sulfonate. Pentaerythritol tetrabenzenesulfonate[19] (1.5 g.), 15 ml. of anhydrous tetrahydrofuran, and 35 ml. of anhydrous trimethylamine were sealed in a Carius bomb tube. The reaction container was immersed in an oil bath and maintained at a temperature of 115° for 5 days during which time the product precipitated. The tube was opened and volatile compounds removed to yield tetrakis(dimethylaminomethyl)methane tetramethobenzenesulfonate. Recrystallization from ethanol–ethyl acetate gave 0.40 g. (20%); m.p. 300° dec. An analytical sample was prepared by repeated recrystallizations from the same solvent.

Anal. Calcd. for $C_{41}H_{64}O_{12}N_4S_4$: C, 52.77; H, 6.91. Found: C, 52.40; H, 7.12.

Other quaternary salts of tetrakis(dimethylaminomethyl)methane have been reported.[20]

Acknowledgment. We are very grateful to the Strasenburgh Laboratories for financial support and for their interest, encouragement, and advice.

SALT LAKE CITY, UTAH

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[19] E. R. Buchman, U. S. Patent 2,703,808 (March 8, 1955).

[20] Evelyn Berlow, R. H. Barth, and J. E. Snow, *The Pentaerythritols*, Reinhold, New York, 1958, pp. 81–82.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Synthesis of 1,5-Di-*O*-benzoyl-3,4-*O*-isopropylidene-D-xylulose from D-Arabitol[1,2]

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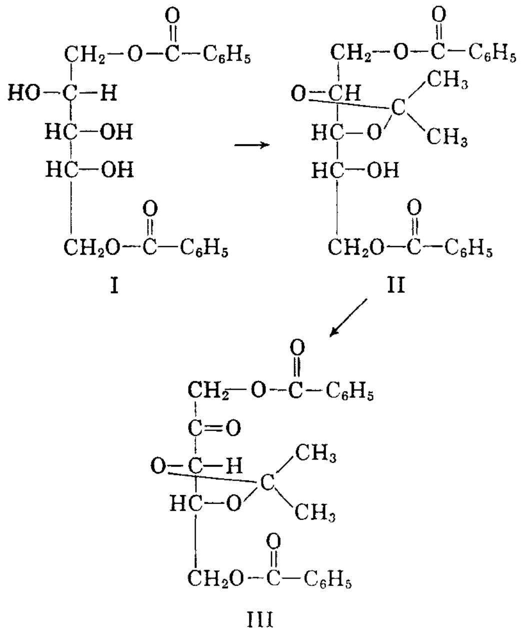
The pentitol derivative, 1,5-di-*O*-benzoyl-2,3-*O*-isopropylidene-D-arabitol, has been prepared and the position of the acetone group established. Oxidation with chromium trioxide gave 1,5-di-*O*-benzoyl-3,4-*O*-isopropylidene-D-xylulose. This confirms the general applicability of this oxidative route to the synthesis of derivatives of the rare ketopentoses.

Although D-xylulose-5-phosphate was shown in 1956 to be an intermediate in the carbohydrate metabolism of both plants and animals,[4] there exists as yet no chemical method for its synthesis. In exploratory studies directed toward this end, we have prepared 1,5-di-*O*-benzoyl-3,4-*O*-isopropylidene-D-xylulose (III) by a route which may be applicable to other xylulose esters. This general method[5] was previously employed in the synthesis of a derivative of another rare ketopentose, D-ribulose.



I II III

In the work herein described, D-arabitol, a readily available starting material, was benzoylated using a modification of the published method.[6] The 1,5-di-*O*-benzoyl-D-arabitol (I) so obtained was acetonated giving 1,5-di-*O*-benzoyl-2,3-*O*-isopropylidene-D-arabitol (II). The position of the acetone group in II was established as C-2–C-3 by comparing the tribenzoate, prepared by benzoylation and subsequent deacetonation, with the tribenzoate prepared by debenzalation of the known 1,4,5-tri-*O*-benzoyl-2,3-*O*-benzylidene-D-arabitol.[6] The two tribenzoates were identical with respect to optical rotation and infrared spectra. Interestingly, the tribenzoate derived from the benzylidene tribenzoate melted at 104° while that derived from the isopropylidene tribenzoate melted at 93–94°. However, infrared spectra and cross-seeding established that the two tribenzoates were dimorphic. The structure assigned to the isopropylidene tribenzoate is consistent with the finding that one mole of periodate was consumed by the acetone compound produced on saponification. Compound II was oxidized using chromium

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[1] This report is based on a portion of the thesis submitted by David H. Rammler to the Graduate School of the University of California, Berkeley, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] Present address: Institute for Enzyme Research, University of Wisconsin, Madison, Wis.

