

from water it forms rather long thick prismatic crystals, which are a monohydrate that is stable in air but which soon becomes anhydrous in a desiccator over lime, passing to a white powder.

(b) (Experiments by Hockett).— α -Methyl-L-fucoside, prepared by refluxing fucose with 1% hydrochloric acid in methanol for twelve hours and isolated as described above, was recrystallized from methanol-ethyl acetate to constant properties readily. The pure substance shows m. p. 154° (corr.) and $[\alpha]^{20D} -197.1$ (*c*, 3.42; 4-dm. tube); a sample which was prepared by deacetylation of its purified triacetate (described below) showed the rotation -197.0 (*c*, 4.16; 4-dm. tube). Analyses for carbon, hydrogen and methoxyl gave the expected values (the substance has been analyzed by previous investigators). The mother liquor from the α -form was treated in absolute alcoholic solution with double the theoretical quantity of dried potassium acetate (CH_3COOK) dissolved in absolute alcohol; silky needles of the 1:1 molecular compound of the β -fucoside separated at once and they were recrystallized from hot absolute alcohol. The β -fucoside was obtained by preparing its triacetate from this molecular compound (as described below) and deacetylating the triacetate with barium methylate, the over-all yield of the two steps being nearly quantitative. The pure β -L-fucoside showed m. p. $121-123^\circ$ and $[\alpha]^{20D} +14.2$ (*c*, 3.9; 4-dm. tube) in water.

The α - and β -Forms of Triacetyl-methyl-L-fucopyranoside.—Two grams of the pure α -fucoside was acetylated by heating for thirty minutes on the steam-bath with 12 cc. of acetic anhydride and 6 cc. of pyridine, followed by isolation according to standard procedure; yield 85%. The substance was recrystallized from hot water; a further recrystallization from aqueous methyl alcohol did not change its rotation, which was $[\alpha]^{20D} -149.1$ (*c*, 0.9) in chloroform (Phelps). The pure α -fucoside was also

acetylated by heating with 5 parts of acetic anhydride and one-quarter part of fused sodium acetate; the triacetate was isolated by standard procedure and recrystallized from absolute alcohol, as brilliant plates, which gave the correct analyses (previously reported by Minsaas) for methoxyl, acetyl, carbon and hydrogen, melted at 67° and showed $[\alpha]^{20D} -149.7$ (*c*, 1.8) in chloroform (Hockett). The β -methyl-L-fucoside triacetate was prepared by heating 5 g. of its pure potassium acetate compound for one hour on the steam-bath with 20 cc. of acetic anhydride, and isolating the substance through standard procedure (yield, quantitative); by recrystallization from absolute alcohol, from which it separates in clear tablets, it is readily brought to constant properties, m. p. $96-97^\circ$ and $[\alpha]^{20D} +7.1$ (*c*, 4.5; 4-dm. tube) in chloroform (Hockett). Its analysis showed the correct values for carbon, hydrogen, methoxyl and acetyl, confirming Minsaas' reported analysis for the substance.

Summary

The α - and β -methylpyranosides of L-fucose (L-galacto-methylose) and their triacetates, previously reported by Minsaas, have been reprepared and their purity carefully controlled. The results confirm Minsaas' rotations except in the case of β -methyl-L-fucoside, the rotation of which is found to be $+14.2$ instead of $+16.0$. Some modifications of E. P. Clark's directions for preparing crystalline fucose from seaweed are presented. The difference of rotations of the glycosides shows the normal value; the difference for their triacetates is decidedly lower than would be expected.

WASHINGTON, D. C.

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The Cleavage of the Carbon Chains of Some Methyl Aldohexamethylo-pyranosides by Oxidation with Periodic Acid¹

By W. DAYTON MACLAY, RAYMOND M. HANN AND C. S. HUDSON

Jackson and Hudson² have described the crystalline dialdehyde (III) that results from the oxidation of α -methyl-L-mannomethylo-pyranoside³ (I) with periodic acid. We have now obtained this same dialdehyde by the similar oxidation of α -methyl-L-galactomethylo-pyranoside (II), and by oxidation of this dialdehyde with bromine water in the presence of strontium carbonate have ob-

tained the crystalline strontium salt of the corresponding dibasic acid (IV). In like manner it has been found that the periodic acid oxidation of α -methyl-D-glucomethylo-pyranoside (V) yields the crystalline enantiomorphous dialdehyde (VI), from which in turn has been prepared the crystalline strontium salt of the corresponding dibasic acid (VII), the enantiomorph of (IV). The hydrolysis of the dibasic acid formed from the strontium salt (IV) yields L-lactic acid⁴ in optical

