

28. *Trityl Derivatives of Xylofuranose.*

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Tritylation of methylxylofuranoside ($\alpha\beta$ -mixture) with trityl chloride in pyridine gave 3 : 5-ditrityl methylxyloside. Tritylation followed by acetylation, gave 2 : 3-diacetyl 5-trityl methylxyloside.

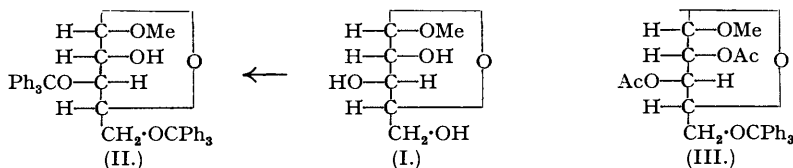
HOCKETT and HUDSON (*J. Amer. Chem. Soc.*, 1931, **53**, 4457) demonstrated that α -methylxyloside, β -methylxyloside, α -methylxyloside, and β -methylarabinoside reacted with trityl (triphenylmethyl) chloride in pyridine although the primary alcoholic hydroxyl group, normally substituted specifically by this reagent, was engaged in ring formation. Jackson, Hockett, and Hudson (*J. Amer. Chem. Soc.*, 1934, **56**, 947) prepared two crystalline isomeric ditrityl derivatives (m. p. 238–240°, $[\alpha]_D^{20}$ –55.5° in pyridine, and m. p. 162.5–163°, $[\alpha]_D^{20}$ –22.5° in pyridine, respectively), and a syrup from β -methylxyloside. Acetylation of the syrup yielded two isomeric crystalline diacetyl monotrityl β -methylxylosides: m. p. 169–170°, $[\alpha]_D^{20}$ –15.7° in chloroform, and m. p. 125–127°, $[\alpha]_D^{20}$ –49.1° in chloroform, respectively. Tritylation of xylose (Zeile and Kruckenberg, *Ber.*, 1942, **75**, 1127) gave a mixture of monotrityl xylose (32%) and ditrityl xylose (49%).

It was anticipated that tritilation of methylxylofuranoside ($\alpha\beta$ -mixture), in which the primary alcoholic hydroxyl group (C₅) is free, would yield a normal 5-trityl derivative and so support the assumption that trityl chloride reacts preferentially with the primary alcoholic hydroxyl group unless that group is engaged in ring formation.

Methylxylofuranoside ($\alpha\beta$ -mixture) (I) prepared from xylose by the method of Haworth and Westgarth (*J.*, 1926, 880), when treated with trityl chloride in pyridine for 12 hours at room temperature, followed by 1 hour on a boiling water-bath, yielded crystalline ditrityl methylxylofuranoside (m. p. 78°, $[\alpha]_D^{20}$ +4.0° in chloroform), identified as 3 : 5-ditrityl methylxyloside (II) by methylation to 2-methyl 3 : 5-ditrityl methylxyloside which, on detritylation and hydrolysis, gave crystalline 2-methyl xylose. Acetylation of tritylated methylxyloside by acetic anhydride in pyridine prior to isolation gave a diacetyl monotrityl methylxyloside (III) as an orange glass, $[\alpha]_D^{20}$ +11.2° in chloroform. The formation of (III) may be explained by the existence of two trityl

derivatives of methylxylofuranoside; namely, 3:5-ditrityl methylxylofuranoside and syrupy 5-trityl methylxylofuranoside. It is this latter substance which gives rise to (III).

Methanolysis of the diacetyl monotrityl methylxyloside (III) removed both acetyl and trityl groups leaving methylxyloside which was characterised by methylation to trimethyl methylxyloside and subsequent hydrolysis to crystalline 2:3:4-trimethyl xylose.



EXPERIMENTAL.

Tritylation of Methylxylofuranoside.—Methylxylofuranoside ($\alpha\beta$ -mixture) (6.5 g.) prepared from xylose (B.D.H. reagent) by the method of Haworth and Westgarth (*loc. cit.*) was dissolved in dry, redistilled pyridine (30 c.c., b. p. 118°). Dry trityl chloride (10.7 g., recrystallised from benzene containing 10% acetyl chloride) was added, and the solution, after standing for 12 hours at room temp., was heated for 1 hour with exclusion of moisture on a boiling water-bath. To the clear solution, at 0°, distilled water was added to permanent turbidity and the solution then poured into ice-water (1 l.). After 3 hours the separated orange gum was removed by decantation and washed with water. The gum was dissolved in ether and the ether solution washed with dilute acetic acid, aqueous bicarbonate (3 times) and finally with water. The ether extract, dried over anhydrous sodium sulphate and evaporated under reduced pressure, yielded an orange-red viscous syrup which from solution in absolute alcohol gave colourless prisms (11.9 g.), m. p. 78°, $[\alpha]_D^{20} + 4.0^\circ$ (in chloroform, c 1.0) (Found: Trityl, 74.7. $\text{C}_{44}\text{H}_{40}\text{O}_5$ requires trityl 74.99%). (The trityl content was estimated by the method of Valentin, *Coll. Czechoslov. Chem. Comm.*, 1931, 3, 499.)

2-Methyl 3:5-Ditrityl Methylxyloside.—Ditrityl methylxyloside (5.0 g.) dissolved in methyl iodide (16 c.c.) was refluxed for 8 hours at 45°, silver oxide (8 g.) being added in 1 g. portions at hourly intervals. After evaporation under reduced pressure, the methylated product was extracted with chloroform and the solvent evaporated, yielding 5.2 g. of syrup, $[\alpha]_D^{16} + 6^\circ$ (in chloroform, c 0.72) (Found: OMe, 9.0. $\text{C}_{48}\text{H}_{44}\text{O}_5$ requires OMe, 9.0%).

