

Experimental⁸

β -Morpholino-2-chloro-chalcone (II).—A solution of 0.7 g. of morpholine in 1 ml. of ether was added to a solution of 1.9 g. of *o*-chlorophenylbenzoylacetylene⁹ in 10 ml. of ether. The mixture was allowed to stand at room temperature while the ether evaporated. The residual solid was recrystallized from petroleum ether (b.p. 65–110°) to yield 2.4 g. (92%) of very pale yellow cubes, m.p. 113–114°.

Anal. Calcd. for C₁₉H₁₅ClNO₂: C, 69.61; H, 5.53. Found: C, 69.29; H, 5.37.

The ultraviolet spectrum, which was determined in ethanol solution with a Cary recording spectrophotometer, showed two maxima, λ 246 μ , ϵ 11,100 and λ 340 μ , ϵ 21,200.

The first time this compound was obtained it crystallized from petroleum ether (b.p. 65–110°) in white plates, m.p. 98–99°.

Anal. Calcd. for C₁₉H₁₅ClNO₂: C, 69.61; H, 5.53; N, 4.27. Found: C, 69.58; H, 5.64; N, 4.02.

Admixture with the latter lower-melting crystalline form did not depress the melting point of the form melting at 113–114°, and the ultraviolet spectra of the two materials were identical.

4-Morpholinoflavylium Chloride (V).—A solution of 2.3 g. of β -morpholino-2-chloro-chalcone in approximately 40 ml. of *n*-butyl ether was heated under reflux for 3.5 hr. During this period a crystalline solid was gradually precipitated. After the precipitate had been removed by filtration, washed with ether and dried, there was obtained 1.0 g. (43%) of light-tan needles, m.p. 235–237° dec. Efforts to find a solvent for recrystallization of this product were unsuccessful. The compound gave an immediate precipitate with aqueous silver nitrate solution.

Anal. Calcd. for C₁₉H₁₅ClNO₂: C, 69.61; H, 5.53; N, 4.27. Found: C, 69.75; H, 5.88; N, 4.31.

When the filtrate from the reaction mixture and the ether used to wash the precipitate were concentrated, 1.1 g. (a 48% recovery) of crude starting material was obtained, m.p.

109–112°. Recrystallization of this material from petroleum ether (b.p. 65–110°) gave the usual light-yellow cubes, m.p. 113–114°.

Preparation of Flavone (VI) Directly from *o*-Chlorophenylbenzoylacetylene (I).—A solution of 5 g. of compound I in 30 ml. of morpholine was heated at the reflux temperature for 10 hr. Morpholine hydrochloride separated when the mixture was cooled. (The morpholine was not dried prior to use and no attempt was made to exclude water during the reaction period.) The cooled mixture was diluted with an equal volume of ether and filtered to remove the morpholine hydrochloride, which melted at 174–175° dec. after it had been washed with ether, and did not depress the melting point of an authentic sample. The filtrate was evaporated to leave a light-red oil, which was triturated first with water, then with a small amount of 6 *N* hydrochloric acid. The resulting sticky brown solid was taken up in ether, but evaporation of the ether again left an oil. The oil was triturated with petroleum ether (b.p. 65–110°), and the resulting brown solid was recrystallized from the same solvent to give two crops of crystals (total weight 2.5 g., a 74% yield) of crude flavone, m.p. ca. 94°. After purification by vacuum sublimation and recrystallization from low-boiling petroleum ether (b.p. 30–60°), the crystals were nearly colorless and melted at 96–97°.

Anal. Calcd. for C₁₅H₁₀O₂: C, 81.06; H, 4.41. Found: C, 81.23; H, 4.43.

The compound did not depress the m.p. of a sample of flavone, m.p. 96–97°, prepared by the method of Mazingo and Adkins,¹⁰ and the infrared spectra of the two samples were identical.

Conversion of 4-Morpholinoflavylium Chloride (V) into Flavone (VI).—A 1.0-g. sample of compound V was added to 20 ml. of water which had been acidified by addition of a small amount of 6 *N* hydrochloric acid. The mixture was extracted three times with 10-ml. portions of ether. After removal of the solvent from the ether extracts and recrystallization of the residual solid from petroleum ether, 0.4 g. (59%) of flavone was obtained in the form of white needles, m.p. 96–97°. The melting point was not depressed when the product was mixed with an authentic sample of flavone.¹⁰

(10) R. Mazingo and H. Adkins, *ibid.*, **60**, 668 (1938).