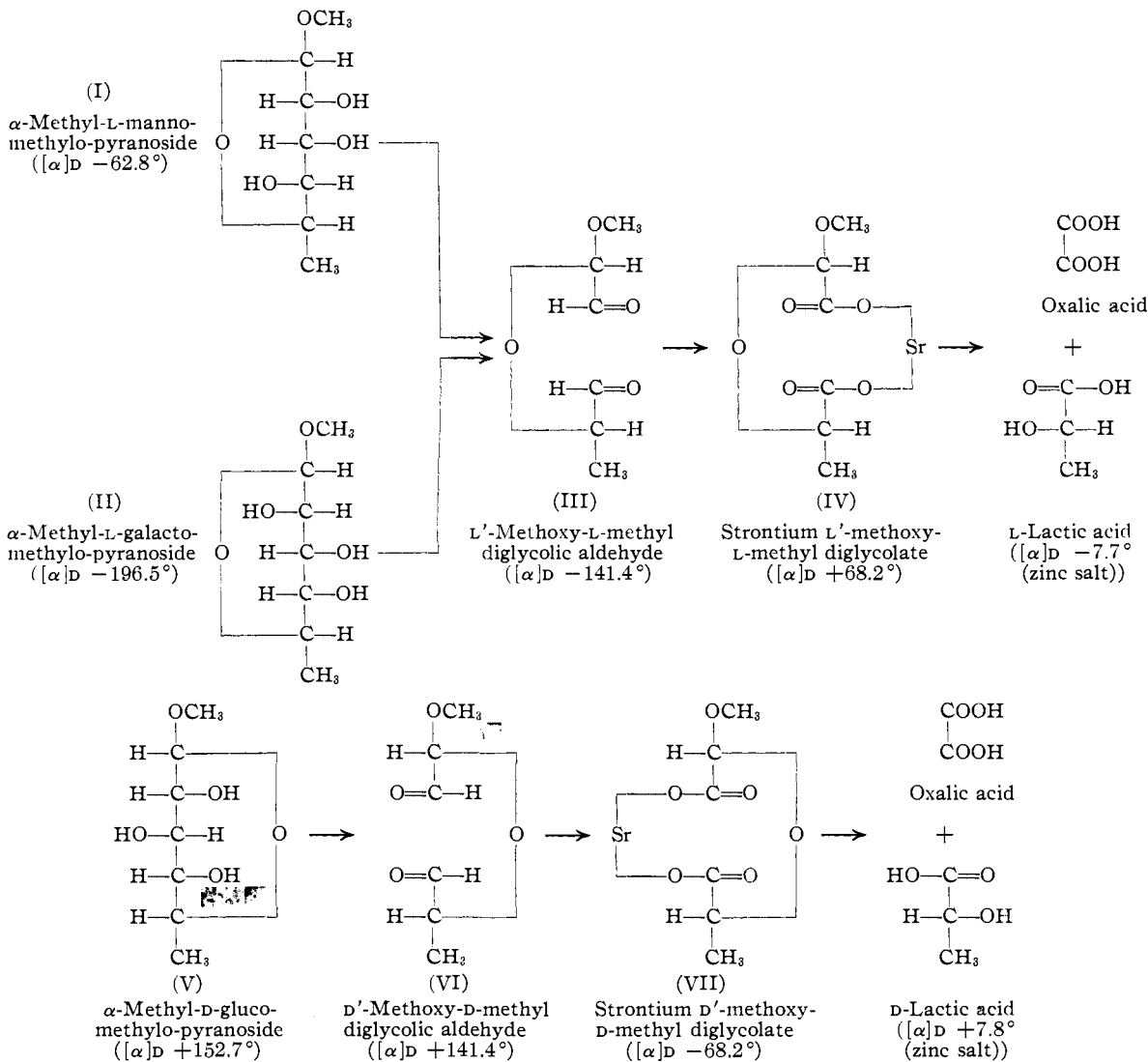
(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Jackson and Hudson, *THIS JOURNAL*, **59**, 994 (1937).

(3) We use the nomenclature for methyl pentoses that was suggested by Votoček: L-mannomethylose = L-rhamnose, L-galactomethylose = L-fucose, D-glucomethylose = D-isorhamnose (syn. D-epirhamnose). The D and L symbols refer throughout to configuration.

(4) In the case of the optically active lactic acids and their zinc salts the L-lactic acid is dextrorotatory and its zinc L-lactate levorotatory, while the D-lactic acid is levorotatory and its zinc D-lactate

dextrorotatory. D-Lactic acid has the configuration $\text{CH}_3-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-\text{COOH}$.