Detritylation of methyl ditrityl methylxyloside. Methyl ditrityl methylxyloside (2.8 g.) was refluxed with methanolic hydrogen chloride (50 c.c., containing 1.5% HCl) for 2 hours at 95°. The solution was neutralised by silver carbonate, filtered, and the filtrate evaporated at 40° under reduced pressure. The residue was extracted exhaustively with warm water and the aqueous extracts were evaporated and extracted with chloroform. Evaporation of the chloroform gave monomethyl methylxyloside (0.53 g.) as a golden brown syrup (Found: OMe, 35.0. Calc. for $\text{C}_7\text{H}_{14}\text{O}_5$: OMe, 34.83%).

Hydrolysis of methyl methylxyloside. The methyl methylxyloside (0.52 g.) was hydrolysed by 2% nitric acid (52 c.c.) at 95°, the hydrolysis being followed polarimetrically: $[\alpha]_D^{19} + 55^\circ$ (30 min.); $+36^\circ$ (90 min.); $+36^\circ$ (120 min., c 1.0). The solution was neutralised by barium carbonate, filtered, the filtrate evaporated at 40° and exhaustively extracted with boiling acetone and boiling ether. Evaporation of the solvent gave 2-methyl xylose (0.42 g.), m. p. 131–132° (from ethyl acetate), $[\alpha]_D^{20} + 36^\circ$ (in water, c 1.0) (Found: OMe, 18.6. Calc. for $\text{C}_6\text{H}_{12}\text{O}_5$: OMe, 18.9%). Cf. 2-methyl xylose, m. p. 132–133°, $[\alpha]_D^{20} + 35.9^\circ$ in water (Robertson and Speedie, *J.*, 1934, 824).

2:3-Diacetyl 5-Trityl Methylxyloside.—To methyl xylofuranoside ($\alpha\beta$ -mixture) (10.0 g.) dissolved in dry pyridine (50 c.c.; b. p. 118°), dry trityl chloride (17 g.) was added. After standing for 12 hours at room temp. the solution was heated 1 hour on a boiling water-bath and allowed to cool. Acetic anhydride (50 c.c.) was added and the solution left at room temp. for a further 24 hours. The mass of white crystals (4.12 g.) was removed by filtration, washed with pyridine and then with distilled water, the pyridine washings being added to the mother-liquor. The crystals were identified as triphenylmethylcarbinol, m. p. 158°. Distilled water was added, to the mother-liquor cooled to 0°, to permanent turbidity. On pouring the solution into ice water (1.5 l.) a creamy gummy material separated; this was removed by decantation, washed thoroughly with water, dissolved in ether and the ether solution washed with aqueous sodium bicarbonate (three times), then with water till free from acid, and dried over anhydrous sodium sulphate. Evaporation of the ether yielded an orange glass (23.7 g.), $[\alpha]_D^{20} + 11.2^\circ$ (in chloroform, c 0.85) (Found: OMe, 6.3; trityl, 49.4. $\text{C}_{28}\text{H}_{30}\text{O}_5$ requires OMe, 6.3; trityl 49.6%).

Conversion of diacetyl monotrityl methylxyloside to trimethyl xylose. Diacetyl monotrityl methylxyloside (23.6 g.) was refluxed for 3½ hours at 95° with methanol (100 g.) containing hydrogen chloride (3 g.), the solution neutralised by silver carbonate, filtered, and the filtrate evaporated to dryness under reduced pressure. The residue was extracted with warm water, the aqueous extracts being evaporated under reduced pressure to give methylxylopyranoside as an impure syrup (6.85 g.) (Found: OMe, 17.8. Calc. for $\text{C}_7\text{H}_{14}\text{O}_5$: OMe, 18.9%). The impure methylxylopyranoside (6.75 g.) was twice methylated with methyl iodide (70 c.c.) and silver oxide (35 g.) during 10 hour periods at 45°. The methylated product, a mobile yellow syrup (7.93 g.), isolated in the usual way, consisted mainly of a mixture of α and β forms of trimethyl methylxylopyranoside, $n_D^{21} 1.4410$, $[\alpha]_D^{16} + 55.1^\circ$ (in methyl alcohol, c 0.99) (Found: OMe, 55.3%. Calc. for $\text{C}_9\text{H}_{18}\text{O}_5$: OMe, 60.2%). Distillation gave a colourless syrup (6.32 g.), $n_D^{17} 1.441$, b. p. 125–130° (bath temp.)/17 mm., $[\alpha]_D^{15} + 57.0^\circ$ (in methanol, c 1.07). The trimethyl methylxyloside (6.32 g.) was hydrolysed by 2% nitric acid (70 c.c.) for 2 hours at 95°, neutralised by barium carbonate, filtered, and the filtrate evaporated under reduced pressure. Extraction of the residue with boiling acetone and boiling ether and evaporation of the solvents gave a colourless syrup (5.5 g.) which slowly deposited crystals of trimethyl xylose, m. p. 88–89°, $[\alpha]_D^{20} + 19.8^\circ$ at equilibrium (in water, c 0.86) (Found: OMe, 48.0; C, 49.9; H, 8.4. Calc. for $\text{C}_9\text{H}_{18}\text{O}_5$: OMe, 48.4; C, 50.0; H, 8.3%). $[\alpha]_D^{17} + 20.4^\circ$ in water (equilibrium value): Haworth and Percival, *J.*, 1931, 2850, give m. p. 90–92°.