Asian Journal of Chemistry Vol. 2, No. 4 (1990), 407–415

Chemical Studies on the Roots of the Saudi Date Palm Tree—*Phoenix dactylifera L.*

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Petroleum ether extracts, ethyl alcohol extracts as well as ashed material of the roots of the date palm tree (*Phoenix dactylifera L.*) of cultivar Maktomey were analysed by gas-liquid chromatography, $^{1}H/^{13}C$ NMR spectroscopy and atomic absorption spectrophotometry. They were found to contain fixed oil, sugars and other significant organic and inorganic compounds. Although a very small quantity of fatty acids was extracted out, carbohydrates were found to be present in significant amounts. Mineral contents like Ca, Fe, K, Mg, Na and Zn were determined in the ashed material, with Na in dominant strength in the range of 2194.42 μg/g.

INTRODUCTION

In most desert areas of the world date palms have been widely grown as staple food. As one of the oldest cultivated tree crops, its benefits to agriculture are well known and many nations have appreciated its importance over centuries because of the economical and nutritional values of its fruits. Additionally the date palm tree has shown an outstanding ecological ability to survive in a climate of hot and dry, thus making it an ideal plant to combat desert expansion which is of much interest these days[14].

The date palm, being economically important in Saudi Arabia, is widely cultivated in the Kingdom making this one of the major date producing countries in the Arab world, Saudi Arabia is known for various environmental and location advantages for cultivation of palms and the production and marketing of dates and related industries. The fruit is of great importance as a source of human food and previously the seeds were utilized by villagers and farmers of Saudi Arabia as a complementary part of cattle diet[3].

Little information is present in the literature concerning the chemistry of date palm roots. Recently few reports have appeared concerning the other parts of the date tree[12]. Seeds of a few date cultivars in certain areas of the Kingdom of Saudi Arabia have been subjected to chemical investigations and were characterised by organic and inorganic analysis, including moisture, ash, proteins, carbohydrates, fibres, fixed oil, fatty acids, sterol, ergosterol and minerals[1,3,11]. Chemical analyses of stems were reported in a recent report[7]. Polyhydroxystilbenes, a mixture of hydrocarbons, esters, β-sitosterol, stigmasterol, campestrol, crude fatty acids and triglycerides were isolated. Stilbenes act as antimicrobiological agents responsible for

the durability of heartwood of various tree species, They have been isolated as well from several higher plants[4,7].

This report covers the study of the roots of the date palm tree cultivar Maktomey, which was collected from Al-Qasim region (Central region of Saudi Arabia) and subjected to chemical analysis (organic as well as inorganic) to isolate and identify its chemical constituents and to compare these with the results of those which were previously reported on seeds of the same cultivar produced in Saudi Arabia[1]. Both were studied with similar techniques such as: GLC, NMR (^1H and ^{13}C) and atomic absorption spectrophotometry.

EXPERIMENTAL

The roots of date palm tree under investigation were isolated from the mature tree of the cultivar Maktomy. Roots were washed thoroughly with distilled water to eliminate dust and soil-contents and dried under direct sunlight for five days and then in an oven at 50°C to complete dryness. The percentage water content was calculated (Table 7). The dried material was broken into small pieces and crushed to a fibric-powder.

For analysis of organic constituents about 100 g portions of the fibric powder were extracted in sequence with the following organic solvents: petroleum ether (60–80°), diethyl ether, chloroform and ethyl alcohol. Successive extractions of each solvent were evaporated in a rotavapor to remove the solvent and the percentage of the crude residue was calculated (Table 1).