[4] P. K. Stumpf and B. L. Horecker, *J. Biol. Chem.*, **218**, 753 (1956).

[5] D. H. Rammler and D. L. MacDonald, *Arch. Biochem. Biophys.*, **78**, 359 (1958).

[6] W. T. Haskins, R. M. Hann and C. S. Hudson, *J. Am. Chem. Soc.*, **65**, 1663 (1943).

trioxide in benzene–acetic acid solution[7] to give crystalline 1,5-di-*O*-benzoyl-3,4-*O*-isopropylidene-D-xylulose (III) in 50% yield. The infrared spectrum of III showed a carbonyl band at 1720 cm.$^{-1}$, aromatic absorption in the region of 1600 cm.$^{-1}$ and a methyl doublet at 1375 cm.$^{-1}$ No hydroxyl absorption was found in the region from 4000 cm.$^{-1}$ to 3000 cm.$^{-1}$ Final proof of the structure was achieved by reduction of the carbonyl group and identification of the pentitols, obtained after removal of blocking groups, as xylitol and D-arabitol.

EXPERIMENTAL[8]

1,5-Di-O-benzoyl-D-arabitol (I). This compound was prepared using a modification of the method described by Haskins *et al.*[6] A solution of 39 ml. (0.334 mole) of freshly distilled benzoyl chloride in 100 ml. of anhydrous pyridine was added with rapid stirring to a solution of 25 g. (0.164 mole) of D-arabitol in 350 ml. of anhydrous pyridine. The time for the total addition was 70 min. and the rate of addition was such that the reaction temperature never exceeded 35°. After standing at room temperature for 18 hr. the reaction mixture was poured into 500 ml. of rapidly stirred ice water. The gummy precipitate which formed was removed, washed with water, and then dissolved in 300 ml. of hot absolute ethanol. Upon cooling, this solution deposited 41 g. (69%) of the dibenzoate which melted at 139–140°. After recrystallization from ethanol, it melted at 140–141°; $[\alpha]_D^{23}$ +7.4° (*c*, 0.81 in pyridine). Previously reported values[6]: m.p. 131–132° and $[\alpha]_D^{20}$ +8.4° (*c*, 0.81 in pyridine).[9]

Anal. Calcd. for $C_{19}H_{20}O_7$ (360.35): C, 63.32; H, 5.59; C_6H_5CO, 58.3. Found: C, 63.17; H, 5.26; C_6H_5CO, 57.1.

1,5-Di-O-benzoyl-2,3-O-isopropylidene-D-arabitol (II). A mixture of 10 g. (0.028 mole) of 1,5-di-*O*-benzoyl-D-arabitol, 60 g. of anhydrous copper sulfate, 1 l. of dry acetone, and 1 ml. of concd. sulfuric acid was shaken for 18 hr. at room temperature. After removal of copper sulfate by filtration the sulfuric acid was neutralized with ammonia gas. The precipitated ammonium sulfate was removed by filtration and the filtrate was concentrated *in vacuo* yielding 11.4 g. of a light oil. A solution in 10 ml. of hot methanol, upon cooling, deposited 7 g. of crystalline 1,5-di-*O*-benzoyl-2,3-*O*-isopropylidene-D-arabitol. A second crop of crystals (2 g.) was obtained from the mother liquors giving a total yield of 9 g. (83.5%), m.p. 79–80°, $[\alpha]_D^{23}$ +20.8° (*c*, 1.36 in dry methanol).

Anal. Calcd. for $C_{22}H_{24}O_7$ (400.41): C, 65.99; H, 6.04. Found: C, 65.61; H, 6.05.

