4-Deoxy-L-Ribose

RECENT investigations¹ of the behaviour of the Dische reagent² towards various deoxysugars and their glycosides have revealed that a coloration is obtained with a number of such compounds, and that the reagent cannot be regarded as specific for 2-deoxyribose. Colorimetric evidence based on the Dische test thus does not preclude the occurrence of deoxysugars other than 2-deoxy ribose³ in the deoxypentose nucleic acid structure. As an extension to the investigations on the known 2-deoxyribose⁴ and 3-deoxyribose⁵ (otherwise known as 3-deoxyxylose), we have synthesized 4-deoxy-L-ribose, with a view to its characterization and the study of its behaviour towards colorimetric reagents.

3: 4-Anhydro-α-methyl-D-lyxoside (II) was formed by treatment of 4-tosyl-a-methyl-D-lyxoside (I) with sodium methoxide. Scission of the ethylene oxide ring with hydrogen bromide in acetone was expected to yield two derivatives, 4-bromo-a-methyl-Dlyxoside (III) and 3-bromo- β -methyl-L-xyloside (IV), although, in fact, only the 4-bromo compound was isolated. Hydrogenation of the latter (III) in the presence of Raney nickel led to the glycoside of the required compound.

 α -Methyl-lyxoside was shaken for 12 hr. with acetone containing concentrated sulphuric acid. After neutralization and removal of the solvent, $2:3\text{-acetone-}\alpha\text{-methyl-}D\text{-lyxoside}$ was distilled as a viscous syrup (b.p. $65^{\circ}/0.02 \text{ mm.}$; n_{D}^{23} , 1.4575). This compound reacted readily with p-toluenesulphonyl-chloride in pyridine to give crystalline 4-tosyl-2: 3-acetone- α -methyl-D-lyxoside (m.p. 96– $07^{\circ} \cdot \Gamma_{\alpha}^{122} = 10.2^{\circ}$ in ethanol (con., 1.85)). When 97°; $[\alpha]_{D}^{22}$, -10.2° in ethanol (con., 1.85)). warmed with dilute acetic acid the isopropylidene group was removed and 4-tosyl-a-methyl-D-lyxoside $([\alpha]_D^{2_1}, + 30.0^\circ \text{ in chloroform (con., 1.4)};$ $n^{21}n$, 1.5140) resulted. Mild alkaline hydrolysis of this 4-tosyl derivative yielded 3:4-anhydro- α -methyl-D-lyxoside (b.p. 115° (bath temp.)/0.02 mm.; $[\alpha]_{2^{\circ}}^{2^{\circ}}$, + 98.6 in acetone (con., 1.4)). The anhydro ring was cleaved when this compound was boiled with hydrogen bromide in acetone for 4 hr., and crystalline 4-bromo-α-methyl-D-lyxoside (III) (m.p. 134-135°) was obtained. Evidence for the structure of this





compound was obtained from its ready oxidation by lead tetra-acetate in glacial acetic acid⁷. Reduction of (III) with hydrogen in the presence of Raney nickel and calcium hydroxide at room temperature and atmospheric pressure gave 4-deoxy-β-methyl-Lriboside ($[\alpha]_{D}^{21}$, + 39° in water (con., 0.22)), which was hydrolysed by dilute aqueous acid to 4-deoxy-Lribose (V) ($[\alpha]_{D}^{21}$, + 23 in water (con., 0.2); n_{D}^{23} , 1.4920) which gave a crystalline α -benzylphenyl hydrazone (m.p. 102-103°).

Comparative Dische tests² performed simultaneously on 2-, 3- and 4-deoxyribose revealed that no coloration was given by the 4-deoxy compound or by ribose itself.

The chromatographic R_G values⁸ of the three deoxyriboses were determined in butanol (40 per cent), ethanol (10 per cent), water (50 per cent) on Whatman No. 1 paper giving the following figures : 2-deoxyribose, 0.50; 3-deoxyribose, 0.60; 4-deoxyribose, 0.53.

The structure of this 4-deoxy compound involves certain problems of nomenclature, since the penultimate carbon atom is, in this case, symmetrical. We propose, therefore, that the configuration of this type of compound be decided by reference to the ultimate asymmetrical carbon atom, and in this instance the compound is therefore named '4-deoxy-L-ribose'

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Modified Newtonian Systems

To the usual assumptions for Newtonian mechanics, we add the following, in order to account for the behaviour of light:

(1) The speed of light is the same in all directions, relative to the emitting source.

(2) If a source moves with constant velocity, relative to a Newtonian origin, the speed of light emitted along the line of motion is the same relative to the origin or the source.

From these two additional assumptions, it is possible to develop transformation equations for two Newtonian frames S and S'. We take V as the velocity of S' relative to S and c the speed of light relative to an emitting source considered fixed in S'. If accented co-ordinates are referred to S' and unaccented to S, we have the following equations

$$ax' = x - Vt, \quad y = y', \quad z = z', \quad \alpha t' = t - Vx/c^2,$$

where

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