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(8) Microanalyses are by Dr. G. Weiler and Dr. F. B. Strauss, Oxford, England.

(9) C. L. Bickel, *THIS JOURNAL*, **69**, 2134 (1947).

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

Reduction of the Products of Periodate Oxidation of Carbohydrates. IV. Hydrogenation with Palladium-Charcoal of the Dialdehydes from Methyl Glycosides^{1,2}

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Hydrogenation in the presence of a palladium-charcoal catalyst of the dialdehyde (II), *D'*-methoxy-*D*-hydroxymethyl-diglycolic aldehyde, obtained from methyl α -*D*-glucopyranoside (I) by periodate oxidation, effects preferential reduction of one aldehyde group to give the monoaldehyde V, the properties of which indicate that it has the dioxane structure VII. The structure of V was established by bromine oxidation to the monocarboxylic acid IV which upon hydrolysis gave rise to glycerol and glyoxylic acid. The same series of reactions has been carried out with methyl β -*D*-glucopyranoside. The dialdehyde (*D'*-methoxydiglycolic aldehyde (IX)) from methyl β -*L*-arabopyranoside, the dialdehyde (*L'*-methoxy-*L*-methyl-diglycolic aldehyde (X)) from methyl α -*L*-rhamnopyranoside and the dialdehyde (*D'*-methoxy-*D*-methoxymethyl-diglycolic aldehyde (XI)) obtained from methyl 6-*O*-methyl- α -*D*-galactopyranoside, did not give rise to monoaldehydes upon hydrogenation in the presence of a palladium-charcoal catalyst. The structural significance of these findings is discussed.

When any one of the methyl α -*D*-hexopyranosides such as methyl α -*D*-glucopyranoside (I) is oxidized with periodate, *D'*-methoxy-*D*-hydroxymethyl-diglycolic aldehyde (II) is formed.^{3,4} Hy-

drogenation of the dialdehyde II in the presence of a Raney nickel catalyst under pressure at 120° has been shown in Part I of this series² and elsewhere⁵ to give the corresponding alcohol III.

It is shown herein that hydrogenation of II under pressure in the presence of a palladium-charcoal catalyst at room temperature brings about a partial reduction and there is formed a monoaldehyde V. The structure of V rests upon the

(1) Paper No. 3581, Scientific Journal Series, Minnesota Agricultural Experiment Station, University of Minnesota, St. Paul, Minnesota.

(2) Part I, *THIS JOURNAL*, **77**, 3091 (1955).

(3) H. Hérissé, P. Fleury and M. Joly, *J. pharm. chim.*, **20**, 149 (1934).

(4) E. L. Jackson and C. S. Hudson, *THIS JOURNAL*, **58**, 378 (1936); **59**, 994 (1937).

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

The observation that II reacts in the cyclic acetal form VI lends support to the view that the dialdehydes formed from glycosides and the polyaldehydes formed from polysaccharides by periodate oxidation tend to form cyclic acetals⁸⁻¹⁰ and hydrates.¹¹ Infrared studies¹² also favor this contention.

Experimental

A. Hydrogenation of D'-Methoxyhydroxymethylglycolic Aldehyde (II) in the Presence of a Palladium-Charcoal Catalyst.—Methyl α -D-glucopyranoside (5.0 g.) was oxidized with periodic acid⁴ to yield D'-methoxy-D-hydroxymethylglycolic aldehyde. This dialdehyde, isolated in the usual manner,^{4,5} was transferred to the hydrogenation bomb, dissolved in absolute ethanol (75-100 ml.) and palladium-charcoal catalyst (2-3 g.) was added. The hydrogenation was performed at a pressure of 1200 lb. per sq. in., with mechanical shaking, at room temperature for 15 hours. The solution, filtered from the catalyst, was concentrated *in vacuo* (bath, 40-45°) to give a clear viscous sirup consisting of the monoaldehyde (V or VII) and unchanged dialdehyde. Distillation of the sirup, b.p. (bath temp.) 120-140°, 0.005 mm., gave a colorless liquid (2.56 g.) consisting principally of the monoaldehyde, n_D^{20} 1.4688, $[\alpha]_D^{25} +128^\circ$ in ethanol (*c* 2) and $[\alpha]_D^{25} +118^\circ$ in water (*c* 2) and R_f 0.53 (methyl ethyl ketone-water azeotrope). This material did not reduce Fehling solution nor did it give a Schiff test. *Anal.* Calcd. for $C_6H_{12}O_6$: OCH₃, 18.9. Found: OCH₃, 17.1, 17.7.

