to the procedure described for the corresponding ethyl compound (II) except that 150 parts of methanol was used in place of the ethanol. A good yield was obtained; m. p. 187–188° (dec.), spec. rot. −19° (30°; *c*, 4.2; $CHCl_3$). The substance crystallized in rod-shaped prisms and showed solubilities and behavior similar to II.

Anal. Calcd. for $C_{32}H_{44}O_{23}(OCH_3)Cl_2P$: OCH_3, 3.35. Found: OCH_3, 3.97.

1,1-Dichloro-*aldehydo-d*-galactose Pentaacetate (IV).—*aldehydo-d*-Galactose pentaacetate (10 g., 1 mol) was dissolved in 100 cc. of pure benzene, 15 g. of Drierite (anhydrous calcium sulfate) added and the whole refluxed in an all-glass apparatus equipped with a drying tube. Powdered phosphorus pentachloride (6.8 g., 1.3 mol) was introduced quickly and the reflux maintained for twelve hours, whereupon the pale yellow solution was filtered and the filtrate washed with ice water and with an aqueous solution of sodium bicarbonate until halogen free (eight to twelve washings). Solvent removal from the dried (decolorizing charcoal) solution left 3 to 5 g. of a pale yellow sirup. This sirup was dissolved in the minimum quantity of hot ethanol and was crystallized on the addition of an equal volume of water. Pure material was obtained on further recrystallization from 80% ethanol; yield 0.8–1.6 g. of m. p. 148–150°; spec. rot. +11° (20°; *c*, 3.2; $CHCl_3$).

The substance was soluble in the common solvents except petroleum ether and cold water. It showed no reduction toward copper acetate (see Table I) and reduced Fehling solution only on long boiling. It gave a positive Schiff test very slowly on standing.

It was found that a reflux period less than specified above (twelve hours) yielded compound I while a longer period yielded only sirups which could not be crystallized and which readily decomposed.

Anal. Calcd. for $C_6H_7O_5(CH_3CO)_5Cl_2$: C, 43.2; H, 4.98; Cl, 15.9. Found: C, 43.3; H, 5.07; Cl, 15.6.

We are indebted to Mr. John Walker (W. P. A. Project 18062) for assistance rendered in the analytical determinations. We also acknowledge the general assistance of Mr. Irving Auerbach (N. Y. A. Project O. S. U. 167).

Summary

1. The action of phosphorus pentachloride upon *aldehydo-d*-galactose pentaacetate in dry benzene produces a crystalline substance (IV) which is shown to be 1,1-dichloro-*aldehydo-d*-galactose pentaacetate.

2. The action of phosphorus pentachloride upon *aldehydo-d*-galactose pentaacetate in ether leads to the isolation of a crystalline substance (I) designated di-(1-chloro-*aldehydo-d*-galactose pentaacetate) chlorophosphate.

3. From I is obtained di-(1-chloro-*aldehydo-d*-galactose pentaacetate) ethyl (and methyl) phosphate, II, and III.

4. The structure assigned to I is made probable by its hydrolysis to *aldehydo-d*-galactose pentaacetate and by its reaction with ethanol to form II, from which *aldehydo-d*-galactose heptaacetate is obtained on acetylation.

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

Crystalline Phenylurethans (Carbanilates) of Sugar Glycosides

BY M. L. WOLFROM AND D. E. PLETCHER

A well-established procedure in organic chemistry is the characterization of carbinols as N-aryl urethans prepared by the reaction of N-aryl isocyanates with the carbinol. Maquenne and Goodwin[1] investigated the extension of this reaction, using phenyl isocyanate, to a number of unsubstituted sugars but obtained only amorphous powders. Jolles and Botrini,[2] likewise employing phenyl isocyanate, obtained as amorphous powders the phenylurethans or carbanilates of several naturally occurring glycosides. Crystalline fully substituted carbanilates of some of the sugar alcohols have been reported.[1,3]

We have now been successful in obtaining in crystalline form the carbanilates of four of the methyl glycosides of the sugars, in which derivatives all of the free hydroxyls have been brought into reaction. These substances melt with decomposition at high temperatures and exhibit correspondingly low solubilities. Under certain conditions they show a pronounced tendency to separate as gels and are in general rather difficult to manipulate.

These polyurethans or polycarbanilates were not sufficiently soluble in chloroform for satisfactory polarizations. Rotations are recorded in acetone solution for all except β-methyl-*d*-glucoside tetracarbanilate, for which pyridine was found to be the only suitable polarization sol-

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(1) L. Maquenne and W. Goodwin, *Bull. soc. chim.*, [3] **31**, 430 (1904).

(2) E. Jolles and M. Botrini, *Gazz. chim. ital.*, **65**, 1217 (1935).

(3) H. Tessmer, *Ber.*, **18**, 968 (1885).

vent. It is of interest to note that the tetracarbanilate of α-methyl-*d*-mannoside (+ 79°, water) exhibits a specific rotation in acetone solution of eighteen degrees to the left. Such a reversal of rotation had been noted by Jolles and Botrini[2] for the amorphous tetracarbanilates of arbutin and esculin in pyridine solution.

