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Crystalline α -Methyl-D-altrosido and Some New Derivatives of D-Altrose¹

BY NELSON K. RICHTMYER AND C. S. HUDSON

In preceding publications² we have described crystalline neolactose,³ D-altrose and D-altrosan, and have established the structure of the altrosan as a $\alpha<1,5>\beta<1,6>$ anhydride analogous to levoglucosan. The present communication continues with the acetylation of altrosan, and the transformation of the triacetate to a number of new derivatives of D-altrose.

2,3,4-Triacetyl-D-altrosan, obtained by the action of acetic anhydride and pyridine, has a high negative rotation,⁴ as might be expected from a consideration of the rotation of altrosan itself. For comparison, the rotations of the known hexosans $\alpha<1,5>\beta<1,6>$ and their acetates are recorded in Table I.

TABLE I
SPECIFIC ROTATIONS OF THE HEXOSANS $\alpha<1,5>\beta<1,6>$
AND THEIR TRIACETATES

| Hexose | Anhydride in H ₂ O | Triacetate in CHCl ₃ |
|--------------------------|-------------------------------|---------------------------------|
| D-Altrose | -213° | -172° |
| D-Mannose ^a | -127.6 | -123.6 |
| D-Glucose | -66.2 ^b | -65.5° |
| D-Galactose ^d | -21.9 | -5.7 |

^a Knauf, Hann and Hudson, *THIS JOURNAL*, **63**, 1447 (1941). Cf. Zemlén, Gerecs and Valatin, *Ber.*, **73**, 575 (1940). ^b Pictet and Sarasin, *Helv. Chim. Acta*, **1**, 87 (1918). ^c Zemlén, Gerecs and Valatin, *Ber.*, **73**, 576 (1940). ^d Micheel, *ibid.*, **62**, 687 (1929).

The acetolysis of triacetylaltrosan by acetic anhydride containing 2% of sulfuric acid resulted in the formation of an equilibrium mixture containing 64% of the α - and 36% of the β -pentaacetates.⁵ The α -pentaacetyl-D-altrose

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(2) (a) Richtmyer and Hudson, *THIS JOURNAL*, **57**, 1716 (1935); (b) *ibid.*, **61**, 214 (1939); (c) *ibid.*, **62**, 961 (1940).

(3) In a recent review in *Fortschritte der Chemie organischer Naturstoffe*, **2**, 202 (1939), Zemlén states that Kunz, who with one of us (C. S. H.) discovered the conversion of lactose octaacetate to acetochloroneolactose by means of aluminum chloride (Kunz and Hudson, *THIS JOURNAL*, **48**, 1978, 2435 (1926)), was unable to duplicate the reaction in Zemlén's laboratory. In our experience the use of a standard technical anhydrous aluminum chloride and the procedure described in Ref. 2a above has produced recrystallized acetochloroneolactose consistently in 35-40% yield.

(4) Throughout the article the rotations are specific rotations at 20° for sodium light; *c* designates concentration in grams per 100 cc. of solution.

(5) The acetolysis of triacetyl levoglucosan is reported by K. Freudenberg and Soff, *Ber.*, **69**, 1245 (1936), to produce an equilibrium mixture containing 88% of the α -pentaacetate. Similarly, the acetolysis of any other triacetyl hexosan $\alpha<1,5>\beta<1,6>$ would be

crystallized readily, but the β -pentaacetate still remains a sirup. Conversion of either pentaacetate to crystalline α -acetochloro-D-altrose was effected in good yield by the action of titanium tetrachloride in chloroform solution, according to the method of Pacsu.⁶ Replacement of the chlorine atom by a hydroxyl group was accomplished by shaking the acetochloro compound with silver carbonate and aqueous acetone. The resulting tetraacetate separates with a molecule of acetone of crystallization. Because of its upward mutarotation in chloroform, from -6.0° to +12.9°, it will be designated as β -tetraacetyl-D-altrose.

