

Chemical Identification of Some Toxic Residues Bioaccumulated in Date Palm Seeds (*Phoenix dactylifera*)

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Abstract: The dangers resulting in the consumption of contaminated elements found on date fruits or seeds products after exposure to pesticides and toxic chemicals are harmful to health. In the present study, the organic extract of date palm seeds was analyzed using gas chromatography coupling-mass spectrometry (GC/MS). The results obtained show a high concentration of fatty substances such as trans-oleic acid, the most abundant unsaturated fatty acid (18.67%) followed by monoenoic fatty acids, such as oleic acid methyl ester (8.87%). Secondary metabolites such as phenol, 2,6-di-tert-butyl- (4.97%), beta-ionone, methyl- (1.05%) and alkaloids such as elaeagnine (1.22%) were measured at low concentrations. Thirteen compounds belonging to linear hydrocarbons were found at a rate of 12.08%. The seeds were also exposed to pesticides such as diethyl parathion (9.84%) and toxic residues such as thiophene,3-butyl-,1,1-dioxide (0.51%) known to be toxic for human consumption.

Keywords: Date palm seeds; GC/MS; fatty substances; hydrocarbons; pesticide residues; hydrocarbons.

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1. Introduction

Particular attention must be given to the role of environmental technologies in monitoring pollutants. Their emissions into the environment, to identify the hazards of pollutants to the environment, and understand the tolerance levels of persistent pollutants in plants [1]. Actually, it is possible to use green plants as rapid biosensors for environmental identification, tracking, and the detection of the effects of pesticides, heavy metal pollutants, and other microbial contaminants [1,2]. For example, contamination of agricultural products by some pesticides residues potentially harmful compounds which could impact human health [3]. Most farms that produce vegetables and fruit are treated with more than one plant protection product or pesticides, the hazards posed by pesticides must be controlled to reduce their entry into the food chain [4,5]. These environmental problems have led to the possible use of various methods such as microextraction, associated with an analysis of micellar electrokinetic chromatography for the determination of pesticides in environmental samples and plants [6]. According to some information on exposure to environmental pollution and chemical mixtures such as toxins of chemical origin, metalloids can often be caused and accumulated during storage conditions [7], the level of toxic residues is revealed by chemical analysis of a food supplement, sometimes it shows some differences between what is indicated

on the label and the detected values [8]. Although the rapid screening methods allow the analysis of a large number of samples, the mass spectrometry methods with multiple analytes led full quantification of the analytes [9]. Risk assessment of individual exposure to pesticides induce mood disorders, and it has been documented that exposure to organophosphate pesticides type affects neuronal regeneration, as results in the mechanism of toxicological action, may lead to the recorded increase in the risk of developing anxiety and depression following occupational exposure to organophosphate pesticides [10]. Therefore, it is important to demand more stringent regulations to set the same quality standards because of preventing the harmful effects they may have on the consumer. The world's population was currently using herbal and natural remedies for medical care [11]. The fruits and seeds of the date palm (*Phoenix dactylifera*) have beneficial properties that can serve as a source of nutraceuticals, dietary and phytotherapeutic purposes, fruits and seeds are rich in alkaloids, proteins, carbohydrates, fatty acids, carotenoids, vitamins, polyphenols, flavonoids, and tannins, as well as various types of nutrients such as potassium, calcium, magnesium and phosphorus and various type of fatty acids [12-14]. The objective of this study is to analyze the chemical composition of date palm seeds (*Phoenix dactylifera*), in order to determine whether these seeds contain potentially toxic elements, in this situation, the consumption of fruit will have a direct effect on human health.

2. Materials and Methods

2.1. Plant Material.

The date fruit of Deglet Nour cultivars (AC) was harvested in autumn 2013, from Tozeur (Tunisia) 33°55'10"N, 8°08"E, the fruits were marketed for human consumption. The seeds were reduced completely fine powder by an electric grinder (type KSW 445 CB) and placed in a hermetically sealed bottle.