The true methoxyl value was determined by the modified method of Gran¹³ wherein the methyl iodide is collected as the quaternary salt with trimethylamine.

In part I of this series it was suggested that the high methoxyl value found for D'- and L'-methoxyhydroxymethyl-diethylene glycol and for D'- and L'-methoxy-diethylene glycol by the usual method, arose from the glycolic aldehyde formed by hydrolysis during the Zeisel determination. From the present investigations into the monoaldehyde (V or VII) and its derivatives, as well as from other work to be published later, it is apparent that the high methoxyl values arise from the glycerol or glycol residue and not the aldehyde moiety. The amount of "extra methoxyl" arising from isopropyl iodide (from glycerol) or ethyl iodide (from ethylene glycol) is variable and depends upon the time and temperature used in the Zeisel determination and, inasmuch as propylene and ethylene are formed at the same time, respectively, as the alkyl iodides, the "extra methoxyl" is seldom equivalent to more than half a methoxyl group.

Properties of the Monoaldehyde. (a) Hydrolysis with Acid.—A solution of the monoaldehyde (V or VII) (0.1043 g.) in 0.1 N HCl (10 ml.), $\alpha_D^{25} +1.29^\circ$ (1 dm. tube) (20 min. at room temperature), heated on the steam-bath, showed the following rotations: $\alpha_D^{25} +1.01^\circ$ (2.5 hr.), $+0.53^\circ$ (10.5 hr.), $+0.25^\circ$ (16.5 hr.), $+0.09^\circ$ (33.5 hr.), $\alpha_D^{25} \pm 0^\circ$ at 45 hr. With the same conditions the dialdehyde (II or VI) was hydrolyzed to a constant rotation $\alpha_D^{25} +0.05^\circ$ (50.3 mg. in 6 ml. 0.1 N HCl, 1 dm. tube) in 15 hours.

(b) Treatment of the Monoaldehyde (V or VII) with Methanolic Hydrogen Chloride.—The monoaldehyde (V or VII) (1.155 g.) was treated with methanolic hydrogen chloride (1%) (25 ml.) at room temperature for 45 days until the rotation had changed from $[\alpha]_D^{25} +134^\circ$ (initial) to the constant value $[\alpha]_D^{25} +58^\circ$. The reaction mixture was neutralized with silver carbonate, filtered and concentrated *in vacuo* to a colorless sirup (1.029 g.) containing the methyl acetal (? VIII or VIIa).

Paper chromatographic analysis using methyl ethyl ketone: water azeotrope revealed the presence of glycerol and some unchanged monoaldehyde in the crude product. By column partition chromatography using methyl ethyl

ketone:water azeotrope as the solvent the mixture was resolved in the usual way to give two methyl acetals: fraction a, a colorless mobile liquid, 170 mg., n_D^{25} 1.4482, $[\alpha]_D^{25} +179^\circ$ in methanol (*c* 2). *Anal.* Calcd. for $C_7H_{14}O_5$: OMe, 34.9. Found: OMe (by the method of Gran),¹³ 37.0. Fraction b, crystalline solid, 49 mg., m.p. 110°, $[\alpha]_D^{25} +39^\circ$ in methanol (*c* 0.5). *Anal.* Calcd. for $C_7H_{14}O_5$: C, 47.2; H, 7.9. Found: C, 47.5; H, 8.0. Fraction a issued from the column before fraction b, which in turn was followed by the unchanged monoaldehyde and then the glycerol. Both the acetals were non-reducing to Tollens reagent. Upon hydrolysis either with dilute mineral acid or methanolic hydrogen chloride both acetals gave rise to glycerol as revealed by paper chromatography. The isomeric acetals are believed to have the formulas shown in VIII or VIIa but the stereochemical arrangement of the group at C₂ is not known.

(c) Treatment of the Monoaldehyde (V or VII) with Benzylphenylhydrazine.—To a solution of the monoaldehyde (0.1422 g.) in 95% ethanol (3 ml.) was added benzylphenylhydrazine (0.5 ml.) and the mixture was refluxed for 10 min. On cooling yellow crystals of glyoxal bis-benzylphenylhydrazone quickly separated (yield 0.266 g. after filtering and washing with 95% ethanol), m.p. and mixed m.p. 193-194°, after recrystallization from chloroform-petroleum ether. A melting point of 197.5°¹⁴ is recorded for this substance. *Anal.* Calcd. for $C_{22}H_{26}N_4$: C, 80.4; H, 6.3; N, 13.4. Found: C, 80.7; H, 6.4; N, 13.7.