This β -tetraacetate furnished a convenient source for the preparation of tetraacetyl- β -methyl-D-altrosido. Purdie and Irvine reported nearly forty years ago⁷ that the free glycosidic hydroxyl group in tetramethylglucose could be etherified by means of methyl iodide and silver oxide. A similar reaction applied now to tetraacetylaltrose has produced tetraacetyl- β -methyl-D-altrosido. The mother liquor from this preparation deposited spontaneously, although in much smaller amounts, a second compound, namely, tetraacetyl- α -methyl-D-altrosido. The latter was obtained also by rearrangement of the β -isomer with titanium tetrachloride in chloroform, by the method of Pacsu.⁸

Since these altrosido acetates were obtained from the same altrose tetraacetate, through a series of other acetylated compounds derived from D-altrosan of known pyranoside ring structure,^{2c} and since the β -form was isomerized to the α -form by titanium tetrachloride, all by reactions which are not known to cause a shift in the size of the ring, it may be assumed that the two altrosido acetates are of the pyranoside ring type. From the rotations of +66.0° and -61.0° for the α - and β -anomers, respectively, the value 2A for the difference in molecular rotations may be calculated as +46,000. The corresponding 2A

expected to produce the same equilibrium mixture that forms when either hexose pentaacetate is treated with the acetic-sulfuric rearranging solution of Montgomery and Hudson, *THIS JOURNAL*, **56**, 2463 (1934). See also Hann and Hudson, *ibid.*, **56**, 2465 (1934).

(6) Pacsu, *Ber.*, **61**, 1508 (1928).

(7) Purdie and Irvine, *J. Chem. Soc.*, **83**, 1021 (1903). See also Irvine and Moodie, *ibid.*, **89**, 1578 (1906).

(8) Pacsu, *Ber.*, **61**, 1513 (1928).

values for the other known pairs of acetylated methylaldohexopyranosides are: glucose +53,900,⁹ galactose +53,500,¹⁰ gulose +46,900,¹¹ and mannose +36,100.¹²

In order to obtain larger amounts of the tetraacetyl- α -methyl-D-altroside we decided to utilize the excellent methods developed by G. J. Robertson and his collaborators in their study of Walden inversion in the sugar series. Thus, Robertson and Griffith,¹³ in continuation of the earlier work of Mathers and Robertson,¹⁴ subjected 2,3-ditosyl-4,6-benzylidene- α -methylglucoside¹⁵ to alkaline hydrolysis. The adjacent tosyl groups were eliminated with the formation of an ethylene oxide ring at carbon atoms 2 and 3, and the new compound was described, for reasons set forth in their original article, as 2,3-anhydro-4,6-benzylidene- α -methyl-D-alloside. More drastic action of hot aqueous caustic potash under pressure then opened the 2,3-anhydro ring of the alloside, and the resulting crystalline product was described correctly as 4,6-benzylidene- α -methyl-D-altroside.

Although Robertson and Griffith removed the benzylidene group by gentle acid hydrolysis, they obtained only a sirupy α -methylaltroside, with $[\alpha]_D^{15} +125.6^\circ$ in methyl alcohol. We were fortunate in obtaining a crystalline product, first, by deacetylation of the α -methyl-D-altroside acetate; later, with seed crystals available, it was more convenient to prepare the desired altroside from its benzylidene derivative.

α -Methyl-D-altroside crystallizes from methyl alcohol in large, clear prisms, melting at 108° , and rotating $+125.8^\circ$ in aqueous solution. α -Methyl-D-altroside is a pyranoside, for upon oxidation according to the procedures of Jackson and Hudson¹⁶ it consumed two equivalents of sodium metaperiodate, liberated one equivalent of formic acid, and the rotation of the product, $+120.8^\circ$, agreed with the rotation $+121.0^\circ$ for D'-methoxy-D-hydroxymethyldiglycolic aldehyde derived from α -methyl-D-glucopyranoside. Furthermore, the oxidation of α -methyl-D-altroside with periodic acid consumed two equivalents of oxidant, and the resulting dialdehyde, upon subsequent oxidation with

bromine water and strontium carbonate, produced the same strontium D'-methoxy-D-hydroxymethyldiglycolate that Jackson and Hudson obtained from the α -methyl-D-galactoside, glucoside, guloside and mannoside of known pyranoside ring structure.^{16a}