TABLE 1

THE PERCENTAGE OF THE FOUR ORGANIC SOLVENT EXTRACTS OF THE ROOTS OF CULTIVAR MAKTOMEY AND THE SEEDS OF THE SAME CULTIVAR STUDIED UNDER SIMILAR ORGANIC EXTRACTIONS[1]

Maktomey cultivar	Pet. Ether	Diethyl ether	$CHCl_3$	EtOH	Fibre dry wt. %
Roots	0.26	0.29	0.13	3.44	91.98
Seeds	7.80	0.46	0.48	10.30	21.65

Carbohydrates Analysis

The ethyl alcohol extraction (the last extraction solvent) of the fibric-powder of the roots was dried prior to analysis. The dry material was sticky and dark-red in colour. About 5 mg were silylated in Tri-Sil-Z (a mixture of Trimethylsilylimidazole in dry pyridine) by heating at 60–70°C. The silylated product was subsequently analyzed by GLC on a Pye Unicam Series 304 chromatograph with FID. The coiled glass column (2 m×2 mm I.D.) was packed with 3% OV 17 on chromosorb W. The

column temperature was initially set at 150°C and increased to 320°C at a rate of 10°C/min. Injector temperature was 400°C while FID temp. was set at 250°C. The flow rate of carrier gas and oxygen free nitrogen was supplied at 40 ml/min. Hydrogen and air flow rate for the detector were 40 ml/min. and 300 ml/min respectively.

Inorganic Analysis

The method used for the analysis of mineral contents in the roots is mainly that one as described therein[1,11]. In brief 5g of fibric-powder of the root was ignited and ashed in a muffle furnace at 750°C for about 15 hrs. The ash was dissolved in 5 ml fuming HNO_3 after calculating its ash content total percentage; and subsequently transferred to a 100 ml volumetric flask filled with deionized water. The solution was then analyzed for its elemental composition in an atomic absorption spectrophotometer of Varian-Model AA-1475 Series. The absorption mode was used according to the Varian Publication of 1978 and the calibration absorption was compared with that of the corresponding standards of the respective elements.

NMR Spectra

(i) *^{1}H NMR Spectra*: ^{1}H observed frequency 100 MHz; pulse width 20 μs (45°): pulse delay auto set, acquisition time auto set, data points 8k; spectral width 1000 Hz; effective resolution 0.10 Hz, probe temperature 28°C, sample tubes 10 mm, probe ^{1}H/^{13}C dual probe and deuterium internal lock.

(ii) *^{13}C NMR Spectra*: ^{13}C observed frequency 25 MHz; pulse width 10 μs (45°); pulse delay 15 s, acquisition time auto set; data points 8k; spectral width 5000 Hz, effective resolution 0.15 ppm, sample tube 10 mm: probe ^{1}H/^{13}C dual probe, ^{1}H noise decoupling and internal lock on the deuterium signal of the solvent.

RESULTS AND DISCUSSION

The dry weight percentage (based on the net weight of any roots) of each extract of roots of the date palm tree under investigation is presented in Table 1. Percentage oil 0.26% extracted with petroleum ether is very small amount in comparison to a similar extraction of date seeds of the same cultivar (7.80%)[1]. Chloroform and ether extracts too have yielded small quantities of material (0.29 and 0.13% respectively) (Table 1). While the ethanol extraction has taken out most of the constituents 3.2 to 3.44% containing carbohydrates, proteins and steroids.

The ethanolic extraction of root was found rich in carbohydrates which constitute a highly significant class of natural product. The GLC analysis on the soluble silylated, extract material in TMSI (Trimethyl-

silylimidazole) revealed an obvious presence of sugars both reducing and non-reducing, upon comparing them with the silylated authentic corresponding standard samples.

The monosaccharides, mannose, fructose and α-β-glucose were prominently observed in the root extract in the quantity (4× more; ±2× more in ±2× more; 2.5× more. Sucrose slightly by (1/3) less, maltose (1/3) less than the date-seeds of the same investigated cultivar (Table 2)[1]. A GLC chromatogram of the silylated ethyl alcohol extract of the root is reproduced in Fig. 1. Inspection of the GLC analysis (Fig. 1) revealed the presence

