones in an excellent yield with a high stereoselectivity.

We expect that the synthesized chalcones might have biological and medicinal activities probably analogous to the biologically active amino chalcones[9], quinolinyl chalcones[6] and some ferrocenyl chalcone[5].

Efficient stirring of an equimolar amount of cyclopropylmethyl ketone (**1**) and 4-methoxyacetophenone (**3**) with aromatic aldehydes, while one equivalent of cyclohexanone (**5**) with two equivalents of aromatic aldehydes in aqueous NaOH solution and in the presence of cetyltrimethylammoium bromide (CTABr) as surfactant at room temperature, underwent stereoselective crossed-aldol condensation with precipitation of 1,3-disubstituted propenones (**2** and **4**) and double condensation with cyclohexanone to give diarylidene cyclohexanones (**6**) in a high yield within a short reaction time (t) as shown in Tables 1, 2 & 3. It is shown from the Tables that electron donating substituents of aromatic aldehydes decrease the reaction period and increase the yield of the products.

TABLE 1. Crossed-Aldol condensation of cyclopropylmethyl ketone (**1**) with aromatic aldehydes: Synthesis of (2*E*)-3-aryl-1-cyclopropylprop-2-en-1-ones (**2a-f**).



(1) **(2)**

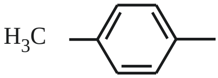
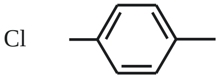
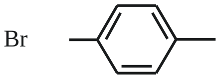
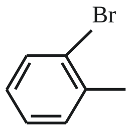
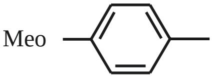
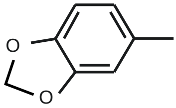
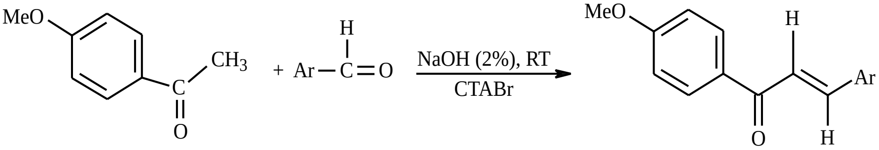
Product no.	Ar	t (min)	Yield (5)
2a		90	93
2b		100	68
2c		120	80
2d		140	78
2e		40	78
2f		30	87

Table 2. Crossed-Aldol condensation of 4-methoxyacetophenone (**3**) with aromatic aldehydes: Synthesis of (2*E*)-3-aryl-1-(4`-methoxyphenyl)prop-2-en-1-ones (**4a-d**).



(3) **(4)**

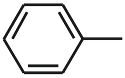
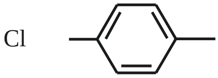
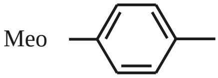
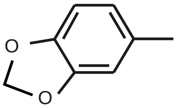
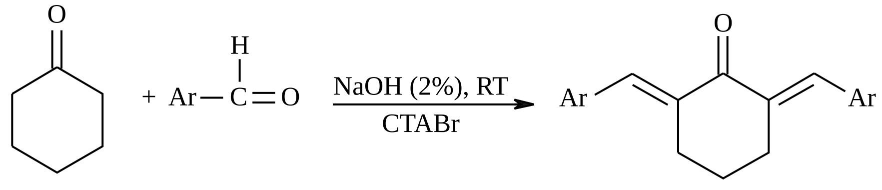
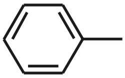
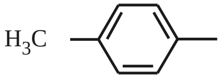
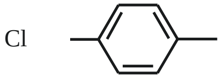
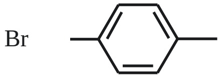
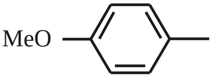
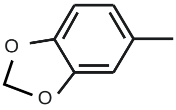
Product no.	Ar	t (min)	Yield (%)
4a		100	65
4b		140	66
4c		40	73
4d		30	78

TABLE 3. Crossed-Aldol condensation of cyclohexanone (**5**) with aromatic aldehydes: Synthesis of 2,6-bis(arylidene) cyclohexanones (**6a-f**).



