TABLE II

ANALYSES OF CELLULOSE ACETATE CARBAMATES FROM CELLULOSE ACETATE OF 38.8% ACETYL

2.352 acetyls/glucose unit and 0.648 hydroxyls/glucose unit

Cellulose acetate carbamates	0.5 Hours		1 Hour		3 Hours		5 Hours		7 Hours		% Ac calcd. for complete reaction
	% Ac	Carb./ g. u.	% Ac	Carb./ g. u.	% Ac	Carb./ g. u.	% Ac	Carb./ g. u.	% Ac	Carb./ g. u.	
Phenyl	32.02	0.465	31.45	0.512	30.28	0.620	30.13	0.635	29.98	0.648	29.90
o-Chlorophenyl	29.15	.561	28.40	.624	28.20	.640	28.20	.640	28.05	.654	28.10
p-Bromophenyl	26.33	.627	26.10	.644	26.10	.644	26.10	.644	26.10	.644	26.00
o-Tolyl	34.48	.246	33.40	.317	31.40	.466	30.43	.536	29.80	.596	29.10
p-Tolyl	32.40	.388	31.35	.470	29.72	.600	29.56	.616	29.52	.619	29.10
α-Naphthyl	29.18	.512	28.17	.583	27.17	.665	27.17	.665	27.17	.665	27.30

Summary

1. Phenyl, o-chlorophenyl, p-bromophenyl, o-tolyl, p-tolyl, and α-naphthyl isocyanates reacted readily with 38.8% cellulose acetate at 60°.

2. The order of relative reaction rates of these isocyanates was as follows: p-bromophenyl (fastest), o-chlorophenyl, α-naphthyl, phenyl, p-tolyl, and o-tolyl (slowest).

3. The completely carbamated esters showed good solubilities in a variety of organic solvents.

4. All cellulose acetate carbamates formed hydrolyzed partially during deacetylation with aqueous alkali at room temperature.

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Methyl Glucoside Carbanilates. II. α-Methyl-d-glucoside-2,3,6-tricarbanilate

BY W. M. HEARON

Carbanilates are excellent derivatives of methyl glucoside since they are readily formed, high melting, insoluble in water, readily crystallized and resistant to hydrolysis.

To the partially substituted methyl glucoside carbanilates previously reported[1] is now added the 2,3,6-tricarbanilate, which is of special interest because of its relation to carbanilated cellulose[2] and starch. The series of reactions for its preparation is given below

α-methyl-d-glucoside-2,3-dicarbanilate (I)

↓

6-trityl-α-methyl-d-glucoside-2,3-dicarbanilate (II)

↓

6-trityl-α-methyl-d-glucoside-2,3-dicarbaniliate-4-acetate (III)

↓

α-methyl-d-glucoside-2,3-dicarbanilate-4-acetate (IV)

↓

α-methyl-d-glucoside-2,3,6-tricarbanilate-4-acetate (V)

↓

α-methyl-d-glucoside-2,3,6-tricarbanilate (VI)

As with methyl-d-glucoside,[3] tritylation and acetylation of α-methyl-d-glucoside-2,3-dicarbanilate could be carried out without isolation of the intermediate. That no migration of acetyl to the primary hydroxyl[4] occurred during detritylation was proved by retritylation of IV to III. No migration of acetyl occurred during carbanilation since (V) melted sharply about 70° below α-methyl-d-glucoside-2,3,4-tricarbanilate-6-acetate which was prepared by acetylation of the 2,3,4-tricarbanilate.[1] Finally, no inversions or loss of methoxyl occurred during this series of reactions since carbanilation of VI gave the previously reported α-methyl-d-glucoside tetracarbanilate.[5]

(1) Hearon, Hiatt, and Fordyce, THIS JOURNAL, **66**, 995 (1944).

(2) Hearon, Hiatt and Fordyce, *ibid.*, **65**, 829 (1943).

(3) Helferich, Klein and Snyder, *Ber.*, **59**, 81 (1926).

(4) Compare Helferich and Bredereck, *ibid.*, **64**, 2413 (1931); Helferich and Müller, *ibid.*, **63**, 2146 (1930); Robertson, *J. Chem. Soc.*, **1933**, 737.