2.2. Detail on the extraction of the organic fraction.

The organic extracts from date seeds were obtained according to protocol optimized by Lebreton and co-workers [15]; in the first order, acid hydrolysis was performed on 20g plant material blinded with 80 mL of hydrochloric acid (2N HCl). After that, the mixture prepared into the Erlenmeyer flask was boiled in a water bath at 100 °C for 40 minutes. To extract chemical compounds, the acid mixture is separated twice into two fractions with diethyl ether (60-60 mL). The colors of fractions obtained are light yellow corresponding to organic fraction, for the first time, it dissolved in methanol and then evaporation host. For chromatographic analysis, the chemical compounds are dissolved in hexane. However, the orange-red fraction was eliminated.

2.3. GC/MS profiling of chemical composition of seeds and pollen extracts.

The chemical analysis of the organic extract was performed by GC/MS using an HP 6800 chromatograph (Agilent Technologies) coupled to a mass spectrometer HP 5973 MSD equipped with a capillary column HP-5MS (5% phenyl and 95% dimethyl polysiloxane) with dimensions of 30 m x 0.25 mm x 0.25 microns. The temperature in the column was programmed at 60 °C to 290 °C at 6 °C. min⁻¹ and then held isothermal for 5 min. The gas carrier is helium and flow at a rate of 0.8 mL.min⁻¹. The injector temperature was at 250 °C,

the volume of extract injected is 1 μ l in split mode (20:1), and the solvent is hexane (within 4 min). The interface temperature was 280 $^{\circ}$ C, and of ionization source was 230 $^{\circ}$ C and the ionization was effected by electron impact (EI) with a potential of 70 eV. The analyzer was a quadrupole (150 $^{\circ}$ C). The mass spectrum is recorded using a mass detector scan mode (34-550 amu). The GC/MS can detect compounds according to their elution order and identify by comparing their mass spectrum and retention time (RT) with those of *Wiley* databases *NIST 7* and *02*. The content of chemicals constituents is expressed by percentages peak-area (Area %). The compounds selected for identification are those with a recognition rate higher than 30%

3. Results and Discussion

The chemical composition of organic extract gives quantitative levels of the content, which is expressed by the distribution area in % (Figure 1). Various compounds were found well as fatty acid, and ester bonds of fatty acids were formed under transesterification into methanol, other fatty compounds, aromatic substances, alkaloids, aliphatic hydrocarbons that were found with very low content such as toxic compounds, and pesticide residues.

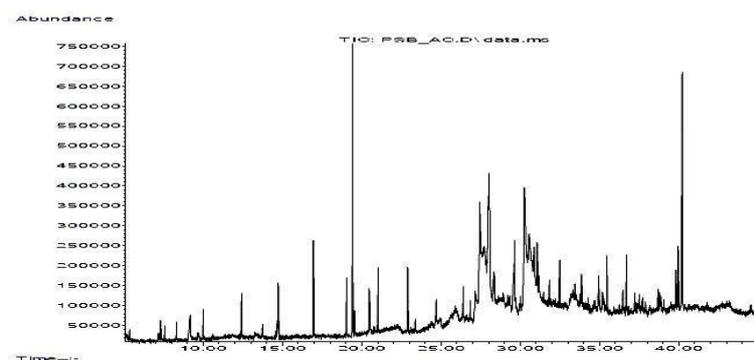


Figure 1. Chromatogram of the organic extract of date seed obtained by GC/MS analyses.

3.1. Fatty acids.

The analyzed date palm seeds extracts (AC) contain methyl esters of saturated and unsaturated fatty acids (%) (Table 1). In general, the presence of a double bond reduces a fatty acid melting point, increases its oxidation susceptibility, and contributes to the existence of several geometric and positional isomers for the same length of the carbon chain, such as trans-oleic acid the most abundant unsaturated fatty acid (18.67%) (Figure 2), followed by monoenoic fatty acids, such as oleic acid methyl ester (8.87%). According to previous works, we can see that the soxhlet extraction of date palm seeds gives better extraction of unsaturated fatty acids compared to other fatty derivatives [16]. A study was performed to assess the chemical composition and the physicochemical properties of the seed oils from 6 varieties of date palm (*Ph. dactylifera*), the average free content of fatty acids was 0.5%. The seed oil also had a mean content tocol and its related compounds (2 tocopherols and 2 tocotrienols) of 70.75 mg/100 g [17]. Our results corroborate with those found by Besbes et al. [18] with a concentration in oleic acid at 39.17%. Nehdi et al. [19] report that the major fatty acid found in the seeds of *Ph. Canariensis* is oleic (50%). The seeds of some Arecaceae such as *Phoenix canariensis* Hort. [19] and *Washingtonia filifera* (Linden ex André) H. Wendl. [20] constantly contains oleic acid (40.60%); it is the most abundant compound compared to other fatty acids. Also, the major fatty acid that is containing in seeds of *Ph. Theophrasti* Gr. [21] is an oleic acid type (17.88%). A study has shown that oleic acid is the precursor of *cis*-vaccenic acid. The

