70. *Trityl Derivatives of* D-*Arabofuranose.*

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Tritylation of methyl-D-arabofuranoside (αβ-mixture) with trityl chloride in pyridine gave crystalline 3 : 5-ditrityl methyl-D-arabofuranoside and trityl methyl-D-arabinoside as a syrup.

Smith (*J.*, 1939, 753) prepared 5-trityl methyl-L-arabofuranoside by allowing methyl-L-arabofuranoside (1 mol.) to react with trityl chloride (0·95 mol.) in pyridine for 5 days at 20°. The compound was obtained as a glass in almost quantitative yield. The location of the trityl group on C_5 was established by methylation followed by detritylation and hydrolysis to give 2 : 3-dimethyl L-arabinose. Zeile and Kruckenberg (*Ber.*, 1942, **75**, 1127) prepared a ditrityl L-arabinose (m. p. 93°, optically inactive) by treating L-arabinose (1 mol.) with trityl chloride (2 mols.) in pyridine. Diacetyl and dibenzoyl derivatives of the ditrityl compound were prepared, but the location of the trityl groups was not established.

In the present investigation methyl-D-arabofuranoside (αβ-mixture) (1 mol.) was treated with trityl chloride (2 mols.) in pyridine for 12 hours at room temperature, followed by 1 hour on a boiling water-bath. 3 : 5-*Ditrityl methyl*-D-*arabofuranoside* was isolated, and identified by methylation to 3 : 5-*ditrityl* 2-*methyl methyl*-D-*arabofuranoside* which on detritylation and hydrolysis gave 2-methyl D-arabinose. Acetylation of the mother liquor after removal of the ditrityl compound yielded *diacetyl trityl methyl*-D-*arabinoside* as an orange glass.

Thus methyl-D-arabofuranoside and methyl-D-xylofuranoside behave similarly on tritylation, the latter yielding crystalline 3 : 5-ditrityl methylxylofuranoside and 5-trityl methylxylofuranoside as a syrup under the same conditions of tritylation (McIlroy, *J.*, 1946, 100).

Experimental.

D-*Arabinose.*—Calcium D-gluconate (120 g.) prepared from D-glucose by electrolytic oxidation (Isbell, Frush, and Bates, *Ind. Eng. Chem.*, 1932, **24**, 375) was converted into D-arabinose by a modification of Ruff's method (Hockett and Hudson, *J. Amer. Chem. Soc.*, 1934, **56**, 1632). The product (40 g.) had m. p. 155°, $[\alpha]_D^{18^\circ}$ − 103° (*c*, 1·5 in water). Hockett and Hudson (*loc. cit.*) give m. p. 155·5—156·5°, $[\alpha]_D^{17^\circ}$ − 103·3° (in water).

Methyl-D-*arabofuranoside.*—Anhydrous D-arabinose (20 g.) was dissolved in methanolic hydrogen chloride (400 c.c., 1%) at room temperature. The solution became non-reducing after 5 hours; $[\alpha]_D^{18^\circ}$ − 66·8° (30 min.), − 35° (3 hrs.), − 32° (4 hrs.), + 40° (16 hrs.), + 43·6° (17 hrs.), + 42° (17½ hrs.), + 40° (18 hrs.). After neutralisation with silver carbonate, the filtrate was evaporated at 40° to a syrup which was then extracted thoroughly with ethyl acetate. Evaporation of the combined extracts gave a hygroscopic yellow syrup (2·0 g.), b. p. 160°/0·025 mm., $[\alpha]_D^{17^\circ}$ + 64·5° (*c*, 0·6 in methyl alcohol) (Found: OMe, 16·8. Calc. for $C_6H_{12}O_5$: OMe, 18·9%). Baker and Haworth (*J.*, 1925, **127**, 365) give $[\alpha]_D$ + 71·3° (*c*, 0·8 in methyl alcohol) for methyl-D-arabofuranoside, a syrup. Montgomery and Hudson (*J. Amer. Chem. Soc.*, 1937, **59**, 992) report $[\alpha]_D$ + 100—105° for α-methyl-D-arabofuranoside. The rotation of the β-form is not recorded. The portion insoluble in ethyl acetate had $[\alpha]_D^{17^\circ}$ − 101° (*c*, 1·0 in water), and was presumed to be αβ-methyl-D-arabopyranoside (Found: OMe, 18·4. Calc. for $C_6H_{12}O_5$: OMe, 18·9%). Hudson (*J. Amer. Chem. Soc.*, 1925, **47**, 265) gives $[\alpha]_D$ − 17° (in water) for α-methyl-D-arabopyranoside, while Purdie and Rose (*J.*, 1906, **89**, 1204) give $[\alpha]_D$ − 245° (in water) for β-methyl-D-arabopyranoside.

