119. *Acetone Compounds of Sugar Mercaptals: Diisopropylidene D-Xylose Diethylmercaptal.*

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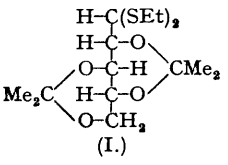
Condensation of D-xylose diethylmercaptal with acetone in presence of phosphoric oxide or copper sulphate gave a diacetone derivative shown to be 2 : 4-3 : 5-*di*iso*propylidene* D-*xylose diethylmercaptal*. Methylation of the latter gave 2 : 4-*dimethyl* 3 : 5-iso*propylidene* D-*xylose diethylmercaptal* which yielded, on demercaptalation and hydrolysis, crystalline 2 : 4-dimethyl D-xylose.

Acetone compounds of the mercaptals of the hexoses, glucose, mannose, and galactose have been prepared by Pacsu and his co-workers (*Ber.*, 1924, **57**, 849; 1929, **62**, 2811, 3104). The mercaptals of both glucose and mannose yielded 2 : 3-*iso*propylidene and 2 : 3-5 : 6-*di*iso-*propylidene* derivatives. Galactose gave two mono-compounds and two di*iso*propylidene compounds. The behaviour of the demercaptalated mono-compounds on periodate oxidation indicated that the *iso*propylidene residues were attached in 4 : 5- and 5 : 6-positions, respectively (Pacsu and Trister, *J. Amer. Chem. Soc.*, 1939, **61**, 2444; 1940, **62**, 2301).

In the present investigation the acetone compound of D-xylose diethylmercaptal has been prepared and characterised. Acetonation of xylopyranose is accompanied by a ring shift, 1 : 2-3 : 5-di*iso*propylidene xylofuranose being the product (Haworth and Porter, *J.*, 1928, 611). β-Methylxyloside yields 3 : 5-*iso*propylidene β-methylxyloside (Robertson and Speedie, *J.*, 1934, 824). Since in xylose diethylmercaptal as in β-methylxyloside there is no hydroxyl group on C_1 available for condensation, the *iso*propylidene residue might, by analogy, be expected to engage the 3 : 5-positions. The absence of an oxide ring, however, makes the hydroxyl group attached to C_4 also available in the mercaptal, and a number of possible mono- and di*iso*propylidene derivatives may be visualised.



(I.)

Treatment of D-xylose diethylmercaptal with acetone in presence of phosphoric oxide or anhydrous copper sulphate gave *di*iso*propylidene* D-*xylose diethylmercaptal* (I) as a syrup. Successive methylations with Purdie's reagents and sodium and methyl iodide in ether converted (I) into impure 2 : 4-dimethyl 3 : 5-*iso*propylidene D-xylose diethylmercaptal, a syrup. Hydrolysis of the latter (0·3N-sulphuric acid in alcohol at 70°) was accompanied by partial demercaptalation. Complete demercaptalation was effected by mercuric chloride and mercuric oxide in methanol according to the method of Pacsu and Green (*J. Amer. Chem. Soc.*, 1936, **58**, 1824). The product reduced Fehling's solution in the cold and ammoniacal silver nitrate and

was presumed to be 2 : 4-*dimethyl* iso*propylidene* aldehydo*xylose*. Methanolysis of the latter gave 2 : 4-dimethyl β-methylxyloside, which gave, on hydrolysis, 2 : 4-dimethyl D-xylose, identified by conversion into the crystalline anilide (Baker, Hirst, and Jones, *J.*, 1946, 783).

The extreme ease of hydrolysis of acetone residues is well known. Irvine and Hynd (*J.*, 1909, **95**, 1220) found it difficult to avoid this during methylation of " diacetone " fructose by methyl iodide and silver oxide unless special precautions were taken to exclude moisture. Although these precautions were taken during the methylation herein described, one such residue was removed in the course of this operation. The isolation of 2 : 4-dimethyl xylose after methylation, demercaptalation, and hydrolysis of the di*iso*propylidene xylose mercaptal proves that the more firmly bound *iso*propylidene residue engages the 3 : 5-positions. This establishes the position of the other residue on carbon atoms 2 and 4. Hence the disubstituted compound is 2 : 4-3 : 5-di*iso*propylidene D-xylose diethylmercaptal.

Experimental.