conversion of *cis*-vaccenic acid from oleic acid is considered to be a secondary isomerization pathway revealed in many fruits [22]. The coconuts (*Cocos nucifera*), African oil palm (*Elaeis guineensis*) and date palm (*Phoenix dactylifera*) are the *Arecaceae* family's three main cultivated species, for which genome sequences have been recently made available to clarify the similarities and differences in lipid metabolism between the three main species of *Arecaceae* [23], it provides valuable details for physiological studies; the genes involved in transforming pyruvate into fatty acid and many of the lipid-related genes were strongly homologous and conserved in homologous segments for the selection of fatty acid composition and oil content in these cultures between the three species [23].

Table 1. Chemical composition of the organic extract of Deglet Nour seeds cultivars analyzed by GC/MS.

N°	Compound	IUPAC name / Synonyme	RT (min)	Area %	Molecular Weight	Molecular Formula
1	Pentanoic acid, 4-oxo-, methyl ester	Levulinic acid, methyl ester	7.324	0,41	130,1418	C ₆ H ₁₀ O ₃
2	Decane	n-Decane	7.577	0,25	142,28	C ₁₀ H ₂₂
3	NI		8.313	0,310		
4	Pentanoic acid, 4-oxo-	Levulinic acid / Laevulinic acid	9.178	1,03	116,11	C ₅ H ₈ O ₃
5	Undecane	n-Undecane	10.002	0,45	156,31	C ₁₁ H ₂₄
6	Dodecane	n-Dodecane	12.420	0,69	170,33	C ₁₂ H ₂₆
7	Pentanoic acid, 4-oxo-, butyl ester	Levulinic acid, butyl ester	13.744	0,21	172,22	C ₉ H ₁₆ O ₃
8	Tridecane	n-Tridecane	14.745	1,21	184,37	C ₁₃ H ₂₈
9	Tetradecane	n-Tetradecane	16.952	1,55	198,38	C ₁₄ H ₃₀
10	Pentadecane	n-Pentadécane	19.047	0,94	212,41	C ₁₅ H ₃₂
11	Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	Phenol, 2,6-di-tert-butyl-	19.424	4,97	206,32	C ₁₄ H ₂₂ O
12	Dodecanoic acid, methyl ester	Lauric acid, methyl ester	19.553	0,47	214,34	C ₁₃ H ₂₆ O ₂
13	1-Methyl-2-trifluoroethyl-1,2,3,4-tetrahydro-.beta.-carboline	Elaeagnine	20.483	1,22	186,25	C ₁₂ H ₁₄ N ₂
14	Hexadecane	n-Hexadecane	21.024	1,06	226,44	C ₁₆ H ₃₄
15	Heptadecane	n-Heptadecane	22.908	1,04	240,48	C ₁₇ H ₃₆
16	Tetradecanoic acid, methyl ester	Myristic acid, methyl ester	23.378	0,19	242,39	C ₁₅ H ₃₀ O ₂
17	Octadecane	n-Octadecane	24.691	0,53	254,49	C ₁₈ H ₃₈
18	NI		25.615	0,95		
19	NI		25.909	1,89		
20	Nonadecane	n-Nonadécane	26.397	0,76	268,52	C ₁₉ H ₄₀
21	Hexadecanoic acid, methyl ester	Palmitic acid, methyl ester	26.845	0,40	270,45	C ₁₇ H ₃₄ O ₂
22	Tertridecanol	Tetradecan-1-ol	27.168	1,89	214,39	C ₁₄ H ₃₀ O
23	Hexadecanoic acid	Palmitic acid / Cetylic acid	27.457	7,85	256,42	C ₁₆ H ₃₂ O ₂
24	Hexadecanoic acid	Palmitic acid / Cetylic acid	27.721	7,11	256,424	C ₁₆ H ₃₂ O ₂
25	Phosphorothioic acid, O,O-diethylO-(4-nitrophenyl) ester	parathion	28.022	9,84	263,20	C ₁₀ H ₁₄ NO ₅ P S
26	Octadecanal	Octadecanaldehyde	28.345	1,59	268,49	C ₁₈ H ₃₆ O
27	9-Octadecenoic acid (Z)-, methyl ester	Oleic acid, methyl ester	29.628	2,82	296,48	C ₁₉ H ₃₆ O ₂
28	Cyclohexane, 1-(1,5-dimethylhexyl)-4-(4-methylpentyl)-	1-(6-methylheptan-2-yl)-4-(4-methylpentyl)cyclohexane	30.011	0,69	280,53	C ₂₀ H ₄₀
29	9-Octadecenoic acid, (E)-	Elaidic acid / trans-Oleic acid	30.264	9,37	282,46136	C ₁₈ H ₃₄ O ₂
30	9-Octadecenoic acid, (E)-	Elaidic acid / trans-Oleic acid	30.558	9,30	282,46	C ₁₈ H ₃₄ O ₂
31	9-Octadecenoic acid (Z)-	Oleic acid, methyl ester	30.864	3,31	296,48	C ₁₉ H ₃₆ O ₂
32	Docosane	n-Docosane	31.070	1,90	310,60	C ₂₂ H ₄₆
33	9-Octadecenoic acid (Z)-	Oleic acid, methyl ester	31.176	2,10	296,48	C ₁₉ H ₃₆ O ₂