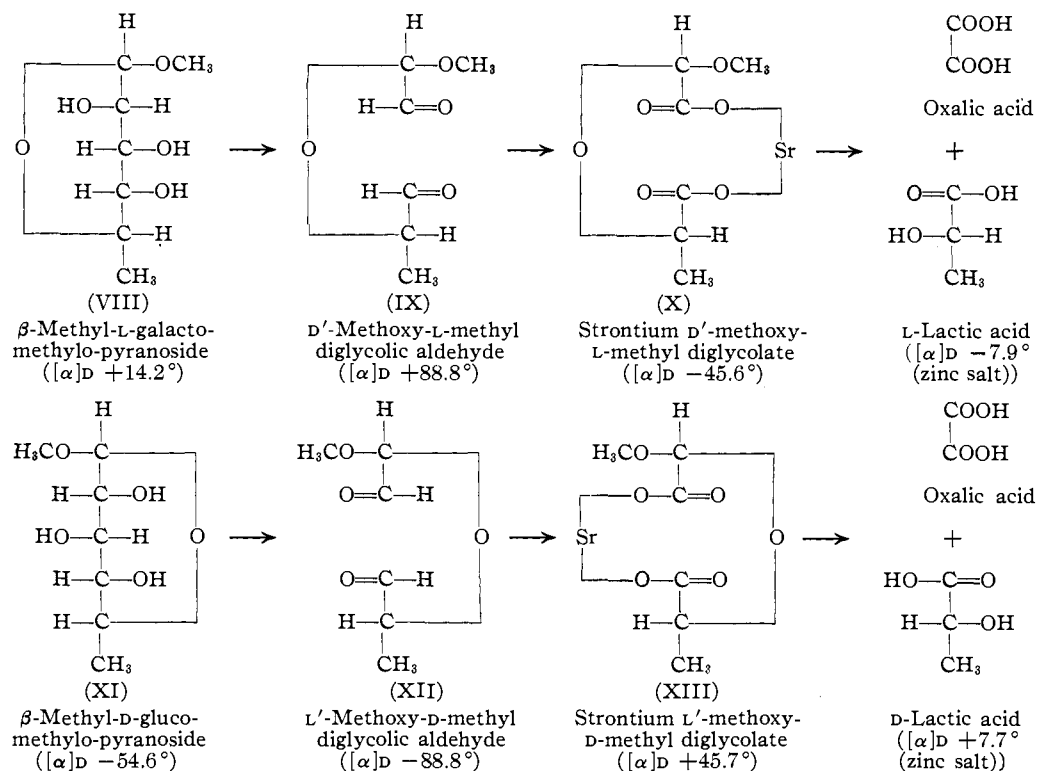
purity, and like treatment of the dibasic acid formed from the strontium salt (VII) yields D-lactic acid. The presence of lactic acid proves that all of these glycosides are pyranosides, and the correlation of the enantiomorphous forms of lactic acid with the known sugar configurations of Fischer proves the configurations of the lactic acids. We believe that this is the most simple and direct way of bringing the lactic acids into Fischer's system of configurations; it supplements the recent proof² of the configurations of the forms of glyceric acid that was obtained from the oxidation of the methyl-aldohexopyranosides with periodic acid. The results also prove that the two methylosides, α -methyl-L-mannomethyloside and α -methyl-L-galactomethyloside, have the same configuration for carbon atom one, enantiomorphous to the

configuration for carbon atom one in α -methyl-D-glucomethyloside, both configurations having been designated alpha (*i. e.*, α -L- and α -D, respectively) in the past from rotatory considerations. The preparation of α -methyl-D-gluco-methylo-pyranoside from α -methyl-D-gluco-pyranoside, by Helferich, Klein and Schafer⁵ and by Compton⁶ (see experimental part) furnishes the structural proof of the alpha classification of the three methylo-pyranosides.

The oxidation of β -methyl-L-galactomethylo-pyranoside (VIII) with periodic acid has yielded a new dialdehyde (IX) which is also crystalline and passes on bromine oxidation to a new dibasic acid, the strontium salt (X) of which

(5) Helferich, Klein and Schafer, *Ber.*, **59**, 84 (1926); *Ann.*, **447**, 19 (1926).

(6) Compton, *THIS JOURNAL*, **60**, 398 (1938).



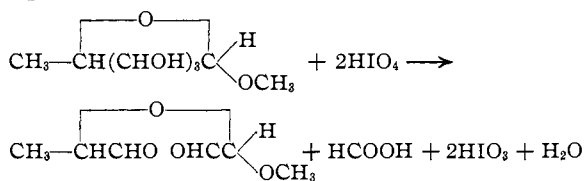
is crystalline. The similar oxidation of β -methyl-D-glucomethylo-pyranoside (XI) has yielded in crystalline state the dialdehyde (XII), which is the enantiomorph of (IX), and the strontium salt (XIII), which is the enantiomorph of (X). Hydrolysis of the dibasic acid of (X) yields L-lactic acid and that of the acid of (XIII) yields D-lactic acid. The two β -glycosides are therefore pyranosides and possess enantiomorphous configurations for carbon atom one, which are the opposites of the configurations for the corresponding α -glycosides. Since β -methyl-D-glucomethylo-pyranoside has been correlated as regards carbon atom one with β -methyl-D-glucoside,⁷ the present results prove that the customary α - and β -designations of these methylosides are correct from the stereo-structural standpoint. It is also evident from the rotatory data of column 3, Table III, and Fig. 1 that these methylosides are pure substances, no one of them being a crystalline molecular combination of α - and β -forms.⁸

The four crystalline dialdehydes (two enantiomorphous pairs) and the four corresponding crystalline strontium salts are reference substances which can be employed to learn the ring structure and the α - or β -classification of any methyl py-

ranoside of the remaining aldohexamethyloses or of any methyl furanoside of the aldopentomethyloses.

