158. *The Ring Structure of Xylal.*

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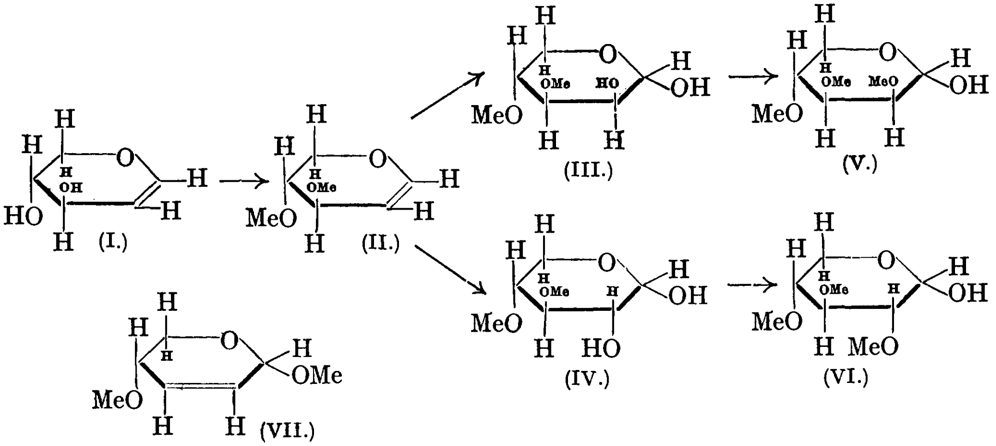
It has been shown previously (Hirst and Woolvin, J., 1931, 1131) that glucal gives on methylation a trimethyl derivative which on treatment with aqueous perbenzoic acid yields 3 : 4 : 6-trimethyl glucopyranose. These observations afforded a direct proof of the pyranose structure of glucal and the present paper is concerned with a similar inquiry into the ring structure of xylal. Methylation of xylal (I) with methyl sulphate and sodium hydroxide gave a syrupy dimethyl derivative which, judging from its physical and chemical properties, consisted almost entirely of *dimethyl xylal* (II). It may have contained, however, a small proportion of the corresponding methylated ψ-xylal (VII) (compare Hirst and Woolvin, *loc. cit.*) and for this reason the physical constants are quoted with reserve.

Dimethyl xylal reacted readily with aqueous perbenzoic acid, giving a mixture of dimethyl xylose (IV) and dimethyl lyxose (III). The behaviour here is normal and is in contrast with that of trimethyl glucal in that under similar conditions the latter substance gave only one of the two expected reaction products, namely, trimethyl glucose, the yield of trimethyl mannose being too small for identification. Further methylation and subsequent hydrolysis of the mixture of methylated pentoses gave rise to a mixture of 2 : 3 : 4-trimethyl xylopyranose (VI) and 2 : 3 : 4-trimethyl lyxopyranose (V), both of which were isolated in the crystalline condition. The isolation of these two sugars in good yield provides a complete proof of the pyranose structure of xylal, since no alteration in ring structure can take place at any stage of the above series of reactions. The presence of trimethyl lyxose in the final product is in itself a guarantee of the structure, since this substance could not in any event be derived from ψ-xylal, because the addition of hydroxyl groups at a double bond by the action of per-acids is known to occur invariably in the *trans*-position.



EXPERIMENTAL.