N°	Compound	IUPAC name / Synonyme	RT (min)	Area %	Molecular Weight	Molecular Formula
34	3-Heptafluorobutyroxypentadecane	1-Ethyltridecyl 2,2,3,3,4,4,4-heptafluorobutanoate	31.829	0,72	424,4	C ₁₉ H ₃₁ F ₇ O ₂
35	Tricosane	n-Tricosane	32.488	0,92	324,62	C ₂₃ H ₄₈
36	9-Octadecenoic acid (Z)-	Oleic acid, methyl ester	33.189	0,64	296,48	C ₁₉ H ₃₆ O ₂
37	cis-2,3-Epoxy cyclohexane-1-methanol	[(1R,6S)-7-oxabicyclo[4.1.0]heptan-5-yl]methanol	33.318	0,96	128,16	C ₇ H ₁₂ O ₂
38	9-Octadecenamide, (Z)-	Oleamide; Oleic acid amide	33.442	0,73	281,47	C ₁₈ H ₃₅ NO
39	Hexadecenoic acid, Z-11-	Z-11-Hexadecenoic acid	33.771	0,38	254,40	C ₁₆ H ₃₀ O ₂
40	Dotriacontane	n-Dotriacontane	33.866	0,78	450,86	C ₃₂ H ₆₆
41	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	Glycerol α-monooleate	34.289	0,22	356,53	C ₂₁ H ₄₀ O ₄
42	NI		34.678	0,38		
43	1H-Indole, 5-methyl-	1H-Indole, 5-methyl-, monohydrate	34.942	1,10	149,19	C ₉ H ₁₁ NO
44	Silane, methylenebis(dimethyl-	(E)-1-(2,6,6-trimethylcyclohexen-1-yl)pent-1-en-3-one	35.184	0,47	132,35	C ₅ H ₁₆ Si ₂
45	1,9-Tetradecadiene	(9Z)-tetradeca-1,9-diene	35.249	0,47	194,36	C ₁₄ H ₂₆
46	.beta.-Ionone, methyl-	(1E)-1-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-1-penten-3-one	35.466	1,05	206,32	C ₁₄ H ₂₂ O
47	Nonahexacontanoic acid	n-Nonahexacontansaeure	36.467	0,78	999,8	C ₆₉ H ₁₃₈ O ₂
48	2-methyl 3-(4-(1'-methylethyl)-phenyl)propanal	3-(4-Isopropylphenyl)-2-methylpropionaldehyde	36.690	1,10	190,28	C ₁₃ H ₁₈ O
49	3-(2,2-dideuterobutyl)-thiophene-1,1-dioxide	Thiophene, 3-butyl-, 1,1-dioxide	37.208	0,51	172,24	C ₈ H ₁₂ O ₂ S
50	1H-Indole, 7-methyl-	7-methyl-1H-indole	37.497	0,49	131,17	C ₉ H ₉ N
51	Thiophene, 2-hexyl-	2-hexylthiophene	37.714	0,75	168,29	C ₁₀ H ₁₆ S
52	.beta.-Ionone, methyl-	(E)-1-(2,6,6-trimethylcyclohexen-1-yl)pent-1-en-3-one	37.897	0,33	206,32	C ₁₄ H ₂₂ O
53	NI		38.679	0,64		
54	NI		38.780	0,48		
55	Dodecane, 1,2-dibromo-	1,2-Dibromododecane	38.862	0,51	300,07	C ₁₀ H ₂₀ Br ₂
56	1H-Indene, 2,3,3a,4,7,7a-hexahydro-2,2,4,4,7,7-hexamethyl-	(3aR,7aR)-2,2,4,4,7,7-hexamethyl-1,3,3a,7a-tetrahydroindene	39.056	0,26	206,37	C ₁₅ H ₂₆
57	Cyclooctene, 4-methylene-6-(1-propenylidene)-	(1Z)-4-methylidene-6-prop-1-enylidenecyclooctene	39.821	0,87	160,25	C ₁₂ H ₁₆
58	Cholesta-4,6-dien-3-ol, (3.beta.)-	[10,13-dimethyl-17-(6-methylheptan-2-yl)-2,3,8,9,11,12,14,15,16,17-decahydro-1H-cyclopenta[a]phenanthren-3-yl] benzoate	39.968	1,30	384,63	C ₂₇ H ₄₄ O
59	Cholest-5-ene, 3-bromo-, (3.beta.)-	(3S,8S,9S,10R,13R,14S,17R)-3-bromo-10,13-dimethyl-17-[(2R)-6-methylheptan-2-yl]-2,3,4,7,8,9,11,12,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthrene	40.210	4,84	449,55	C ₂₇ H ₄₅ Br
Number of substances detected				59		
Total area (%)				99,98		
Number of unidentified substances (NI)				6		