The rotational relationships of the aldohexamethylo-pyranosides and their products of oxidation are shown in Table I.

The oxidation of these aldohexamethylo-pyranosides by periodic acid is practically quantitative, one mole of the glycoside consuming 2 moles of periodic acid according to the reaction equation



The distinction between a pyranoside and a furanoside probably can be made very readily in the aldohexamethylose series, since a mole of the pyranoside consumes 2 moles of periodic acid and generates one mole of formic acid, but a mole of the furanoside can be expected to consume only one mole of the acid and produce no formic acid.

It has been known in the past from methylation data⁹ and some correlations that three of the

(7) Fischer and Zach, *Ber.*, **45**, 3761 (1912).

(8) Cf. Jackson and Hudson, *THIS JOURNAL*, **61**, 959 (1939).

(9) Hirst and Macbeth, *J. Chem. Soc.*, 22 (1926); Charlton, Haworth and Peat, *ibid.*, 89 (1926), and refs. 5, 6 and 7.

TABLE I
PRODUCTS OF OXIDATION OF THE ALDOHEXOMETHYLO-PYRANOSIDES

Substance	Methyl glycoside [α] ₂₀ ^D	Dialdehyde (monohydrate) ^a [α] ₂₀ ^D	Dibasic acid ^b [α] ₂₀ ^D	Strontium salt ^c [α] ₂₀ ^D	Resulting zinc lactate ^d [α] ₂₀ ^D
α -Methyl-L-galactomethylo-pyranoside	-196.5°	-141.4°	-23.3°	+68.2°	-7.7°
α -Methyl-D-glucomethylo-pyranoside	+152.7°	+141.4°	+23.5°	-68.2°	+7.8°
β -Methyl-L-galactomethylo-pyranoside	+14.2°	+88.8°	-41.6°	-45.6°	-7.9°
β -Methyl-D-glucomethylo-pyranoside	-54.6°	-88.8°	+41.9°	+45.7°	+7.7°

^a See Table III, note (a). ^b Determined by liberating the acid (c, 0.92-1.05) from its pure, anhydrous strontium salt with an equivalent of hydrochloric acid. ^c See Table IV, note a. ^d See Table V, note a.

substances here studied (α -methyl-L-mannomethylo-pyranoside and α - and β -methyl-D-glucomethylo-pyranosides) are pyranosides; the present work confirms these ring allocations, extends the proof of the pyranoside structure to the two other glycosides (α - and β -methyl-L-galactomethylo-pyranosides) and proves the α - and β -classification by structural correlation.

We are indebted to Dr. A. E. Knauf for preparing the α - and β -methyl-D-glucomethylo-sides used in the present investigation. We also express our appreciation to Dr. W. T. Haskins for performing the micro-analyses in connection with this work.

Experimental

Preparation of the Methyl Aldohexomethylo-pyranosides.—The α - and β -methyl-L-galactomethylo-pyranosides were prepared from L-galactomethylose and methyl alcohol containing 1.5% of dry hydrochloric acid gas according to Hockett, Phelps and Hudson.¹⁰ The α -methylside melted at 157-158° (corr.) and rotated -196.5 ± 0.5 ¹¹ in water, and the β -isomer melted at 122° (corr.) and rotated $+14.2^\circ$ in water.

The α -methyl-D-glucomethylo-pyranoside was obtained by deacetylation of its triacetate, which was prepared by Compton's⁶ procedure of tosylation and acetylation of α -methyl-D-gluco-pyranoside and subsequent iodination and reduction of the terminal carbon atom. The purified triacetate melted at 78-79° (corr.) and rotated $+153.4^\circ$ in chloroform, in good agreement with Compton's values of 77-78° and $+153.6^\circ$; Helferich, Klein and Schafer⁵ reported a melting point of 75° and a rotation of $+159.2^\circ$ in chloroform for the triacetate, which they prepared by reduction of α -methyl-6-bromo-gluco-pyranoside triacetate. Pure α -methyl-D-glucomethylo-pyranoside was found to melt at 98-99°, in agreement with Helferich and his co-workers; the rotation, which apparently has not been recorded, was found to be $+152.7^\circ$ (c, 1.75; l, 4) in water.

(10) Hockett, Phelps and Hudson, *THIS JOURNAL*, **61**, 1658 (1939).

(11) Unless otherwise stated all rotations are constant specific rotations at 20° for sodium light.

