

aqueous sodium hydroxide. The white solid was collected and washed with water, giving 2.91 g. melting 214–215° dec., R_f 0.39; chilling the mother liquors overnight afforded an additional 3.09 g., m.p. 208–211° dec., bringing the total yield of product to 6.00 g. (77.8%). Crystallization from methanol-ethyl acetate did not raise the melting point of the first crop. It was soluble in water (positive silver nitrate test), methanol, and warm ethanol, but insoluble in other organic solvents; R_f 0.39; pK_a 3.5 (80% methyl Cellosolve). Molecular weight determinations by isothermal distillation suggested that the compound was not dimeric, but the results were not completely satisfactory (therefore, see below).

Anal. Calcd. for $C_{12}H_{15}N_2Cl_4Br$ (409.01): C, 35.24; H, 3.70; N, 6.85. Found: C, 35.11; H, 3.71; N, 7.05.

Reaction of 3,4,5,6-tetrachloro-*o*-xylylene dibromide and 2-dimethylaminoethylamine in dioxane according to the method of Wenner^{16f} gave the same product.

Nitrate Salt (VIIIb).—A 1.00-g. sample of VIIIa was refluxed for 30 minutes with 0.50 g. of silver nitrate in 15 ml. of methanol. After removal of silver bromide by filtration, solvent was removed *in vacuo*, and the white solid residue, m.p. 223–225° dec. (no mixed melting point depression of starting bromide), was recrystallized from methanol-ethyl acetate. The white crystalline nitrate salt, m.p. 224–227° dec., R_f 0.38, gave a negative silver nitrate test. The infrared spectrum showed all the bands of the starting material plus those characteristic of ionic nitrate (1350 and 846 cm^{-1}).²²

Anal. Calcd. for $C_{12}H_{15}O_3N_3Cl_4 \cdot CH_3OH$ (423.15): C, 36.90; H, 4.53; N, 9.93. Found: C, 37.53; H, 4.10; N, 10.09.

Molecular Weight Determination; Picrate Salt.—A solution of 0.40 g. of VIIIa in 4 ml. of methanol was added to a solution of 0.80 g. of picric acid in 8 ml. of methanol. The immediate precipitate of 0.40 g. of yellow solid was removed by filtration (m.p. 140–144°). After standing overnight, the filtrate deposited 0.16 g. of yellow crystals, m.p. 235–236° dec., which proved to be 7,8,9,10-tetrachloro-1,2,3,4,5,6-hexahydro-2,2-dimethyl-2,5-benzodiazocinium dipicrate.

Anal. Calcd. for $C_{24}H_{20}O_{14}N_8Cl_4 \cdot \frac{1}{2}CH_3OH$ (802.34): C, 36.68; H, 2.76; N, 13.97. Found: C, 36.91; H, 3.04;

N, 14.30. A spectrophotometric determination of the molecular weight¹⁹ gave 812.94.

7,8,9,10-Tetrachloro-1,2,3,4,5,6-hexahydro-2,2,5-trimethyl-2,5-benzodiazocinium Dibromide (IX).—Gaseous methyl bromide was bubbled for 1 hour through a refluxing solution of 3.00 g. of VIIIa in 24 ml. of 95% ethanol. Solvent was removed *in vacuo* and the yellow oily residue was taken up in 24 ml. of methanol. After the solution had been chilled overnight, the white crystals which had separated were collected and washed with methanol, giving 1.05 g. of IX, m.p. 284–286° dec., R_f 0.41. The infrared spectrum showed absorption in the 2500–2700 cm^{-1} region, typical of acid salts. The mother liquors contained more IX and a small amount of X, according to paper chromatographic examination.

Anal. Calcd. for $C_{13}H_{18}N_2Cl_4Br_2 \cdot H_2O$ (521.98): C, 29.91; H, 3.86; N, 5.37. Found: C, 29.23; H, 3.82; N, 5.73.

7,8,9,10-Tetrachloro-1,2,3,4,5,6-hexahydro-2,2,5,5-tetramethyl-2,5-benzodiazocinium Dibromide (X).—A solution of 3.09 g. of VIIIa in 31 ml. of 50% methyl bromide in dimethylformamide was warmed on the steam-bath with stirring for 1 hour in the presence of 0.77 g. of sodium acetate. The solution was cooled and 3.30 g. of white solid was collected. Crystallization from methanol gave 2.55 g. (65.2%) of dibromide product, m.p. 226–229° dec., R_f 0.12, whose infrared spectrum was completely different from the isomeric dimethobromide of IIB (m.p. 245–247° dec.).