*Di*iso*propylidene* D-*xylose diethylmercaptal*. Phosphoric oxide (44 g.) was added with vigorous shaking to a solution of D-xylose diethylmercaptal (28 g., m. p. 63°, $[\alpha]_D^{18°}$ −30° in water, prepared from D-xylose by the method of Wolfrom, *J. Amer. Chem. Soc.*, 1931, **53**, 4379) dissolved in dry acetone (750 c.c.). The mixture was shaken for 1 hour, the reaction being controlled by cooling in ice-water. Inorganic material was then filtered off and washed with acetone. Water (10 c.c.) was added to the combined extracts, which were then neutralised by sodium carbonate. Filtration, followed by evaporation under diminished pressure, left a stiff syrup. This was extracted with chloroform, and the extract dried (Na_2SO_4) and evaporated to a viscous red syrup which was contaminated by acetone auto-condensation products. Distillation of the syrup gave the following fractions: (1) 2 g., b. p. 40°/1 mm. (bath temp.), $n_D^{20°}$ 1·4439 (I.C.T.); (2) 5 g., b. p. 60°/0·02 mm. (bath temp.), $n_D^{15°}$ 1·4970, optically inactive [mesitylene has $n_D^{17°}$ 1·4980 (I.C.T.)]; (3) 27 g. (85%), b. p. 115—120°/0·02 mm. (bath temp.), a yellow syrup, $n_D^{20°}$ 1·5004, $[\alpha]_D^{18°}$ −62·3° in acetone (*c*, 2·62), which gave a positive iodoform test when hydrolysed with hydrochloric acid (5N) (Found: C, 53·6; H, 8·3; S, 18·7. *Di*iso*propylidene xylose diethylmercaptal*, $C_{15}H_{28}O_4S_2$, requires C, 53·6; H, 8·3; S, 19·1%).

Condensation of D-xylose diethylmercaptal with acetone in presence of anhydrous copper sulphate gave an identical product but in much lower yield (48%).

2 : 4-*Dimethyl* 3 : 5-iso*propylidene* D-*xylose diethylmercaptal*. The above syrup (14 g.), dissolved in methyl iodide (50 c.c.), was refluxed for 9 hours at 45° with exclusion of moisture, dry silver oxide (28 g.) being added in equal portions at hourly intervals. After evaporation under reduced pressure the methylated product was extracted with chloroform and the solvent evaporated, yielding 13·6 g. of syrup (Found: OMe, 13·8%). After 2 further methylations the syrup (11 g.; OMe, 16·8%) was dissolved in dry ether (150 c.c.), and sodium wire (2 g.) added. After the initial reaction had subsided, the solution was shaken for 36 hours, kept for 12 hours at room temperature, and decanted rapidly into a distilling flask containing methyl iodide (15 c.c.). Evaporation under diminished pressure gave a paste, which was dissolved in methyl iodide (25 c.c.), shaken vigorously for 24 hours, and kept at room temperature for 12 hours. An equal volume of dry ether was added, and the sodium iodide removed by filtration through activated carbon and washed with dry ether. Evaporation of the combined filtrate and washings gave an impure deep red syrup (7·2 g.), $n_D^{20°}$ 1·4689, $[\alpha]_D^{20°}$ −6·4° in water (*c*, 1·22) (Found: OMe, 18·3; S, 17·6. Calc. for $C_{14}H_{28}O_4S_2$: OMe, 19·1; S, 19·4%). A sample of the product decomposed at 85°/0·1 mm. on distillation. Two methylations of di*iso*propylidene xylose diethylmercaptal by methyl sulphate and sodium hydroxide (30%) gave a syrup; $n_D^{16°}$ 1·4780; OMe, 17·6%. Subsequent treatment with sodium and methyl iodide in ether raised the methoxyl content to 18·3%; $[\alpha]_D^{17°}$ −5·8° in water (*c*, 2·05) (61% yield).

Hydrolysis of dimethyl iso*propylidene xylose diethylmercaptal*. The syrup (6 g.), dissolved in sulphuric acid (50 c.c., 0·5N) and alcohol (25 c.c.), was heated for 2 hours at 70°. The solution darkened in colour and a strong smell of ethylthiol was detected. After neutralisation with barium carbonate and filtration through activated carbon, evaporation of the filtrate under diminished pressure at 40° gave a syrup which was further purified by extraction with chloroform. Removal of the solvent (dried, Na_2SO_4) gave a deep red syrup (4 g., $n_D^{20°}$ 1·5123) with a negative iodoform reaction (Found: S, 15·7; OMe, 26·4. *Dimethyl xylose diethylmercaptal*, $C_{11}H_{24}O_4S_2$, requires S, 22·5; OMe, 21·8%). It was apparent that partial demercaptalation had occurred.

