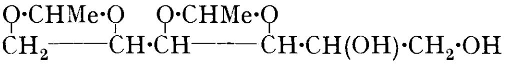
92. *An Easy Method for the Preparation of* l-*Xylose.*

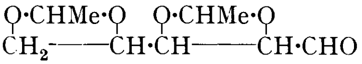
By Herbert Appel.

AFTER Haworth (*J. Soc. Chem. Ind.*, 1933, **52**, 645) and Reichstein (*Helv. Chim. Acta*, 1933, **16**, 1019) and their respective co-workers had shown that *l*-xylose (or *l*-xylosazone) was a useful material for the synthesis of *l*-ascorbic acid, the author worked out, and completed in December, 1933, an easy method for the preparation of the sugar, previously accessible only by the complicated process of Fischer and Ruff (*Ber.*, 1900, **33**, 2145). Triethylidene sorbitol, prepared by treating sorbitol with paraldehyde and hydrochloric acid (compare Helferich and Appel, *Ber.*, 1931, **64**, 1841), lost one acetaldehyde group when heated with 50% acetic acid, yielding 1 : 2 : 3 : 4-*diethylidene sorbitol* (I). Oxidation of (I) with lead tetra-acetate produced diethylidene *l*-xylose (II) (not isolated), and after hydrolysis with dilute sulphuric acid *l*-xylose was obtained. Vargha has recently (*Ber.*, 1935, **68**, 18) prepared *l*-xylose by the similar method of oxidising 1 : 3-monobenzylidene sorbitol with lead tetra-acetate.



$$\overbrace{\text{CH}_2\text{——CH}}^{\text{O·CHMe·O}}\text{·}\overbrace{\text{CH——CH}}^{\text{O·CHMe·O}}\text{·CH(OH)·CH}_2\text{·OH}$$

(I.)



$$\overbrace{\text{CH}_2\text{——CH}}^{\text{O·CHMe·O}}\text{·}\overbrace{\text{CH——CH}}^{\text{O·CHMe·O}}\text{·CHO}$$

(II.)

1 : 2 : 3 : 4-*Diethylidene Sorbitol.*—Sorbitol (50 g.) was shaken for 10 hours with paraldehyde (50 c.c.) and hydrochloric acid (17 c.c., *d* 1·19), chloroform (100 c.c.) added, the mixture washed successively with water, dilute aqueous sodium hydroxide, and water, and the chloroform–paraldehyde solution dried over calcium chloride and evaporated under diminished pressure. The residual thick syrup, consisting of triethylidene sorbitol (it could be obtained crystalline, m. p. 174—176°, but recrystallisation at this stage was wasteful and unnecessary), was dissolved in 50% acetic acid (300 c.c.) and heated for 50 minutes on the water-bath; the solvent was then removed quickly under diminished pressure at 70°. The residue was recrystallised from methyl alcohol, and addition of ether and light petroleum increased the yield (17 g.); m. p. 212—214°, $[\alpha]_D^{17°}$ − 11·1° (*c* = 2·3 in water) (Found : C, 51·1; H, 7·7. $C_{10}H_{18}O_6$ requires C, 51·25; H, 7·75%).

β-*Tetra-acetyl* l-*Xylose.*—A mixture of diethylidene sorbitol (4 g.), lead tetra-acetate (8·6 g.), benzene (40 c.c.), and glacial acetic acid (20 c.c.) was left over-night with occasional shaking, the solvent then removed under diminished pressure, 2*N*-sulphuric acid (60 c.c.) added, and the mixture heated during 1½ hours on the water-bath. The filtered solution was nearly neutralised (litmus) with alkali (the free *l*-xylose can be obtained by neutralisation with barium carbonate and extraction of the residue with absolute alcohol) and evaporated under diminished pressure. The dry residue was extracted thrice with 25 c.c. of hot alcohol. These extracts, on removal of the solvent under diminished pressure, left a dry residue, which was heated during 15 minutes on the water-bath with 6 g. of sodium acetate and 30 c.c. of acetic anhydride. The mixture was poured into ice-water and the β-tetra-acetyl *l*-xylose (2 g.), which crystallised after a few minutes, was filtered off. Extraction of the aqueous solution with ether gave a further 0·6 g. of less pure material. After recrystallisation from dilute alcohol the β-tetra-acetyl *l*-xylose had m. p. 127—128·5° (corr.), $[\alpha]_D^{15°}$ + 25·7° (*c* = 3·6 in chloroform). Vargha (*loc. cit.*) gives m. p. 126° and $[\alpha]_D^{20°}$ + 25·7°.

l-*Xylosazone.*—4 G. of diethylidene sorbitol were treated as described above. The residue from the alcoholic solution was heated during 2½ hours on the water-bath with 45 c.c. of water, 8 g. of phenylhydrazine hydrochloride, and 5 g. of sodium acetate. The yield of pure *l*-xylosazone, m. p. 159—161°, was 2·4 g.

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