Anal. Calcd. for $C_{14}H_{20}N_2Cl_4Br_2 \cdot 2H_2O$ (554.02): C, 30.35; H, 4.37; N, 5.06. Found: C, 30.51; H, 4.21; N, 5.23.

Conversion of IX to X.—A suspension of 3.7 g. of IX and 0.77 g. of sodium acetate in 37 ml. of 50% methyl bromide in dimethylformamide was refluxed on the steam-bath for 1 hour. The 3.2 g. of white crystals (R_f 0.17) which separated on cooling was crystallized twice from methanol, giving 1.79 g. of X, m.p. 232–234.5° dec. (yellow-orange melt, foamed).

Anal. Calcd. for $C_{14}H_{20}N_2Cl_4Br_2$ (517.99): C, 32.46; H, 3.89. Found: C, 32.39; H, 4.18.

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[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL BIOCHEMISTRY, UNIVERSITY OF MINNESOTA]

The Structure of the Dialdehyde Formed by Periodate Oxidation of Methyl α -L-Rhamnopyranoside^{1,2}

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Infrared, optical rotation and methylation data show that the crystalline monohydrate of the dialdehyde, formed by periodate oxidation of methyl α -L-rhamnopyranoside, possesses a cyclic acetal structure Va or Vb.

In a previous communication³ it was established that hydrogenation at room temperature in the presence of a palladium-charcoal catalyst of the dialdehyde II from the aldohexopyranosides such as methyl α -D-glucopyranoside (I) effected preferential reduction of the aldehyde group at C₄⁴ to give III. This behavior of II was attributed to the presence of a ring which engaged the hydroxyl group at C₆ and the aldehyde function at C₂ as in IIa. It was further noted³ that if the hydroxyl group at C₆ was blocked by a methyl group or was other-

wise suitably modified as in the case of a 6-deoxy sugar glycoside, such as methyl α -L-rhamnopyranoside (IV), the corresponding dialdehyde V resisted reduction under those conditions which transformed II into III. In order to explain this result it was suggested that the dialdehyde exists in the cyclic form Va in which the two aldehydic groups at C₂ and C₄ are mutually involved in cyclic hemiacetal formation through the agency of a molecule of water.

This paper is concerned with further evidence in support of the contention that the so-called "dialdehyde"^{5,6} obtained upon periodate oxidation of methyl α -L-rhamnopyranoside (IV) exists in the cyclic form.

(1) Paper No. 3803, Scientific Journal Series, Minnesota Agricultural Experiment Station, University of Minnesota.

(2) Presented in part at the 129th A.C.S. Meeting, Dallas, Texas, April, 1956.

(3) J. E. Cadotte, G. G. S. Dutton, I. J. Goldstein, B. A. Lewis, F. Smith and J. W. Van Cleve, *THIS JOURNAL*, **79**, 691 (1957).

(4) Unless stated otherwise the numbering of the carbon atoms corresponds to that of the parent glycoside.

(5) E. L. Jackson and C. S. Hudson, *THIS JOURNAL*, **59**, 994 (1937).

(6) W. D. Maclay, R. M. Hann and C. S. Hudson, *ibid.*, **61**, 1660 (1939).

TABLE I

RELATIONSHIP BETWEEN THE SPECIFIC ROTATION AND STRUCTURE OF METHYL GLYCOSIDES, THEIR "DIALDEHYDES," AND THE OXIDATION AND REDUCTION PRODUCTS OF THE DIALDEHYDES

Compound, methyl pyranoside	Glycoside in water	"Dialdehyde" in water	Dibasic acid in water	Alcohol in ethanol (water)
α -D-Gluco-	+159 ^o 12	+121 ^o 5.8	+26 ^o 8	-10 ^o 8
β -D-Gluco-	-34 ^o 12	-150 ^o 5.3	+45 ^o 6	+11 ^o 8
α -D-Xylo-	+154 ^o 12	+125 ^o 5.8	-12 ^o 5	-7 ^o 8
α -L-Rhamno-	-63 ^o 12	-143 ^o 5.3	-23 ^o 9	+35 ^o 10
6-O-Methyl- α -D-galacto-	+165 ^o 3	+143 ^o 3.11	...	-12 ^o 11

