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CARBOHYDRATE CONSTITUENTS OF ZAHDI DATES (PHOENIX DACTYLIFERA L.)

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Abstract. Zahdi dates contain D-glucose and D-fructose in equimolar proportion, as major sugar constituents, with a small amount of sucrose. Pectic substances, hemicelluloses and cellulose are present as cell-wall polysaccharides. The soluble sugars have been isolated on a preparative scale from the samples of Zahdi dates and some preliminary investigations have been done on these carbohydrate constituents.

Date plams in general are very important plants and have been known to mankind for more than 4000 years. It is thought that Iraq was their original place and the Middle East and North Africa are considered the most important growing areas.

The dates are used as a food constituent by millions of people particularly in Arabia, Persia, Egypt and nearby countries where hundreds of varieties of all sizes and flavours are grown commercially. The best of these varieties is 'soft date' having a sugar content of more than 60%. The common varieties of dates include Zahdi, Suyer, Hillawi, Khadrawi, Khistawi, Burban, Ashrasi, Maktoom, Braim, Tabrazal, Barhi and Sultani.[1]

Iraq has been one of the major countries producing dates. It produces about 35% of the world's date fruit. Among more than 450 varieties which are found in Iraq, the most common variety is Zahdi and forms about 43% of the total number of date plams in Iraq . Zahdi dates are grown mostly in the middle part of Iraq and approximately 7 million trees are grown in middle Euphratus and 3.8 million trees in Baghdad and Dyala.[2] Zahdi date is a cheaper variety and good proportion of it is exported;[3] it is also used for the production of commercial products like Dibis, wine and alcohol.

A preliminary investigation of chemical constituents present in Zahdi date has been carried out[4] and the percentage of sugar in the samples of this variety of date is also determined.[5–7] It has been shown that the amounts of various sugars vary during the different maturity stages of this fruit.[9] It is also reported that the relative amounts of monosaccharides and the disaccharide change during different ripening stages of the fruit and the relationship between these carbohydrates has been determined.[9]

For the preparation of commercial products with increased market potential, a complete examination of important carbohydrate constituents, which form the major chemical components of the dates, is essential. It is a matter of experience that some of the carbohydrate constituents, for example pectins are undesirable in some of the date-products, on the one hand, and the same may be used, after searching for an economical method, for the production of other commercial products like jelly powder, on the other.

Results and Discussion

Duplicate samples of Zahdi date fruit were extracted exhaustively with boiling water.

The extract showed the absence of starchy material and was found to contain some polysaccharide(s) which resembled the typical pectins [10–13] and constituted about one per cent of the fruit material. The supernatant extract left after removal of the polysaccharide was analysed for: (a) total sugar content [14] and (b) reducing sugar content which were found to be 63 and 59.5% respectivley, showing that the percentage of the nonreducing sugar (sucrose) in the date fruit is 3.5%. Total sugar and reducing sugar contents were also determined in the other direct exhaustive extracts of Zahdi date fruit and same results were obtained. Small portion of each extract was concentrated to a reasonable volume and examined by paper chromatography. Each sample was found to contain D-glucose and D-fructose in equimolar proportion and a small amount of sucrose. The monosaccharides, D-glucose and D-fructose were separated by preparative daper chromatography, estimated by the phenol–sulphuric acid colorimetric method[14] and found to be present in 1:1 proportion. All attempts to separate the mixture of sugars by fractional crystallization or precipation failed.

D-glucose, D-fructose and sucrose were fully characterized after separation of the mixture, obtained from the date extract, on charcoal–Celite (1:1) followed by preparative paper chromatography, by criteria of melting points as well as melting points of the derivatives of these sugars.

The residue left after removal of water extract, was further extracted with ammonium oxalate solution[11] and furnished another polysaccharide fraction which resembled the sample of pectic material extracted with water. These polysaccharide fractions need detailed investigations. Further extraction of the residue with alkali furnished a fraction of hemicelluloses,[15] which was not examined further.

The residue was examined for fibre content and apparently represented the pure cellulose. The fibre, moisture and ash contents[16] were also deter-

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mined in the samples of the date fruits and found to be 12, 16 and 4% respectivley.

Experimental.