(5) **(6)**

Product no.	Ar	t (min)	Yield (%)
6a		90	83
6b		100	63
6c		120	83
6d		140	40
6e		60	80
6f		30	80

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تكاثف ألدول المتصالب الانتقائي لبعض مركبات الميثيلين النشطة مع ألدهيدات أروماتية في وسط مائي. تحضير (2E)-1,3-Disubstituted Propenones

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المستخلص. تكاثف ألدول للسيكلوبروبيل ميثيل كيتون و ٤- ميثوكسي أسيتوفينون و سيكلوهكسانون مع الألدهيدات الأروماتية المختلفة ، تم إجراؤه في الماء في طور غير متجانس في وجود سيتيل تراي ميثيل أمونيوم برومايد كخافض توتر سطحي كاتيوني عند درجة حرارة الغرفة. جميع التفاعلات تمت خلال فترة قصيرة و أعطت مردوداً عالياً لمشتقات البروبينون الانتقائية في الماء كمذيب صديق للبيئة.

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Determination of Some Elements in Local Food Products in Kingdom of Saudi Arabia

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Abstract. Vegetable and fruit samples were collected from their major area of Kingdom of Saudi Arabia (KSA), together with locally bred fish and meat and locally manufactured products as cheese and macaroni. These samples were analysed for Na, K, Mg, Ca, Fe, Zn, Cu and Mn using Flame Photometer and Atomic Absorption Spectrometer. The results showed that the level of Na & K in local foodstuff do not vary greatly from the reported values. But Mg shows much higher concentration than the reported value. On the contrary, levels of Ca, Fe, Zn, Cu and Mn are lower than the reported values.

The daily intake of essential elements was calculated taking into account the concentration of these elements in the edible part and the daily consumption data which were derived from two sources: (a) the food balance sheet of KSA given by Food and Agriculture Organization FAO and (b) from questionnaire distributed to 200 families in Jeddah. The results show that the daily intake of these essential elements according to FAO satisfy the daily requirements except Ca & Zn. But according to the questionnaire the daily intake of these elements are less than the required daily intake except for Mg.

Introduction

Essential elements are those if removed from diet result in consistent and reproduceable impairment of physiological function[1]. The deficiencies of these elements result from a combination of poor availability and low intake[2].

Metals in human body are divisible into two groups the major elements (Na, K, Mg and Ca) form the main proportion of the total elements content of the body and trace elements (Fe, Cu, Mn and Zn) which found in low or even minute, quantities[3].

Sodium and potassium are the principle cations in the extra and intracellular fluid, respectively. They regulate nerves and muscles function.

Magnesium enters in the constituent of bone and teeth. It is important in the hydrolysis and energy storage reaction of phosphate derivatives, also it plays important role in enzymatic reaction catalyzed by certain kinase. In plant, magnesium ion plays a pivotal role in the process of photosynthesis. All of the chlorophylls which participate in photosynthesis are coordination compound of Mg^{2+}[4].

Calcium beside its constituent of bone and teeth it plays a major regulatory role in numerous biochemical and physiological processes, it involves in photosynthesis, oxidative phosphorylation, blood clotting, muscle contraction, cell division, transmission of nerve impulses, enzyme activity, cell membrane function and hormone secretion[2].

Iron plays many key roles in biological systems, including oxygen transport and storage, ATP (adenosine triphosphate) generation, DNA synthesis and chlorophyll synthesis[2].

Zinc enters in many physiological function as, taste sensation, metabolism of skin, reproductive process, bone formation, wound healing, brain function and metabolism of carbohydrate, protein and nucleic acid. It enters in many metallo enzymes[1].

Copper is a cofactor in many enzymes including phenolase and is at active center of hemocyanin, an oxygen carrying protein in some erthropods. It has critical importance in hemosynthesis, bone development, nerve function and connective tissues[1].

Manganese plays an essential role in cellular metabolism where a number of enzymes require the presence of this elements for their function. These include enzymes for the synthesis of mucopolysaccharides, for protein and energy metabolism and for cell protection from free radical damage[5].

Due to the importance of these elements several researchers had determined them in different food matrix during the last years[6-16].