The β -methyl-D-glucomethylo-pyranoside was prepared from levoglucosan by way of levoglucosan triacetate, 1,6-dibromo-glucose triacetate, β -methyl-6-bromo-glucoside triacetate and β -methyl-D-glucomethylo-side triacetate followed by deacetylation. The purified substance melted at 131-132° (corr.) and rotated -54.6° in water,

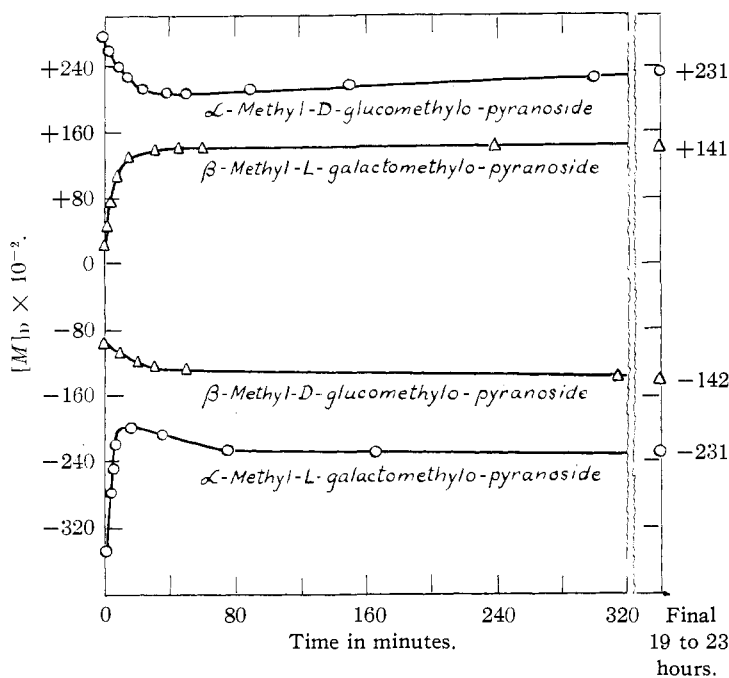


Fig. 1.—Rotatory changes during the oxidation of the methyl aldohexomethylo-pyranosides.

in agreement with the values of 131-132° and -55.1° reported by Fischer and Zach.⁷

Rotatory Changes during the Oxidation of the Methyl Aldohexomethylo-pyranosides.—To a solution of 0.25 g. of the methylside in 20 cc. of water was added 4.83 cc. of 0.610 M periodic acid (2.1 molecular equivalents). As quickly as possible the solution was diluted to 25 cc., thoroughly shaken, transferred to a 4-dm. tube and the rotatory changes observed. The solution was kept in a 20° room during the course of the reaction. The rotatory changes during the oxidation are recorded in Table II, and shown in Fig. 1. When the rotation of the solution had become constant, 5 cc. of it was analyzed for periodic acid.¹² The results showed that one mole of the aldohexomethylo-pyranosides (in the order listed in Table II)

(12) Fleury and Lange, *J. pharm. chim.*, [8] **17**, 107 (1933).

had consumed 1.99, 1.98, 1.99 and 1.99 moles, respectively, of periodic acid. This conforms with the equation previously stated.

TABLE II

ROTATORY CHANGES DURING THE OXIDATION OF THE METHYL HEXOMETHYLO-PYRANOSIDES TO DIALDEHYDES

α -Methyl-L-galactomethylpyranoside	α -Methyl-D-glucomethylpyranoside	β -Methyl-L-galactomethylpyranoside	β -Methyl-D-glucomethylpyranoside				
Time ^a [M] _D × 10 ⁻²⁶	Time [M] _D × 10 ⁻²⁶	Time [M] _D × 10 ⁻²⁶	Time [M] _D × 10 ⁻²⁶				
0	-350 ^c	0	+272 ^c	0	+25.3 ^c	0	-97.3 ^c
3	-281	2	+265	2	+46.3	2	-99.1
4	-252	4	+258	4	+75.5	4	-102
5	-238	7	+247	6	+94.0	6	-106
6	-218	10	+238	8	+108	9	-110
8	-205	15	+225	10	+116	12	-113
10	-199	25	+213	12	+121	15	-116
12	-199	40	+209	15	+126	19	-118
15	-200	45	+208	20	+133	25	-122
25	-203	50	+209	30	+138	30	-123
35	-208	90	+214	45	+140	40	-126
75	-226	150	+219	60	+141	50	-129
165	-228	300	+227	240	+141	315	-138
19	-231	22	+231	23	+141	22	-142
hrs.		hrs.		hrs.		hrs.	

^a Minutes after addition of the periodic acid. ^b Although the solutions were kept in a 20° room throughout the course of the reactions, there were temperature changes in the solutions due to the heat evolved in the oxidation reactions. ^c Calculated from the specific rotations in water of the methyl hexomethylpyranosides (mol. wt. 178.1) in the order listed: $-196.5 \pm 0.5^\circ$, $+152.7^\circ$, $+14.2^\circ$, -54.6° .