1,5-Di-O-benzoyl-3,4-O-isopropylidene-D-xylulose (III). To a solution of 2.0 g. (0.005 mole) of 1,5-di-*O*-benzoyl-2,3-*O*-isopropylidene-D-arabitol in 20 ml. of anhydrous benzene was added a hot solution of 0.51 g. (0.005 mole) of chromium trioxide in 45 ml. of glacial acetic acid and 0.5 ml. of water. The reaction mixture was warmed on a steam bath for 5 min. and then concentrated *in vacuo* at 50°. The colored sirup which remained was dissolved in 50 ml. of chloroform and extracted with cold 1*N* potassium carbonate until no further color could be removed from the chloroform layer. It was then washed with water and dried over sodium sulfate. Removal of chloroform *in vacuo* left 1.9 g. of sirup. This was dissolved in methanol and upon slow evaporation of the solvent, 1.1 g. (56%) of a crystalline material deposited from solution, m.p. 76–77°. Upon recrystallization from benzene-heptane solution, the ketose derivative gave an analytically pure sample, m.p. 77.8–78°; $[\alpha]_D^{23}$ −21.9° (*c*, 1.02 in chloroform). The infrared spectrum of this compound indicated the presence of aromatic, carbonyl and methyl groups, but no hydroxyl absorption could be detected.

Anal. Calcd. for $C_{22}H_{22}O_7$ (398.40): C, 66.32; H, 5.57. Found: C, 66.67; H, 5.84.

Proof of structure of 1,5-di-O-benzoyl-3,4-O-isopropylidene-D-xylulose. A sample (0.2 g.) of 1,5-di-*O*-benzoyl-3,4-*O*-isopropylidene-D-xylulose was dissolved in 50 ml. of dioxane and to this was added 0.2 g. of sodium borohydride dissolved in 1 ml. of water. After 3 hr. at room temperature, the solution was concentrated at reduced pressure, the residue extracted with chloroform, and the chloroform removed *in vacuo*. The resulting sirup was saponified with a small amount of potassium hydroxide, following which the solution was made acidic with glacial acetic acid and hydrolyzed for 2 hr. on the steam bath. The hydrolysate was then passed through a column containing Dowex-1 (OH^- form) and Dowex-50 (H^+ form). The effluent was concentrated to dryness *in vacuo*, and the residue, dissolved in a small amount of water, was subjected to paper ionophoresis in a water cooled apparatus.[10] The sample, together with authentic pentitols and a caffeine marker, was run on Whatman 3 MM paper in saturated aqueous boric acid previously adjusted to *p*H 5.9 with sodium hydroxide solution. Ionophoresis was continued for 2 hr. at 2400 volts and a current of 36 ma. As measured from the caffeine marker, authentic xylitol, D-arabitol, and ribitol moved 17.2, 15.3, and 9.0 cm., respectively, while the components from the ketose derivative moved 17.4 and 15.3 cm. The polyols were detected using the periodate benzidine spray.[11]

1,4,5-Tri-O-benzoyl-2,3,-O-isopropylidene-D-arabitol. To a cold solution of 1.5 g. (3.7 mmoles) of 1,5-di-*O*-benzoyl-2,3-*O*-isopropylidene-D-arabitol in 15 ml. of anhydrous pyridine was added 1.5 ml. (0.103 mole) of freshly distilled benzoyl chloride and a drop of 60% perchloric acid. After 18 hr. at room temperature, the excess benzoyl chloride was destroyed with a small amount of ice and the reaction mixture was dissolved in 50 ml. of chloroform. The chloroform solution was washed successively with cold 1*N* sulfuric acid, cold 1*N* potassium carbonate, and finally with water. After drying over sodium sulfate, chloroform was removed *in vacuo*, yielding 2 g. of an oil which crystallized from ether-heptane solution (1.6 g. 86%). The 1,4,5-tri-*O*-benzoyl-2,3-*O*-isopropylidene-D-arabitol so obtained melted at 77–78°; $[\alpha]_D^{23}$ +15.7° (c, 1.2 in chloroform).

Anal. Calcd. for $C_{29}H_{28}O_8$ (504.51): C, 69.04; H, 5.59. Found: C, 69.36; H, 5.93.