Experimental

2,3,4-Triacetyl-D-altrosan.—To a well-cooled solution of 25 g. of crystalline altrosan in 500 cc. of pyridine was added 250 cc. of acetic anhydride in 25-cc. portions. The mixture was kept in the refrigerator overnight, at room temperature for two days, then poured into ice water and extracted with chloroform. The chloroform solution was washed in succession with water, cold dilute hydrochloric acid until free from pyridine, water, aqueous sodium bicarbonate, and water, dried with granular calcium chloride, and the chloroform evaporated *in vacuo*. The sirup was dissolved in ether, diluted with isopentane, and inoculated with a crystal obtained in a preliminary experiment. Triacetylaltrosan separated in clusters of elongated prisms in practically quantitative yield. After one recrystallization from ether-isopentane the rotation⁴ of the product was -172° in chloroform (*c*, 1.0), and was unchanged by two additional recrystallizations. The melting point was $100-101^\circ$.

Anal. Calcd. for $C_{15}H_{16}O_8$: C, 50.00; H, 5.60; acetyl, 10.41 cc. of 0.1 N NaOH per 100 mg. Found: C, 50.14; H, 5.64; acetyl, 10.42 cc.

α -Pentaacetyl-D-altrose.—The acetolysis of triacetylaltrosan was carried out by dissolving 31 g. of the triacetate in 300 cc. of acetic anhydride containing 6 cc. of concentrated sulfuric acid. A preliminary experiment had shown that the reaction was complete within five minutes, since the equilibrium rotation of $+32^\circ$, calculated as pentaacetylaltrose, was unchanged overnight. After one hour, therefore, the acetolysis mixture was poured on ice, the acids neutralized by the addition of solid sodium bicarbonate, and the aqueous solution extracted thoroughly with chloroform. The chloroform solution, washed with water, dried with granular calcium chloride, filtered, and concentrated *in vacuo* to 200 cc., all as quantitatively as possible, had a rotation of $+24.4^\circ$. On the assumptions that $A_{AC} = 20,600$ ¹⁷ and that the only products are altrose pentaacetates, this rotation would indicate a mixture of 64% α -pentaacetate and 36% β -pentaacetate. To isolate the former, the chloroform was removed *in vacuo*, the residual sirup dissolved in ether, and crystallized by the addition of isopentane. The yield was 23.8 g. of α -pentaacetate, or 57% of the theoretical.¹⁸ The rotation, $+62.7^\circ$, was

(16a) Note added May 27, 1941. If D-altrose and its derivatives should prove to resemble in rotatory relations the compounds of the D-mannose series rather than those of the D-glucose series, as appears now from the data available, we may calculate that the D-altrose of specific rotation $+32.6^\circ$ in water, reported previously from this Laboratory, represents the nearly pure β -form of this sugar in spite of its apparent lack of mutarotation (*cf.* Austin and Humoller, *THIS JOURNAL*, **56**, 1153 (1934)). Experiments designed to test this hypothesis are now in progress.

(17) This is the average value of A_{AC} obtained from the cellobiose and neolactose series (Richtmyer and Hudson, *ibid.*, **58**, 2535 (1936)).

(18) If it is desirable to obtain additional crystalline α -pentaacetate, the concentrated and dried sirupy mother liquor may be treated with the rearranging mixture of Montgomery and Hudson (Ref. 5), and about 50% of the remaining pentaacetate will then separate as the α -form. The new mother liquor may be treated likewise.

(9) Hudson and Dale, *THIS JOURNAL*, **40**, 997 (1918).

