but in considerably lower yield. The **amide**, prepared in 60% yield as described for 7-methyloctoic acid, after crystallization from ligroin (75–90°), methyl alcohol and acetone, separated in rosets of small white blades; m. p. 100.2–101.3°.

Anal. Calcd. for $C_{19}H_{39}ON$: C, 76.71; H, 13.21. Found: C, 77.01; H, 13.39.

The **tribromoanilide** was prepared in 74% yield (m. p. 111.5–112.5°) by heating the acid chloride from 0.50 g. of acid with 0.58 g. of tribromoaniline for one and one-half hours on the steam-bath. After two crystallizations from ethyl alcohol, slender white needles were obtained; m. p. 112.0–112.5°.

Anal. Calcd. for $C_{25}H_{40}ONBr_3$: C, 49.21; H, 6.60. Found: C, 49.13; H, 6.62.

The **lead salt** was prepared by pouring an alcoholic solution of the sodium salt into aqueous lead acetate.

Anal. Calcd. for $C_{38}H_{74}O_4Pb$: Pb, 25.81. Found: Pb, 25.65.

This salt was very sparingly soluble in ether (15–20 mg. per 100 cc.).

Summary

Ethyl 10-keto-17-methyloctadecanoate has been synthesized by the reaction of di-isononyl cadmium with ω-carbethoxynonoyl chloride. This keto ester has been converted to 17-methyloctadecanoic acid by Clemmensen reduction. 4-Keto-7-methyloctoic acid was prepared as an intermediate in this synthesis.

NASHVILLE, TENN. RECEIVED FEBRUARY 4, 1942

[COMMUNICATION NO. 844 FROM THE KODAK RESEARCH LABORATORIES]

The Synthesis of Some New Glucose and Gentiobiose Derivatives

BY DELBERT D. REYNOLDS AND WILLIAM O. KENYON

Many esters of glucose derived from monobasic organic acids are known, and intramolecular or cyclic carbonic acid esters of glucose have been synthesized.[1] However, as far as the authors are aware, the intermolecular esters containing two glucose units and one dibasic acid, or a derivative of such interesters, are not known. Recently, the authors had occasion to prepare di-(1,2,3,4-tetraacetyl-β-*d*-glucosyl) carbonate, and it was obtained in good yields. This paper describes the method of preparing this compound and some of its derivatives.

As substantiation for the structures assigned, the di-(1,2,3,4-tetraacetyl-β-*d*-glucosyl) carbonate was converted to di-(1,2,3,4,2′,3′,4′-heptaacetyl-β-gentiobiosyl) carbonate as illustrated in Fig. 1. The latter compound was hydrolyzed to gentiobiose which was converted to β-gentiobiose octaacetate and compared with a specimen of pure octaacetate synthesized by another method.[2]

The unusual stability of the di-(1-bromo-2,3,4-triacetyl-β-*d*-glucosyl) carbonate is worthy of note. A sample of the pure compound was exposed to laboratory conditions for several months without any noticeable decomposition or change of melting point.

A similar series of compounds has been prepared from other sugars and other dibasic acids. We hope to report these in subsequent papers.

The plan of the experimental work and the structures of the compounds produced are shown in Fig. 1.

Experimental

Di-(1,2,3,4-tetraacetyl-β-*d*-glucosyl) Carbonate (II).—Twenty grams of β-*d*-glucose 1,2,3,4-tetraacetate (I), prepared as described by Reynolds and Evans,[2] and 5 g. of Drierite were added to 50 cc. of dry pyridine. This mixture was cooled in an ice-water-bath and a solution of 2.8 g. of phosgene in 10 cc. of dry toluene was added slowly. The mixture soon formed a firm gel. Fifty cc. of pyridine was added, the mixture shaken at room temperature for fifteen hours, and then warmed on the steam-bath for two hours. The resulting solution was poured into ice water containing acetic acid in excess of the pyridine used. The precipitate was dried and recrystallized by dissolving in chloroform and adding ether until crystallization began; average yield 17 g. (82% of theory); m. p. 195–196°; twice recrystallized by the above method, the m. p. was 198–199°; $[\alpha]^{20.5}_{546.1}$ +12.15°[3] (*c*, 4.026; *l*, 2; $CHCl_3$). *Anal.* Calcd. for $C_{29}H_{38}O_{21}$: C, 48.17; H, 5.30. Found: C, 48.06; H, 5.23.

Di-(1-bromo-2,3,4-triacetyl-β-*d*-glucosyl) Carbonate (III).—Twenty grams of II dissolved in 200 cc. of a 32% solution of hydrogen bromide in glacial acetic acid was allowed to stand two hours at room temperature and then 200 cc. of chloroform was added. The solution was poured into 1 liter of ice water. The resulting chloroform layer containing III was separated, washed well with ice

(1) W. N. Haworth and C. R. Porter, *J. Chem. Soc.*, 151 (1930).

(2) D. D. Reynolds and W. L. Evans, THIS JOURNAL, **60**, 2559 (1938).

