sulfuric acid, aqueous sodium bicarbonate and water. Moisture was removed with sodium sulfate and the solution concentrated; dropwise addition of pentane yielded a fine powder (3.60 g., 99%) which was reprecipitated from diisopropyl ether by the addition of pentane and dried *in vacuo* (0.1 mm.) at 80° for 5 hr. Attempts to obtain this amorphous product in crystalline form failed. After chromatography on alumina it showed $[\alpha]^{20}D$ −24.3° in glacial acetic acid (c 4.85) and $[\alpha]^{20}D$ −28.3° in ethanol (c 4.26).

Anal. Calcd. for $C_{31}H_{42}O_4(O_2C_2H_3)_7COOH$: neut. equiv., 117.1. Found: neut. equiv., 116.7.

Cleavage of Steviolbioside Heptaacetate with Hydrogen Bromide in Glacial Acetic Acid.—A solution of 65 mg. of the heptaacetate in 1.5 ml. of glacial acetic acid was mixed with 0.13 ml. of a solution containing ca. 30% by weight of hydrogen bromide in glacial acetic acid. Polarimetric observations showed a minimum rotation at 5 minutes followed by a slow dextromutarotation to a positive value. After 36 hr. crystallization began and, after 50 hr., the crystals were removed. Recrystallized from dichloromethane-ether and dried *in vacuo* at 90°, the material (15 mg., 31%) melted with decomposition at 195-197° and rot::.ed $[\alpha]^{20}D$ +94.2° in chloroform (c 0.43). Freudenberg and his coworkers[6] have reported m.p. 196° and $[\alpha]^{20}D$ +95.6° (CHCl₃) for α-acetobromosophorose.

In another experiment wherein a solution containing 1.100

g. of steviolbioside heptaacetate, 6.5 ml. of glacial acetic acid, 2.2 ml. of AcOH–HBr and 0.8 ml. of acetic anhydride was held at 20° for 3 days and then chilled, α-acetobromosophorose was obtained in 8% yield. The filtrate was diluted with ether, washed with aqueous sodium bicarbonate and extracted with aqueous sodium hydroxide. After acidification to pH 4 the alkaline extract was immediately extracted with ether which, in turn, was washed with sodium bicarbonate, water and then dried over sodium sulfate. Concentration and the addition of pentane gave 24 mg. of prisms which, recrystallized from ether–pentane, melted at 231-232° and did not depress the melting point of keto-isostevic acid (isosteviol).

β-Sophorose Octaacetate.—A mixture of 60 mg. of α-acetobromosophorose, 20 mg. of silver acetate and 0.5 ml. of glacial acetic acid was heated at 100° for 1 hr. After cooling and diluting with ethyl acetate, the silver bromide was filtered off and the filtrate concentrated *in vacuo* to a thick sirup. Upon addition of methanol crystallization took place. Recrystallized from dichloromethane–pentane, the product melted at 192° either alone or in admixture with a sample of authentic β-sophorose octaacetate.

Acknowledgment.—We wish to express our indebtedness to Professor Karl Freudenberg for his gift of authentic sophorose derivatives.

Bethesda 14, Maryland

Evidence that the Supposed 3,5-Di-*O*-benzoyl-1,2-*O*-(1-hydroxybenzylidene)-α-D-ribose is Actually 1,3,5-Tri-*O*-benzoyl-α-D-ribose

By Robert K. Ness and Hewitt G. Fletcher, Jr.

The more dextrorotatory of the two D-ribofuranose tribenzoates obtained in the acidic or neutral hydrolysis of tri-*O*-benzoyl-D-ribofuranosyl bromide has been shown to be 1,3,5-tri-*O*-benzoyl-α-D-ribose. Some implications arising from this conclusion particularly the probable non-existence of stable cyclic orthoacid structures in the carbohydrate field, are discussed.

In earlier papers[1,2] we have described the hydrolysis of amorphous 2,3,5-tri-*O*-benzoyl-D-ribosyl bromide as giving rise to two crystalline ribofuranose tribenzoates, one melting at 142–143°[3] and rotating +85.3°[3] in chloroform and the other melting at ca. 111–112° and rotating +68.8→ 66.2° (CHCl₃, 2 days). The structure of the latter ester was unequivocally proved by a synthesis involving the hydrogenolysis of benzyl β-D-ribofuranoside tribenzoate. The former, more dextrorotatory substance[4] proved to be stable in acidic solution but was rapidly converted by mild alkali into 2,3,5-tri-*O*-benzoyl-β-D-ribose. These properties plainly indicated that the substance was not simply an anomeric form of 2,3,5-tri-*O*-benzoyl-D-ribose but strongly suggested the possibility of a cyclic orthoacid structure, a 2-hydroxy-1,3-dioxolane. Such structures, while rarely mentioned in the literature, have nevertheless been postulated