(10) Dale and Hudson, *ibid.*, **52**, 2534 (1930).

(11) Isbell, *Bur. Standards J. Research*, **8**, 1 (1932).

(12) Harris, Hirst and Wood, *J. Chem. Soc.*, 2108 (1932).

(13) Robertson and Griffith, *ibid.*, 1193 (1935).

(14) Mathers and Robertson, *ibid.*, 1076 (1933).

(15) The word "tosyl" is the commonly accepted contraction of "p-toluenesulfonyl."

(16) Jackson and Hudson, *THIS JOURNAL*, **59**, 994 (1937); **61**, 1532, Note 8 (1939).

not changed appreciably by four recrystallizations from a mixture of chloroform, ether and isopentane, and the value $+63.0^\circ$ in chloroform (c , 5.0) is accepted for pure α -pentaacetyl-D-altrose. The crystals separate as rectangular, plate-like prisms, melting at $118-119^\circ$.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: C, 49.23; H, 5.68; acetyl, 12.79 cc. of 0.1 N NaOH per 100 mg. Found: C, 49.45; H, 5.73; acetyl, 12.89 cc.

α -Acetochloro-D-altrose.—To a solution of 10 g. of α -pentaacetylaltrose¹⁹ in 75 cc. of alcohol-free, dry chloroform was added 2.9 cc. of titanium tetrachloride in 40 cc. of absolute chloroform. A yellow precipitate formed, then redissolved during three and one-half hours of heating in a water-bath at $70-75^\circ$; the final solution was dark in color, and accompanied by a small amount of brownish gum on the walls of the flask. The mixture was poured on ice, the chloroform solution separated, washed thrice with water, dried over granular calcium chloride, and concentrated *in vacuo*. Crystalline material was obtained readily with the aid of ether and isopentane, in a yield of 8.0 g. After one recrystallization from a mixture of chloroform, ether and isopentane, the rotation of the α -acetochloroaltrose was $+103^\circ$, rising to $+110.0^\circ$ in chloroform (c , 5.0) after five recrystallizations, and remaining unchanged by three additional recrystallizations. The pure material separated as large, flat prisms melting at $101-102^\circ$.

Anal. Calcd. for $C_{14}H_{19}O_9Cl$: C, 45.85; H, 5.22; Cl, 9.67; acetyl plus chlorine, 13.63 cc. of 0.1 N NaOH per 100 mg. Found: C, 46.00; H, 5.16; Cl, 9.75; acetyl plus chlorine, 13.54 cc.

β -2,3,4,6-Tetraacetyl-D-altrose.—A solution of 9.7 g. of acetochloroaltrose in 100 cc. of acetone and 5 cc. of water was shaken for two hours with 10 g. of silver carbonate. The mixture was filtered, and the halogen-free filtrate concentrated *in vacuo* as far as possible with the bath temperature at 30° . During the concentration, crystals appeared spontaneously in the neck of the flask. From their low melting point of 65° , the presence of acetone of crystallization was suspected. Accordingly, the sirupy residue was dissolved in a small amount of dry acetone, and isopentane added cautiously. The tetraacetate separated in clusters of large, flat prisms. The mother liquor was decanted, and the crystals washed with a mixture of isopentane and acetone in which they appeared to be less soluble than in either solvent alone. The yield was 5.8 g. After one recrystallization in the same manner, the crystals were spread on a watch glass and exposed to the air at room temperature. The transparent crystals began to lose weight and in about six weeks two samples reached constancy after the loss of 14.33 and 14.35% of their original weights, respectively. Calcd. for 1 molecule of acetone of crystallization: 14.29%. The final product was white, but maintained its original crystalline appearance. It melted at $85-90^\circ$, and showed mutarotation -6.0° changing to $+12.9^\circ$ (constant) in chloroform (c , 4.0) in the course of six weeks at 20° . It is readily soluble in water.