(d) Reduction of the Monoaldehyde (V or VII). (1) With Sodium Borohydride.—To a solution of the sirupy monoaldehyde ($[\alpha]_D^{25} +130^\circ$ in ethanol (*c* 1.5)) (0.2161 g.) in methanol (15 ml.) was added sodium borohydride (0.075 g.). The rotation fell rapidly, becoming constant at $[\alpha]_D^{25} -7^\circ$ after 10 min. Addition of sodium borohydride (0.02 g.) did not change the rotation. After 2 hr. the reaction mixture was neutralized with dilute acetic acid and concentrated *in vacuo* to dryness.

To a solution of the sirupy residue in pyridine (15 ml.) was added *p*-nitrobenzoyl chloride (0.7 g.). The mixture was heated for 40 min. at 90°, cooled and poured into saturated sodium bicarbonate solution (150 ml.). The reaction mixture was extracted with chloroform. The chloroform extract was washed successively with dilute sulfuric acid, sodium bicarbonate solution, water and dried over sodium sulfate. Removal of solvent yielded the characteristic tris-*O-p*-nitrobenzoyl derivative² of D'-methoxyhydroxymethyl-diethylene glycol (III) (0.44 g.), m.p. and mixed m.p. 109°, $[\alpha]_D^{25} -23^\circ$ in chloroform (*c* 1).

(2) With Raney Nickel and Hydrogen.—Raney nickel (5 g.) was added to a solution of the monoaldehyde (0.2775 g.) in dry ethanol (80 ml.) and hydrogenation commenced at 1000 lb. per sq. in. After one hour at 25° the temperature was adjusted to 110°. After 12 hr. the reaction mixture was allowed to cool, filtered and concentrated to a mobile sirup. Extraction with acetone and concentration *in vacuo* gave D'-methoxyhydroxymethyl-diethylene glycol (III) (0.2067 g.) as a colorless liquid which showed $[\alpha]_D^{25} -4^\circ$ in ethanol (*c* 4). When treated with *p*-nitrobenzoyl chloride as described above, III yielded the corresponding tris-*O-p*-nitrobenzoate,² m.p. and mixed m.p. 110°, $[\alpha]_D^{25} -24^\circ$ in chloroform (*c* 1.3).

(e) Oxidation of the Monoaldehyde (V or VII) with Bromine.—The monoaldehyde (0.85 g.) was dissolved in water (150 ml.) and treated with bromine (1.5 ml.) and strontium carbonate (10 g.) for 4 days in the dark. The excess bromine was removed by aeration and the bromide ions were precipitated with silver carbonate. The silver salts were removed by filtration and the excess silver ions with hydrogen sulfide. A small amount of strontium carbonate was added to the filtered solution which was then concentrated *in vacuo* (bath temperature, 45°) to a small volume (50 ml.), filtered and concentrated to a glass-like solid. To an aqueous solution (8 ml.) of this glass were added ethanol and ether to precipitate the strontium salt of the monocarboxylic acid IV. The salt was purified by reprecipitation from aqueous solution with ethanol to give a white amorphous solid (0.450 g.), $[\alpha]_D^{25} -25^\circ$ in water (*c* 1).

Characterization of the Monocarboxylic Acid IV.—A portion of the strontium salt of the monocarboxylic acid (0.0521 g.) was converted to the free acid by passing it through a column of Amberlite IR 120 cation-exchange resin and the

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

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

(10) Cf. R. Criegee, *Ann.*, **495**, 211 (1932).

(11) J. K. Hamilton, R. Montgomery and F. Smith, *THIS JOURNAL*, in press.

(12) J. W. Rowen, F. H. Forziati and R. E. Reeves, *ibid.*, **73**, 4484 (1951).

(13) G. Gran, *Svensk Papperstidning*, **19**, 702 (1954).

(14) O. Ruff and G. Ollendorf, *Ber.*, **33**, 1809 (1900).

neutralization equivalent was determined by titration of the eluate. *Anal.* Calcd. for $C_6H_{12}O_6$: equiv. wt., 180. Found: equiv. wt., 173.

