specific color reaction described by Dische and Borenfreund.[8] The major portion of the hydrolysis mixture was neutralized with aqueous barium hydroxide, filtered and concentrated to a sirup that was benzoylated with benzoyl chloride and pyridine in the usual manner. The four grams of product thus obtained was identified as erythritol tetrabenzoate, melting at 190–191° and showing no depression of m.p. when mixed with an authentic specimen.

Acetolysis of 1,7-Anhydro-D-*glycero*-β-D-*gulo*-heptopyranose (III).—In the same way as had been done previously with the 1,6-anhydride,[5] a 0.5-g. sample of the new 1,7-anhydride was dissolved in a 2:1 mixture of acetic anhydride and glacial acid containing 2.5% (v./v.) of concentrated sulfuric acid. After the rotation had become constant at $[\alpha]^{20}_{\mathrm{D}}$ +20.2° (calcd. as heptose hexaacetate) in the course of 5 days at 20°, the reaction mixture was decomposed in the usual manner. The product was fractionally crystallized from chloroform–pentane to yield the known α- and β-anomers of D-*glycero*-D-*gulo*-heptose hexaacetate, which were identified by m.p. and mixed m.p. with authentic materials prepared especially for that purpose.

Hexa-*O*-acetyl-D-*glycero*-α-D-*gulo*-heptopyranose has been reported by Fischer[9] to melt at 156°. Hudson and Yanovsky[10] later prepared the substance by the zinc chloride–acetic anhydride rearrangement of the β-anomer and reported m.p. 164° (uncor.) and $[\alpha]^{20}_{\mathrm{D}}$ +87.0° for the pure substance. One of us has now repeated the zinc chloride procedure[10] and, after five recrystallizations from a mixture of chloroform, ether, and pentane, obtained a product with m.p. 171–172° (cor.) and $[\alpha]^{20}_{\mathrm{D}}$ +94.7° in chloroform (*c* 1.6, *l* 4); these values were unchanged by five additional recrystallizations. Independently, the second author then acetylated 10 g. of D-*glycero*-D-*gulo*-heptose with 150 ml. of acetic anhydride containing 1% sulfuric acid. The rotation, after 3 days, was $[\alpha]^{20}_{\mathrm{D}}$ +22° and corresponded roughly to the presence of 20% of the α-form. The crude product, from chloroform–pentane, weighed 15.6 g. and melted at 116–136°. One recrystallization from a large volume of ether yielded 6.2 g. with m.p. 140–155°. A second recrystallization, from chloroform–ether, produced cauliflower-like aggregates of small needles weighing 2.7 g. and melting at 166–168°. Five additional recrystallizations from chloroform–ether finally yielded 0.5 g. of flattened, shiny, prismatic needles, with m.p. 171–172° (cor.) and $[\alpha]^{20}_{\mathrm{D}}$ +94.8° in chloroform (*c* 2.5; *l* 2) in excellent agreement with the values obtained for the product isolated in the first preparation.

Anal. Calcd. for $C_{19}H_{26}O_{13}$: C, 49.35; H, 5.67; CH_3CO, 55.9. Found: C, 49.41; H, 5.83; CH_3CO, 55.7.

Acknowledgment.—The authors wish to thank Mr. John T. Sipes for preparing the D-*glycero*-D-*gulo*-heptose and Mr. Edward W. Tracy for his aid in the preparation of the anhydrides; Dr. James W. Pratt for his determination of the molecular weights; and Dr. William C. Alford and his associates of the Institutes' microanalytical laboratory for carrying out the microanalyses.

BETHESDA 14, MARYLAND

---

[8] Z. Dische and E. Borenfreund, *J. Biol. Chem.*, **180**, 1297 (1949).

[9] E. Fischer, *Ann.*, **270**, 64 (1892).

[10] C. S. Hudson and E. Yanovsky, THIS JOURNAL, **38**, 1575 (1916).

[CONTRIBUTION FROM THE STARCH AND DEXTROSE SECTION, NORTHERN UTILIZATION RESEARCH BRANCH[1]]

The Polyesterification of 2,4;3,5-Di-*O*-methylene-D-gluconic Acid[2]

BY C. L. MEHLTRETTER AND R. L. MELLIES

RECEIVED AUGUST 25, 1954

The polyesterification of the difunctional substituted sugar acid 2,4;3,5-di-*O*-methylene-D-gluconic acid is reported. Rapid condensation of this substance occurs in dry pyridine solution on addition of an equivalent amount of benzoyl chloride or benzoic anhydride. Other aromatic acid chlorides also were effective for this purpose. The molecular size of polymer fractions isolated, established by elementary analysis and end-carboxyl-group determination, was in the range of 3 to 45 basic monomer units. The behavior of the products in various solvents also was indicative of polymer formation.