Experimental

6-Trityl-α-methyl-d-glucoside-2,3-dicarbanilate (II).—A solution of 3.0 g. of α-methyl-d-glucoside-2,3-dicarbanilate[1] and 1.93 g. of trityl chloride in 6 ml. of dry pyridine was heated in a stoppered flask on a steam-bath for one hour. After cooling the solution was diluted with 20 ml. of ordinary pyridine and poured into cold water. The white precipitate, amounting to 4.8 g. or 98%, was recrystallized from hot methanol giving 3.1 g. or 63% yield melting at 121–122°; $[\alpha]^{25}D$ +57.3° (acetone, *C* 0.1).

Anal. Calcd. for $C_{40}H_{38}O_8N_2$: C, 71.2; H, 5.63; N, 4.16; trityl, 36.1. Found: C, 71.1; H, 5.75; N, 4.15; trityl, 36.2.

6-Trityl-α-methyl-d-glucoside-2,3-dicarbanilate-4-acetate (III). **A. By Acetylation of 6-Trityl-α-methyl-d-glucoside-2,3-dicarbanilate.**—A solution of 2.0 g. of 6-trityl-α-methyl-d-glucoside-2,3-dicarbanilate and 4.5 ml. of acetic anhydride in 10 ml. of dry pyridine was heated in a stoppered flask on a steam-bath for thirty minutes. After cooling to room temperature water was added to a permanent cloudiness and the mixture was poured into cold water. The precipitate, amounting to 2.1 g. or 99%, crystallized from hot alcohol giving 1.9 g. or a 90% yield, m. p. 134–135°, $[\alpha]^{25}D$ +77.8° (acetone, *C* 0.1).

Anal. Calcd. for $C_{42}H_{40}O_9N_2$: C, 70.4; H, 5.58; N, 3.91; trityl, 33.9. Found: C, 70.0; H, 5.80; N, 3.75; trityl, 33.8.

(5) Wolfrom and Pletcher, THIS JOURNAL, **62**, 1151 (1940).

B. By Tritylation and Acetylation of 6-Trityl-α-methyl-*d*-glucoside-2,3-dicarbanilate.—A mixture of 15 g. of α-methyl-*d*-glucoside-2,3-dicarbanilate and 9.7 g. of trityl chloride in 30 ml. of dry pyridine was heated in a stoppered flask on a steam-bath for one hour. After cooling 15 ml. of acetic anhydride was added and the solution allowed to stand at room temperature for fifteen hours. After dilution with 45 ml. of ordinary pyridine the mixture was poured into cold water. The white precipitate was crystallized from hot alcohol giving 23.7 g. or 95.7% yield, m. p. 134–135°; mixed melting point with the material from A, above, 134–135°.

α-Methyl-*d*-glucoside-2,3-dicarbanilate-4-acetate (IV).—A cold solution of 6.2 g. of 6-trityl-α-methyl-*d*-glucoside-2,3-dicarbanilate in 18 ml. of glacial acetic acid was treated with 18 ml. of hydrobromic acid in acetic acid (made by adding 11 ml. of 42% hydrobromic acid to 46 ml. of cooled acetic anhydride). The heavy precipitate of trityl bromide (2.3 g.) was sucked off and the filtrate run immediately into ice water. The white precipitate was sucked off, washed with water and dried; weight, 3.9 g., or 95%. Crystallization from alcohol and water gave 3.8 g. or 93%. Recrystallization by dissolving in chloroform and precipitating with *n*-butyl ether gave 3.5 g. or 85% yield melting at 119–120°, $[\alpha]^{25}D$ +85.3° (acetone, *C* 0.1).

Anal. Calcd. for $C_{23}H_{26}O_9N_2$: C, 58.2; H, 5.48; N, 5.90. Found: C, 58.3; H, 5.50; N, 5.89.

A small amount of the product, when treated in pyridine with the theoretical quantity of trityl chloride, gave a precipitate in water which melted at 133–134° (from alcohol) and did not depress the melting point of 6-trityl-α-methyl-*d*-glucoside-2,3-dicarbanilate-4-acetate.

α-Methyl-*d*-glucoside-2,3,6-tricarbanilate-4-acetate (V).—A solution of 1.5 g. of α-methyl-*d*-glucoside-2,3-dicarbanilate-4-acetate in 3 ml. of dry pyridine was treated with 0.5 g. of phenyl isocyanate (1.4 times theory) and heated in a stoppered flask on a steam-bath for one hour. After cooling, the solution was diluted with 1 ml. of methanol and allowed to stand ten minutes. Five ml. of ordinary pyridine was then added and the mixture poured into cold water. The precipitate was sucked off, washed and dried. After washing with hot ligroin to remove methyl carbanilate the precipitate weighed 1.7 g. or 91%. Crystallization from *n*-butanol gave 1.2 g. or 64% melting at 166–167°, $[\alpha]^{25}D$ +75.0° (acetone, *C* 0.1).