Hydrolysis of the Monocarboxylic Acid IV. (1) **Identification of the Glycerol Moiety.**—An aqueous solution of the salt of the monocarboxylic acid IV (0.050 g.) was deionized with Amberlite IR 120 resin, concentrated to a small volume (5 ml.) and heated on the steam-bath for 2 hours to autohydrolyze the acid. The optically inactive hydrolyzate was passed through Duolite A4 to remove the glyoxylic acid and concentrated to a sirup which, by paper chromatography using methyl ethyl ketone–water azeotrope, was shown to be glycerol. The glycerol was dissolved in pyridine (3 ml.) and treated with *p*-nitrobenzoyl chloride (0.150 g.) at 80° for 30 min. The glycerol-tris-*p*-nitrobenzoate (0.060 g.) which crystallized when the reaction mixture was poured into sodium bicarbonate solution was recrystallized from chloroform–petroleum ether, m.p. and mixed m.p. 192–194°.

(2) **Identification of the Glyoxylic Acid Moiety.**—To a solution of the strontium salt of the monocarboxylic acid IV (0.070 g.) in water (5 ml.) was added concentrated sulfuric acid (0.1 ml.) to precipitate the strontium as sulfate. The salts were filtered, washed with water and the filtrate was heated (70°) for 1 hr. to hydrolyze the monocarboxylic acid. To this hot hydrolyzate was added a hot (70°) solution of 2,4-dinitrophenylhydrazine (0.050 g.) in water (2 ml.) containing concentrated sulfuric acid (0.5 ml.) and the reaction was held at 70° for 15 min. until yellow crystals of glyoxylic acid 2,4-dinitrophenylhydrazone separated. The solution was allowed to cool and after 36 hr. the crystals were filtered, washed with water and recrystallized from hot water (yield 0.045 g.), m.p. and mixed m.p. 194°. A melting point of 190° dec. was reported by Brady⁶ for this substance. The monohydrate of this hydrazone was obtained by Rabassa.¹⁵ For the monohydrate he reported¹⁵ m.p. 194–195° dec. and for the anhydrous form, which is the only form encountered in this work, m.p. 192° dec. *Anal.* Calcd. for $C_8H_8O_6N_4$: C, 37.8; H, 2.4; N, 22.0. Found: C, 37.7; H, 2.8; N, 22.2.

B. Hydrogenation of L'-Methoxy-D-hydroxymethylglycolic Aldehyde in the Presence of Palladium-Charcoal Catalyst.—Methyl β -D-glucopyranoside (2.0 g.) was oxidized with periodic acid⁴ giving L'-methoxy-D-hydroxymethylglycolic aldehyde. The dialdehyde was dissolved in absolute ethanol (100 ml.) and hydrogenated (1000 p.s.i.) in the presence of palladium-charcoal (2 g.) at room temperature for 20 hr. The solution was filtered and concentrated *in vacuo* to a sirup (1.66 g.) composed of the monoaldehyde and unchanged dialdehyde. Since the monoaldehyde did not readily distil the mixture was resolved by chromatography on a hydrocellulose column with methyl ethyl ketone–water azeotrope as the solvent giving the pure monoaldehyde (0.515 g.) as a colorless sirup having $[\alpha]^{25D} -148^\circ$ in ethanol (*c* 2) and R_f 0.53 (methyl ethyl ketone–water azeotrope). It was found from a comparison of yields that the dialdehyde from the methyl β -glucoside was more difficultly reduced to the corresponding monoaldehyde than was the dialdehyde from the α -anomer.

Oxidation of the Monoaldehyde with Bromine.—The monoaldehyde (0.35 g.) was dissolved in water (75 ml.) and treated with bromine (0.5 ml.) and barium carbonate (10 g.) for 2–3 days after which the reaction mixture was aerated to remove excess bromine, filtered and neutralized with silver carbonate. Hydrogen sulfide was passed through the solution to remove the excess silver and the filtered solution was concentrated *in vacuo* to a glassy solid which was dissolved in a small amount of water. Ethanol was added to precipitate the white barium salt of the monocarboxylic acid which had $[\alpha]^{27D} +23^\circ$ in water (*c* 1), after purification by reprecipitation.

Characterization of the Monocarboxylic Acid. (1) **Identification of Glycerol Moiety.**—The barium salt of the monocarboxylic acid (0.094 g.) was deionized with Amberlite IR 120 resin and heated on the steam-bath for 4 hr. The optically inactive hydrolyzate was passed through a Duolite A4 resin column and concentrated *in vacuo* giving glycerol which was identified chromatographically and as the crystalline tris-*p*-nitrobenzoate, m.p. and mixed m.p. 193–194°.

