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Protein and Amino Acid Composition of Three Varieties of Iraqi Dates at Different Stages of Development

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Protein contents and amino acid composition of date fruits were determined in three Iraqi varieties (Khastawi, Khadhrawi, and Zahdi) at different stages of development. Protein concentration for the three varieties was highest at the green stage. Seventeen total amino acids were detected and determined; their concentrations (dry basis) varied. Khastawi and Khadhrawi showed a higher concentration than the Zahdi variety. At the green stage, concentrations of glutamic acid, aspartic acid, lysine, leucine, alanine, and serine were highest. At the yellow and ripe stages, glutamic acid, aspartic acid, lysine, leucine, proline, and glycine were present at a high concentration. For most amino acids, the concentration of amino acids is higher at the yellow stage than at the ripe stage.

Iraq annually produces a considerable amount of dates, two-thirds of which is exported and the remainder of which is utilized locally for consumption or production of vinegar, syrup, and some alcoholic beverages. Several important varities grow in different parts of Iraq. These varieties differ in their color, taste, texture, sugar, protein, and amino acid contents. Date fruits are edible only when they are in the yellow or ripened stage and quite undesirable by man when they are at the green stage. Dates and date syrup are consumed by a large number of Iraqi's and in some low income families they are considered as an important source of food mainly because of their carbohydrate contents.

Qualitative and quantitative studies on the constituents of dates, such as carbohydrates, fats, proteins, and amino acids, at the ripe stage were reported: Ashmawi et al. (1956), Ragab et al. (1956), and Auda et al. (1974).

Amino acid and oligopeptide contents of California dates at different stages of development have been reported by Globbelaar et al. (1955) and Rinderknecht (1959). The amino acid composition of three varities of Iraqi dates at the ripe stage has also been reported by Al-Rawi et al. (1967) and Al-Aswad (1971).

There is very little information on the changes in proteins and amino acids that occur during development and ripening of some varieties of dates. Therefore, we measured changes in proteins and amino acids as a part of a study on the preservation and extension of the market life beyond the harvest season for these varieties which are grown in the Republic of Iraq.

MATERIALS AND METHODS

Sampling. Samples of three common varieties (Khastawi, Khadhrawi, and Zahdi) were obtained from Za'afarania Horticultural Experiment Station. For each

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Table I. Protein and Moisture Content of Three Varieties of Iraqi Dates at Different Stages of Fruit Maturation

Variety	Stage	Moisture %	Protein, % Fresh wt.	Protein, % Dry wt.
Khastawi	Green	81	0.7	4.4
	Yellow	48	1.1	2.2
	Ripe	11	2.0	2.3
Khadhrawi	Green	83	0.8	4.9
	Yellow	65	1.0	2.9
	Ripe	10	1.8	2.0
Zahdi	Green	81	0.7	3.9
	Yellow	63	1.7	2.0
	Ripe	10	1.8	1.9

stage of development fresh bunches were cut and immediately transported to the laboratory. Uniform fruits in shape, size, and color were brushed free of dust and stored in plastic bags at −20°C until analyzed.

The stages of development used in this study were green, fully yellow, and ripe. Fruits representing all stages were removed from the trees and analyzed immediately without allowing them to turn artificially to the other advanced stages.

Moisture and Total Nitrogen Determination. Moisture was determined by drying (oven method) samples (10 g) of date (in duplicate) in an oven at 65°C until they reached a constant weight (48 h was sufficient); the final results were standardized by the method of Bidwell and Sterling (1925).

Total nitrogen was determined by the Kjeldahl method, using 30% hydrogen peroxide in the digestion process as an oxidizing agent (Koch and McMeekin, 1924).

Amino Acid Analysis. *Amino Acids and Oligopeptides.* Samples of dates (4 g) were homogenized in a Virtis high speed homogenizer with 60 ml of deionized water for 6 min. The homogenate was mixed and placed in a graduate cylinder, and the volume brought to 80 ml.

Homogenate (20 ml) was taken and mixed with 80 ml of absolute ethanol. The mixture was then stoppered and stored overnight at 0°C in order to precipitate the protein. The sample was centrifuged at 10000*g* for 15 min. The supernatants were taken and evaporated to dryness in a rotary evaporator at 35–40°C. The residue was dissolved in 5 ml of citrate buffer (pH 2.2) and then filtered. One-milliliter aliquots were then used for analysis in a Beckman Model 120C Amino Acid Analyzer.