in certain cases.[5,6] The most firmly established of these at the time of our earlier work appeared to be the D-talose monobenzoate which Pigman and Isbell[7] had obtained in 1937 through the perbenzoic acid oxidation of D-galactal. Like our ribose tribenzoate, this D-talose monobenzoate was relatively stable in dilute acid solution but mutarotated rapidly in the presence of very dilute alkali. In order to throw light upon the structure of our D-ribofuranose tribenzoate we attempted the deliberate synthesis of 3,5-di-*O*-benzoyl-1,2-*O*-(1-hydroxybenzylidene)-α-D-ribofuranose (I). To this
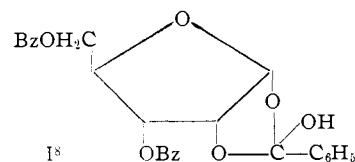
end, tri-*O*-benzoyl-D-ribofuranosyl bromide was condensed with benzyl alcohol in the presence of

(1) R. K. Ness, H. W. Diehl and H. G. Fletcher, Jr., This Journal, **76**, 763 (1954).

(2) R. K. Ness and H. G. Fletcher, Jr., *ibid.*, **76**, 1663 (1954).

(3) Melting points are corrected. Unless otherwise specified rotations are specific rotations for the D line of sodium at 20°, concentration being expressed in g. per 100 ml. of solution.

(4) F. Weygand and F. Wirth [*Chem. Ber.*, **85**, 1000 (1952)] had previously and independently obtained this substance through the acidic hydrolysis of a partially benzoylated adenosine and designated it as 2,3,5-tri-*O*-benzoyl-D-ribose.

(5) N. K. Richtmyer and C. S. Hudson, This Journal, **58**, 2534 (1936).

(6) *Cf.* E. Pacsu, *Advances in Carbohydrate Chem.*, **1**, 77 (1945), for a review.

(7) W. W. Pigman and H. S. Isbell, *J. Research Natl. Bur. Standards*, **19**, 189 (1937).

(8) The ring-attached hydrogen atoms in this and succeeding formulas have been omitted for greater clarity.

quinoline to give a crude amorphous 3,5-di-O-benzoyl-1,2-O-(1-benzyloxybenzylidene)-α-d-ribofuranose, which was then hydrogenolyzed in the presence of palladium. The product proved to be a mixture of the two isomeric ribofuranose tribenzoates, a fact which was interpreted as supporting the cyclic orthoacid structure I.

The unusual nature of this structure prompted us to attempt the synthesis of analogs. For this purpose crystalline 1,2-O-(1-benzyloxybenzylidene)-α-d-ribopyranose was synthesized in crystalline form[9] and treated with hydrogen in the presence of palladium; no well-defined product was obtained. A parallel attempt to hydrogenolyze 1,4,6-tri-O-benzoyl-2,3-O-(1-benzyloxybenzylidene) α-d-fructofuranose, a substance first prepared by Helferich and his co-workers,[10,11] similarly failed.[12]

At the time of the above researches a separate project was being pursued in this Laboratory with the object of elucidating the structure of the intensely sweet, natural product stevioside.[13] In the course of this research, methanolic ammonia at 0° was shown to cause the migration of a mesitoyl group from the α-C_1 position in d-glucopyranose to C_2.[14] This somewhat surprising migration of a sterically hindered acyl group from C_1 to a cis-C_2 position strongly suggested that non-hindered acyl groups would be even more prone to migrate under such circumstances.[15] As pointed out at that time,[14] the behavior of the known, supposed cyclic orthoacids could equally well be rationalized on the assumption that they were 1-acyl sugars having a hydroxyl group free at C_2 and cis to the C_1-acyl.[16] 1,3,5-Tri-O-benzoyl-α-d-ribose (IV), for instance, would be stable in acid or neutral solution but should rearrange to 2,3,5-tri-O-benzoyl-d-ribose (II) under mildly alkaline conditions. At this juncture Isbell and his co-workers demonstrated[17] that the "d-talose orthobenzoic acid" is actually a normal d-talose monobenzoate since it shows strong carbonyl absorption in the 5.77 μ region. With this background we have now re-examined the structure of the more dextrorotatory ribofuranose tribenzoate and obtained the following evidence.