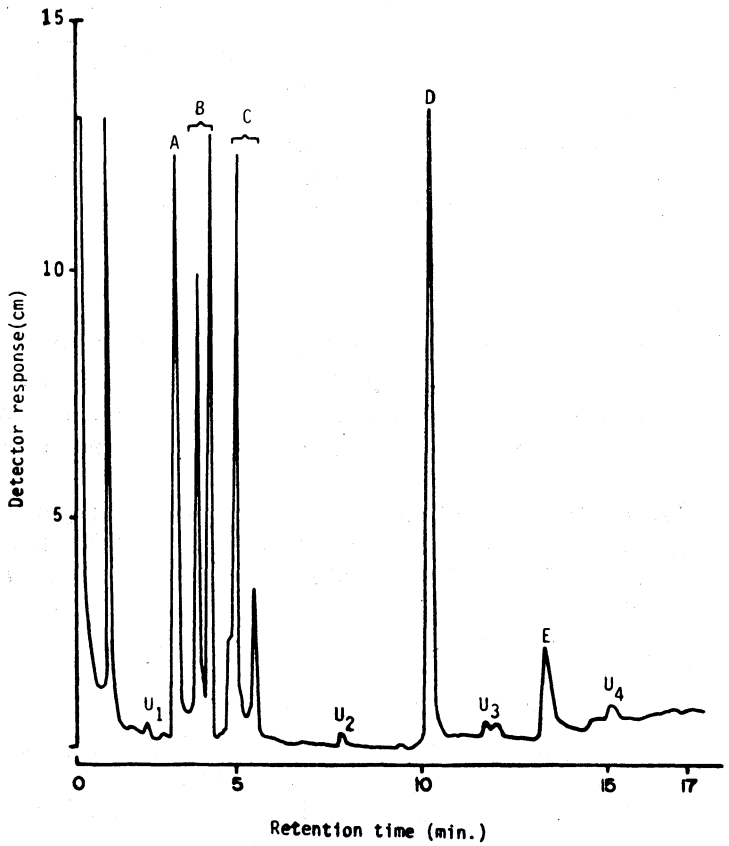

Fig. 1. Chromatogram tracing of sugar contents of alcohol extraction from the roots of date palm tree (Cultivar Maktomey) where alphabet for each peak refers to name of the sugar.

of some additional peaks (U_1–U_4) which could probably be some other compounds present as traces in the extract attributed as unknown (Table 2). However the observed result in Table 2 clearly indicates that the most available percentage of sugar among others is sucrose (22.38%)

which agrees well with that of the previous reports on the date seeds[1,3]; while maltose comes in a fair amount.

TABLE 2

RELATIVE SUGAR CONTENTS IN THE ALCOHOL EXTRACT OF THE INVESTIGATED SEEDS OF THE CULTIVAR MAKTOMEY[1] WITH THAT OF THE ROOTS OF THE SAME CULTIVAR UNDER INVESTIGATOR

Sugar / Maktomey	Mannose (A)	Fructose (B)	Glucose (C)	Sucrose (D)	Maltose (E)	Unknown			
						U_1	U_2	U_3	U_4
Roots	17.09	13.76	16.93	22.38	8.87	0.30	1.10	1.12	0.67
Seeds	4.43	7.37	6.40	30.80	12.11				

Further steps were undertaken using ^1H and ^{13}C NMR spectroscopy to determine the structures of the sugars observed in the roots. The ^1H and ^{13}C NMR chemical shifts assignments were ensured by comparing them with that of authentic standard samples of the corresponding sugars (Tables 3 and 4). The ^1H NMR spectrum for the investigating root shows

TABLE 3

^1H NMR CHEMICAL SHIFTS FOR SUGAR CONTENTS OF THE ROOTS OF MAKTOMEY CULTIVAR WITH AUTHENTIC STANDARD SAMPLES FOR THE SUGARS IN DMSO-d_6 AT 28°C

Name	Chemical Shifts
Roots	1.05; 3.44; 4.43; 5.88; 6.69
Mannose	3.41; 3.47; 3.52; 4.47; 4.63; 4.85; 4.90; 6.19; 6.23
Fructose	3.29; 3.49; 3.60; 4.42; 4.67; 5.14; 5.3; 5.6
Glucose	3.12; 3.5; 4.43; 4.65; 4.77; 4.9; 6.12; 6.23
Sucrose	3.17; 3.41; 3.59; 3.87; 4.38; 4.48; 4.79; 5.03; 5.19
Maltose	3.33; 3.59; 4.48; 4.90; 5.43; 6.33; 6.66

its signals at δ 1.05; 3.44; 4.43; 5.88 and 6.69 in solvent DMSD-d_6 at room temperature. By examining however the available data for the standard samples of different sugars in Table 3 the presence of mannose, for example, can be confirmed on the basis of two peaks available at δ 3.44 and 4.43 considering the solute effects on chemical shifts. However, as the five observed sugars are present together, an obvious probability of signals overlapping each other could be expected[1].