Total Amino Acids. The open flask method of Mondino and Bongiovanni (1970) was used. A sample of date (2 g) was placed in a round-bottomed flask with 250 ml of constant boiling, glass-distilled 6 N HCl. The mixture was bubbled with a fine stream of nitrogen gas and hydrolyzed under nitrogen atmosphere at a reflux temperature for approximately 24 h. The mixture was then cooled to room temperature, filtered, and evaporated to dryness in a rotary evaporator at 35–40°C. The residue was washed with 2 ml of distilled water and reevaporated. This process was repeated three times. The residue then was dissolved in 15 ml of citrate buffer (pH 2.2), refiltered, and washed with further 5 ml of the same buffer. The mixed filtrate (0.25 ml) was taken and analyzed on a Beckman Model 120C Amino Acid Analyzer.

RESULTS AND DISCUSSION

Moisture contents of all varieties examined were similar in the same stages of development except for Khastawi at the yellow stage where the moisture content was higher in the green stage followed by a rapid decrease during ripening (Table I). These results show a close similarity between the varieties studied and indicate that total solids

Table II. Total and Free Amino Acids in Three Varieties of Iraqi Dates in Different Stages of Development [Milligrams of Amino Acid per 100 g of Date (Dry Weight Basis)]

AA	Khastawi Green Free	Khastawi Green Total	Khastawi Yellow Free	Khastawi Yellow Total	Khastawi Ripe Free	Khastawi Ripe Total	Khadhrawi Green Free	Khadhrawi Green Total	Khadhrawi Yellow Free	Khadhrawi Yellow Total	Khadhrawi Ripe Free	Khadhrawi Ripe Total	Zahdi Green Free	Zahdi Green Total	Zahdi Yellow Free	Zahdi Yellow Total	Zahdi Ripe Free	Zahdi Ripe Total
Lys	10.0	461.6	2.2	262.2	6.8	83.8	8.2	460.4	3.5	200.5	3.4	66.5	3.9	357.0	2.7	144.0	9.8	93.7
His	1.9	116.5	1.5	65.4	0.8	36.8	1.2	131.3	1.6	64.6	0.2	0.1	1.3	103.0	1.6	39.0	0.1	26.5
Arg	6.7	271.3	4.0	145.6	5.3	80.9	9.8	299.5	4.7	131.9	2.1	62.3	6.9	224.0	4.7	91.8	4.6	74.4
Asp	22.7	423.0	88.5	352.2	3.9	161.2	20.3	558.8	52.6	285.6	2.9	159.9	46.2	369.2	97.3	194.7	8.6	129.8
Thr	10.3	187.3	2.4	109.7	1.4	62.8	10.7	209.4	3.8	108.6	2.2	55.0	6.2	155.4	2.7	61.8	1.9	46.4
Ser	28.1	317.8	10.9	133.7	7.6	67.4	92.0	367.8	11.7	134.8	6.7	69.0	52.7	224.2	14.8	77.5	6.0	64.1
Glu	245.0	640.8	54.0	417.7	40.7	226.8	134.5	738.5	45.5	357.9	52.5	257.5	88.7	496.8	93.0	268.8	101.4	257.2
Pro	11.4	253.2	11.4	140.1	12.4	126.6	9.7	255.8	34.6	152.2	14.7	108.1	16.3	203.6	9.3	96.5	30.3	76.5
Gly	5.4	228.9	1.2	165.1	5.0	120.1	7.7	284.6	2.1	150.8	4.1	113.4	7.1	198.0	2.4	112.6	8.7	117.5
Ala	60.8	329.6	10.9	130.4	27.6	92.7	67.4	278.4	6.1	147.1	8.8	116.2	42.2	227.0	21.7	80.1	46.9	148.1
Cys				93.1		58.7				60.4		40.0				34.4		59.0
Val	7.0	140.9	1.4	138.3	1.1	85.6	10.0	238.9	2.6	139.7	0.5	80.9	7.1	184.8	4.6	81.5	1.7	72.4
Met	2.6	11.1	0.4	25.3	0.5	15.9	2.5		2.2	11.6	0.2	22.6	Trace	6.7	0.8	16.6	0.2	12.1
Ile	3.5	155.4	0.7	8.2	0.5	61.7	5.5	164.0	1.3	104.6	0.2	60.8	1.4	145.5	1.0	61.3	0.7	47.5
Leu	6.2	370.5	0.8	181.0	1.3	114.6	7.4	427.2	1.7	196.0	0.5	110.8	2.3	264.2	1.1	111.2	1.2	84.4
Tyr	4.1	66.6	1.2	66.1	1.7	36.6	5.0	88.2	1.8	34.4	2.2	43.8	2.3	72.0	1.6	42.4	4.0	27.7
Phe	5.0	177.0	1.1	98.8	0.8	62.0	4.7	208.0	1.5	101.4	1.0	62.2	2.9	157.9	1.0	66.8	0.9	53.8
	430.7	4151.50	192.6	2622.9	117.4	1494.2	396.6	4710.8	177.3	2432.1	102.2	1437.10	287.5	3416.3	206.3	1589.0	227.0	1391.1

increased at a faster rate when fruits approached the ripe stage. All varieties attained almost the same percentage, about 90% of dry matter when ripe.