(2) **Identification of Glyoxylic Acid Moiety.**—The glyoxylic acid obtained from the barium salt of the mono-

carboxylic acid by hydrolysis with sulfuric acid was identified as the crystalline 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 192°.

C. Hydrogenation of L'-Methoxydiglycolic Aldehyde.—Methyl β -D-arabopyranoside (2.12 g.) was oxidized with periodic acid⁴ to yield L'-methoxydiglycolic aldehyde ($[\alpha]^{25D} -122.5^\circ$ in water) which was isolated in the usual way. The sirupy dialdehyde dissolved in absolute ethanol (60–75 ml.) was transferred to the glass liner of the hydrogenation bomb and palladium-charcoal catalyst (2 g.) was added. The hydrogenation was carried out at room temperature and at a pressure of 850 lb. per sq. in. of hydrogen for 20 hr. After filtering and concentrating (*in vacuo*, bath temp. 35–40°) the ethanol solution, a colorless, viscous sirup was obtained. This sirup distilled, b.p. (bath temp.) 82–88°, 0.006 min., with considerable decomposition to give a liquid, $n^{25D} 1.4393$, $[\alpha]^{25D} -133.5^\circ$ in water (*c* 1.0), which restored the color to Schiff reagent but did not reduce Fehling solution. *Anal.* Calcd. for $C_8H_8O_4$: OCH₃, 23.5. Found: OCH₃, 23.7. The sirup (0.220 g.) was dissolved in water (50 ml.) and treated with strontium carbonate (3.8 g.) and bromine (0.3 ml.) for 18 hr. in the dark. The solution was aerated, filtered, treated with silver carbonate and refiltered. The silver ions were precipitated as silver sulfide and the filtered solution was concentrated *in vacuo* (bath, 40–45°) to a hard sirup which crystallized slowly upon dissolving in water (5 ml.) and adding a few drops of ethanol. The crystalline product (strontium L'-methoxydiglycolate) (0.085 g.) when recrystallized from 50% ethanol had $[\alpha]^{25D} +53.7^\circ$ in water, (*c* 0.5). *Anal.* Calcd. for $C_8H_8O_4 \cdot Sr$: OCH₃, 11.6. Found: OCH₃, 11.8. The product from the hydrogenation experiment was therefore largely unchanged starting material.

D. Hydrogenation of D'-Methoxydiglycolic Aldehyde.—Methyl β -L-arabopyranoside was oxidized with periodic acid to yield D'-methoxydiglycolic aldehyde ($[\alpha]^{25D} +124^\circ$ in water) which was subsequently treated with hydrogen and a palladium-charcoal catalyst following the procedure described previously for methyl β -D-arabopyranoside. The crude sirupy product which appeared to be principally unchanged dialdehyde restored the color to Schiff reagent but did not reduce Fehling solution. It distilled, b.p. (bath temp.) 60–66° (0.003 min.), with considerable decomposition to give a sirup, $n^{25D} 1.4463$ and $[\alpha]^{25D} +125.5^\circ$ in water (*c* 1). *Anal.* Calcd. for $C_8H_8O_4$: OCH₃, 23.5. Found: OCH₃, 28.0. The high methoxyl value is probably due to the fact that the product contained a small amount of the fully reduced compound.

Oxidation of the crude sirup (0.50 g.) from the above hydrogenation reaction with bromine–water in the presence of strontium carbonate in the usual way gave the crystalline hydrate (0.40 g.), strontium D'-methoxydiglycolate, $[\alpha]^{25D} -48.5^\circ$ in water (*c* 1). Jackson and Hudson report⁴ for this compound $[\alpha]^{25D} -55.5^\circ$ in water, after repeated recrystallization from water–ethanol.

Autohydrolysis of the acid, derived from the strontium salt by the addition of dilute sulfuric acid, gave a hydrolyzate which did not contain any ethylene glycol (tested by paper chromatographic analysis). The dialdehyde from methyl β -L-arabopyranoside therefore was not converted into a monoaldehyde under the hydrogenation conditions employed.

E. Hydrogenation of L'-Methoxy-L-methylglycolic Aldehyde.—Methyl α -L-rhamnopyranoside (5 g.) was oxidized with periodic acid⁴ to yield L'-methoxy-L-methylglycolic aldehyde as the crystalline monohydrate ($[\alpha]^{25D} -144^\circ$ in water (*c* 1.0) and m.p. 95°).