Demercaptalation. A solution of mercuric chloride (22 g.) in absolute methanol (50 c.c.) was added during 30 minutes to a mixture of dimethyl *iso*propylidene xylose diethylmercaptal (9 g.), yellow mercuric oxide (18 g.), and anhydrous sodium sulphate (5 g.) in absolute methanol (80 c.c.). After being stirred for 6 hours at 45°, the solution was filtered, the residue extracted with warm alcohol, and the combined filtrate and washings treated with pyridine (5 c.c.) and kept at 0° for 2 hours. After removal of the pyridine–mercuric chloride complex by filtration, the filtrate was evaporated under reduced pressure to a syrup which was freed from inorganic material by extraction with warm benzene. Evaporation of the extracts gave a syrup (5·4 g., 90%) which distilled at 85°/0·05 mm. (bath temp.). The syrup had $n_D^{20°}$ 1·4535, $[\alpha]_D^{16°}$ −52° in chloroform (*c*, 0·96), reduced Fehling's solution and ammoniacal silver nitrate, and gave a positive iodoform test for acetone and a negative Lassaigne test for sulphur (Found: C, 55·4; H, 8·9; OMe, 26·5. *Dimethyl* iso*propylidene* aldehydo*xylose* $C_{10}H_{18}O_5$, requires C, 55·1; H, 8·3; OMe, 28·4%).

Hydrolysis of the aldehydo*xylose*. The syrup (3 g.) was heated with methanolic hydrogen chloride (250 c.c. containing 0·5% HCl) for 7 hours at 40°. Neutralisation with silver carbonate, filtration through activated carbon, and evaporation yielded a viscous syrup which gave on high-vacuum distillation a pale yellow liquid (1·2 g.), $n_D^{14°}$ 1·4530, b. p. 100—105°/0·06 mm. Trituration with ether–

light petroleum gave long colourless needles, m. p. 60°, $[\alpha]_D^{17°}$ −83·3° in chloroform (*c*, 0·82) [Robertson and Speedie, *loc. cit.*, give m. p. 60—61°, long colourless needles, $[\alpha]_D^{20°}$ −82·4° (chloroform), $n_D^{15°}$ 1·4534 for 2 : 4-dimethyl β-methylxyloside] (Found : OMe, 47·5. Calc. for $C_8H_{16}O_5$: OMe, 48·4%).

2 : 4-*Dimethyl* D-*xylose*. The xyloside (1 g.) was heated with aqueous methanol (10 c.c.) containing hydrochloric acid (10 c.c., 3%) for 6 hours at 50°, and the solution neutralised with barium carbonate, filtered, and evaporated to dryness at 45°. Ether extraction of the residue and evaporation of the extracts gave a straw-coloured reducing syrup which crystallised from acetone–light petroleum; m. p. 107—108°, $[\alpha]_D^{15°}$ −28° (initial) ⟶ +21·2° (const., 29 hours) (*c*, 0·83 in water). Barker, Hirst, and Jones (*J.*, 1946, 783) report m. p. 108°, $[\alpha]_D$ −30° (initial) ⟶ +22° (24 hours) for 2 : 4-dimethyl D-xylose (Found : OMe, 33·1. Calc. for $C_7H_{14}O_5$: OMe, 34·8%). The product, refluxed with alcoholic aniline for 3 hours on a steam-bath, gave 2 : 4-dimethyl xylose anilide, m. p. 168—169° (from alcohol–light petroleum), $[\alpha]_D^{20°}$ −80·7° in dioxan (*c*, 0·8). Barker, Hirst, and Jones (*loc. cit.*) give m. p. 170°, $[\alpha]_D^{20°}$ −82° in dioxan (Found : OMe, 23·0. Calc. for $C_{13}H_{19}O_4N$: OMe, 24·5%).

Micro-combustion analyses were done by C. L. Carter, Dunedin, and Weiler and Strauss, Oxford.

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