In the present work, it is proposed to determine the concentration of essential major (Na, K, Mg and Ca) and trace (Fe, Zn, Cu and Mn) elements in local foodstuff of KSA. From the results the daily intake of these elements by KSA people can be estimated and compared with the requirement of these elements according to recommended dietary allowances (RDA)[17].

Experimental

Materials

Samples from local foodstuff of Kingdom of Saudi Arabia (KSA) were collected during 1998-1999. The vegetables, fruits and grains were collected from their major growing area in KSA together with fish and meat from animals which have been bred in KSA and locally manufactured products.

The groups of foodstuff studied were:

– Meat (chicken, lamb, beaf, camel and fish) “edible part”.

– Leafy vegetable (mallow, spinach, garden rocket, lettuce, parsley curly, cabbage, mint and sweet basil).

– Non leafy vegetable (squash, okra, green pepper, egg plant (black), stringed beans, cucumber and cauliflower).

– Tubers (potato white and carrots).

– Fruits (mandarine, dried dates, pumpkin and tomatoes).

– Grains (wheat and corn).

– Manufactured products (macaroni and cheese).

From each sample 5 specimens were analysed. Two hundred grams of edible part from each specimen were taken, rinsed with tap water and then washed with double distilled water (except wheat and corn), dried at 100ºC till constant weight and ground with special mills with provision to prevent contamination (wearing parts made of aluminum and titanium).

The water used was double distilled water of high quality and all reagents used were of analytical grade from BDH Poole England. Measurements were done against metal standard solution, Spec pure from Alfa - Aesar - Ubichem - England.

The instruments used are Flame Emission Spectrometry (FES) Corning model 410. Atomic Absorption Spectrometer (AAS) with deuterium back ground correction model UNICAM-939 Supply with Flame system from England.

Methods

The representative samples, performed by quartering process, were digested using the Official Method AOAC. In nargent beaker 40 ml of conc. nitric acid (Analar) was added to 4 g of sample and allow to stand overnight at room temperature. Heat at 70ºC till the volume of nitric acid was reduced to about 5 ml, after cooling 3 ml of 60% $HClO_4$ was added and heating was continued till near dryness. The residue was dissolved by double distilled water, then the solution was filtered quantitatively in 100 ml measuring flask. The filterate was diluted to mark with deionised water. The same previous procedure was performed without sample to give blank[18].

Sodium and potassium concentrations were measured using flame emission spectrometry against standard solution of NaCl and KCl. AAS with flame system was used for Mg, Ca, Fe, Zn, Cu and Mn concentration measurements. Hallow cathod lamps of Mg, Ca, Fe, Zn, Cu and Mn were used and the measurements were performed at wave lengths 285.2, 422.7, 248.3, 213.9, 324.8, and 279.5 nm respectively against metal standard solution[19].

Measurements were performed at Center Laboratory of Radiation Technology Center, Cairo, Egypt.

A questionnaire was distributed among two hundred families in Jeddah. The answers on the quantities of food they consumed independent of financial situation were collected and the mean values were calculated.

Results and Discussion

The level of Na, K, Mg and Ca in the local foodstuff of KSA are presented in Table 1. The concentrations were calculated in mg/kg fresh weight ± standard deviation of five species per each kind of food.

TABLE 1. Level of some major elements in mg/kg fresh weight in local foodstuff of KSA.

No.	Samples	Concentration in mg/kg fresh weight			
		Na	K	Mg	Ca
	Meat				
1	Chicken	669 ± 21	2155 ± 18	689 ± 44	96 ± 11
2	Lamb	460 ± 8	1980 ± 8	676 ± 37	107 ± 4
3	Beef	560 ± 10	2430 ± 9	537 ± 36	64 ± 6
4	Camel	680 ± 7	2170 ± 10	500 ± 30	46 ± 2
5	Fish	634 ± 9	1642 ± 11	445 ± 26	106 ± 3
	Leafy vegetables				
6	Mallow	407 ± 12	4950 ± 41	1770 ± 91	2122 ± 80
7	Spinach	370 ± 8	4697 ± 17	7572 ± 284	2437 ± 68
8	Garden rocket	557 ± 13	2110 ± 8	1065 ± 24	990 ± 8
9	Lettuce	383 ± 5	1780 ± 22	280 ± 8	190 ± 16
10	Parsley curly	2120 ± 71	5137 ± 13	1250 ± 83	1275 ± 78

TABLE 1. Contd.