A solution of the dialdehyde (0.3 g.) in ethanol (60 ml.) was transferred to the glass liner of the hydrogenation bomb. Palladium-charcoal catalyst (1.4 g.) was added and the hydrogenation was allowed to proceed at 1000 lb. per sq. in. of hydrogen for 24 hr. at room temperature. The solution was filtered and concentrated *in vacuo* (bath, 40°) to give a crystalline product which proved to be the starting material. L'-methoxy-L-methylglycolic aldehyde m.p. and mixed m.p. 95°, $[\alpha]^{25D} -134^\circ$ in water (*c* 1).

F. Hydrogenation of D'-Methoxy-D-methoxymethylglycolic Aldehyde. Methyl 6-O-Methyl- α -D-galactopyranoside.—A solution of 1,2:3,4-di-O-isopropylidene-D-galactopyranose¹⁶ (50 g.), in acetone (50 ml.), was methylated in the

(15) S. V. Rabassa, *Rev. acad. cienc. exact. fis-quim. y nat. Madrid*, **31**, 435 (1934).

(16) A. L. Raymond and E. F. Schroeder, *THIS JOURNAL*, **70**, 2785 (1948).

usual way with methyl sulfate (162 ml.) and sodium hydroxide (405 ml. of 30%). The reagents were added in tenths during 2 hr. The methylation was completed by heating the reaction mixture for 30 min., after which it was cooled, mixed with chloroform (200 ml.) and filtered to remove sodium sulfate, the latter being washed with small amounts of chloroform. The chloroform layer was separated and the aqueous phase re-extracted twice with chloroform (50 ml.). The combined chloroform extracts were dried (sodium sulfate), freed from the solvent and the residual liquid distilled giving: 1,2;3,4-di-*O*-isopropylidene-6-*O*-methyl-*D*-galactopyranose, a colorless liquid, b.p. 125° (bath temp.), 0.001 mm., n_D^{25} 1.4525, $[\alpha]_D^{25}$ -64° in chloroform (*c* 5) (yield almost quantitative); literature¹⁷ $[\alpha]_D$ -63.2° in tetrachloroethane.

Hydrolysis of the 1,2;3,4-di-*O*-isopropylidene-6-*O*-methyl-*D*-galactopyranose (30 g.) was described previously¹⁸ with aqueous acetone containing hydrochloric acid gave 6-*O*-methyl-*D*-galactose (10.3 g.), m.p. and mixed m.p. 127.5° (after recrystallization from aqueous ethanol); literature¹⁸ in.p. 128° and $[\alpha]_D^{25} +114° \rightarrow +77°$ in water.

A solution of 6-*O*-methyl-*D*-galactose (5 g.) in 2% methanolic hydrogen chloride (25 ml.) was refluxed for 13 hr. when the rotation had become constant. Removal of acid (Ag_2CO_3) and solvent (*in vacuo*) gave a sirupy product which crystallized spontaneously. Recrystallization from methanol gave methyl 6-*O*-methyl- α -*D*-galactopyranoside, m.p. 138°, $[\alpha]_D^{25} +165°$ in water (*c* 1). *Anal.* Calcd. for $C_8H_{16}O_6$: OCH₃, 29.8. Found: OCH₃, 29.8.

Oxidation of Methyl 6-*O*-Methyl- α -*D*-galactopyranoside with Periodate.—Methyl 6-*O*-methyl- α -*D*-galactopyranoside (1 g.) was oxidized with periodic acid in the usual way to give the sirupy dialdehyde, *D'*-methoxy-*D*-methoxymethylidiglycolic aldehyde, $[\alpha]_D^{25} +145°$ in water (*c* 1.5) changing in 40 hr. to +119°. The dialdehyde was treated with hydrogen in the presence of palladium-charcoal as described in the previous experiments. The sirupy product (0.74 g.) thus obtained appeared to consist only of unchanged dialdehyde recognized by its characteristic mutarotation, $[\alpha]_D^{25} +153°$ in water (*c* 1.5) changing in 50 hr. to +116°.

Bromine oxidation of the product from the hydrogenation reaction in the presence of barium carbonate yielded the barium salt of the corresponding dicarboxylic acid. Hydrolysis of this dicarboxylic acid and chromatography of the hydrolyzate using 1-butanol:acetic acid:water (2:1:1) revealed glyoxylic acid and 3-*O*-methyl-*D*-glyceric acid. The former was characterized as glyoxylic acid-2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 192-193°, while the latter was recognized by comparison of its R_f value with that of an authentic specimen. No 3-*O*-methyl-*D*-glycerol, which would arise by reduction of the C_1 aldehydic group as in the case of methyl α -*D*-glucopyranoside, was found.