1,5-Di-O-benzoyl-2,3-O-benzylidene-D-arabitol. This compound was prepared according to the published method.[6] The m.p., 107.8–108°, and $[\alpha]_D^{23}$, +11.1° (*c*, 0.86), are in agreement with the values (108–109° and +12.6°) recorded.

Anal. Calcd. for $C_{26}H_{24}O_7$ (488.45): C, 69.63; H, 5.39. Found: C, 69.82; H, 5.55.

1,4,5-Tri-O-benzoyl-2,3-O-benzylidene-D-arabitol. Preparation according to Haskins *et al.*[6] with a single modification, namely, the addition of a drop of 60% perchloric acid

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(7) K. Heyns and W. Stein, *Ann.*, 558, 194 (1947).

(8) All melting points were taken with total immersion thermometers. The analyses reported here were performed by the Microchemical Laboratory, Department of Chemistry, University of California, Berkeley. Periodate consumption was determined by a spectrophotometric method (G. V. Marinetti and G. Rouser, *J. Am. Chem. Soc.*, 77, 5345 (1955)) and optical rotations were taken using a Rudolph recording polarimeter Model 202, S-80.

(9) A sample of the dibenzoate prepared by Haskins *et al.*[6] was obtained as a gift from the Hudson Collection, National Institutes of Health, Bethesda, for comparison with our sample. They were identical with respect to melting point and infrared spectrum. It thus appears that the previously reported melting point was in error by 10°.

(10) A. M. Crestfield and F. W. Allen, *Anal. Chem.*, 27, 422 (1955).

(11) H. Viscontini, D. Hoch, and P. Karrer, *Helv. Chim. Acta*, 38, 642 (1955).

to the benzoylation mixture, afforded the fully blocked compound in 96% yield. The compound melted at 101–103° as reported.[3]

*1,4,5-Tri-O-benzoyl-*D*-arabitol.* A solution of 1 g. of 1,4,5-tri-*O*-benzoyl-2,3-*O*-isopropylidene-D-arabitol in 80% acetic acid was heated on the steam bath until a constant optical rotation was obtained. Acetic acid and water were removed *in vacuo* yielding 0.6 g. (65%) of a crystalline material which could be recrystallized from ether-heptane; m.p. 93–94°; $[\alpha]_D^{23}$ −7.6° (*c*, 0.88 in dry methanol).

Anal. Calcd. for $C_{26}H_{24}O_8$ (464.45): C, 67.23; H, 5.21; C_6H_5CO, 67.5. Found: C, 67.58; H, 5.68; C_6H_5CO, 66.3.

*1,4,5-Tri-O-benzoyl-*D*-arabitol* (*allotropic form*). A solution of 1 g. of 1,4,5-tri-*O*-benzoyl-2,3-*O*-benzylidene-D-arabitol in 80% acetic acid was heated on the steam bath until a constant optical rotation was obtained. The acetic acid and water were removed *in vacuo* yielding 0.62 g. of a crystalline material which melted at 104° after recrystallization from ether–petroleum ether (b.p. 60–70°); $[\alpha]_D^{23}$ −7.3° (*c*, 0.96 in dry methanol). If an ether–petroleum ether solution of this compound was seeded with the tribenzoate melting at 93° the crystalline material obtained melted at 93–94°. If the conditions were reversed, the compound which crystallized melted at 104°. The infrared spectra of the two compounds differ when taken in potassium bromide, but are identical in chloroform solution.

Anal. Calcd. for $C_{26}H_{24}O_8$ (464.45): C, 67.23; H, 5.21. Found: C, 67.58; H, 5.28.

*2,3-O-Isopropylidene-*D*-arabitol.* To a sample (1 g.) of 1,5-di-*O*-benzoyl-2,3-*O*-isopropylidene-D-arabitol dissolved in 50 ml. of dry methanol was added 0.5 ml. of 0.8*N* barium methoxide. After 18 hr. at room temperature the methanol was removed *in vacuo* and the amorphous residue was dissolved in water and chromatographed, ascendingly, on large sheets of Whatman 3MM paper. The upper phase of a 4:1:5 (v./v.) mixture of *n*-butyl alcohol, ethanol, and water was the developing solvent. The sugar, which was chromatographed as a single component, was eluted with water and concentrated to dryness *in vacuo*. After 3 days of drying under high vacuum, a crystalline substance was obtained which consumed 0.94 mole of periodate per mole of sugar when oxidized in ammonium acetate buffer *p*H 5.8. The crystalline material melted near room temperature and was very hygroscopic.