No.	Samples	Concentration in mg/kg fresh weight			
		Na	K	Mg	Ca
11	Cabbage	317 ± 9	2250 ± 8	389 ± 14	241 ± 8
12	Mint	546 ± 5	4700 ± 16	2653 ± 40	1790 ± 66
13	Sweet basil	830 ± 8	5747 ± 13	3421 ± 84	2117 ± 83
	Non leafy vegetables				
14	Squash	210 ± 10	2963 ± 13	789 ± 18	90 ± 5
15	Okra	540 ± 8	3437 ± 12	2073 ± 62	733 ± 51
16	Green pepper sweet	433 ± 9	1840 ± 22	312 ± 3	72 ± 2
17	Egg plant (black)	280 ± 7	2897 ± 13	302 ± 7	108 ± 2
18	Stringed beans	340 ± 10	3180 ± 22	1029 ± 49	336 ± 34
19	Cucumber	220 ± 6	1880 ± 25	340 ± 16	143 ± 13
20	Cauliflower	410 ± 8	3117 ± 13	491 ± 27	197 ± 6
	Tubers				
21	Potato white	250 ± 9	3163 ± 17	604 ± 13	71 ± 7
22	Carrots	930 ± 7	2410 ± 8	360 ± 5	193 ± 8
	Fruits				
23	Mandarine	123 ± 5	1513 ± 5	394 ± 16	318 ± 6
24	Dry dates	610 ± 8	7707 ± 13	1942 ± 116	482 ± 24
25	Pumpkin	173 ± 5	2260 ± 16	243 ± 6	211 ± 7
26	Tomatoes	297 ± 9	3110 ± 23	390 ± 8	86 ± 3
	Grains				
27	Wheat	520 ± 7	3620 ± 16	3354 ± 225	340 ± 37
28	Maize (corn)	430 ± 8	3650 ± 8	5064 ± 374	90 ± 14
	Manufactured products				
29	Macaroni	440 ± 6	2257 ± 13	1522 ± 131	194 ± 23
30	White cheese	7820 ± 9	587 ± 49	682 ± 31	2617 ± 72

From the table it is clear that the higher concentration of Na in cheese while the lower in mandarine. In contrast to Na, K shows lower concentration in cheese but the higher level was in dry dates.

Also from the table it is clear that leafy vegetables have higher concentration of Mg. This is due to the presence of Mg as essential element in chlorophyll formation[4,20].

The highest Ca concentration was found in cheese while camel meet shows the lowest one. In vegetables there is a positive correlation between Ca and Mg concentration this can be explained that Ca involves in photosynthesis as Mg[2], this result confirms with the results obtained by Salah *et al.* (1996)[21].

The level of trace elements in mg/kg fresh weight in Saudi Arabia foodstuff are presented in Table 2.

TABLE 2. Level of some trace elements in mg/kg fresh weight in local foodstuff of KSA.