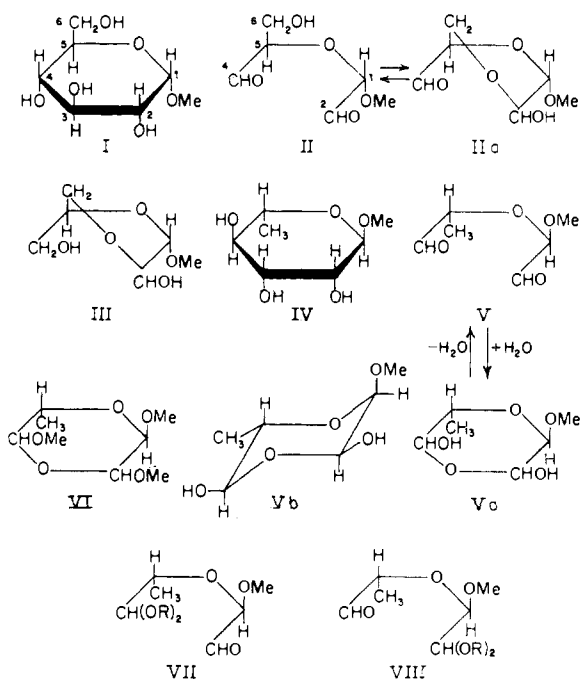
The crystalline monohydrate of the "dialdehyde" V formed from methyl α -L-rhamnopyranoside (IV) by oxidation with periodic acid was found by the Rast method to be monomolecular. The usual methods of dehydration failed to remove the molecule of water thus indicating that the water molecule was of structural significance. The role played by the water was apparent from the observation that infrared analysis revealed the presence of strong hydroxyl absorption at 3500 cm^{-1} , but no carbonyl band was detected. Moreover, methylation of V with silver oxide and methyl iodide introduced two methyl groups to give an almost quantitative yield of the crystalline product VI thus showing that V was behaving not as a dialdehyde but as a dihydroxy compound. Infrared analysis showed that VI contained no hydroxyl groups. The presence of two hydroxyl groups in V also was recognized by the fact that V gave a crystalline di-*p*-nitrobenzoate. It is clear, therefore, that the dialdehyde V in the form of its crystalline monohydrate must be represented as the 1,4-dioxane compound Va, namely, 2-L''-methoxy-3,5-dihydroxy-6-D''-methyl-1,4-dioxane.⁷

Other although less likely isomeric forms of the dialdehyde V represented in VII and VIII (R = H) were eliminated by the fact that the methylated derivative of V was unaffected by treatment with sodium borohydride,⁸ thus showing that the crystalline dimethyl derivative prepared from the monohydrate of V did not possess the structure VII or VIII (R = CH₃).

While the stereochemistry at C₁ and C₅ in Va follows from the structure of the parent compound IV, the disposition of the two hydroxyl groups in Va is not known. However, from a consideration of conformational analysis, the hydroxyl groups probably are in the equatorial positions and hence the monohydrate of the dialdehyde is believed to have the structure shown in Vb; it also follows that the methylated derivative, VI, will have the same conformation as Vb.

Pertinent to the argument that the so-called dialdehydes exist as derivatives of 1,4-dioxane is the observation that the specific rotations of the dialdehydes^{5,8} are generally similar to or larger in magnitude than those of the parent glycosides in all those cases where the dialdehyde may exist in a

1,4-dioxane form, such as Va and IIa. Elimination of the possibility of ring formation by oxidation or reduction usually produces a marked decrease in the magnitude of rotation and often results in a change in the sign of rotation.⁹ When the dialde-



hyde II is reduced to the corresponding alcohol the asymmetric center at C₅ is destroyed, but that this is not the main cause for the change in optical activity is demonstrated by the observation that the dialdehyde D'-methoxy-D-methoxymethyl diglycolic aldehyde,³ obtained from methyl 6-O-methyl- α -D-galactopyranoside, has $[\alpha]_D +143^\circ$ while the corresponding alcohol shows only $[\alpha]_D -12^\circ$ even though the product still possesses dissymmetry at C₅ on account of the methoxyl group at C₆ (see Table I). Similarly the so-called dialdehyde from methyl α -L-rhamnopyranoside exhibits a rotation of $[\alpha]_D -143^\circ$ while the corresponding acyclic acid and alcohol show -23 and $+35^\circ$, respectively,

(9) M. Abdel-Akher, J. E. Cadotte, B. A. Lewis, R. Montgomery, F. Smith and J. W. Van Cleve, *Nature*, **171**, 474 (1953).