Anal. Calcd. for $C_{14}H_{20}O_{10}$: C, 48.27; H, 5.79; acetyl,

(19) It is not essential to use the α -pentaacetate, since a 79% yield of crystalline acetochloroaltrose was isolated following the action of titanium tetrachloride directly on the well-washed and dried chloroform solution of mixed pentaacetates obtained from triacetylaltrosan as described above.

11.48 cc. of 0.1 N NaOH per 100 mg. Found: C, 48.45; H, 5.82; acetyl, 11.65 cc.

Tetraacetyl- β -methyl-D-altroside.—A mixture of 20.9 g. of crystalline β -tetraacetate, 200 cc. of methyl iodide and 19 g. of silver oxide was shaken mechanically for several days in the cold room at about $+2^\circ$. The silver salts were removed by filtration, washed with ether, and the combined filtrates concentrated *in vacuo*. The sirup, crystallized from ether-isopentane, deposited 14.6 g. of rectangular prisms melting at $94-95^\circ$ and rotating -61.0° in chloroform (c , 5.0); neither melting point nor rotation was changed by four additional recrystallizations.

Anal. Calcd. for $C_{18}H_{24}O_{10}$: C, 49.72; H, 6.12; OCH_3 , 8.56; acetyl, 11.04 cc. of 0.1 N NaOH per 100 mg. Found: C, 49.91; H, 6.28; OCH_3 , 8.69; acetyl, 10.97 cc.

Tetraacetyl- α -methyl-D-altroside.—The mother liquor from the crystallization of the tetraacetyl- β -methylaltroside was concentrated to a thick sirup weighing 7.2 g. Dissolved in ether the material rotated $+18^\circ$, corresponding to about 62% α - and 38% β -methylaltroside acetates. Upon dilution with isopentane, and inoculation with a crystal of the α -form which had separated spontaneously from a similar earlier preparation of the sirupy residue, the solution deposited 3.0 g. of tetraacetyl- α -methylaltroside.²⁰ The pure substance separates as prisms melting at $88-89^\circ$; its rotation, $+66.0^\circ$ in chloroform (c , 5), was unchanged by five recrystallizations from a mixture of chloroform, ether and isopentane.

Anal. Calcd. for $C_{18}H_{24}O_{10}$: C, 49.72; H, 6.12; OCH_3 , 8.56; acetyl, 11.04 cc. of 0.1 N NaOH per 100 mg. Found: C, 49.66; H, 6.18; OCH_3 , 8.54; acetyl, 11.07 cc.

Rearrangement of Tetraacetyl- β -methyl-D-altroside to Tetraacetyl- α -methyl-D-altroside.—The method of Pacsu²¹ was used. Thus, 7.0 g. of the β -isomer in 55 cc. of absolute chloroform was heated with 3.7 g. of titanium tetrachloride for forty-five minutes at 70° . The mixture was cooled, dried into ice water, and the chloroform extract washed, dried and concentrated. The chloroform solution rotated $+20^\circ$, corresponding to about 64% α - and 36% β -methylaltroside acetates. From this solution was isolated 3.0 g. of product identified by melting point, mixed melting point and rotation as tetraacetyl- α -methyl-D-altroside.

4,6-Benzylidene- α -methylglucoside was prepared according to the directions of Freudenberg, Toepffer and Andersen.²² The yield of crude product, melting at $161-163^\circ$, was 60-70%. A sample, twice recrystallized from water, then thrice recrystallized from a mixture of chloroform and ether, melted at $163-164^\circ$. The rotation, constant at 110.4° in chloroform (c , 2.0), is lower than the value $+117.5^\circ$ in chloroform reported by Mathers and Robertson,²³ but is in agreement with the rotation $+110.0^\circ$ observed for a carefully-purified sample obtained from 2,3-anhydro-4,6-benzylidene- α -methylalloside (see below).