No.	Samples	Concentration in mg/kg fresh weight			
		Fe	Zn	Cu	Mn
	Meat				
1	Chicken	6.15 ± 1.44	13.92 ± 2.96	0.42 ± 0.04	0.13 ± 0.02
2	Lamb	16.71 ± 2.19	24.34 ± 4.01	0.90 ± 0.06	0.04 ± 0.1
3	Beef	12.46 ± 2.26	30.71 ± 6.38	0.50 ± 0.03	0.12 ± 0.02
4	Camel	9.55 ± 1.60	24.14 ± 5.85	0.33 ± 0.02	0.06 ± 0.02
5	Fish	2.56 ± 0.35	4.47 ± 0.27	0.19 ± 0.05	0.07 ± 0.01
	Leafy vegetables				
6	Mallow	31.40 ± 3.66	6.18 ± 0.19	1.83 ± 0.17	10.76 ± 0.76
7	Spinach	82.94 ± 5.45	6.77 ± 0.20	1.98 ± 0.53	6.67 ± 0.81
8	Garden rocket	27.56 ± 0.35	3.20 ± 0.29	0.22 ± 0.01	1.40 ± 0.11
9	Lettuce	9.06 ± 0.71	1.91 ± 0.04	0.30 ± 0.02	0.60 ± 0.08
10	Parsley curly	34.96 ± 0.52	3.26 ± 0.25	1.09 ± 0.01	5.34 ± 0.51
11	Cabbage	3.11 ± 0.18	0.89 ± 0.02	0.19 ± 0.01	0.62 ± 0.05
12	Mint	134.11 ± 0.73	5.76 ± 0.84	1.30 ± 0.14	9.51 ± 1.11
13	Sweet basil	137.21 ± 1.97	5.51 ± 0.11	1.79 ± 0.12	11.42 ± 0.36
	Non leafy vegetables				
14	Squash	6.38 ± 0.29	5.45 ± 0.11	0.70 ± 0.05	0.82 ± 0.01
15	Okra	11.76 ± 1.08	5.85 ± 0.23	1.59 ± 0.02	3.55 ± 0.15
16	Green pepper sweet	9.53 ± 0.27	1.25 ± 0.13	0.35 ± 0.02	0.35 ± 0.01
17	Egg plant (black)	4.33 ± 0.11	2.42 ± 0.13	0.80 ± 0.06	0.70 ± 0.03

TABLE 2. Contd.

No.	Samples	Concentration in mg/kg fresh weight			
		Fe	Zn	Cu	Mn
18	Stringed beans	7.31 ± 0.27	1.76 ± 0.01	0.40 ± 0.02	0.78 ± 0.02
19	Cucumber	2.55 ± 0.22	1.24 ± 0.12	0.22 ± 0.02	0.31 ± 0.02
20	Cauliflower	7.25 ± 0.65	3.42 ± 0.20	0.29 ± 0.01	0.63 ± 0.04
	Tubers				
21	Potato white	3.13 ± 0.06	4.37 ± 0.07	1.19 ± 0.01	0.68 ± 0.01
22	Carrots	3.08 ± 0.08	1.19 ± 0.14	0.27 ± 0.03	0.46 ± 0.02
	Fruits				
23	Mandarine	2.02 ± 0.21	0.81 ± 0.13	0.30 ± 0.02	0.19 ± 0.02
24	Dry dates	19.26 ± 0.67	4.08 ± 0.34	3.09 ± 0.07	1.13 ± 0.04
25	Pumpkin	0.88 ± 0.07	1.70 ± 0.24	0.12 ± 0.01	0.03 ± 0.01
26	Tomatoes	3.37 ± 0.13	1.22 ± 0.11	0.68 ± 0.02	0.24 ± 0.02
	Grains				
27	Wheat	28.75 ± 1.38	20.03 ± 0.94	3.21 ± 0.20	10.76 ± 0.23
28	Maize (corn)	44.81 ± 1.06	25.28 ± 2.19	3.10 ± 0.21	6.40 ± 0.11
	Manufactured products				
29	Macaroni	17.62 ± 0.74	12.82 ± 2.76	2.97 ± 0.29	3.97 ± 0.18
30	White cheese	3.40 ± 0.22	16.10 ± 2.17	0.25 ± 0.06	0.20 ± 0.02

Based on the data presented in Table 2 the higher concentration of Fe in green vegetable can easily be noticed this can be explained by the assimilation of Fe in chlorophyll and stored as ferritien[2].

Regarding Zn, the higher concentration of this element was recorded in meat due to its binding with proteins and albumin[1,4]. Also grains show high concentration of Zn and the lower concentration is in fruits, these results confirm with the previous results[1,11,15].

Concerning Cu level in different foodstuff, Table 2 shows that dates and grains are the richest food samples with Cu while fish is the poorest one. It can be also considered that the vegetables are good source of Cu whereas it is found in plastocyanin (Cu-containing protein) which is essential electron carrier in photosynthesis[20].

Grains show a remarkable higher concentration of Mn than other samples this is in agreement with the previous studies of Owen[2] and Farady *et al.*[11]. The lower concentration of Cu was found in tubers, meat and fish this result is confirmed by the results of Farady *et al.*[8] and Mcdonald[22].

