somewhat more soluble in organic solvents than the corresponding β-glucoside derivative.

The α-methyl mannoside was regenerated from this tetracarbanilate according to the procedure of Salmon and Powell[6] and was identified by melting point and mixed melting point.

Anal. Calcd. for $C_{35}H_{34}O_{10}N_4$: C, 62.67; H, 5.07; N, 8.35. Found: C, 62.60; H, 5.05; N, 8.29.

We are indebted to Mr. John Walker (W. P. A. Project 18062) and to Mr. H. S. Clark for all analytical determinations. We also acknowledge the assistance and counsel of Dr. John C. Sowden.

Summary

1. The tetracarbanilates of α-methyl-*d*-mannoside, α-methyl-*d*-glucoside, β-methyl-*d*-glucoside and the tricarbanilate of β-methyl-*d*-xyloside have been synthesized in crystalline condition.

COLUMBUS, OHIO RECEIVED MARCH 9, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

aldehydo-Maltose Octaacetate

BY M. L. WOLFROM AND M. KONIGSBERG

The crystalline octaacetate of maltose diethyl mercaptal was reported[1] from this Laboratory some time ago. At the time, efforts to demercaptalate this substance yielded no crystalline product but the application of certain recent improvements[2] in the demercaptalation procedure has yielded the *aldehydo*-maltose octaacetate in crystalline form. A preliminary report[2] to this effect has been made and the details will now be communicated. The substance gives a positive Schiff aldehyde test and readily forms a crystalline oxime without loss of acetyl.

aldehydo-Maltose octaacetate exhibits no detectable mutarotation in ethanol solution but crystallizes as a compound with one mole of ethanol. This ethanol compound shows no detectable mutarotation in chloroform or ethanol solution and thus differs from the ethanol addition compounds of the *aldehydo*-acetates of galactose,[3] fucose[4] and mannose,[2] which have been demonstrated clearly to be true carbonyl addition compounds or ethyl hemiacetals. Table I indicates that the molecular rotations of *aldehydo*-maltose octaacetate and its ethanol compound are identical within the limits of experimental error. The ethanol compound is thus apparently not an ethyl hemiacetal but is a secondary valence compound with one mole of ethanol of crystallization. An alternative view would be that a change in the configuration of carbon one in this open chain derivative of maltose has little effect upon the rotation of the compound as a whole. This viewpoint receives some support in that the diethyl mercaptal of maltose octaacetate has practically the same rotation (specific, +88°; molecular, +69,000) in chloroform as the *aldehydo*-acetate. The fact that these maltose derivatives are α-glucosides might lead to the lactol carbon of the glucosidic portion making the controlling contribution to the rotation.

aldehydo-Maltose octaacetate is the first crystalline *aldehydo*-acetate in the disaccharide series.

TABLE I

ROTATIONS OF *aldehydo*-MALTOSE OCTAACETATE AND ITS ETHANOL COMPOUND

	$[\alpha]^{21}D$, $CHCl_3$ (alcohol free)	Mol. rotn.	$[\alpha]^{25}D$, EtOH	Mol. rotn.
aldehydo-Maltose octaacetate	+93.5°	+63,000	+96°	+65,000
The monoethyl alcoholate	+85	+62,000	+90	+65,000

Experimental

***aldehydo*-Maltose Octaacetate.**—Maltose diethyl mercaptal octaacetate[1] (20 g.) was dissolved in 300 cc. of acetone and added to a mixture of 60 g. of mercuric chloride, 70 g. of cadmium carbonate, and 7 cc. of water in 500 cc. of acetone. This mixture was stirred vigorously and refluxed for eight hours. The cold solution was filtered into a flask containing 75 g. of cadmium carbonate and the filtrate was concentrated under reduced pressure (35–40°) in the presence of the cadmium carbonate. The residue was extracted with warm chloroform (alcohol free) and the extract washed free of halogen, treated with decolorizing charcoal, dried over calcium chloride and concentrated to a thick sirup under reduced pressure. The sirup was dissolved in ether, one-fourth its volume of low boiling petroleum ether added, and cooled. The crystalline product was filtered and washed with cold ether; 8.5 g. m. p. 112–113°. A second crop was obtained from the mother liquors; 4.9 g. or 13.4 g. (78%) total, m. p. 105–113°. Pure material was obtained on two recrystallizations from absolute ether; m. p. 116–117°, spec. rot.

(1) M. L. Wolfrom and E. E. Stahly, THIS JOURNAL, **53**, 4379 (1931).
(2) M. L. Wolfrom and M. Konigsberg, *ibid.*, **61**, 574 (1939).
(3) M. L. Wolfrom, *ibid.*, **53**, 2275 (1931).
(4) M. L. Wolfrom and J. A. Orsino, *ibid.*, **56**, 985 (1934).

+93.5° (22°; *c*, 5; abs. $CHCl_3$),[5] spec. rot. +96° (25°; *c*, 1; EtOH; no mutarotation).

The compound crystallized as elongated prisms and was very soluble in chloroform and acetone and was moderately soluble in ether, alcohol and boiling water. It reduced Fehling solution on warming and reduced a neutral solution of copper acetate. In aqueous solution at room temperature it quickly restored the color to Schiff reagent.