Anal. Calcd. for $C_8H_{16}O_5$ (192.21): C, 49.99; H, 8.39. Found: C, 48.8; H, 8.5.

BERKELEY 4, CALIF.

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

The Composition of Pyrodextrins. III. Thermal Polymerization of Levoglucosan[1]

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The di- and trisaccharide portions of the thermal polymers of 1,6-anhydro-β-D-glucopyranose were isolated as acetates by carbon and silicate chromatography and the peracetates of 4-*O*-α-D-glucopyranosyl-1,6-anhydro-β-D-glucopyranose (1,6-anhydromaltose), 4-*O*-β-D-glucopyranosyl-1,6-anhydro-β-D-glucopyranose (1,6-anhydrocellobiose), 2-*O*-α-D-glucopyranosyl-1,6-anhydro-β-D-glucopyranose (1,6-anhydrokojibiose), 2-*O*-β-D-glucopyranosyl-1,6-anhydro-β-D-glucopyranose (1,6-anhydrosophorose), and three peracetylated anhydrotrisaccharides were identified therein. All save the maltose and cellobiose derivatives are hitherto undescribed.

The thermal polymerization of 1,6-anhydro-β-D-glucopyranose was studied[4] by Pictet, Pringsheim and Schmalz, Irvine, and Oldham, and more recently by da Silva Carvalho, Prins, and Schuerch.[5] Wolfrom, Thompson, and Ward[1] studied the thermal polymerization of 1,6-anhydro-β-D-glucopyranose and its possible relation to reactions taking place during the roasting of starch to produce pyrodextrins. They isolated gentiobiose, isomaltose, maltose, cellobiose, sophorose, and 1,6-anhydro-β-D-glucopyranose as their acetates from the fragments present in the partial hydrolyzate of the ethanol-insoluble portion of the thermal polymer. The isolation of these hydrolytic fragments indicates the presence of 6-*O*-α-(and β)-D-, 4-*O*-α-(and β)-D-, 2-*O*-β-D-linkages, and 1,6-anhydro-β-D-glucopyranose end groups in the polymer.

We wish to describe herein a study of the ethanol-soluble portion of the thermal polymer of 1,6-anhydro-β-D-glucopyranose, which contains low molecular weight carbohydrates with 1,6-anhydro-β-D-glucopyranose end groups. These substances were isolated by carbon column elution chromatography and further refractionation of the acetylated fractions by silicate column chromatography to give the individual sugar acetates. Four anhydrodisaccharides, 4-*O*-α-D- and 4-*O*-β-D-, 2-*O*-α-D-, and 2-*O*-β-D-glucopyranosyl-1,6-anhydro-β-D-glucopyranose were isolated as their hexaacetates, the latter pair of substances for the first time. 4 - *O* - (2,3,4,6 - Tetra - *O* - acetyl - β - D - glucopyranosyl) - 2, 3 - di - *O* - acetyl - 1,6 - anhydro-β-D-glucopyranose (1,6-anhydrocellobiose hexaacetate) was obtained in two crystalline forms: m.p.

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[1] Previous communication in this series: M. L. Wolfrom, A. Thompson, and R. B. Ward, *J. Am. Chem. Soc.*, 81, 4623 (1959). Preliminary communication: *Abstracts Papers Am. Chem. Soc.*, 138, 5D (1960).

[2] Postdoctoral Fellows of the Corn Industries Research Foundation (O. S. U. Proj. 11168-5241).

[3] R. H. Moore gratefully acknowledges a travel grant from The Wellcome Trust, 52 Queen Anne St., London W 1.

[4] A. Pictet, *Helv. Chim. Acta*, 1, 226 (1918); H. Pringsheim and K. Schmalz, *Ber.*, 55, 3001 (1922); J. C. Irvine and J. W. H. Oldham, *J. Chem. Soc.*, 127, 2903 (1925).

[5] J. da Silva Carvalho, W. Prins, and C. Schuerch, *J. Am. Chem. Soc.*, 81, 4054 (1959).