Comparing our results with the reported values, it was found that the levels of Na and K are similar to those reported values[2,13]. According to the same references Mg concentration was found much higher than the reported values. This higher concentration of Mg could be attributed to the high level of Mg in the underground water of arid country which is used in irrigation[23]. It was found also that the levels of Ca, Fe, Zn, Cu and Mn in Saud Arabia foodstuff are lower than that in the other reported values[2,11-13,15]. This lower concentration may be referred to the sandy soil that does not contain organic materials which work towards buffering the pH of soil. The pH increases as CaO is added and the result is the formation of calcium phosphate which is not absorbed by plant. In addition as the pH increases above 7 the elements Fe, Zn, Cu, and Mn are less absorbable by plants[20].

From the concentration of major and trace elements in food the daily intake of these elements by KSA inhabitants were calculated in correlation with: a) food balance sheet of KSA (FAO 1994-1996)[24], b) questionnaire data. Tables 3 & 4 represent the daily intake of major and trace elements in mg/day. According to FAO the results show that the daily intake of major and trace elements exceeds the daily requirements except Ca and Zn where their daily intake is less than the daily requirements.

TABLE 3. Daily intake* of major elements by KSA inhabitants from local foodstuff.

No.	Foodstuff	Daily* consumption of food in g	Daily intake of elements in mg/day			
			Na	K	Mg	Ca
1	Chicken meat	78.10	52.25	168.31	53.81	7.50
2	Lamb meat	20.80	9.57	41.18	14.06	2.23
3	Beef meat	11.80	6.61	28.67	6.34	0.76
4	Camel meat	6.50	4.42	14.11	3.25	0.30
5	Fish meat	17.80	11.29	29.23	7.92	1.90
6	Vegetables	289.50	146.78	296.00	393.43	199.18
7	Potatoes	47.60	11.90	150.56	28.75	3.38
8	Carrots	0.26	0.25	0.65	0.10	0.05
9	Mandarine	56.00	6.89	84.73	22.06	17.81
10	Dry dates	74.70	45.57	575.71	145.07	36.01

Table 3. Contd.

No.	Foodstuff	Daily* consumption of food in g	Daily intake of elements in mg/day			
			Na	K	Mg	Ca
11	Pumpkin	16.40	2.84	37.06	3.99	3.46
12	Tomatoes	82.50	24.50	256.58	32.18	7.10
13	Wheat	332.00	172.64	1201.84	1113.53	112.88
14	White cheese	50.00	391.00	29.35	34.10	130.85
	Sum		686.50	3513.98	1858.59	523.41
	Daily requirement*		500.00	2000.00	222.00	600.00 - 1200.00

*In accordance with FAO[23].

Table 4. Daily intake * of trace elements by KSA inhabitants from local foodstuff.

No.	Foodstuff	Daily* consumption of food in g	Daily intake of elements in mg/day			
			Fe	Zn	Cu	Mn
1	Chicken meat	78.10	0.4803	1.0872	0.0328	0.0102
2	Lamb meat	20.80	0.3476	0.5063	0.0187	0.0008
3	Beef meat	11.80	0.1470	0.3624	0.0059	0.0014
4	Camel meat	6.50	0.0621	0.1589	0.0021	0.0004
5	Fish meat	17.80	0.0376	0.0662	0.0021	0.0011
6	Vegetables	289.50	5.3036	0.9698	0.2287	0.7180
7	Potatoes	47.60	0.1490	0.2080	0.0566	0.0324
8	Carrots	0.26	0.0008	0.0003	0.0001	0.0001
9	Mandarine	56.00	0.1131	0.0454	0.0168	0.0106
10	Dry Dates	74.70	1.4387	0.3048	0.2308	0.0844
11	Pumpkin	16.40	0.0144	0.0279	0.0019	0.0005
12	Tomatoes	82.50	0.2780	0.1007	0.0561	0.0198
13	Wheat	332.00	9.5450	6.6500	1.0657	3.5723
14	White cheese	50.00	0.1700	0.8050	0.0125	0.0100
	Sum		18.0872	11.2929	1.7308	4.4620
	Daily requirement*		10 - 15	12 - 15	1.5 - 3	2 - 5

*In accordance with FAO[23].