(3) We wish to thank Mr. T. F. Murray, Jr., of these Laboratories, for the optical rotation measurements.

water, dried over anhydrous sodium sulfate, decolorized with charcoal, filtered, and the chloroform removed by a current of dry air. The sirupy residue was dissolved in 50 cc. of ether. Crystallization began after one-half hour in the refrigerator. The yield was 17 g. (80%); after recrystallizing by dissolving in chloroform and adding

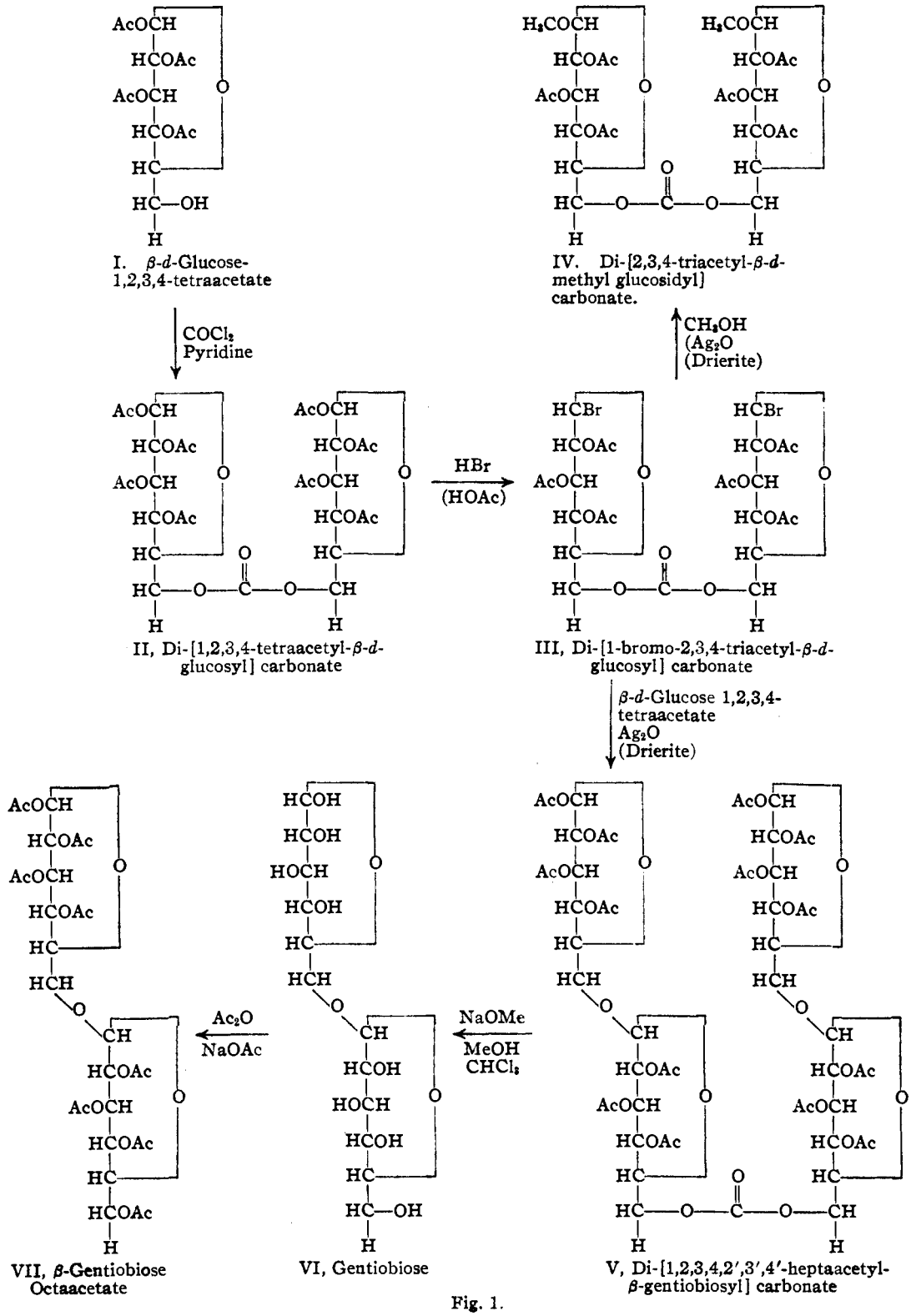

Fig. 1.

ether, the m. p. was 147–148°; $[\alpha]^{26.5}_{546.1}$ +258° (*c*, 4.018; *l*, 2; $CHCl_3$). *Anal.* Calcd. for $C_{25}H_{32}O_{17}Br_2$: Br, 20.92. Found: Br, 20.87.

Di-(2,3,4-triacetyl-β-*d*-methylglucosidyl) Carbonate (IV).—Four grams of silver oxide, 10 g. of Drierite, and 75 cc. of absolute methanol were placed in a 200-cc. round-bottom, three-neck flask equipped with a calcium chloride drying tube, sealed glass stirrer, and dropping funnel. The flask was wrapped with black paper. The mixture was stirred for one hour to dry the reactants. Five grams of III in 25 cc. of dry, alcohol-free chloroform (see ref. 2 for purifying the chloroform) were added through the dropping funnel over a one-hour period to the well-stirred reaction mixture. Stirring was continued overnight at room temperature. The mixture was filtered and the solution crystallized upon evaporation. After recrystallization from methanol, the m. p. was 191–192°; yield 3.8 g. (87%); $[\alpha]^{23}_{546.1}$ −75.0°. *Anal.* Calcd. for $C_{27}H_{38}O_{19}$: C, 48.64; H, 5.75. Found: C, 48.59; H, 5.75.