General Methods of Investigation. Paper partition chromatography was carried out on Whatman paper No. 1, using the following solvent systems (a) butanol – ethanol – water (4:1:5; upper layer) (b) butanol–acetic acid–water (4:1:5; upper layer) (c) ethyl acetate–pyridine–water (10:4:3) (*d*) ethyl acetate–acetic acid–water (10:5:6)

Chromatograms were developed by spraying with aniline phthalate. For the separation of mono- and disaccharides the chromatography was carried out on a charcoal–Celite (1:1) column, which was successively eluted with water (for monosaccharides) and 5% ethanol (for disacchride).

Cations were removed by Amberlite resin IR-120 (H), and anions by IR-45(OH).

Samples of polysaccharides (10–20 mg) were hydrolysed with NH_2SO_4 (10–20 ml) at 100° for 18 hr. The hydrolysates were neutralized with $Ba(OH)_2$ and $BaCO_3$. Insoluble inorganic salts were removed by centrifugation. The supernatant solution was deionized with IR-120(H) resin, concentrated and examined by paper chromatography.

The amount of reducing sugars in the sample was estimated with Fehling solution (copper method) and total sugar content was estimated by the phenol–sulphuric acid colorimetric method.[14] Uronic acid anhydride content (uaa) was determine by (a) Anderson's decarboxylation method[17] and (b) Carbazole method.[18] Samples of the date were analysed for moisture, fibre and ash contents by the method described by Pearson.[16]

Extraction and Examinations of the Carbohydrates of Zahdi Dates. A sample of date fruit material (without stone; 10 g) was extracted with boiling water (3 × 100 ml; for 2 hr). The extracts were removed by filtration. A portion of the combined extracts was tested for the presence of starch with iodine solution and gave a negative test with this reagent. The polysaccharide present in the combined extracts was precipitated with an equal volume of acetone, removed at the centrifuge, dried by the solvent exchange method,[11] and weighed (0.10 g) (Found: uaa 83% sp. rot. 210°; constituent sugars, examined by paper cromatography in solvent systems (b) and (d): galacturonic acid, galactose and arabinose).

A portion of the supernatant solution left after removal of acetone was analysed for: (i) total sugar content (63%) and (ii) reducing sugar content (59.3%) The rest of the solution was concentrated to a syrup (7.2 g). The paper chromatographic examination of the syrup in solvent systems (a), (b) and (c) showed the presence of (1) D-glucose, (2) D-fructose and (3) sucrose (small amount). The first two sugars seemed to be in 1:1 proportion by visual examination. A portion of the syrup (50 mg) was subjected to preparative paper partition chromatography in solvent system (a). The three component sugars after having been chromatographed, were extracted from the paper with water in the usual way and estimated by the phenol–sulphuric acid method.[10] (Found: D-glucose 29.5%; D-fructose 29.3% and sucrose 3.5% of the date fruit).

Another portion of the syrup (1.5 g) was separated on a preparative scale on a charcoal–Celite column, as described in the general methods, followed by preparative paper chromatography in solvent system (a) The following fractions were obtained.

Fraction I. (0.42 g; sp. rot.—92°; m.p. and mixed m.p. 104°). It was chromatographically indistinguishable from D-fructose. A derivative 1,2:4, 5-di-*o*-isopropylidene-D-fructose (m.p. 119°) was prepared.

Fraction II. (0.40 g.m.p. 146°). It was chromatographically indistinguishable from D-glucose. It was converted to 2,4-dinitrophenylhydrazone (m.p. and mixed m.p. 120°–122°).

Fraction III. (0.038 g). It was chromatographically indistinguishable from sucrose and was converted to the octaacetate (m.p. 70°).

Extraction with ammonium oxalate and sodium hydroxide: The date residue left after extraction with water, was further extracted with ammonium oxalate solution (0.5%; 2×100 ml; at 90° for 1.5 hr). The polysaccharide (0.08 g) from the combined extracts was precipitated with acetone (1:1, v/v); removed by filtration and dried by the solvenet exchange method. (Found: uaa 85%; sp. rot. 206°; constituent sugars examined by paper partition chromatography in solvent systems (b) and (d): galacturonic acid, galactose and arabinose). The residual plant material was further extracted with sodium hydroxide solution (2%; 2× 100 ml; at room temperature; for 1 hr) and furnished another polysaccharide fraction (0.5 g) which was not further investigated. The weight of the residue left after these successive extractions was 1.2 g.

Similar investigations were done on a duplicate sample of Zahdi dates and the same type of results were obtained.

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