(10) Bertha A. Lewis and F. Smith, unpublished results.

(11) I. J. Goldstein, J. K. Hamilton and F. Smith, *THIS JOURNAL*, **79**, 1190 (1957).

(12) "Polarimetry, Saccharimetry and the Sugars," by F. J. Bates and Associates, Circular C-410 of the Natl. Bur. of Standards, 1942.

(7) Groups designated by D''- and L''- in this formulation correspond to positions below and above the plane of the ring of the original formula written according to the Haworth convention.

(8) F. Smith and J. W. Van Cleve, *THIS JOURNAL*, **77**, 3091 (1955).

even though both possess an asymmetric center at C₅ in addition to that at C₁.

It is also of interest to note that the aldehyde, obtained by periodate oxidation of 1,2-*O*-isopropylidene-*D*-glucofuranose, and its reduction product 1,2-*O*-isopropylidene-*D*-xylofuranose display little difference in rotation¹⁸ since there is no chance for either compound to undergo cyclization.

The phenomenon of cyclization established herein for the dialdehyde V from methyl α -L-rhamnopyranoside (IV) and postulated previously in a number of instances¹⁴⁻²¹ is a general one for the products of periodate oxidation of the simple and complex carbohydrates.

Experimental

Oxidation of Methyl α -L-Rhamnopyranoside with Periodic Acid.—Methyl α -L-rhamnopyranoside was oxidized with periodic acid in the usual way^{5,6} to give the crystalline monohydrate of *L*'-methoxy-*L*-methylidiglycolic aldehyde, m.p. 102° and $[\alpha]^{23D} -144^\circ$ in water (*c* 1); lit.⁶ m.p. 101–102°, $[\alpha]^{20D} -143^\circ$ in water. The product showed a strong hydroxyl absorption but no carbonyl absorption in the infrared region of the spectrum. The molecular weight determined in camphor by the Rast method using $K = 26$ was 160 (calcd. for C₆H₁₂O₅ 164). The *K*-value was ascertained with methyl β -L-arabinopyranoside.

Methylation of *L*'-Methoxy-*L*-methylidiglycolic Aldehyde Monohydrate (Va) with Silver Oxide and Methyl Iodide.—

(13) G. W. Huffman, Bertha A. Lewis, F. Smith and D. R. Sprietsbach, *THIS JOURNAL*, **77**, 4346 (1955).

(14) H. E. Carter, R. K. Clark, Jr., S. R. Dickman, Y. H. Loo, P. S. Skell and W. A. Strong, *Science*, **103**, 540 (1946).

(15) J. H. Michell and C. B. Purves, *THIS JOURNAL*, **64**, 589 (1942).

(16) B. A. Lewis, R. Montgomery, F. Smith and J. W. Van Cleve, presented at the 121st American Chemical Society Meeting, Milwaukee, Wisc., March, 1952.

(17) C. D. Hurd, P. J. Baker, Jr., R. P. Holysz and W. H. Saunders, Jr., *J. Org. Chem.*, **18**, 186 (1953).

(18) Von E. Schreier, G. Stöhr and E. Hardegger, *Helv. Chim. Acta*, **37**, 574 (1954).

(19) V. C. Barry and P. W. D. Mitchell, *J. Chem. Soc.*, 3631 (1953).

(20) L. Mester and E. Moczar, *Chemistry & Industry*, 761 (1957).

(21) R. C. Hockett, M. H. Nickerson and W. H. Reeder, *THIS JOURNAL*, **66**, 472 (1944).

Silver oxide (3 g.) was added to a suspension of the crystalline dialdehyde monohydrate (0.797 g.) in methyl iodide (20 ml.). After standing at room temperature for 1 hr. when no visible reaction occurred, the reaction mixture was boiled under reflux for 24 hr. Evaporation of the solvent at room temperature gave a colorless crystalline residue in almost quantitative yield, which after two recrystallizations from light petroleum ether yielded 2-*L*'',3,5-trimethoxy-6-*D*''-methyl-1,4-dioxane (VI) as fine, flat needles (0.300 g.), m.p. 73–74.5° with sublimation and $[\alpha]^{22D} -142^\circ$ in ethanol (*c* 1). In the infrared, the compound showed a strong ether absorption but no carbonyl absorption.