3.2. Other fatty compounds and phytosterols.

Certain fatty compounds have been found in date palm seeds (Figure 2) such as α-monooleate glycerol (0.22%), it is an amphiphilic lipid and biodegradable compound, with

many useful applications [24-26]. The α -monooleate glycerol is a friction agent commonly used in the lubricant industry. It is thought to have lubricated metallic surfaces by its hydrolyzing to oleic acid, glycerol, and calcium oleate (CaOl_2) [27]. Also, the oleamide (*cis*-9,10-octadecenoamide) is found in date palm seeds at 0.73%. It is a fatty acid amide discovered in cerebrospinal fluid in sleep-deprived animals [28], has a variety of effects that impart as signaling molecules potential in some biological activities [28,29].

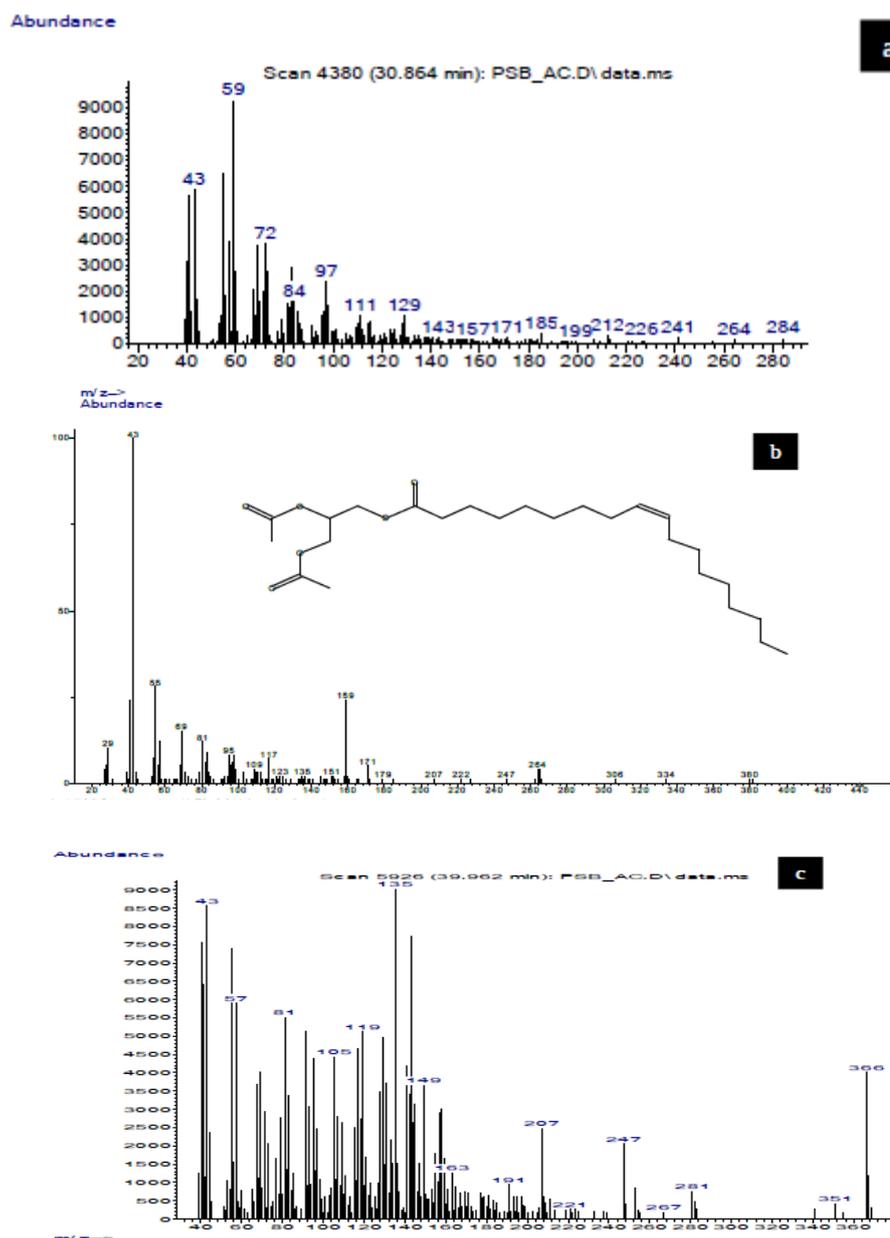


Figure 2. Mass spectrum of principal fatty compounds found in date palm seeds: a-oleamide; b- glycerol α -monooleate; c- 4,6-cholestadien-3 β -ol.

Indeed, 4,6-cholestadien-3 β -ol (1.3%) identified in date palm seeds was also found in some crude extracts from Brazilian and Spanish marine species (*Condrosia reniformes*, *Tethya rubra*, and *Tethya ignis*) [30]. However, the 3 β -bromo-5-cholestene (4.84%) was isolated (Figure 3) for the first time from the date seeds.