Isolation of the Dialdehydes.—The oxidation of β -methyl-D-glucomethylpyranoside and the subsequent isolation of crystalline L'-methoxy-D-methyl diglycolic aldehyde will be described as typical of the procedures used in the oxidation of the four glycosides and the isolation of the corresponding dialdehydes. To a solution of 5.0 g. of pure β -methyl-D-glucomethylpyranoside in 148 cc. of water in a 250-cc. volumetric flask was added 99.1 cc. of 0.595 M periodic acid (2.1 molecular equivalents). The solution was kept in a 20° room for eighteen hours; it was then made up exactly to 250 cc. with water and its rotatory power determined, which was found to be in agreement with the end-value recorded in Table II for the oxidation of this glycoside. The solution was neutralized to methyl red with a 10% solution of hot strontium hydroxide, and the strontium iodate and periodate salts that precipitated were filtered and washed with water. One gram of strontium carbonate was added and the solution concentrated *in vacuo* to 100 cc. in a water-bath at 50–60°. The strontium carbonate was filtered off and the concentration continued to dryness, partial crystallization of the dialdehyde taking place. The dry residue was extracted with two 50-cc. and two 25-cc. volumes of absolute ethanol, complete extraction being confirmed by the absence of optical activity of an aqueous solution of the crystalline salts remaining after the extraction. The alcoholic extract was concentrated *in vacuo* to a dry sirup which was dissolved in 20 cc. of ether; after shaking for a few minutes, crystals of the dialdehyde began to separate. Twenty-five cubic centimeters of petroleum ether was then added and on standing at room temperature for sixteen hours 2.55 g. of crystalline

dialdehyde was obtained. The mother liquor was concentrated to dryness and dissolved in 8 cc. of ethyl acetate, yielding an additional 1.0 g. of crystals. The yield of crystalline product was 3.55 g. (77%) and the rotation of the mother liquor indicated an over-all yield of 95%. Recrystallized from 5 parts of ethyl acetate the L'-methoxy-D-methyl diglycolic aldehyde monohydrate separates in the form of long needles melting at 101–102° (corr.) and rotating -88.8° (*c*, 0.71; *l*, 4) in water.

The four crystalline dialdehydes resulting from the oxidation of their respective parent glycosides form two sets of enantiomorphs. Not only are the properties of the members of each enantiomorphous pair similar in nature, as would be expected of course, but a marked similarity is also found in the properties of the two pairs. Thus, the melting points are nearly the same and the four compounds are readily crystallizable from 5 parts of ethyl acetate or by dissolving them in 10 parts of ether and adding an equal volume of petroleum ether, separating from these solvents as needle-like crystals. Analysis of each of the compounds corresponds to the monohydrate and on heating at 65° over anhydrous in a vacuum (Hyvac pump) they readily sublime without loss of water, which therefore is to be regarded as water of constitution. The yields of crystalline products were 70–80% with over-all yields of 90–95%. The rotations, melting points and analyses of these dialdehydes are listed in Table III. The crystallization of the four dialdehydes presents the first opportunity to test an assumption which was made by Jackson and Hudson² that the rotation of the non-crystallizable dialdehydes from the periodic acid oxidation of alpha methyl mannopyranoside, etc., is closely given by the constant end rotation of the oxidized solution. In the present case the specific rotations of the dialdehyde monohydrates (mol. wt. 164), as found from the constant end rotations of Table II, are $\pm 23100/164 = \pm 140.9$ and $\pm 14150/164 = \pm 86.3$, in satisfactory agreement with the data of Table III.

Oxidation of the Dialdehydes.—The oxidation of L'-methoxy-D-methyl diglycolic aldehyde to L'-methoxy-D-methyl diglycolic acid and the isolation of the latter in the form of its strontium salt will be described as typical of the technique employed in the oxidation of the four diglycolic aldehydes.

To 10.0 g. of L'-methoxy-D-methyl diglycolic aldehyde monohydrate in 800 cc. of water was added 80 g. of strontium carbonate and 10 cc. of bromine. The oxidation mixture was shaken intermittently for two hours and allowed to stand for an additional fifteen hours. The excess bromine was removed by aeration, the strontium carbonate filtered off and the bromide ions precipitated by shaking with 80 g. of silver carbonate. The silver ions were removed with hydrogen sulfide and the excess hydrogen sulfide by aeration. The solution was concentrated *in vacuo* in a water-bath at 60–70° to a volume of 40 cc. A volume of 40 cc. of absolute ethanol was added and the crystallization of the strontium salt began in a few minutes. After standing in a refrigerator for sixteen hours 11.6 g. of strontium L'-methoxy-D-methyl diglycolate had separated and an additional 0.9 g. was obtained by concentrating the mother liquor to 15 cc. and adding ethanol to saturation; total yield, 12.5 g.

TABLE III
 ROTATIONS, MELTING POINTS AND ANALYSES OF THE DIALDEHYDES

Methylo-pyranoside oxidized	Diglycolic aldehyde formed	[α] _D ²⁰ ^a (monohydrate)	M. p., °C.	C ₈ H ₁₀ O ₄ ·H ₂ O		
				(Calcd. C)	H	OCH ₃
α -Methyl-L-galacto-	L'-Methoxy-L-methyl-	-141.4°	98-99.5	43.83	7.56	18.89
α -Methyl-D-gluco-	D'-Methoxy-D-methyl-	+141.4°	98-99	43.83	7.54	18.98
β -Methyl-L-galacto-	D'-Methoxy-L-methyl-	+88.8°	100-101	43.78	7.22	18.91
β -Methyl-D-gluco-	L'-Methoxy-D-methyl-	-88.8°	101-102	44.02	7.31	19.07
α -Methyl-L-manno-	L'-Methoxy-L-methyl ^b	-143° ^c	101-102	43.88	7.22	18.89

^a (*c*, 0.77-1.03; *l*, 4) in water. ^b Jackson and Hudson, ref. 2. ^c (*c*, 0.42; *l*, 2) in water.