Nevertheless ^{13}C chemical shifts are more reliable and accurate in structure elucidation than ^{1}H NMR because of its relative sensitivity to chemical environment. In the similar way the presence of different sugars in the extract can be confirmed by picking up the known carbon and co-migrating it with that of the corresponding ^{13}C signals (Table 4). As

TABLE 4

^{13}C CHEMICAL SHIFTS FOR SUGAR CONTENTS OF THE ROOTS OF MAKTOMEY CULTIVAR WITH AUTHENTIC STANDARD SAMPLES FOR THE SUGARS IN DMSO-d_6 AT 28°C

Name	Chemical shifts
Roots	18.62; 29.13; 56.15; 63.14; 70.66; 76.88; 144.60
Mannose	61.41; 67.28; 70.45; 71.07; 72.98; 93.82
Fructose	62.88; 69.74; 75.61; 81.72; 97.81; 101.80
Glucose	61.00; 70.34; 71.69; 72.09; 72.86; 91.94
Sucrose	60.53; 62.11; 69.86; 71.62; 72.85; 74.32; 77.14; 82.54; 91.70; 104.03
Maltose	69.80; 70.15; 71.80; 72.39; 73.27: 74.97; 76.32; 80.31; 90.94; 100.68

such the available data in Table 4 indicates the presence of five types of known sugars which are mannose, fructose, glucose, sucrose and maltose. Here too the overlapping of signals of each other could not be routed out as they are present together along with some additional signals of other compounds present as traces in the extract.

Fatty acids, the natural derivatives of lipids, which constitute an important factor to plant world, are usually a mixture of complex triesters of glycerol (triglycerides). Most seeds of the date palm trees were found to have natural fatty acids both saturated and unsaturated[1,3,10,11] along with essential fatty acids like linoleic acid etc. which is a dietary requirement for the healthy growth of animals[3,8]. The neutral fraction of dewaxed hexane from the stems of Phoenix dactylifera contained mixtures of hydrocarbons, fatty acids, triglycerides, steroid ketones, hydroxy ketones etc.[7]. To isolate, identify and determine the different fatty acids present in the roots, our study concentrated on the petroleum ether extraction of the roots which gave the fixed oil content[1,11]. The ^{1}H and ^{13}C NMR spectroscopy were performed on the cited successive organic solvent extraction which yielded only small amounts (Table 1) to determine the configuration of different fatty acids present therein. The saturated ester like methyl ester showed its signals in ^{1}H NMR spectrum of the extract at δ 0.88 (W-CH_3); while the β-CH_2-α-CH_2 and ester methyl groups appear in the spectrum at δ 1.26; 1.60; 2.28 and 3.83 respectively in the solvent $CDCl_3$ at 28°C under 100 MHz spectrometer (Table 5). The

methyl oleate signal shows for olefinic protons at δ 5.34 (a triplet) and a singlet for allylic proton at δ 2.01 (cis) in the same solvent.

TABLE 5

^{1}H NMR CHEMICAL SHIFTS OF FATTY ACIDS FROM THE PETROLEUM ETHER EXTRACTION OF THE DATE PALM ROOTS (MAKTOMEY CULTIVAR) IN SOLVENT $CDCl_3$ AT 28°C

Maktomey	Chemical Shifts			
	—CH_3	—CH_3 and OCH_3	Olefinic	Others
Roots	0.88	1.26; 1.60; 2.01; 2.28; 2.77; 3.83; 4.14	5.34	4.96; 5.09