The protein content at the green stage as shown in Table I is the highest and it is twofold higher than the concentration of the ripe stage (dry weight basis). There is no significant difference in the protein content of the three varieties studied with the same stage.

Amino acid compositions of the three varieties are given in Table II. In all varieties there are identical patterns of amino acid composition and 17 amino acids were detected. The protein-rich green stage contained the highest concentration of amino acids with more glutamic acid, aspartic acid, lysine, leucine, alanine, and serine than the other two stages of maturity. The data in Table II show that total and free amino acids concentrations are considerably different in the three varieties for the three stages of maturity. This seems to be associated with the protein contents of the three stages of development (Table I). The data also show for the three varieties at the yellow and completely ripened stages that glutamic acid, aspartic acid, lysine, leucine, proline, and glycine were present at high concentrations.

The concentrations of essential amino acids in the protein hydrolysates for the two stages of development where date is mostly consumed (yellow and ripened) differ significantly in the two stages for the three varieties. They total to approximately 1125, 1059, and 674 mg per 100 g of dry date for Khastawi, Khadhrawi, and Zahdi, respectively, at the yellow stage as compared to 604, 529, and 511 mg per 100 g of dry date at the ripe stage.

At the yellow stage lysine was the predominant essential amino acid for the three varieties followed by leucine, while at the ripe stage lysine was predominant in the variety Zahdi and leucine was predominant for the varieties Khastawi and Khadhrawi. The data show that Khastawi is higher in the essential amino acids than Khadhrawi and Zahdi. The difference between Khastawi and Zahdi is very significant at the yellow stage and becomes less at the ripe stage.

For most amino acids the concentration is higher at the yellow stage than the ripe stage and also the varieties (Khastawi and Khadhrawi) are significantly higher than Zahdi. From these results it can be concluded that date fruits are not very poor in protein and amino acid composition and that the highest concentration of amino acids, for the two stages in which dates are generally eaten, is in the yellow stage.

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Long-Term Exposure of Swine to a [14C]Dichlorvos Atmosphere

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Young swine have been exposed for 24 days to an atmosphere containing between 0.10 and 0.15 μg of [*1-vinyl*-14C]dichlorvos per l. of air. As in feeding experiments with the same labeled compound, the 14C content varied widely among different tissues, but none contained dichlorvos. The relative specific activities of isolated key intermediates are compatible with the degradation pathway postulated by Page et al. [Page, A. C., DeVries, D. M., Young, R., Loeffler, J. E., *Toxicol. Appl. Pharmacol.* **19**, 378 (1971); Page, A. C., Loeffler, J. E., Hendrickson, H. R., Huston, C. K., DeVries, D. M., *Arch. Toxicol.* **30**, 19–27 (1972)] which proceeds from dichlorvos after cleavage of the P–O–vinyl bond and dechlorination through a hypothetical symmetrical two-carbon intermediate to glycine and serine, and from there through well-established metabolic pathways to other naturally occurring tissue constituents.

Besides its application in various areas of animal husbandry, dichlorvos (2,2-dichlorovinyl *O,O*-dimethyl phosphate) is also used extensively in the NO-PEST Insecticide Strip from which dichlorvos is released.

Short-term pulmonary administration of 32P-labeled dichlorvos to pigs has shown that dichlorvos is degraded under these conditions by cleavage at the oxygen atom bonding the vinyl group to the dimethyl phosphate moiety (Loeffler et al., 1971). This is the same pathway as experimentally found after gastric or intestinal infusion of [32P]dichlorvos (Loeffler et al., 1972), and as the one which has to be postulated to account for the results with [*1-vinyl*-14C]dichlorvos after intestinal infusion and after single or multiple oral administration to swine (Page et al., 1971).

Work with rodents (Hutson et al., 1971a,b) has confirmed that in short-term experiments even at much higher than normal use concentrations the degradation pathway of inhaled and of orally administered dichlorvos was independent of the route of application and that the metabolism in the rat proceeded essentially in the same way as in swine.

Prolonged feeding of dichlorvos to swine did not change the degradation pathway from that seen after a single oral

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