Dimethyl Xylal.—Diacetyl xylal (14·3 g., prepared by Levene and Mori's method) in acetone (150 c.c.) was simultaneously deacetylated and methylated at 29° by methyl sulphate (41 c.c.) and 30% aqueous sodium hydroxide (101 c.c.). The reagents were added slowly during 2 hours and towards the end the temperature was raised to 40°. In this way decomposition was avoided and the final solution was only slightly yellow (dark coloured products are formed if higher initial temperatures are employed). After a further 90 minutes at 40° the acetone was removed by distillation and the aqueous solution was then shaken with chloroform, which removed the methylated xylal, the latter being obtained as a yellow mobile syrup (4·5 g.) on evaporation of the solvent (Found : OMe, 30%). Methylation was completed by use of Purdie's reagents and on fractional distillation of the product *dimethyl xylal* was obtained as a colourless mobile liquid, b. p. *ca.* 73°/17 mm., $n_D^{20^\circ}$ 1·4566, $[\alpha]_D^{19^\circ}$ − 180° in chloroform (*c*, 0·2) (Found : OMe, 42·4. $C_7H_{12}O_3$ requires OMe, 43·0%. 0·0187 G. of the substance required 0·0203 g. of bromine for saturation of the double bond, corresponding to 98% of the calculated quantity for dimethyl xylal). Dimethyl xylal was very soluble in water and the usual organic solvents.

Action of Perbenzoic Acid on Dimethyl Xylal.—To a solution of dimethyl xylal (4·1 g.) in water (20 c.c.), perbenzoic acid (4·4 g.) in ethereal solution (30 c.c.) was added with cooling. This mixture was shaken at 0° for 5 hours and then kept overnight at room temperature. The aqueous layer was separated and the pale yellow ethereal layer was extracted five times with water. The combined aqueous extracts were neutralised with sodium bicarbonate and the solution was extracted with chloroform. On removal of the solvent the syrupy product was dissolved in ether and after filtration the solution was evaporated again, leaving a colourless syrup (3·7 g.). The latter syrup was dissolved in acetone (40 c.c.) and methylated in the usual way with methyl sulphate (30 c.c.) and 30% aqueous sodium hydroxide (65 c.c.), the temperature being kept low until reducing action disappeared. The product (1·8 g.) was further methylated by silver oxide and methyl iodide and distilled, giving a colourless mobile liquid (1·4 g.), b. p. *ca.* 110°/20 mm., $n_D^{17^\circ}$ 1·4427, $[\alpha]_D$ −34° in water (*c*, 4·0) (Found : OMe, 57·8. Calc. for $C_9H_{18}O_5$: OMe, 60·2%).

When this distillate (1·37 g.) was heated on the boiling water-bath with 3% hydrochloric acid, the rotation changed in the course of 1 hour from $[\alpha]_D$ − 34° to the constant value + 2° (a mixture containing 57% of trimethyl xylose and 43% of trimethyl lyxose would have $[\alpha]_D$ + 2° in water). The hydrochloric acid was then neutralised by barium carbonate, and the neutral solution evaporated to dryness under diminished pressure. The mixed methylated sugars were extracted with boiling ether and on removal of the ether were obtained as a viscid colourless syrup (1·1 g.). On inoculation with a sample of authentic 2 : 3 : 4-trimethyl lyxose rapid crystallisation ensued and a semi-solid paste was obtained. The syrup (0·8 g.) was drained away on porous tile and the crude trimethyl lyxose (0·30 g., m. p. alone or in admixture with an authentic specimen, 76—77°) was recrystallised from light petroleum, giving characteristic crystals of 2 : 3 : 4-trimethyl lyxose, m. p. alone or when mixed with an authentic specimen of similar m. p., 79°; $[\alpha]_D^{23^\circ}$ − 22° in water (equilibrium value, *c*, 0·9).

The material absorbed in the porous tile was extracted by boiling chloroform and on removal of the solvent was recovered as a stiff colourless syrup. After inoculation with a crystal of

2 : 3 : 4-trimethyl xylose rapid crystallisation took place. After some days the syrupy portion was removed by absorption in porous tile, leaving a hard crystalline mass (0·33 g.), which consisted mainly (80—90%) of 2 : 3 : 4-trimethyl xylose, some 2 : 3 : 4-trimethyl lyxose being present also. Recrystallisation did not effect a separation of the two sugars, but crystallographic measurements, for which we are indebted to Dr. E. G. Cox of this department, established the identity of both and enabled an estimate of their relative proportions to be made. No other crystalline sugar was observed during this examination.

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