Di-(1,2,3,4,2′,3′,4′-heptaacetyl-β-gentiobiosyl) Carbonate (V).—Ten grams of silver oxide, 20 g. of Drierite, 9.2 g. of I, and 65 cc. of dry, alcohol-free chloroform were stirred for one hour in the reaction flask described in the preparation of IV. Ten grams of III in chloroform was added with stirring during one hour. After twenty-two hours of stirring, the reaction mixture was filtered through a layer of kieselguhr and the residue washed well with chloroform. The combined filtrate and washings were concentrated to a sirup when the solvent was removed by a current of dry air. The sirup was dissolved in methanol and crystallization began at once. The yield of V was 6.9 g. (40% based on III); m. p. 220–222°; after two recrystallizations from methanol, m. p. was 237–238° $[\alpha]^{23}_{546.1}$ −28.8° (*c*, 2.31; *l*, 1; $CHCl_3$). *Anal.* Calcd. for $C_{53}H_{70}O_{37}$: C, 48.97; H, 5.43. Found: C, 48.78; H, 5.30.

Conversion of V to β-*d*-Gentiobiose Octaacetate (VII).—Four grams of V was dissolved in a mixture of 20 cc. of chloroform and 15 cc. of methanol. Five cubic centimeters of sodium methylate solution (1 g. of sodium in 200 cc. of methanol) was added and the reaction solution was stirred at room temperature for one hour. The β-*d*-gentiobiose (VI) which precipitated was separated and dried over phosphorus pentoxide *in vacuo;* yield 1.6 g. (76%). This was mixed with 1 g. of fused sodium acetate and 10 cc. of acetic anhydride. After heating on the steam-bath for two hours, the product was precipitated in ice water, yielding 1.3 g. of VII (53%). Twice recrystallized the material had a m. p. of 195–196° and a mixed m. p. with a sample of VII prepared by another method[2] showed no depression of m. p.

Summary

1. Some new crystalline sugar derivatives have been prepared and characterized: di-(1,2,3,4-tetraacetyl-β-*d*-glucosyl) carbonate, di-(1-bromo-2,3,4-triacetyl-β-*d*-glucosyl) carbonate, di-(1,2,3,4,2′,3′,4′-heptaacetyl-β-gentiobiosyl) carbonate and di-(2,3,4-triacetyl-β-*d*-methyl glucosidyl) carbonate.

2. Evidence is presented to substantiate the structures assigned to these new compounds.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO STATE UNIVERSITY]

Optically Active Phenylurethan Anesthetics[1]

BY MAYNARD S. RAASCH[2] AND WALLACE R. BRODE

Asymmetric local anesthetics which have been prepared in their enantiomorphic forms and physiologically tested include cocaine and pseudococaine,[3] eucaine and isoeucaine,[4] tutocaine,[5] and stovaine.[6] The present work provides examples of the phenylurethan type.

Diothane (*dl*-1-piperidinopropane-2,3-diol dicarbanilate hydrochloride)[7,8] was prepared in optically active forms by first resolving the intermediate *dl*-1-piperidinopropane-2,3-diol with *l*-menthoxyacetic acid. This gave the *levo* form of the amino alcohol which melted at 20°. Since the *dl*-form melts at 83°, it was possible to obtain the *dextro* form very nearly pure by isolating the crude *dextro* form from the resolution mother liquors and filtering the racemate from it at 25°. This unusual fractional filtration procedure provides a means for obtaining both enantiomorphic forms pure with the use of only one resolving agent.

The active piperidinopropanediols were allowed to react with phenyl isocyanate to form the dicarbanilate and then with hydrogen chloride to form the optically active diothanes. The products were readily recrystallized from methyl ethyl ketone with which they formed a solvate containing one molecule of the ketone to one of the active diothane. Recrystallization from other

(1) Presented before the Organic Division at the Atlantic City meeting of the American Chemical Society, September, 1941.

(2) Wm. S. Merrell Fellow, 1939-1941.

(3) Gottlieb, *Arch. Exptl. Path. Therap.*, **97**, 113 (1923).

(4) King, *J. Chem. Soc.*, **125**, 41 (1924).

(5) Waser, "Synthese der organischen Arzneimittel," Ferdinand Enke, Stuttgart, 1928, p. 82.

(6) Fourneau and Ribas, *Bull. soc. pharmacol.*, **35**, 273 (1928).

(7) Rider, THIS JOURNAL, **52**, 2115 (1930); *J. Pharmacol.*, **47**, 255 (1933).

(8) Rider and Cook, THIS JOURNAL, **59**, 1741 (1937); *J. Pharmacol.*, **64**, 1 (1938).