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Improvements in the Preparation of Crystalline D-Mannose from the Doum Palm Kernel*

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D-Mannose is usually prepared¹⁻⁵ by acid hydrolysis of the D-mannan of the ivory nut, followed either by direct crystallisation of the sugar from the hydrolysate, or preparation and recrystallisation of methyl α -D-mannopyranoside,^{6,7} from which it is recovered by acid-hydrolysis.^{8,9} Like ivory nut, the kernel of the African doum palm (*Hyphaene thebaica*) has been used for the manufacture of buttons, and contains a D-mannan.¹⁰⁻¹²

In a recent publication,¹³ the doum palm kernel was described as an alternative source

of D-mannose, obtained by acid hydrolysis of the kernel shavings and direct crystallisation from glacial acetic acid, in 20 % overall yield.

In the present work the method is improved by first preparing crystalline methyl α -D-mannopyranoside from the doum palm kernel shavings by methanolysis, in a good yield (50–52 %). Methyl α -D-mannopyranoside is then hydrolysed with sulfuric acid to give crystalline D-mannose in 70 % yield from the mannoside. The overall yield is about 34 % of the doum palm kernel.

Experimental. Melting points are uncorrected. Concentrations were performed at reduced pressure below 50 °C. Thin-layer chromatography (TLC) was performed on silica gel (Kiesel gel G, Merck) using butanol–pyridine–water (10:3:3) as a solvent and ceric sulfate as a spray reagent.

Methyl α -D-mannopyranoside. The doum palm kernels (500 g) were defatted with light petroleum (b.p. 60–80 °C) for a week, then ground in a mill. The dry, finely-ground kernels (100 g) were added in small portions to 75 % sulfuric acid (100 ml) in a mortar, at such a rate that the temperature was not allowed to exceed 30 °C, and the meal was well kneaded after each addition. The meal was kept for 15 h at 25–30 °C with occasional kneading until the suspension was nearly a homogeneous paste. At the end of this period, a mixture of dry, acetone-free methyl alcohol (100 ml) and concentrated hydrochloric acid (25 ml) was added under vigorous mixing, and the soft paste was transferred to a 2 l flask and diluted with absolute methyl alcohol (600 ml). The mixture was boiled under reflux for 8 h, and after addition of charcoal (15 g), it was refluxed for a further 1 h, and filtered hot. The residue was washed with hot absolute methyl alcohol (50 ml). The filtrate and washings were combined and kept at room temperature for 24 h whereupon methyl α -D-mannopyranoside crystallised in colourless cubes. After 3 days the crystals were collected, washed with absolute methyl alcohol (25 ml), dry acetone, and dried; yield, 50 g. After concentration of the mother liquor in a current of air, another 2 g was obtained. The total yield was 52 % of the original meal. m.p.* 158–165 °C, $[\alpha]_{\text{D}}^{20} + 72^\circ$ (c 2, water). This product was recrystallised from 85 % ethanol with 87 % recovery. It was chromatographically pure (TLC), R_F 0.48, m.p. 193 °C, $[\alpha]_{\text{D}}^{20} + 82^\circ$ [lit. m.p. 195 °C, $[\alpha]_{\text{D}}^{20} + 80^\circ$ (c 1, water)].

When the unextracted meal was used, the yield of methyl α -D-mannopyranoside was 36 % of the original meal, and 16–20 % of unreacted meal was recovered.

D-Mannose. A solution of methyl α -D-mannopyranoside (20 g) in 2 N sulfuric acid (320 ml)

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* M.p. of the crude methyl α -D-mannopyranoside isolated from the ivory nut; 170 °C.

was hydrolysed by steam distillation.⁹ After 2 h, TLC showed the hydrolysis to be complete. Charcoal (1 g) was added, and the solution neutralised with barium hydroxide and barium carbonate. The precipitated barium sulfate was filtered off and washed with hot water. The solution and washings were combined and evaporated to a syrup which was dissolved in hot glacial acetic acid (25 ml). The solution was cooled, nucleated with a few crystals of D-mannose, and kept for 2 days with occasional stirring, and then for one day in a refrigerator. The crystalline D-mannose was filtered off, washed with cold ethanol, then ether and dried, yield 13 g; m.p. 130–131 °C, $[\alpha]_D^{20} + 14^\circ$ (equil., water) {lit.³ $[\alpha]_D^{20} + 14.2^\circ$ (equil., water)}.

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Triterpenes. *p*-Toluenesulfonic Acid Catalysed Rearrangement of 18 α ,19 α and 18 β ,19 β Isomers of 3 β ,28-Diacetoxy-epoxylupane

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In a previous communication¹ we reported the BF₃-catalysed rearrangement of the 18 α ,19 α - and 18 β ,19 β -epoxylupane derivatives 1 and 2. This paper deals with the rearrangement of the same epoxides 1 and 2 catalysed by the protic acid *p*-toluenesulfonic acid (TosOH). The reaction of either epoxide with BF₃·Et₂O or TosOH afforded the same E-ring opened rearrangement product, *i.e.* the baccharane derivative 3, the other products consisting of a number of dienes. In general, TosOH yields more dehydration products and less skeletally rearranged compound 3 than the BF₃-etherate.