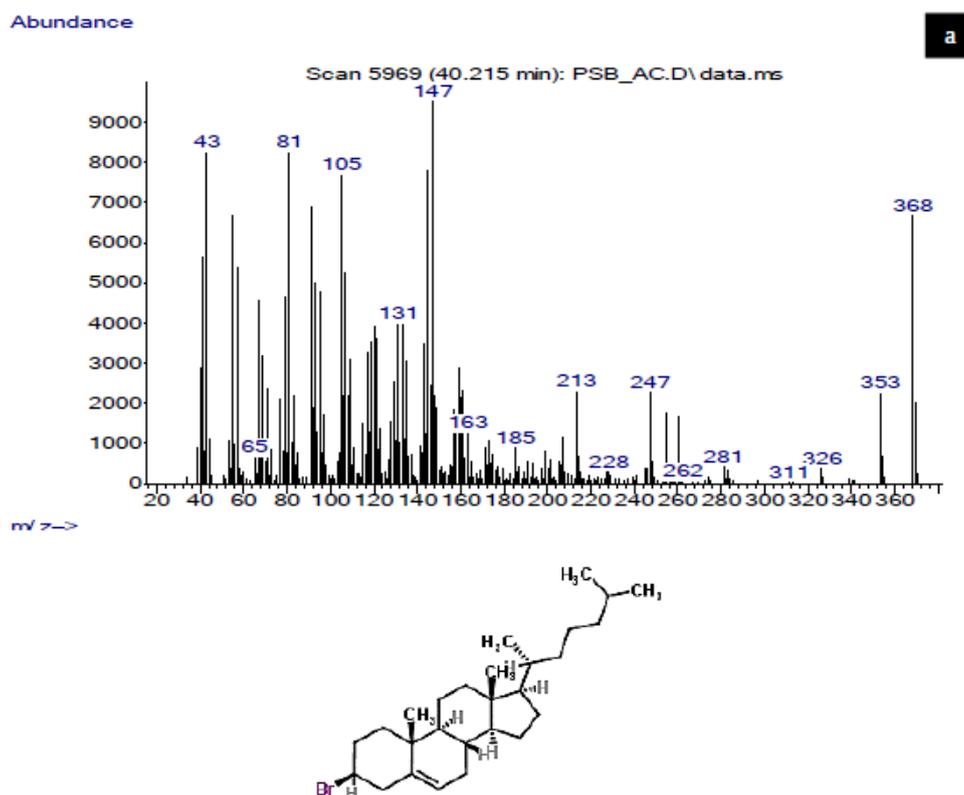


Figure 3. Mass spectrum, cholest-5-ene 3-bromo-, (3.beta.)-(a) and its structural formula (b) found in seed date.

3.3. Aromatics and secondary metabolites.

The analyzes using CG/SM revealed the presence of secondary metabolites (Figure 4) such as phenol 2,6-di-tert-butyl-(4.97%); 3-(4-isopropylphenyl)-2-methylpropionaldehyde (1.1%) a cyclamen aldehyde a colorless liquid may turn to pale yellow. It is considered a strong floral aroma [31].

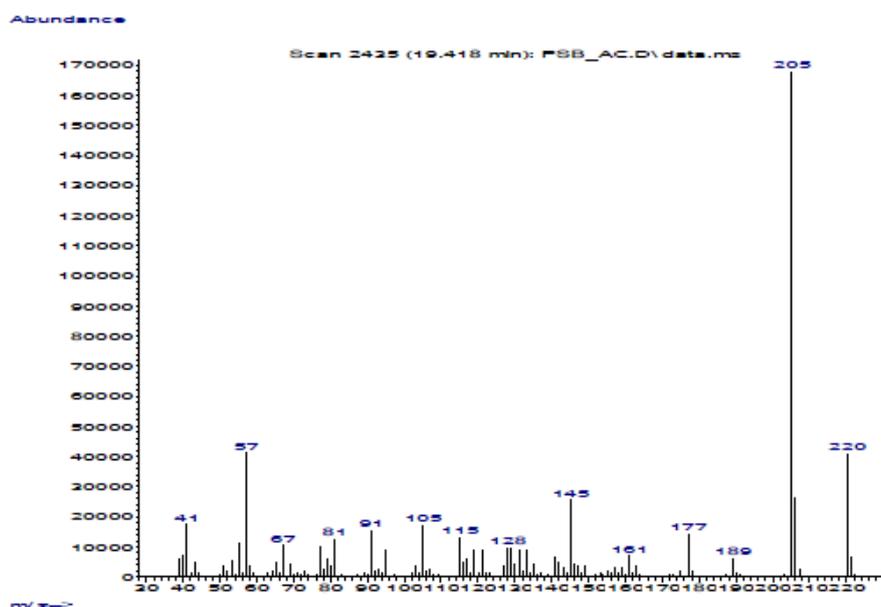


Figure 4. Mass spectrum of phenol, 2,6-bis (1,1-dimethylethyl) -4-methyl- found in date palm seeds.

A terpene molecule beta-ionone, methyl-(1.05%) has also been identified, and it is used in many perfumes. According to some studies, the average skin content resulting from the use of isomethyl-b-ionone and its derivatives in fine fragrance formulae would be used at a rate of 1.18% [32,33] in the final product. However, alkaloids elaeagnine (1.22%) is found in date palm seeds for the first time.