Tritylation of Methyl-D-*arabofuranoside.*—Methyl-D-arabofuranoside (αβ-mixture) (1·4 g.) was dissolved in dry pyridine (15 c.c., b. p. 116°). Dry trityl chloride (4 g.) was added, and the solution, after standing for 12 hours at room temperature, was heated for 1 hour with exclusion of moisture on a boiling water-bath. To the solution at 0° distilled water was added to permanent turbidity, and the solution then poured into ice–water (700 c.c.). After 3 hours the separated red gum was washed with water by decantation and dissolved in ether, and the ether solution washed with dilute acetic acid, aqueous sodium hydrogen carbonate, and finally with water. The ether extract, dried (Na_2SO_4) and evaporated under reduced pressure, yielded a red syrup which, from solution in chloroform, deposited colourless crystals (3·4 g.) of *ditrityl methyl*-D-*arabofuranoside*, m. p. 148—149°, $[\alpha]_D^{17^\circ}$ + 11·9° (*c*, 1·95 in chloroform) (Found: trityl, 74·99; OMe, 4·6. $C_{44}H_{40}O_5$ requires trityl, 74·90; OMe, 4·78%).

Diacetyl Trityl Methyl-D-*arabofuranoside.*—The mother liquor, which did not crystallise after several weeks, was dissolved in dry pyridine (10 c.c.), and acetic anhydride (12 c.c.) added. After standing at 0° for 24 hours, the solution was poured into ice–water (500 c.c.). The creamy gum which separated was washed with water by decantation and dissolved in ether, and the ether solution washed with aqueous sodium hydrogen carbonate until acid-free and then with water. The ether extract, dried (Na_2SO_4) and evaporated under reduced pressure, yielded *diacetyl trityl methyl*-D-*arabinoside* (0·7 g.) as an orange glass, $[\alpha]_D^{18^\circ}$ + 27·2° (*c*, 0·55 in chloroform) (Found: trityl, 49·1; acetyl, 17·6; OMe, 6·3. $C_{29}H_{30}O_7$ requires trityl, 49·6; acetyl, 17·6; OMe, 6·3%).

3 : 5-*Ditrityl 2-Methyl Methyl*-D-*arabofuranoside.*—Ditrityl methyl-D-arabofuranoside (3·3 g.) dissolved in methyl iodide (15 c.c.) was refluxed for 8 hours at 45°, silver oxide (10 g.) being added in 1 g. portions at hourly intervals. The methylated *product* was extracted with chloroform and the solvent evaporated under reduced pressure, yielding colourless crystals (3·4 g.), m. p. 107—108°, $[\alpha]_D^{18^\circ}$ + 23·1° (*c*, 0·65 in methyl alcohol) (Found : OMe, 9·0. $C_{45}H_{42}O_5$ requires OMe, 9·4%).

Detritylation of Ditrityl Methyl Methyl-D-*arabofuranoside.*—Ditrityl methyl methyl-D-arabofuranoside (3·2 g.) was dissolved in dry chloroform (25 c.c.), and the solution saturated at 0° with hydrogen chloride. After standing for 1 hour at 0° and 1 hour at 20° the chloroform solution was exhaustively extracted with warm water. The combined aqueous extracts were neutralised with silver carbonate, and the filtrate evaporated at 40° under reduced pressure to a thick syrup which was converted into the glycoside by refluxing it with methanolic hydrogen chloride (50 c.c., 1%) for 6 hours. Hydrogen chloride was removed by silver carbonate, and the filtrate, evaporated under reduced pressure, yielded colourless crystals (0·62 g.), m. p. 44—45° (from ether), $[\alpha]_D^{17^\circ}$ − 205° (*c*, 1·6 in methyl alcohol). Drying in a vacuum for 12 hours raised the m. p. to 62—63°. Oldham and Honeyman (*J.*, 1946, 986) give m. p. 46—47°, raised to 63—65° on vacuum drying, $[\alpha]_D^{18^\circ}$ + 208° (in methyl alcohol), for 2-methyl β-methyl-L-arabinoside. The elevation of the m. p. on vacuum drying is attributed to dehydration of the monohydrate (Found : OMe, 35·0. Calc. for $C_7H_{14}O_5$: OMe, 34·8%).

2-*Methyl Arabinose.*—2-Methyl β-methyl-D-arabinoside (0·6 g.) was hydrolysed by aqueous sulphuric acid (60 c.c., 3%) during 3 hours at 95°. After neutralisation with barium carbonate, filtration, and evaporation, the residue was extracted with ether and boiling methyl alcohol. Evaporation of the combined extracts yielded a thick syrup (0·46 g.), $[\alpha]_D^{18^\circ}$ − 102° (*c*, 1·5 in water) (Found : OMe, 18·7. Calc. for $C_6H_{12}O_5$: OMe, 18·9%). Schmidt and Simon (*J. pr. Chem.*, 1939, **152**, 190) give $[\alpha]_D^{20^\circ}$ − 102° ± 3° (in water) for 2-methyl D-arabinose. The product, on treatment with phenylhydrazine, gave arabinosazone, m. p. 154·5—155° (decomp.), not depressed by authentic arabinosazone, m. p. 155° (decomp.) (Found : OMe, Nil). The compound is thus 2-methyl arabinose.

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