2,3-Ditosyl-4,6-benzylidene- α -methylglucoside.—The well-dried, crude benzylidene compound was tosylated according to Ohle and Spencker.²⁴ The product obtained by

(20) It is probable that a larger amount of the α -form could be obtained at this point by allowing the β -tetraacetate to mutarotate completely before the methylation is begun.

(21) Pacsu, *Ber.*, **61**, 1513 (1928).

(22) Freudenberg, Toepffer and Andersen, *ibid.*, **61**, 1758 (1928).

(23) Mathers and Robertson, *J. Chem. Soc.*, 698 (1933).

(24) Ohle and Spencker, *Ber.*, **61**, 2392 (1928).

pouring the mixture on ice was extracted with chloroform, the pyridine removed by shaking the solution with ice-cold dilute hydrochloric acid, and the ditosyl compound crystallized from chloroform-ether. The yield was about 70%. Recrystallized from chloroform-ether, it melted at 147–148°, and rotated +11.8° in U. S. P. chloroform; this rotation confirms the data of Mathers and Robertson,²⁵ and of Littmann and Hess,²⁶ rather than the value +66.5° reported by Ohle and Spencker. Evidence for a less stable modification melting at 132–133° was obtained when the first sample was recrystallized from methyl alcohol; later crystallizations from this solvent and from chloroform-ether produced only the previously known higher melting form.

From the mother liquor of the ditosyl compound there was isolated in one instance a substance with the composition of a monotosyl compound. *Anal.* Calcd. for $C_{21}H_{24}O_8S$: C, 57.79; H, 5.54. Found: C, 57.85; H, 5.61. From the melting point of 152–153° and rotation of +64.5° it was identified as the 2-tosyl-4,6-benzylidene- α -methylglucoside, whose preparation and proof of structure have been described by Robertson and Griffith.²⁷

2,3-Anhydro-4,6-benzylidene- α -methyl-D-alloside.—To obtain a practically quantitative yield of the anhydroalloside, which Robertson and Griffith²⁸ obtained as a secondary product, the following modification was adopted. A solution of 100 g. of ditosyl compound (0.17 mole) in 1250 cc. of chloroform was cooled in ice, and 315 cc. of cold 2.7 *N* sodium methylate (0.85 mole) added. The mixture was kept in the refrigerator for three days, with occasional shaking, then allowed to stand at room temperature for an additional day. The solution was diluted with water, and the chloroform layer and extracts washed with water, dried over granular calcium chloride, and concentrated. Crystalline benzylidene-anhydro- α -methylalloside separated readily, and was filtered and washed with the aid of ether. The yield was about 41 g. of product melting at 200°, the exact temperature depending somewhat on the rate of heating. A sample thrice recrystallized from chloroform-ether rotated +140° in chloroform (*c*, 2.2) in agreement with the value +140.4° reported by Robertson and Griffith.

4,6-Benzylidene- α -methyl-D-altroside.—The anhydroalloside was converted to altroside by boiling for forty-eight hours with aqueous potassium hydroxide, according to Robertson and Whitehead.²⁹ The resulting solution was neutralized to phenolphthalein with carbon dioxide, then extracted exhaustively with chloroform, the chloroform solution dried with granular calcium chloride, concentrated *in vacuo*, and the product crystallized with the aid of ether and isopentane. From 210 g. of anhydroalloside was obtained 208 g. of crystalline material which, upon recrystallization from methyl alcohol, yielded 176 g. of benzylidene- α -methylaltroside in large prisms. The melting point 169–170° is in agreement with that of Robertson and Whitehead, and Robertson and Griffith, but the rotation, +115.0° in chloroform (*c*, 2.0), unchanged by three additional recrystallizations, is somewhat lower than the value +126.8° reported for a small sample prepared by

Robertson and Griffith. The composition of our product was confirmed by analysis.

Anal. Calcd. for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.66; H, 6.36.

