

sodium amalgam. No rearrangement was involved in this reaction since the isomeric chloride was shown to yield an entirely different metallic compound when treated with the alloy.

2. Di-*tert.*-butyltetraphenylethane absorbs oxygen rapidly in solution at 25°. On heating a dilute solution to 55° a reversible color change indicative of dissociation appears. On heating for a few minutes in solution at 100°, in the absence of air, it disproportionates completely. These results show that the effect of the tertiary alkyl group in promoting the dissociation of the carbon linkage is similar to the effect of the secondary groups studied in the dioxanthyl series.

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RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP.

XVIII. ALPHA-METHYL *d*-LYXOSIDE TRIACETATE^{1,2}

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In Article VII³ it was assumed that the alpha forms of methyl *d*-xyloside and *d*-lyxoside possess the same ring structure and the rotation of the latter was calculated from that of the former by use of the known difference of rotation between the alpha forms of methyl *d*-glucoside and *d*-mannoside, which at that time were supposed to have like ring structures. Subsequent results⁴ indicated, however, that the glucoside possesses a 1,4-ring and the mannoside a 1,5-ring and consequently in Article XII⁵ it was suggested that α -methyl *d*-lyxoside does not possess the 1,5-ring of methyl *d*-xyloside but rather a 1,4-ring. The 1,3-ring appeared to be excluded because 1,3-ring glycosides in the mannose and rhamnose series are hydrolyzed very rapidly by dilute acids, whereas α -methyl lyxoside is hydrolyzed far more slowly even by stronger acid solutions. It has now been sought to obtain further evidence on this question of the possibility of a 1,3-ring structure in α -methyl *d*-lyxoside by examining the behavior of its fully acetylated derivative, a triacetate, toward alkaline saponification. It has been found that the acetates of methyl mannoside⁶ and methyl rhamnoside,⁷ of the 1,3-ring type, retain one acetyl group (presumably that

¹ Publication approved by the Director of the Bureau of Standards.

² Article XVII was published in THIS JOURNAL, 48, 2435 (1926).

³ Hudson, *ibid.*, 47, 272 (1925).

⁴ Hudson, *ibid.*, 48, 1424, 1434 (1926).

⁵ Phelps and Hudson, *ibid.*, 48, 503 (1926).

⁶ Dale, *ibid.*, 46, 1046 (1924).

⁷ Fischer, Bergmann and Rabe, *Ber.*, 53, 2362 (1920).

attached to carbon atom 2) under conditions of strong alkalinity and it would therefore be supposed that a triacetate of α -methyl lyxoside, of the 1,3-ring type, would behave similarly since the configurations of mannose, rhamnose and lyxose are alike with respect to carbon atoms 1, 2, 3 and 4. The experimental results now to be reported show that the three acetyl groups of α -methyl *d*-lyxoside triacetate are easily removed by alkali, and we therefore conclude that the ring is not in the 1,3-position. It must, therefore, be a 1,4- or a 1,5-ring if ring 1,2 is excluded as an improbable structure for stable, difficultly hydrolyzable glycosides of the true sugars.

Since the molecular rotation (+ 25,240) of α -methyl *d*-xyloside of the 1,5-ring type⁸ differs from that of α -methyl *d*-lyxoside ((59.4)(164) = + 9740) by a value (15,500) that is far removed from the "epimeric difference of rotation"⁹ (6700) for glycosides, it is concluded that the substances are not epimeric structures and that, therefore, α -methyl *d*-lyxoside possesses the 1,4-ring. The value now reported ((30.1)(290) = + 8730) for the molecular rotation of the triacetate of this substance leads to the same conclusion, since it differs from that of α -methyl *d*-xyloside triacetate (+ 34,700) by an amount (25,970) far removed from the epimeric difference of rotation (11,300) for acetylated glycosides.