Crystalline carbanilates and thionocarbanilates on carbon one of glucose and other sugars have been synthesized through the Fischer[4] procedure of treating acetobromosugars with silver cyanate or silver thiocyanate and subsequent treatment with an alcohol.[5]

When the work herein reported was practically completed, we were pleased to note the publication of Salmon and Powell.[6] These workers found that phenyl isocyanate formed readily crystallizable, easily purified, derivatives with two partially substituted glucose structures in which only one or two hydroxyl groups remained free and which failed to form crystalline acetates or tosylates (*p*-toluenesulfonates). In fact, they were able to crystallize 5,6-dimethyl-monoacetoneglucose only by seeding with crystals obtained by the hydrolysis of the corresponding urethan (carbanilate). The sodium methylate hydrolysis procedure of Salmon and Powell was applied to one of our derivatives and the parent glycoside was regenerated. We did not find any of the N,N-diphenylallophanate derivatives mentioned by these workers when pyridine was used as a reaction catalyst.

It would appear that the carbanilates (phenylurethans) are worthy of further consideration by investigators in the carbohydrate field, especially when derivatives are desired of structures containing only one or two free hydroxyl groups.

Experimental

β-Methyl-*d*-glucoside Tetracarbanilate.—β-Methyl-*d*-glucoside (5.0 g., 1 mol, previously dried over phosphorus pentoxide in a vacuum desiccator) was dissolved by heating in 30 cc. of dry pyridine in an apparatus equipped with a reflux condenser and a drying tube. To the solution, cooled to room temperature, was added 12.5 cc. (4.5 mols) of phenyl isocyanate. A reaction was immediately initiated with the liberation of considerable heat. The solution was refluxed for three hours and on cooling a crystalline product separated which was removed by filtration and washed with cold pyridine and finally with ether or petroleum ether; yield 4.5 g., m. p. 223–225°[7] (dec.), preliminary softening at 220°. Pure material could be obtained on recrystallization from pyridine, acetone or ethyl acetate; m. p. 225° (dec.), mixed m. p. with diphenyl urea (m. p. 235°), 210–211°, spec. rot. +13° (23°; *c*, 0.7; pyridine).[8]

The substance crystallized in long, fine needles. It was slightly soluble hot in acetone, chloroform, alcohol, ethyl acetate and pyridine. It was practically insoluble in water, ether and petroleum ether. It was not sufficiently soluble in acetone or chloroform for a satisfactory polarization.

Anal. Calcd. for $C_{35}H_{34}O_{10}N_4$: C, 62.67; H, 5.07; N, 8.35. Found: C, 62.68; H, 5.21; N, 8.38.

β-Methyl-*d*-xyloside Tricarbanilate.—β-Methyl-*d*-xyloside (5 g.) was treated exactly as described for the synthesis of β-methyl-*d*-glucoside tetracarbanilate and the crystalline reaction product was isolated in the same manner; yield 2.5 g., m. p. 233–235° (dec.). Pure material could be obtained on recrystallization from pyridine or alcohol–acetone (1:1); m. p. 234° (dec.), spec. rot. −23° (22°; *c*, 1; acetone).

The substance crystallized in long, fine needles and exhibited solubilities similar to those of the corresponding β-glucoside derivative except that it was more acetone-soluble.

Anal. Calcd. for $C_{27}H_{27}O_8N_3$: C, 62.19; H, 5.18; N, 8.06. Found: C, 62.00; H, 5.10; N, 8.24.

α-Methyl-*d*-glucoside Tetracarbanilate.—α-Methyl-*d*-glucoside (5 g.) was treated as described for the synthesis of the corresponding β-glucoside derivative except that the reaction product did not separate on cooling. The pyridine was then removed under reduced pressure and the amorphous residue washed repeatedly with warm ether; yield 11.5 g. The product was dissolved in a hot mixture of two parts of ethanol and one part of acetone, most of the acetone was then removed by boiling and to the residual hot ethanol solution water was added to incipient turbidity. The product crystallized on standing at room temperature and was removed by filtration. A second crop of approximately the same purity was obtained on mother liquor concentration; total yield 8 g., m. p. 210–214° (dec.). Pure material was obtained by repeating the above process several times; m. p. 227° (dec.), spec. rot. +73° (23°; *c*, 3; acetone).

The substance crystallized in long, fine needles and was somewhat more soluble in organic solvents than the corresponding β-glucoside derivative.

Anal. Calcd. for $C_{35}H_{34}O_{10}N_4$: C, 62.67; H, 5.07; N, 8.35. Found: C, 62.63; H, 5.10; N, 8.38.

α-Methyl-*d*-mannoside Tetracarbanilate.—α-Methyl-*d*-mannoside (5 g.) was treated with phenyl isocyanate as described for the β-methyl-glucoside but was isolated and crystallized by the procedure described for the α-methylglucoside derivative. The substance also could be recrystallized from absolute ethanol or isopropyl alcohol by the addition of water to the hot solution until incipient turbidity was produced; yield 3.4 g. of m. p. 189–190° (dec.); spec. rot. −18° (20°; *c*, 3; acetone).

The substance crystallized in long, fine needles and was

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[4] E. Fischer, *Ber.*, **47**, 1377 (1914).

[5] T. B. Johnson and W. Bergmann, THIS JOURNAL, **54**, 3360 (1932); **60**, 1916 (1938).

[6] M. R. Salmon and G. Powell, *ibid.*, **61**, 3507 (1939).

[7] All melting points are uncorrected and were taken on a 360° thermometer with immersion to the −10° mark.

[8] All rotations are recorded to the D-line of sodium light: 23° is the temperature; *c* is the concentration in g. per 100 cc. soln.

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.

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[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.

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[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).