Intermolecular condensation of ω-hydroxyaliphatic acids to form polymers has been demonstrated adequately.[3,4] Examples of condensation polymerization of structurally related acids derived from natural sugars, however, is limited to that of 2,3,4-tri-*O*-methyl-L-arabonic acid.[5] It was of interest, therefore, to study the polyesterification of the difunctional substituted sugar acid 2,4;3,5-di-*O*-methylene-D-gluconic acid.[6,7] Efforts to achieve such condensation by heating *in vacuo* by the method of Lycan and Adams[3] gave only decomposition products, while attempts to transesterify the methyl ester caused methylene cyclic acetal rearrangement and produced methyl 2,4;5,6-di-*O*-methylene-D-gluconate.[8] However, in an attempt to benzoylate 2,4;3,5-di-*O*-methylene-D-gluconic acid, it was found that this substance was rapidly polymerized in dry pyridine solution on addition of an equivalent amount of benzoyl chloride or benzoic anhydride.[9] An extension of the study showed that such highly electronegative acid chlorides as *m*- and *p*-nitro-, 3,5-dinitro- and *p*-chlorobenzoyl chloride and *p*-toluenesulfonyl chloride also favored polyesterification. On the other hand, thionyl chloride, acetyl chloride and acetic anhydride were ineffective for this purpose.

Polyesterification of dimethylenegluconic acid presumably involves intermediate formation of a mixed anhydride from dimethylenegluconic acid and acid chloride or anhydride used.[10–12] Both functional groups of dimethylenegluconic acid must be present to effect polymerization. Neither the methyl ester nor the 6-acetyl derivative of dimethylenegluconic acid in pyridine solution gave a precipitate on addition of benzoyl chloride. As

---

[1] One of the Branches of the Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] Presented before the Division of Carbohydrate Chemistry at the 126th National Meeting of the American Chemical Society, New York, N. Y., September, 1954.

[3] W. H. Lycan and R. Adams, THIS JOURNAL, **51**, 625 (1929).

[4] W. H. Carothers and J. W. Hill, *ibid.*, **54**, 1559 (1932).

[5] H. D. K. Drew and W. N. Haworth, *J. Chem. Soc.*, 775 (1927).

[6] C. L. Mehltretter, R. L. Mellies, C. E. Rist and G. E. Hilbert, THIS JOURNAL, **69**, 2130 (1947).

[7] M. Zief and A. Scattergood, *ibid.*, **69**, 2132 (1947).

[8] C. L. Mehltretter, R. L. Mellies and C. E. Rist, *ibid.*, **70**, 1064 (1948).

[9] C. L. Mehltretter, U. S. Patent 2,453,150 (Nov. 9, 1948).

[10] Knoll and Co., German Patent 117,267 (1901) [*Chem. Zentr.*, **72**, I, 347 (1901)].

[11] A. E. Tschitschibabin, *J. Russ. Phys.-Chem. Soc.*, **33**, 404 (1901) [*Chem. Zentr.*, **72**, II, 543 (1901)].

[12] N. O. V. Sonntag, J. R. Trowbridge and I. J. Krems, *J. Am. Oil Chem. Soc.*, **31**, 151 (1954).

was to be expected, presence of an equivalent amount of water in pyridine solution of dimethylenegluconic acid prevented polyesterification with the theoretical amount of benzoyl chloride. Introduction of an additional quantity of benzoyl chloride to this solution, however, gave an immediate precipitate of polymer.

The main fraction of polyester produced with benzoyl chloride was a white amorphous product and was obtained in a yield of 57% of theoretical. It consisted of an average of 36 anhydrodimethylenegluconyl units and its terminal hydroxyl group was benzoylated. Molecular size was calculated from the elementary analysis for carbon and hydrogen and carboxyl content as determined by reaction of product with calcium acetate solution and titration of acetic acid liberated.[13] End-carboxyl-group determination by direct titration could not be used because of water insolubility of the polymer and its sensitivity to alkali. A saponification equivalent of 220 was obtained for the main fraction which corresponds with the neutral equivalent for dimethylenegluconic acid. Upon acidification of a saponified solution, crystalline dimethylenegluconic acid was precipitated and recovered in a yield of 75% of theoretical.

TABLE I

PROPERTIES OF POLYESTER FRACTIONS OF DIMETHYLENEGLUCONIC ACID PRODUCED WITH BENZOYL CHLORIDE

Polyester fraction	Carbon, %	Hydrogen, %	Average monomer units: Calcd. from carbon anal.	Average monomer units: Calcd. from end-carboxyl-group detmn.	Decompn. temp., °C.[a]	Rel. viscosity[b]
1	47.85	4.98	38	36	268	1.67
2	49.82	4.91	3	3	240	1.05

[a] Products softened about 10° before decomposing with effervescence. [b] Determined with 0.5% solution of polymer in formamide.