Anal. Calcd. for $C_{30}H_{31}O_{10}N_3$: C, 60.7; H, 5.22; N, 7.08. Found: C, 60.6; H, 5.36; N, 6.98.

α-Methyl-*d*-glucoside-2,3,6-tricarbanilate (IV).—A solution of 1.0 g. α-methyl-*d*-glucoside-2,3,6-tricarbanilate-4-acetate in 20 ml. of methanol containing 0.5% hydrochloric acid was refluxed for two hours. After cooling the hydrochloric acid was removed with barium carbonate, and the solution evaporated to dryness by an air stream. The white solid was purified by solution in acetone, addition of benzene and heating to remove most of the acetone. On cooling the product crystallized out and was sucked off. This purification, when repeated, gave 0.8 g. or 86% melting at 190–191°; $[\alpha]^{25}D$ +56.0° (acetone, *C* 0.1).

Anal. Calcd. for $C_{28}H_{29}O_9N_3$: C, 61.0; H, 5.27; N, 7.62. Found: C, 60.8; H, 5.32; N, 7.56.

α-Methyl-*d*-glucoside-2,3,4-tricarbanilate-6-acetate.—Acetylation of 1.5 g. of α-methyl-*d*-glucoside-2,3,4-tricarbanilate[1] in 10 ml. of dry pyridine with 5 ml. of acetic anhydride at room temperature for fifteen hours gave 1.5 g. crude (94%) and 1.0 g. pure (63%) of white crystals from hot alcohol melting at 235–237°; $[\alpha]^{25}D$ +71.0° (acetone, *C* 0.1).

Anal. Calcd. for $C_{30}H_{31}O_{10}N_3$: C, 60.7; H, 5.22; N, 7.08. Found: C, 60.7; H, 5.35; N, 7.16.

α-Methyl-*d*-glucoside-2,3,4,6-tetracarbanilate.—A small quantity of α-methyl-*d*-glucoside-2,3,6-tricarbanilate in pyridine with an excess of phenyl isocyanate was heated on a steam-bath for one hour. After cooling a little methanol was added to remove excess isocyanate and the mixture poured into cold water. The resulting white precipitate, after recrystallization twice from hot acetic acid, melted at 227° and did not depress the melting point of an authentic sample of α-methyl-*d*-glucoside-2,3,4,6-tetracarbanilate.[5]

Summary

1. Crystalline α-methyl-*d*-glucoside-2,3,6-tricarbanilate has been prepared by a five-step series of reactions from α-methyl-*d*-glucoside-2,3-dicarbanilate.

2. The intermediates in this synthesis, all crystalline, have been described and identified.

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[CONTRIBUTION FROM THE FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

Branched-Chain Fatty Acids. V. The Synthesis of Optically Active 10-Methyloctadecanoic Acids[1]

BY FRANKLIN S. PROUT,[2,3] JAMES CASON[4] AND A. W. INGERSOLL

The synthesis of 10-methyloctadecanoic acid was undertaken as a continuation of the program to synthesize and compare the properties of the complete series of methyloctadecanoic acids.[5] The 10-methyl member of this series is particularly interesting, moreover, since tuberculostearic acid, a C_{19} branched-chain fatty acid isolated from the lipids of tubercle bacillus by Anderson and Chargaff,[6] has been assigned this structure.[7] The assignment of structure by Spielman was based on oxidative degradation of the natural acid and the synthesis of *dl*-10-methyloctadecanoic acid. The synthetic acid melted some ten degrees higher (20–21°) than the melting point (10–11°) reported for tuberculostearic acid. There was, however, close agreement in other properties, and it appeared probable that tuberculostearic acid, although reported to be optically inactive,

(1) Preceding paper in this series: Cason, THIS JOURNAL, **68**, 2078 (1946).

(2) Constructed from a thesis submitted by Franklin S. Prout in partial fulfilment of the requirements for the Ph.D. degree, Vanderbilt University, March, 1947.

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(5) (a) Cason, THIS JOURNAL, **64**, 1106 (1942); (b) Cason and Prout, *ibid.*, **66**, 46 (1943); (c) Cason, Adams, Bennett and Register, *ibid.*, **66**, 1764 (1944).

(6) Anderson and Chargaff, *J. Biol. Chem.*, **85**, 77 (1929).

(7) Spielman, *ibid.*, **106**, 87 (1934).