Although Robertson and Whitehead reported a practically quantitative yield of the altroside derivative, we have found that the mother liquor from the 176 g. of altroside above contained a mixture, from which could be isolated by fractional crystallization an additional 14 g. of benzylidene- α -methylaltroside, and 15 g. of 4,6-benzylidene- α -methylglucoside. The latter, recrystallized once from chloroform-ether and once from water, rotated +110.0° in chloroform (*c*, 2.0). This value was unchanged by three additional recrystallizations from water, followed by two additional recrystallizations from chloroform-ether. The melting point, 163–164°, was not depressed when the sample was mixed with an authentic specimen. The presence of this glucoside derivative is not surprising in view of the findings in the case of most other ethylene oxide ring openings studied by Robertson and other investigators, and the small yield of this product might be overlooked easily in the hydrolysis of the 10-g. sample reported previously.

α -Methyl-D-altroside.—Crystalline altroside was obtained first by deacetylation of the altroside acetate with barium methylate in the usual manner. The sirup crystallized after several weeks in a desiccator.

For the preparation of α -methylaltroside from its 4,6-benzylidene derivative, the following procedure was employed. A solution was prepared by warming 25 g. of benzylidene compound in 1000 cc. of water; 50 cc. of 0.1 *N* sulfuric acid was added and the mixture heated in a water-bath for one hour at 60°. The liberated benzaldehyde was removed by distillation under diminished pressure. No further amount of benzaldehyde could be obtained by longer heating. At this stage the material in solution, calculated as methylaltroside, had a specific rotation of +124°. Enough aqueous barium hydroxide was added to make the solution barely alkaline to phenolphthalein, and the precipitated barium sulfate was removed by filtration. The filtrate was concentrated *in vacuo* to a thick sirup which was dissolved in methyl alcohol, diluted with ether and inoculated with a seed crystal. The α -methylaltroside crystallized readily in large, clear prisms. From a concentrated methyl alcohol solution in the ice-box one crystal has grown to 35 mm. in length, and about 10 mm. in width and thickness. The rotation of the first crop was +125.8 \pm 0.5° in water (*c*, 3.0) and remained unchanged after four recrystallizations. In methyl alcohol a rotation of +135.1° was observed (*c*, 2.0). The melting point was 107–108°, and the yield practically theoretical.

Anal. Calcd. for $C_7H_{14}O_6$: C, 43.30; H, 7.27. Found: C, 43.48; H, 7.35.

Reacetylation of this α -methylaltroside with acetic anhydride and pyridine yielded a tetraacetyl- α -methylaltroside identical with that prepared from altrosan as described above.

Oxidation of α -Methyl-D-altroside with Sodium Metaperiodate.—To 0.4377 g. of pure α -methylaltroside in about 25 cc. of water was added 12 cc. of 0.4125 molal aqueous sodium periodate (2.2 equivalents), and the solution diluted later exactly to 50 cc. with water. After

(25) Mathers and Robertson, *J. Chem. Soc.*, 696 (1933).

(26) Littmann and Hess, *Ber.*, **67**, 524 (1934).

(27) Robertson and Griffith, *J. Chem. Soc.*, 1193 (1935).

(28) Robertson and Griffith, *Ref. 27*, p. 1196.

(29) Robertson and Whitehead, *J. Chem. Soc.*, 321 (1940).

twenty-four hours the rotation, calculated as the expected dialdehyde, was $+120.8^\circ$; this value was unchanged at the end of forty hours. At that time titration of a 10-cc. portion for excess periodate revealed that 2.01 equivalents of oxidant had been consumed. Titration of another 10-cc. portion with 0.1 *N* sodium hydroxide, and methyl red as indicator, showed the presence of 0.97 equivalent of acid, presumably formic acid.