Identification of *D'*-Methoxy-*D*-hydroxymethylidiglycolic Acid. (a) **The Glyoxylic Acid Moiety.**—To a solution of the strontium salt of *D'*-methoxy-*D*-hydroxymethylidiglycolic

acid (0.2005 g.)¹⁹ in water (15 ml.) was added concentrated sulfuric acid (0.5 ml.) and the precipitated strontium sulfate was filtered off. The filtrate was warmed on the water-bath at 70-75° for 1.5 hr. until it was no longer optically active and treated with a solution of 2,4-dinitrophenylhydrazine (0.2509 g., or two equivalent proportions) in water (10 ml.), containing concentrated sulfuric acid (1.5 ml.), for 10 min. at 70-75° as described above. After 48 hr. at room temperature a large crop of long, silky, yellow needles had separated along with a small amount of a microcrystalline orange-colored precipitate. These two crystalline products were separated by dissolving the yellow needles in water at 60-65°; the insoluble orange crystals were filtered off. On cooling the aqueous extract it afforded glyoxylic acid-2,4-dinitrophenylhydrazone (yield 0.1186 g., or 54.5% of the theoretical) m.p. 192°. *Anal.* Calcd. for $C_8H_6O_6N_4$: C, 37.8; H, 2.4; N, 22.0. Found: C, 38.1; H, 2.4; N, 22.0.

It would seem that the above procedure is more advantageous for the identification of small amounts of *D'*-(or *L'*)-methoxy-*D*-(or *L*)-hydroxymethylidiglycolic acid than the method used by Jackson and Hudson⁴ who identified the glyoxylic acid moiety of the dicarboxylic acid, after hydrolysis of the latter, by oxidation with bromine to give oxalic acid. Thus for example, starting with 15 g. of the hydrated strontium salt of the dicarboxylic acid, these authors report a yield of 5.7 g. of barium oxalate. Experiments with 0.2-0.4 g. of the strontium salt of the dicarboxylic acid furnished negligible amounts of barium oxalate. On the other hand, according to the procedure described here, 0.4 g. of the hydrated strontium salt of *D'*-methoxy-*D*-hydroxymethylidiglycolic acid yielded approximately 0.24 g. of glyoxylic acid 2,4-dinitrophenylhydrazone and about 0.01 g. of the 2,4-dinitrophenylhydrazone of pyruvic acid-2,4-dinitrophenylhydrazide, amounts that were adequate for identification purposes.

(b) **The Glyceric Acid Moiety.**—When the orange, water-insoluble crystals, separated from the glyoxylic acid 2,4-dinitrophenylhydrazone in the preceding preparation, were recrystallized from hot ethyl acetate the crystalline 2,4-dinitrophenylhydrazone of pyruvic acid 2,4-dinitrophenylhydrazide was obtained m.p. 316° dec. From two experiments, each starting with 0.2 g. of the strontium salt of *D'*-methoxy-*D*-hydroxymethylidiglycolic acid, a total of 0.01 g. was obtained. The pyruvic acid is formed from glyceric acid by a rearrangement of the pinacol type.²⁰ *Anal.* Calcd. for $C_{15}H_{12}O_9N_8$: C, 40.2; H, 2.7; N, 25.0. Found: C, 40.6; H, 2.8; N, 25.3.

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(19) Prepared from methyl α -*D*-glucopyranoside by the method of Jackson and Hudson.⁴

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

Structure of Corn Hull Hemicellulose. Part III. Identification of the Methylated Aldobiouronic Acid Obtained from Methyl Corn Hull Hemicellulose^{1,2}

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Corn hull hemicellulose has been methylated and the methyl derivative hydrolyzed. The cleavage fragments were separated by means of ion-exchange resins into a neutral and an acidic component. The latter was esterified and the resulting ester reduced to give methyl 2-*O*-(2,3,4-tri-*O*-methyl-*D*-glucopyranosyl)-3-*O*-methyl-*D*-xylopyranoside, m.p. 166-168°, $[\alpha]_D^{25} +85°$ in water. This proved that the aldobiouronic acid cleavage fragment of the methylated hemicellulose was methyl 2-*O*-(2,3,4-tri-*O*-methyl-*D*-glucopyranosyl)uronic acid-3-*O*-methyl-*D*-xylopyranoside and that the *D*-glucuronic acid end groups are linked directly to the main structural xylan framework of the polysaccharide.

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(2) This research was done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing

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