3.4. Hydrocarbons.

Hydrocarbons (Table 1) are quite found in date palm seeds. They are mainly represented by saturated linear alkanes such as n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentadecane, n-hexadecane, n-heptadecane, n-octadecane, n-nonadecane, n-docosane, n-tricosane and n-dotriacontane with a rate of 12.08%. The hydrocarbons can be found in food due to contamination from various origins [32-37], they have been found in many food products, including edible vegetable oils which, due to their lipophilic nature, are easily contaminated and widely distributed in the environment and known to be carcinogens [33]. Therefore environmental management requires an understanding of the bioaccumulation and the using of various analytic methods to estimate the rate of hydrocarbon in plants [33,34]. Two main routes of hydrocarbon pollution in vegetable oils have been suggested [35,36]: interaction with the contaminated atmosphere and the method of drying the raw material by combustion fumes and natural gas. Air pollution from dust and particles containing large quantities of hydrocarbons can contaminate plants by air emissions during the growth vegetation phase [32]. It can be found in diesel engine exhaust particles [36]. This surface contamination can be passed to the final product or during the food packaging process [38].

3.5. Toxic chemical compounds and pesticide residues.

Concentrations of pollutants and potentially toxic elements in seeds are represented in low contents, such as thiophene, 3-butyl-,1,1-dioxide (0.51%). Also, it has been revealed the presence of residues of pesticides such as diethyl parathion (9.84%) (Figure 5).

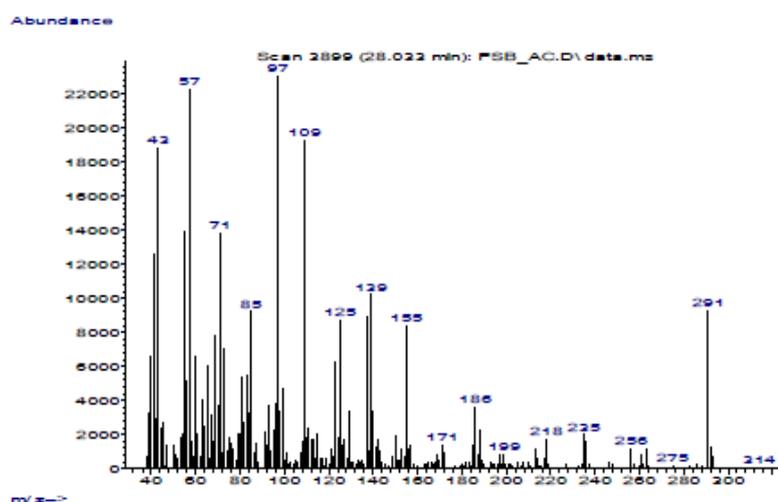


Figure 5. Mass spectrum of phosphorothioic acid, O,O-diethylO-(4-nitrophenyl) ester found in date palm seeds.

Due to its introduction into the general environment, pesticide residues are found in food and are toxic to insects [39]. Indeed, organophosphate pesticides are often used to control insect perforations that can pose a risk to bees [40]. The latest studies on the risks associated

with organic phosphate exposure have been reported [41,42] pesticides have a wide range of physicochemical properties. However, they are particularly difficult to extract in order to facilitate their analysis from various vegetation and environment sources in different samples [43]. So, we can deduce that organic contaminants can enter the vegetation by the absorption process from the atmospheric and environmental contaminants, and in general, it depends on the type of toxic compounds [44,45]. At the same time, co-extraction of fats and other components of the matrix is very difficult to avoid, the isolation of pesticides and other chemical pollutants from high-fat food samples before subsequent analytical measures is still a challenging problem to which a great deal of effort has been made in the development of methods [46], especially given that the majority of pesticides are lipophilic compounds [47].

4. Conclusions

Plants are constantly exposed to a variety of disturbances caused by air and soil pollution, drought, deficiency, or excess of nutrients. However, over a long period, only certain plants react quickly to environmental stress. The risks resulting from the exposure to toxic chemicals elements of the fruits of the date palm (*Phoenix dactylifera*) were analyzed using the gas chromatography coupling mass spectrometry (GC/MS). The concentrations of various class fatty substances were detected, secondary metabolites including phenol, 2,6-di-tert-butyl, and alkaloids such as eleagnine were also identified at low concentration. However, date palm seeds have been exposed to pesticides, such as thiophene, 3-butyl, and 1,1-dioxide, and about thirteen linear hydrocarbons compounds have also been found in date palm seed. Based on this study, human consumption of date palm seeds may have harmful effects; however, it can be used as rapid biosensors for the detection of pesticide, hydrocarbons, and its pollutant effects in surface water or a contaminated environment.

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Conflicts of Interest

The authors declare no conflict of interest.

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