The ^{13}C NMR spectroscopy provided unambiguously more accurate informations with reliable clues for determining the structures of fatty acids in this study where the unsaturated carbons are unaffected by the influence of deshieldings. In the ^{13}C NMR spectrum of the extract of the roots, the signals for alkenes appeared at δ 127.92 and 130.0 for cis and trans respectively; while saturated methyl ester carbon showed signals at δ 29.82. The signals for W–CH_3 were at δ 14.09 and for CH_2 carbons were at δ 22.77; 24.95; 27.30; 29.82; 31.95; 34.07. The ester methyl carbon signals appeared at δ 62.08, while the signal for carbon of carbonyl showed at δ 173.26 (Table 6). However in this study too the chemical shifts

TABLB 6

^{13}C NMR CHEMICAL SHIFTS OF FATTY ACIDS FROM THE EXTRACTION OF PETROLEUM ETHER OF THE DATE PALM ROOTS (MAKTOMEY CULTIVAR) IN SOLVENT $CDCl_3$ AT 28°C

Maktomey	Chemical shifts				
	—CH_3	—CH_2 and OCH_3	Olefinic	—C=O	Others
Roots	14.10	22.77; 24.96; 25.77	127.92	173.26	62.08
		27.30; 29.82; 31.65; 32.05; 34.11	129.98		75.85

assignments were verified with the corresponding samples of the pure fatty acids[1].

The ionic contents of the investigated roots were studied in relation to their inorganic constituents in the instrument atomic absorption spectrophotometer (Inorganic Analysis) where the results were recorded in μg/g amounts of dry fibric powder of the root (Table 7). It was

apparent that the roots were rich in macro and trace minerals essential for healthy growth of the plant. Many cations like Ca^{++}, Fe^{+++}, K^{+}, Mg^{++}, Na^{+} and Zn^{++} were observed in the acid digested solution of the ashed material of the root. The consecutive result in Table 7 indicates the significant presence of Na^{+}, Mg^{++}, K^{+} and Ca^{++} quite in large amount when compared with similar contents in the seeds of the same cultivar (Table 7)[1]. The root system was found to contain more Ca rather than the other sections of the plant, i.e., leaves, stem shoots and fruits, holding true the observation when the level of the nutrient supply changes and incubated for a short period to study the ionic content of seedlings of the likewise cultivars[2]; and that the differences could be due to cultivar difference as the same was noted by many previous workers in the different species[6,15]. Further the high ratio of Ca in the root may be attributed due to its poor mobility[5]; while potassium (K^{+}) being an essential element and mobile ion was evenly distributed in the root[2]. Moreover the roots were observed to have possessed a greater ability for the absorption of Ca in the presence of which other ions like K and Mg are markedly enhanced in the rate of absorption. In the absence of Ca, it was found that the normal functioning of cellular membrane was impaired[10]. It is generally accepted that Ca is essential for maintenance of the roots' functional integrity of cell membrane and any omission of it was observed to cause abnormalities in the membrane functioning[10,16].

TABLE[1]

THE MINERAL CONTENTS IN μg/g OF THE ROOTS OF CULTIVAR MAKTOMEY WITH ASH % AND WATER % TOGETHER WITH ALREADY INVESTIGATED DATE SEEDS OF THE SAME CULTIVAR, MAKTOMEY[1]

Maktomey	Elements										
	Water %	Ash %	Al^{+++}	Ca^{++}	Cd^{++}	Cu^{++}	Fe^{+++}	K^{+}	Mg^{++}	Na^{+}	Zn^{++}
Roots	15.0	7.0	—	1714.0	—		20.0	1360.0	500.0	2194.22	1.22
Seeds	7.25	1.42	2.0	489.13	1.02	1.33	15.45	98.30	68.14	31.45	7.35

However, the rate of ions uptake by the roots from soil is different from cultivar to cultivar, differing in mineral contents as well as in the distribution of minerals[2]; while in the case of the Maktomey cultivar the roots were found to have (Table 7) the higher ratio of ion content showing the increased tolerance for the ions absorption. Among them they show the highest rate of tolerance for the absorption of Na in this cultivar (Table 7).

ACKNOWLEDGEMENTS

This research (Chem/1408/08) was supported by the Research Center, College of Science, King Saud University, Riyadh, Saudi Arabia. The authors would like to thank the University for financial support and Mr. Madana Gopal for running the NMR spectra.

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[*Received*: 31 October 1989; *Accepted*: 2 January 1990] AJC-129