Anal. Calcd. for $C_{12}H_{14}O_{11}$ $(CH_3CO)_3$: C, 49.56; H, 5.64; CH_3CO, 11.8 cc. 0.1 *N* NaOH per 100 mg. Found: C, 49.49; H, 5.63; CH_3CO, 11.8 cc.

aldehydo-Maltose Octaacetate Monoethyl Alcoholate.—This substance was obtained on recrystallization of *aldehydo*-maltose octaacetate from absolute ethanol or on working up the demercaptalation reaction with absolute ethanol in place of ether and petroleum ether. Pure material was obtained on several recrystallizations from absolute ethanol; m. p. 66–67°, spec. rot. +85° (21°; *c*, 5; abs. $CHCl_3$; no mutarotation), spec. rot. +90° (25°; *c*, 1; abs. EtOH; no mutarotation).

The substance was not very stable and slowly decomposed on long standing, with the liberation of alcohol and acetic acid. The product crystallized as long, lustrous needles and was very soluble in chloroform and acetone, moderately so in alcohol and warm ether, and was practically insoluble in water and ligroin. It reduced Fehling solution.

Anal. Calcd. for $C_{12}H_{14}O_{11}(CH_3CO)_3(C_2H_5OH)$: C, 49.7; H, 6.12; OC_2H_5, 6.22; CH_3CO, 11.0 cc. 0.1 *N* NaOH per 100 mg. Found: C, 49.5; H, 6.14; OC_2H_5, 6.16; CH_3CO, 11.0 cc.

aldehydo-Maltose Oxime Octaacetate.—*aldehydo*-Maltose octaacetate (4 g.) was dissolved in 400 cc. of boiling water, filtered and a solid mixture of 0.9 g. of hydroxylamine hydrochloride and 1.8 g. of potassium acetate was added to the filtrate. A crystalline product separated on cooling; yield 1.5 g., m. p. 89–92°, spec. rot. +100° ($CHCl_3$). Pure material was obtained on two recrystallizations from water; yield 0.7 g., m. p. 93–94°, spec. rot. +107° (24°; *c*, 3; U. S. P. $CHCl_3$), spec. rot. +100° (24°; *c*, 3; EtOH). Recrystallization of the product from ether or aqueous alcohol did not alter the constants.

The product crystallized as fine rectangular rods and was soluble in chloroform, acetone, alcohol, ether and boiling water. It was insoluble in the hydrocarbon solvents.

Anal. Calcd. for $C_{12}H_{15}O_{11}N(CH_3CO)_3$: N, 2.02; CH_3CO, 11.5 cc. 0.1 *N* NaOH per 100 mg. Found: N, 2.00; CH_3CO,[6] 11.5 cc.

We are indebted to Mr. John Walker (W. P. A. Project 18062) for assistance rendered in the analytical determinations. We also acknowledge assistance rendered by Mr. F. B. Moody.

Summary

1. The synthesis of the first crystalline *aldehydo*-acetate in the disaccharide series, *aldehydo*-maltose octaacetate, is reported.

2. *aldehydo*-Maltose octaacetate forms a crystalline oxime and a crystalline compound containing one mole of ethanol.

3. *aldehydo*-Maltose octaacetate shows no detectable mutarotation in ethanol solution and its ethanol compound shows no detectable mutarotation in chloroform or ethanol solution.

(5) All rotations are recorded to the D-line of sodium light, 22° is the temperature, *c* is the concentration in g. per 100 cc. soln.

(6) M. L. Wolfrom, M. Konigsberg and S. Soltzberg, THIS JOURNAL, **58**, 490 (1936).

COLUMBUS, OHIO RECEIVED MARCH 11, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Disproportionation in Aryloxymalonic Acid Syntheses

BY JOSEPH B. NIEDERL AND ROSLYN T. ROTH[1]

In the course of the studies of substituted phenylmalonic acids[2,3] studies of various phenoxymalonic acids were undertaken as well. Mono- and di-phenoxymalonic acids, with and without substituents in the phenyl or the malonyl radical, were prepared.

In the preparation of the mono-phenoxymalonic acids from the diethyl mono-bromomalonate by the Williamson synthesis, a "disproportionation" phenomenon was encountered. Thus it was found that the di-phenoxy compounds result in about equal quantities with the monophenoxy products despite the use of equimolar quantities of sodium phenolate and diethyl mono-bromomalonate. On the other hand, no such disproportionation took place when the diethyl mono-chloromalonate was used instead of the bromo compound.

Although the mono- and diphenoxy-malonic acid esters had been prepared previously by Conrad and Brueckner[4] and the mono- and di-*p*-

(1) The material presented in this paper is taken from Part III of the thesis presented by Roslyn T. Roth to the Faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) J. B. Niederl, R. T. Roth and A. Plentl, THIS JOURNAL, **59**, 1901 (1937).

(3) J. B. Niederl and R. T. Roth, *ibid.*, **60**, 2140 (1938).

(4) M. Conrad and C. A. Brueckner, *Ber.*, **24**, 2993 (1891).