 TABLE IV
 ROTATIONS AND ANALYSES OF THE ANHYDROUS STRONTIUM SALTS

Diglycolic aldehyde oxidized	Strontium-diglycolate formed	[α] _D ²⁰ ^a	C ₈ H ₈ O ₈ Sr			
			(Calcd. C)	H	OCH ₃	Sr
L'-Methoxy-L-methyl-	L'-Methoxy-L-methyl-	+68.2°	27.29	3.20	11.66	33.24
D'-Methoxy-D-methyl-	D'-Methoxy-D-methyl-	-68.2°	27.45	3.25	11.81	33.33
D'-Methoxy-L-methyl-	D'-Methoxy-L-methyl-	-45.6°	27.37	3.25	11.60	33.03
L'-Methoxy-D-methyl-	L'-Methoxy-D-methyl-	+45.7°	27.20	3.18	11.93	33.06

^a (*c*, 1.2-1.5; *l*, 4) in water.

(80%). The compound may be recrystallized in a yield of 80% by dissolving in 10 parts of water and adding a like volume of warm 95% ethanol, separating in the form of plate-like crystals rotating +45.7° (*c*, 1.3; *l*, 4) in water. Strontium L'-methoxy-D-methyl diglycolate and its enantiomorph, strontium-D'-methoxy-L-methyl diglycolate, crystallize in the anhydrous form while strontium L'-methoxy-L-methyl diglycolate and its enantiomorph, strontium D'-methoxy-D-methyl diglycolate, when recrystallized by dissolving in 4 parts of warm water and adding 5 parts of warm 95% ethanol, separate in the form of hydrated rhomboid crystals. Although the latter two salts, after being air-dried at room temperature for forty-eight to seventy-two hours, give reproducible specific rotations of +56.3 and -56.2°, respectively, analyses show the substances to contain a small amount of ethyl alcohol in addition to water of hydration. The salts become anhydrous and free of alcohol on heating *in vacuo* (Hyvac pump) over anhydrous at 138° for six hours. The yields of crystalline strontium salts from the oxidations were 80-90%. Rotatory and analytical data concerning them are listed in Table IV.

Hydrolysis of the Acids from the Strontium Salts.—To a solution of 11.2 g. of strontium L'-methoxy-D-methyl diglycolate in 272 cc. of water was added 42.26 cc. of 2.01 *N* sulfuric acid to balance exactly the strontium ions. A volume of 314 cc. of 95% ethanol was added and after standing for eighteen hours the strontium sulfate was filtered off and washed with 50% ethanol. The filtrate was concentrated *in vacuo* to 50 cc. and diluted with 50 cc. of 95% ethanol. The mixture was filtered and the filtrate concentrated to a thick sirup. The sirup was dissolved in 20 cc. of water and reconcentrated to dryness to remove alcohol. The L'-methoxy-D-methyl diglycolic acid sirup was dissolved in 100 cc. of water and heated on a steam-bath for three hours, the rotatory power of the solution becoming constant at the end of two hours. The hydrolyzed solution was diluted to 275 cc., 4 cc. of bromine was added and the reaction mixture allowed to stand for forty-eight hours. The excess bromine was removed by aeration and the oxalic acid precipitated as barium oxalate

by neutralizing the solution to phenolphthalein with 0.45 *N* barium hydroxide. The dried barium oxalate (5.0 g., yield 52%) was dissolved in hot dilute hydrochloric acid and the barium ions precipitated with sulfuric acid. On concentration of the filtrate to a small volume the oxalic acid dihydrate crystallized. After recrystallization from water the oxalic acid was identified by its m. p. and its titration with alkali.

The filtrate from the barium oxalate precipitate was balanced with sulfuric acid to remove the barium ions and then shaken with 50 g. of silver carbonate to remove the bromide ions. The silver was removed by precipitation with hydrogen sulfide and the hydrogen sulfide by aeration. The solution was concentrated to 250 cc. and boiled for three minutes with 3 g. of zinc hydroxide. The excess zinc hydroxide was filtered off and the filtrate concentrated *in vacuo* at 60° to a volume of 20 cc. On standing for sixteen hours, 3.2 g. of zinc D-lactate dihydrate separated (yield 59%). Recrystallized from 4 parts of water the zinc D-lactate separated in the form of needle-like crystals and rotated +7.7° (*c*, 3.2; *l*, 4) in water.

Each of the other three strontium salts was treated in the same manner; in each case oxalic acid and an optically active form of zinc lactate were isolated in like yields. The rotations and analyses of the zinc lactates isolated are listed in Table V.