It becomes possible from the preceding conclusions to calculate the rotations of several members of the *d*-xylose series of the 1,4-ring type and likewise several of those of the *d*-lyxose series of the 1,5-ring type, by the use of the epimeric difference of rotation. Thus the specific rotation of the unknown α -methyl *d*-xyloside (1,4) is calculated to be (9740 + 6700) \div 164 = + 100 in water, and that of its *triacetate* to be (8730 + 11,300) \div 290 = + 69 in chloroform. Likewise the specific rotation of the unknown α -methyl *d*-lyxoside (1,5) is calculated to be (25,240 - 6700) \div 164 = + 113 in water, and that of its *triacetate* to be (34,700 - 11,300) \div 290 = + 80 in chloroform. These calculations can obviously be extended to the α - and β -forms of xylose and lyxose, of both the 1,4- and 1,5-ring types, and to various derivatives of these pentoses other than those just considered. Since the rotation of α -*d*-lyxose (+ 5.5) differs normally from that of α -methyl *d*-lyxoside,^{3,5} it is concluded that this crystalline form of the pentose possesses the 1,4-ring structure.

Experimental

Preparation of α -Methyl *d*-Lyxoside Triacetate.—One g. of pure α -methyl *d*-lyxoside ($[\alpha]_D^{20} = +59.4^\circ$ in water) was heated with 6 cc. of acetic anhydride and 3 cc. of dry pyridine for half an hour on the steam-bath. On pouring the solution into ice water a sirup separated and quickly crystallized, yielding 0.9 g. of crystalline triacetate ($[\alpha]_D = +29.2^\circ$ in CHCl_3). Extraction of the mother liquor with CHCl_3 yielded 0.6

⁸ Hirst and Purves, *J. Chem. Soc.*, **123**, 1352 (1923).

⁹ Hudson, *THIS JOURNAL*, **48**, 1439 (1926).

g. of crystals of nearly the same rotation. Three grams of the substance was thus prepared in two experiments. One recrystallization from hot water gave a pure product, the rotation of which was not changed by four subsequent recrystallizations; m. p. 96°. The rotation measurements on the final product are recorded in the table, the tube length being 2 dm. and the solvent being pure chloroform. The angles are in all cases dextro-rotations.

TABLE I

ROTATION OF PURE α -METHYL *d*-LYXOSIDE TRIACETATE IN CHLOROFORM SOLUTION

Concn., g./100 cc. of soln.	Sodium yellow $\lambda = 589$		Mercury yellow $\lambda = 578$		Mercury green $\lambda = 546$		Mercury blue $\lambda = 436$	
	α	$[\alpha]_D^{20}$	α	$[\alpha]_{578}^{20}$	α	$[\alpha]_{546}^{20}$	α	$[\alpha]_{436}^{20}$
0.745	+0.438	+29.4	+0.461	+31.0	+0.530	+35.6	+0.705	+61.0
1.307	+ .803	+30.7	+ .838	+32.1	+ .941	+36.0	+1.62	+62.0
1.776	+1.074	+30.2	+1.137	+32.0	+1.274	+35.8		
1.908			+1.208	+31.7	+1.358	+35.6	+2.40	+62.9
	Average	+30.1		+31.7		+35.8		+62.0

A Zeisel analysis showed 10.4% of methoxyl (0.3222 g. of substance yielded 0.1552 g. of AgCl) in comparison with the value 10.7 required by the formula $C_{11}H_{13}O_7OCH_3$ (m. w., 290).

An acetyl estimation by the method of Kunz¹⁰ agreed with this formula for a triacetate (0.2126 g. of substance was equivalent to 21.5 cc. of 0.1 *M* HCl).

Summary

Pure α -methyl *d*-lyxoside triacetate has been prepared and it is concluded from a comparison of its rotation with that of α -methyl *d*-xyloside triacetate that the lyxoside derivative possesses a 1,4-ring structure, and that crystalline α -lyxose ($[\alpha]_D = +5.5$) also has this ring structure since its rotation differs normally from that of α -methyl *d*-lyxoside.

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NEW BOOKS

A Comprehensive Study of Starch Chemistry. Volume I. Compiled and edited by ROBERT P. WALTON in collaboration with twenty other authors. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1928. 240 + iv + 360 pp. Illustrated. 18 × 26 cm. Cloth. Price, \$10.00.

In the introductory paragraph of the Preface the compiler writes: "The most prominent aspects of the subject have been treated by authorities who have contributed significantly to the advancement of the field and who are actively engaged in further investigations or developments." This statement describes adequately the nature of the first part of the book and the material presented in it.

The nineteen papers comprising the symposium and the first 235 pages of the volume range in subject matter from various aspects of the molecular constitution and physical and chemical properties of starches and

¹⁰ Kunz and Hudson, *THIS JOURNAL*, **48**, 1978 (1926).