Anal. Calcd. for C₈H₁₆O₅: C, 50.0; H, 8.4; OCH₃, 48.5. Found: C, 50.0; H, 8.3; OCH₃, 48.7.

Treatment of 2-*L*'',3,5-Trimethoxy-6-*D*''-methyl-1,4-dioxane (VI) with Sodium Borohydride.—Sodium borohydride (0.200 g.) was added to a solution of 2-*L*'',3,5-trimethoxy-6-*D*''-methyl-1,4-dioxane (0.100 g.) in water (5 ml.). After 5 hr. the reaction mixture was extracted with diethyl ether (4 × 30 ml.). Concentration of the combined ethereal extracts gave the starting material, m.p. and mixed m.p. 73–74° and $[\alpha]^{22D} -141^\circ$ in ethanol (*c* 1), after recrystallization from light petroleum ether.

Reaction of *L*'-Methoxy-*L*-methylidiglycolic Aldehyde with *p*-Nitrobenzoyl Chloride.—A solution of the dialdehyde, *L*'-methoxy-*L*-methylidiglycolic aldehyde (0.062 g.), in dry pyridine (3 ml.) was treated with *p*-nitrobenzoyl chloride (0.230 g.) at 80° for 0.5 hr. Upon pouring the cooled reaction mixture into a saturated aqueous solution of sodium bicarbonate, the product crystallized immediately. After being filtered, the product was washed with water and dried (crude yield 0.180 g.). Recrystallization from a mixture of ethanol, chloroform and light petroleum ether gave the di-*p*-nitrobenzoate of *L*'-methoxy-*L*-methylidiglycolic aldehyde, m.p. 170.5° and $[\alpha]^{22D} +39^\circ$ in chloroform (*c* 0.8).

Anal. Calcd. for C₂₀H₁₈O₁₁N₂: C, 52.0; H, 3.9; N, 6.1. Found: C, 52.2; H, 3.8; N, 6.1.

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[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY, AND THE WOOD CHEMISTRY DIVISION, PULP AND PAPER RESEARCH INSTITUTE OF CANADA]

The Polysaccharides of White Birch (*Betula papyrifera*). III. Determination of Composition and Identification of 2-*O*-(4-*O*-Methyl-*D*-glucopyranosyluronic acid)-*D*-xylopyranose¹

BY C. P. J. GLAUDEMANS AND T. E. TIMELL

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Alkaline extraction of a holocellulose from white birch (*Betula papyrifera*) has yielded a hemicellulose in an amount closely corresponding to the anhydroxylose and uronic anhydride content of the wood. Hydrolysis of the hemicellulose gave xylose, galacturonic acid, 4-*O*-methyl-*D*-glucuronic acid and 2-*O*-(4-*O*-methyl-*D*-glucopyranosyluronic acid)-*D*-xylopyranose, together with traces of galactose, glucose, arabinose and rhamnose.

Previous studies in this series dealt with methods for isolating an unchanged holocellulose from white birch (*Betula papyrifera*)² and with the molecular properties of its cellulose component.³ This paper is concerned with the general chemical composition

(1) Paper presented before the Division of Cellulose Chemistry at the 132nd Meeting of the American Chemical Society in New York, N. Y., September, 1957.

(2) T. E. Timell and E. C. Jahn, *Svensk Papperstidn.*, **54**, 831 (1951).

(3) T. E. Timell, *ibid.*, **59**, 1 (1956).

of the wood and with the isolation and characterization of an aldobiouronic acid obtained on partial hydrolysis of its hemicellulose portion.

Delignification by a chlorination procedure² of the wood followed by extraction with alkali, afforded a hemicellulose which upon acid hydrolysis yielded galacturonic acid, 4-*O*-methyl-*D*-glucuronic acid, 2-*O*-(4-*O*-methyl-*D*-glucopyranosyluronic acid)-*D*-xylopyranose, and a mixture of sugars. Chromatographic analysis indicated that this mix-