Zinc D-Lactate from Morphine D-Lactate.—The zinc lactates prepared from the four strontium salts exhibited larger rotations (see Table V) than those recorded by Irvine¹³ ([α]_{D15} +6.84° (*c*, 5.6) for zinc D-lactate; [α]_{D20} -6.83° (*c*, 7) for zinc L-lactate) for the same compounds which were obtained from racemic lactic acid by resolution with morphine. In order to further establish the rotational values for the optically active zinc lactates a sample of the D-salt was prepared from pure morphine D-lactate. A quantity of morphine D-lactate prepared according to the directions of Irvine¹³ was furnished the authors by Dr. E. L. Jackson. Recrystallized twice from 4 parts of 50% ethanol, morphine D-lactate rotates

(13) Irvine, *J. Chem. Soc.*, **89**, 935 (1906).

TABLE V
 ROTATIONS AND ANALYSES OF ZINC LACTATES FROM THE STRONTIUM SALTS

	Zinc lactate isolated	$[\alpha]_{D}^{20}$ ^a	C ₈ H ₁₀ O ₆ Zn·2H ₂ O		
			C (Calcd. 25.75)	H 5.05	Zn 23.39
Strontium diglycolate	Zinc L-lactate	-7.7°	25.66	5.06	23.30
L'-Methoxy-L-methyl-	Zinc D-lactate	+7.8°	25.73	5.10	23.54
D'-Methoxy-D-methyl-	Zinc L-lactate	-7.9°	25.66	5.12	23.31
D'-Methoxy-L-methyl-	Zinc D-lactate	+7.7°	25.75	5.16	23.56

^a (*c*, 3.0-3.8; *l*, 4) in water.

-92.2° (*c*, 5.0) in water, in good agreement with the value of -91.8° (*c*, 5) reported by Irvine for this substance. In order to eliminate the possibility of partial racemization by conversion of the D-lactic acid into its calcium salt as done by Irvine, the morphine D-lactate was decomposed and the resultant D-lactic acid isolated according to the directions of Freudenberg and Rhino.¹⁴ To a solution of 9.7 g. of pure morphine D-lactate in 100 cc. of water was added 5 cc. of concentrated ammonium hydroxide. The precipitated morphine was filtered and the filtrate made acid to congo red by the addition of 7.2 cc. of 5.85 *N* sulfuric acid. The solution was then extracted successively with twenty 100-cc. and a like number of 50-cc. volumes of ether. The ethereal extracts were combined, concentrated to a dry sirup and the zinc D-lactate prepared and isolated in a yield of 1.2 g. in the same manner as the zinc lactates obtained from the strontium salts. Recrystallized from 4 parts of water, the zinc D-lactate rotated +7.9° (*c*, 3.2; *l*, 4) in water, in good agreement with the rotational values of the zinc D-lactates obtained from the strontium salts. The specific rotation was the same in a concentration of 5.2.

Summary

The oxidation of α -methyl-L-galactomethylpyranoside with periodic acid yields the same crystalline dialdehyde as Jackson and Hudson obtained from the oxidation of α -methyl-L-mannomethylpyranoside by the same reagent. A crystalline enantiomorphous dialdehyde is obtained from the periodic acid oxidation of α -methyl-D-glucomethylpyranoside. These two dialdehydes, on oxidation by bromine water in the presence of strontium carbonate, form crystalline enantiomorphous strontium salts, derivatives of L'-methoxy-L-methyl diglycolic and D'-methoxy-D-methyl diglycolic acids, respec-

tively. Hydrolysis of these dibasic acids yields L-lactic acid from the former and D-lactic acid from the latter, proving these aldohexamethylsides to be pyranosides and establishing the configurations of the lactic acids through correlation with the known sugar configurations of Fischer. The designation of these three glycosides as α -forms, based in the past upon rotatory considerations, is now proved conclusively through their oxidation by periodic acid.

In like manner, the periodic acid oxidation of β -methyl-L-galactomethylpyranoside and β -methyl-D-glucomethylpyranoside yields two crystalline enantiomorphous dialdehydes which, in turn, yield two crystalline strontium salts, derivatives of D'-methoxy-L-methyl diglycolic and L'-methoxy-D-methyl diglycolic acids, respectively. Hydrolysis of these dibasic acids yields L-lactic acid from the former and D-lactic acid from the latter, proving the two β -aldohexamethylsides to be pyranosides and their designation as β -forms to be correct from the stereostructural standpoint.

Rotatory data of the oxidation of the four aldohexamethylpyranosides show them to be pure substances and not crystalline molecular combinations of α - and β -forms.

The four crystalline dialdehydes and the four corresponding crystalline strontium salts are reference substances which can be employed to learn the ring structure and the α - or β -classification of any methyl pyranoside of the remaining aldohexamethylsides or of any methyl furanoside of the aldopentomethylsides.

(14) Freudenberg and Rhino, *Ber.*, **57**, 1551 (1924).