According to the questionnaire,Tables 5 and 6 represent the daily intake of major and trace elements in mg/day. The results show that except Mg the daily intake of major and trace elements are lower than the required values.

TABLE 5. Daily intake of essential major elements by KSA inhabitants from local foodstuff in correlation with questionnaire.

No.	Kind of food	Sample	Daily consum. of food in g/d	Daily intake mg/day			
			Edible	Na	K	Mg	Ca
	Meat						
1		Chicken	59.8	40.01	128.89	41.20	5.72
2		Lamb	54.8	25.24	108.50	37.04	5.86
3		Beef	9.2	51.52	22.36	4.94	0.59
4		Camel	2.6	1.77	5.64	1.30	0.12
5		Fish	16.7	10.58	27.41	7.42	1.78
	Leafy vegetables						
6		Mallow	5.5	2.24	27.23	9.74	11.67
7		Spinach	3.3	1.20	15.50	24.99	8.04
8		Garden rocket	2.7	1.50	5.70	2.88	2.67
9		Lettuce	11.8	4.52	21.00	3.30	2.30
10		Parsley curly	6.3	13.36	32.36	7.88	8.03
11		Cabbage	8.2	2.60	18.45	3.19	1.98
12		Mint	3.7	2.02	17.39	9.82	6.62
13		Sweet basil	1.6	1.33	9.20	5.47	3.39
	Non leafy vegetables						
14		Squash	22.6	4.75	66.96	17.83	2.03
15		Okra	13.0	7.02	44.68	26.95	9.53
16		Green pepper sweet	12.7	5.50	23.37	3.96	0.91
17		Egg plant (black)	12.3	3.44	35.63	3.71	1.33
18		Stringed beans	15.4	5.24	48.97	15.85	5.17
19		Cucumber	32.4	7.13	60.91	11.02	4.63
20		Cauliflower	7.0	2.87	21.82	3.44	1.38
	Tubers						
21		Potato white	40.9	10.23	129.37	24.70	2.90
22		Carrots	20.3	18.88	48.92	7.31	3.92

TABLE 5. Contd.

No.	Kind of food	Sample	Daily consum. of food in g/d	Daily intake mg/day			
			Edible	Na	K	Mg	Ca
	Fruits						
23		Mandarine	20.2	2.48	30.56	7.96	6.42
24		Dry dates	19.9	12.14	153.37	38.65	9.59
25		Pumpkin	2.5	0.43	5.65	0.61	0.53
26		Tomatoes	63.7	18.92	198.11	24.84	5.48
	Grains						
27		Wheat	47.46	24.68	171.81	159.18	16.14
	Manufactured products						
28		Macaroni	24.7	10.87	55.75	37.59	4.79
29		White cheese	15.9	124.34	9.33	10.84	41.61
	Sum			416.81	1544.84	553.61	175.13
	Daily requirement			500	2000	222	600 - 1200

TABLE 6. Daily intake of essential trace elements by KSA inhabitants from local foodstuff in correlation with questionnaire.

No.	Kind of food	Sample	Daily consum. of food in g	Daily intake mg/day			
			Edible	Fe	Zn	Cu	Mn
	Meat						
1		Chicken	59.8	0.3676	0.8322	0.0251	0.0078
2		Lamb	54.8	0.9157	1.3338	0.0493	0.0022
3		Beef	9.2	0.1146	0.2825	0.0046	0.0011
4		Camel	2.6	0.0248	0.6354	0.0009	0.0001
5		Fish	16.7	0.0352	0.0621	0.0020	0.0009
	Leafy vegetables						
6		Mallow	5.5	0.1727	0.0034	0.0010	0.0592
7		Spinach	3.3	0.2737	0.0223	0.0065	0.0220

TABLE 6. Contd.