Oxidation of α -Methyl-D-altroside with Periodic Acid.—To 3.112 g. of pure α -methylaltroside in 50 cc. of water was added 150 cc. of 0.2355 molal aqueous periodic acid (2.2 equivalents). After three days the solution was diluted exactly to 250 cc. The rotation, calculated as the dialdehyde, was $+117.7^\circ$. Titration of an aliquot portion for excess periodic acid showed that 2.08 equivalents had been consumed. The lowered rotation, and the extra oxidizing agent consumed, indicate a slow continuing oxidation probably due to cleavage of the aldehyde because of the acidity of the solution. The remainder of the solution was neutralized with strontium hydroxide, the dialdehyde isolated, oxidized with bromine water and strontium carbonate as described by Jackson and Hudson,¹⁸ and the strontium salt isolated in 60% yield. This salt was recrystallized, dried to constant weight at room temperature *in vacuo* over calcium chloride, and identified as strontium D'-methoxy-D-hydroxymethylidglycolate dihydrate. *Anal.* Calcd. for $C_8H_{10}O_7Sr \cdot 2H_2O$: Sr, 27.75; H_2O , 11.41. Found: Sr, 27.61, 27.61; H_2O (dried at 138° *in vacuo*), 11.24. The rotation of the strontium salt, calculated as anhydrous (*c*, 0.6), was -53.1° , and the rotation of the dibasic acid (*c*, 1.4) liberated from the salt with an equivalent amount of hydrochloric acid was $+26.0^\circ$. These values are in agreement with those reported by Jackson and Hudson.¹⁶

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Summary

1. D-Altrosan $\langle 1,5 \rangle \beta \langle 1,6 \rangle$ has been converted to the following new crystalline substances: 2,3,4-triacetyl-D-altrosan; α -pentaacetyl-D-altrose; α -acetochloro-D-altrose; β -2,3,4,6-tetraacetyl-D-altrose; tetraacetyl- β -methyl-D-altroside; tetraacetyl- α -methyl-D-altroside; α -methyl-D-altroside.

2. α -Methyl-D-altroside, of $[\alpha]^{20D} +125.8^\circ$ in water, has been proved by periodic acid oxidation methods to possess the α -configuration and a pyranoside ring.

3. The series of reactions developed by G. J. Robertson and his collaborators for the transformation of α -methyl-D-glucoside to α -methyl-D-altroside has been modified to facilitate the preparation of crystalline α -methyl-D-altroside.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Blocking Effects in Condensation Reactions*

By JOSEPH B. NIEDERL AND JOHN S. MCCOY

In the course of studies on condensations of aldehydes with phenols, only the alkylidene-diphenol type of condensation involving one mole of the aldehyde with two moles of the phenol has been exhaustively studied.¹ A one to one ratio condensation has been described by J. B. Niederl and co-workers.² Aliphatic aldehydes and monohydroxy phenols in such condensations yielded polymers which upon pyrolysis gave the respective saturated alkylated phenols. With resorcinol a one to one ratio condensation was observed, the condensation products being tetramers.³

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(1) Schmedlin and Lang, *Ber.*, **43**, 2806 (1910); Claus and Trainer, *ibid.*, **19**, 3009 (1886); Moehlan and Kock, *ibid.*, **11**, 283 (1878); L. Claus, *Ann.*, **237**, 261 (1887); Th. Zincke, *ibid.*, **363**, 255 (1908).

(2) J. B. Niederl and co-workers, *THIS JOURNAL*, **59**, 1113 (1937).

(3) J. B. Niederl and H. Vogel, *ibid.*, **62**, 2512 (1940).

The purpose of the investigation presented in this paper was to determine what molar ratios between aldehydes and phenols are possible when only one ring position is available for reaction. Thus particular emphasis was placed on the condensation of equi- and multimolar quantities of the aldehyde. In the ensuing studies representative aldehydes of the three fundamental types, *i. e.*, saturated and unsaturated aliphatic and aromatic aldehydes were chosen. As properly blocked phenols, the 2,4- and 2,6-dimethylphenols were selected. The aldehydes subjected to condensation were acetaldehyde, crotonaldehyde and benzaldehyde.

It was found that, regardless of the mole ratio, only alkylidene-di-phenol type¹ of crystalline condensation products were obtained with blocked