Further proof of polyester formation was behavior of the product toward various solvents. When treated with aqueous pyridine, gelation occurred. Solution appeared to be effected in hot aqueous ammonia, formamide and formic acid with gradual gelation of polymer on standing. The main fraction was practically insoluble in water, pyridine and usual organic solvents. Fractionation of pyridine filtrate of the main product gave a benzoylated polyester of lower degree of polymerization which dissolved in formic acid but did not gel on standing. Gelation and viscosity studies, carbon and carboxyl analyses and solubility data all indicate the first fraction to be of relatively high molecular weight and the second fraction to be a low polymer (Table I).

Yields and analytical and physical data on the main fraction of polymers formed utilizing benzoic anhydride (A), *m*-nitro- (B), *p*-nitro- (C), 3,5-dinitro- (D), *p*-chlorobenzoyl chloride (E) and *p*-toluenesulfonyl chloride (F) are given in Table II.

Experimental

Polyesterification of 2,4;3,5-Di-*O*-methylene-D-gluconic Acid with Benzoyl Chloride.—A solution of 220.2 g. (1.0 mole) of 2,4;3,5-di-*O*-methylene-D-gluconic acid in 2,500 ml. of boiling dry pyridine was cooled to room temperature and filtered from 5.6 g. of the substituted gluconic acid which had crystallized out. To the 214.6 g. (0.97 mole) of dimethylenegluconic acid in solution was added with stirring 113 ml. (0.97 mole) of benzoyl chloride. The solution became warm and in a short time a gelatinous precipitate formed. The mixture was kept at 10° overnight, protected from atmospheric moisture, and was then decanted through a fritted glass funnel. The residual precipitate was washed several times by mixing with ethyl acetate in a blendor, and filtered through the funnel. The crude product was then washed with hot water until free of chloride ions. The yield of product was 112 g. (57%).

TABLE II

DATA ON DIMETHYLENEGLUCONIC ACID POLYESTERS FORMED WITH BENZOIC ANHYDRIDE AND VARIOUS ACID CHLORIDES

Polyester[a]	Yield, %	Analyses, %: Carbon	Hydrogen	Nitrogen	Chlorine	Sulfur	Average monomer units: Calcd. from carbon anal.	Calcd. from N, Cl or S anal.	Calcd. from end-carboxyl-group detmn.	Decompn. temp., °C.[b]
A[c]	51	47.82	5.02	..	..	..	42	..	..	270
B	60	47.68	4.85	0.34	..	..	13	18	12	280
C	53	47.45	4.87	.35	..	..	..	18	12	280
D	38	47.00	4.68	.86	..	..	13	13	..	280
E	68	47.88	4.87	..	0.84	..	12	18	..	270
F	52	47.60	5.10	..	..	0.32	25	48	45	260

[a] Terminal hydroxyl group of polyester had reacted with polymerizing agent. [b] Products softened about 10° before decomposing with effervescence. [c] Relative viscosity of 0.5% solution of polymer in formamide was 1.74.

Anal. Calcd. for a benzoylated polyester containing 38 anhydrodimethylenegluconyl units: C, 47.85; H, 4.98; neut. equiv., 7804; sapn. equiv., 220. Found: C, 47.85; H, 4.98; neut. equiv., 7757; sapn. equiv., 220.

The pyridine solution which had been decanted from the first polymer fraction was concentrated *in vacuo* to 500 ml. and treated with 800 ml. of ethyl acetate to effect precipitation. After standing overnight at room temperature, the precipitate was filtered and washed free of chloride ions with hot water. The white product was dried at 100° for 8 hours when it weighed 10.0 g.

Anal. Calcd. for a benzoylated polyester containing 3 anhydrodimethylenegluconyl units: C, 49.82; H, 4.98; neut. equiv., 1130. Found: C, 49.82; H, 4.91; neut. equiv., 1140.

Essentially the same procedure was used on a 0.01-mole scale for polymerization of dimethylenegluconic acid with benzoic anhydride and various acid chlorides.

Acknowledgment.—The authors are indebted to C. H. Van Etten and Mrs. Mary Wiele of the Analytical, Physical-Chemical, and Physics Section of this Laboratory for the microanalyses.

PEORIA, ILLINOIS

---

(13) E. C. Yackel and W. O. Kenyon, THIS JOURNAL, **64**, 121 (1942).