No.	Kind of food	Sample	Daily consum. of food in g	Daily intake mg/day			
			Edible	Fe	Zn	Cu	Mn
8		Garden rocket	2.7	0.0744	0.0086	0.0006	0.0038
9		Lettuce	11.8	0.1069	0.0225	0.0035	0.0071
10		Parsley curly	6.3	0.2202	0.0205	0.0069	0.0034
11		Cabbage	8.2	0.0255	0.0073	0.0016	0.0051
12		Mint	3.7	0.4962	0.0213	0.0048	0.0352
13		Sweet basil	1.6	0.2771	0.0088	0.0029	0.0343
	Non leafy vegetables						
14		Squash	22.6	0.1442	0.1232	0.0158	0.0185
15		Okra	13.0	0.1529	0.0761	0.0207	0.0462
16		Green pepper sweet	12.7	0.1210	0.0159	0.0044	0.0044
17		Egg plant (black)	12.3	0.0533	0.0298	0.0098	0.0086
18		Stringed beans	15.4	0.1126	0.0271	0.0061	0.0012
19		Cucumber	32.4	0.0826	0.0402	0.0071	0.0100
20		Cauliflower	7.0	0.0653	0.0239	0.0020	0.0044
	Tubers						
21		Potato white	40.9	0.1280	0.1787	0.0487	0.0278
22		Carrots	20.3	0.0810	0.0242	0.0548	0.0093
	Fruits						
23		Mandarine	20.2	0.4080	0.0164	0.0061	0.0038
24		Dry dates	19.9	0.3833	0.0812	0.0615	0.0225
25		Pumpkin	2.5	0.0022	0.0425	0.0003	0.0001
26		Tomatoes	63.7	0.2147	0.0777	0.0433	0.0153
	Grains						
27		Wheat	47.46	1.3645	0.9506	0.1523	0.5107
	Manufactured products						
28		Macaroni	24.7	0.4352	0.3167	0.0734	0.0953
29		White cheese	15.9	0.0541	0.2550	0.0040	0.0032
	SUM			6.9074	5.5409	0.6200	0.9635
	Daily requirement	0- 15	12 - 15	1.5 - 3	2 - 5		

Conclusion

The levels of Na & K elements in Saudi Arabian foodstuff do not differ greatly from the reported values. At the same time, Mg is much higher than the reported values. In case of Ca, Fe, Zn, Cu and Mn their concentrations are little lower than the reported values. These results are suggested to be due to the nature of soil and irrigation water. The daily intake of most essential elements are lower than requirement values due to the low concentration of these elements in food and the low consumption of vegetables and grains which are rich in these elements.

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تقدير العناصر الأساسية في السلسلة الغذائية المحلية للمملكة العربية السعودية

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المستخلص. تم تحليل المعادن الأساسية الثانوية منها والضئيلة في السلسلة الغذائية المحلية للمملكة العربية السعودية وذلك بجمع عينات من الخضراوات والفواكه من أماكن زراعتها في المملكة ولحوم حيوانات وأسماك تمت تربيتها في المملكة بالإضافة إلى منتجات صناعية محلية.

وتم استخدام جهاز طيف الانبعاث اللهبي في تعيين الصوديوم والبوتاسيوم ، أما باقي العناصر (الكالسيوم - المغنيسيوم - الحديد - الزنك - النحاس - المنجنيز) فقد استخدم جهاز الامتصاص الذري لتعيينها.

ولقد دلت النتائج على أن مستوى الصوديوم والبوتاسيوم في السلسلة الغذائية المحلية لا يختلف كثيرا عن مثيلاتها في الدراسات السابقة خارج المملكة. ولكن مستوى المغنيسيوم وجد أنه أعلى بكثير من الدراسات المرجعية السابقة في جميع العينات ما عدا الأسماك.

وعلى النقيض وجد أن مستوى كل من الكالسيوم والحديد والزنك والنحاس والمنجنيز أقل من مستواه في الدراسات السابقة خارج المملكة.

ولقد تم حساب المتناول اليومي للفرد السعودي حسب كمية الطعام المستهلكة بواسطة الفرد السعودي بناء على ما أقرته منظمة الأغذية والزراعة. ودلت النتائج على أن المتناول اليومي لهذه العناصر من الأغذية المحلية كاف لاحتياج الفرد اليومي ما عدا الكالسيوم والزنك.

كما تم حساب المتناول اليومي للفرد السعودي بناء على استبيان تم توزيعه على ٢٠٠ أسرة في مدينة جدة. ودلت النتائج على أن المتناول اليومي من هذه العناصر أقل من احتياج الفرد ما عدا المغنيسيوم.