1. In the earlier work[2] it was pointed out that 2,3,5-tri-O-benzoyl-d-ribose with its three ester carbonyls ought to show an absorption peak

about 50% greater than an isomeric structure such as I with only two ester carbonyls. Actually, the more dextrorotatory ribofuranose tribenzoate was found to have a molecular extinction coefficient at 230 mμ of 38,600 while 2,3,5-tri-O-benzoyl-d-ribose gave a value of 42,000, absolute ethanol being the solvent in both cases. These results being equivocal, the apparent molecular extinction coefficients in chloroform of 1,2,3,5-tetra-O-benzoyl-β-d-ribose, 2,3,5-tri-O-benzoyl-β-d-ribose and the ribofuranose tribenzoate in question, have now been determined under strictly comparable conditions in the 5.78–5.79 μ range. Values of 1633, 1229 and 1247, respectively, have been obtained; these stand in the ratio of 4.00:3.01:3.05, indicating strongly that all the benzoyl groups present in the more dextrorotatory ribofuranose tribenzoate are normal.

2. In the earlier paper[2] we mentioned that acetylation and benzoylation of the ribofuranose tribenzoate in pyridine solution provided dextrorotatory products from which no crystalline material could be obtained. These amorphous products have now been obtained in chromatographically homogeneous form and the acetate has been investigated further.[18] Treatment with titanium tetrachloride followed by condensation with silver acetate gave the known[2] 1,2-di-O-acetyl-3,5-di-O-benzoyl-β-d-ribose (VII).[19] While this fact cannot be construed as strong evidence for either form (I or IV), the sequence IV → V → VI → VII seems more acceptable than any which can be envisioned as arising from I.

3. Mesylation of the more dextrorotatory ribofuranose tribenzoate provided a crystalline, dextrorotatory mesylate which was treated with an excess of sodium methoxide. The product was found to be methyl α-d-arabinopyranoside (VIII), identification being confirmed through the tribenzoate. Isolation of a d-arabinose derivative from a d-ribose derivative requires inversion at C_2 and implies that the mesyl group was attached at C_2 as in formula III; hence the more dextrorotatory ribofuranose tribenzoate is 1,3,5-tri-O-benzoyl-d-ribose (IV). The dextrorotation ([α]^{20}d +85.3° in CHCl$_3$) and ease of migration of the 1-benzoyl group to C_2 speak for the α-configuration. The mechanism of conversion of III to VIII may be rationalized in the manner shown.

4. In the earlier work[2] hydrogen bromide was shown to cleave one benzoyl group from the more dextrorotatory ribofuranose tribenzoate and the crystalline product was demonstrated to be 3,5-di-O-benzoyl-d-ribofuranosyl bromide. Subsequently, we have found that the corresponding chloride, IX, also a readily crystalline material, is somewhat more stable and, therefore, more convenient to work with experimentally. If it be assumed that the structures of the bromide and the chloride are

(9) H. G. Fletcher, Jr., and R. K. Ness, This Journal, **77**, 5337 (1955).

(10) B. Helferich and L. Bottenbruch, Chem. Ber., **86**, 651 (1953).

(11) B. Helferich and W. Schulte-Hürmann, ibid., **87**, 977 (1954).

(12) R. K. Ness and H. G. Fletcher, Jr., This Journal, **78**, 1001 (1956).

(13) (a) H. B. Wood, Jr., R. Allerton, H. W. Diehl and H. G. Fletcher, Jr., J. Org. Chem., **20**, 875 (1955); (b) E. Mosettig and W. R. Nes, ibid., **20**, 884 (1956); (c) H. B. Wood, Jr., and H. G. Fletcher, Jr., This Journal, **78**, 207 (1956).

(14) H. B. Wood, Jr., and H. G. Fletcher, Jr., ibid., **78**, 2849 (1956).

(15) On the basis of wholly different evidence, R. U. Lemieux and C. Brice [Can. J. Chem., **33**, 109 (1955)] have predicted that 1,3,4,6-tetra-O-acetyl-α-d-glucose ought to rearrange readily to 2,3,4,6-tetra-O-acetyl-α-d-glucose.

(16) It is not excluded, of course, that hydroxyl groups elsewhere in the molecule may be in a favorable position to participate in the wandering of a C_1-acyl group.

(17) H. S. Isbell, J. E. Stewart, H. L. Frush, J. D. Moyer and F. A. Smith, J. Research Nat. Bur. Standards, in press.

(18) Weygand and Wirth (ref. 4) reported the acetylation of the ribofuranose tribenzoate in pyridine solution to give 1-O-acetyl-2,3,5-tri-O-benzoyl-β-d-ribose; apparently rearrangement had taken place prior to acetylation under their (unspecified) conditions.

(19) While the anomeric configuration of this substance was left unspecified in the earlier paper (ref. 2) it seems highly likely that it possesses the β-configuration since its rotation ([α]^{20}d −3° in CHCl$_3$) is near to that of closely related β-d-ribose derivatives and the action of silver acetate on acylhalogenosugars normally leads to the C_1-C_2 trans configuration.
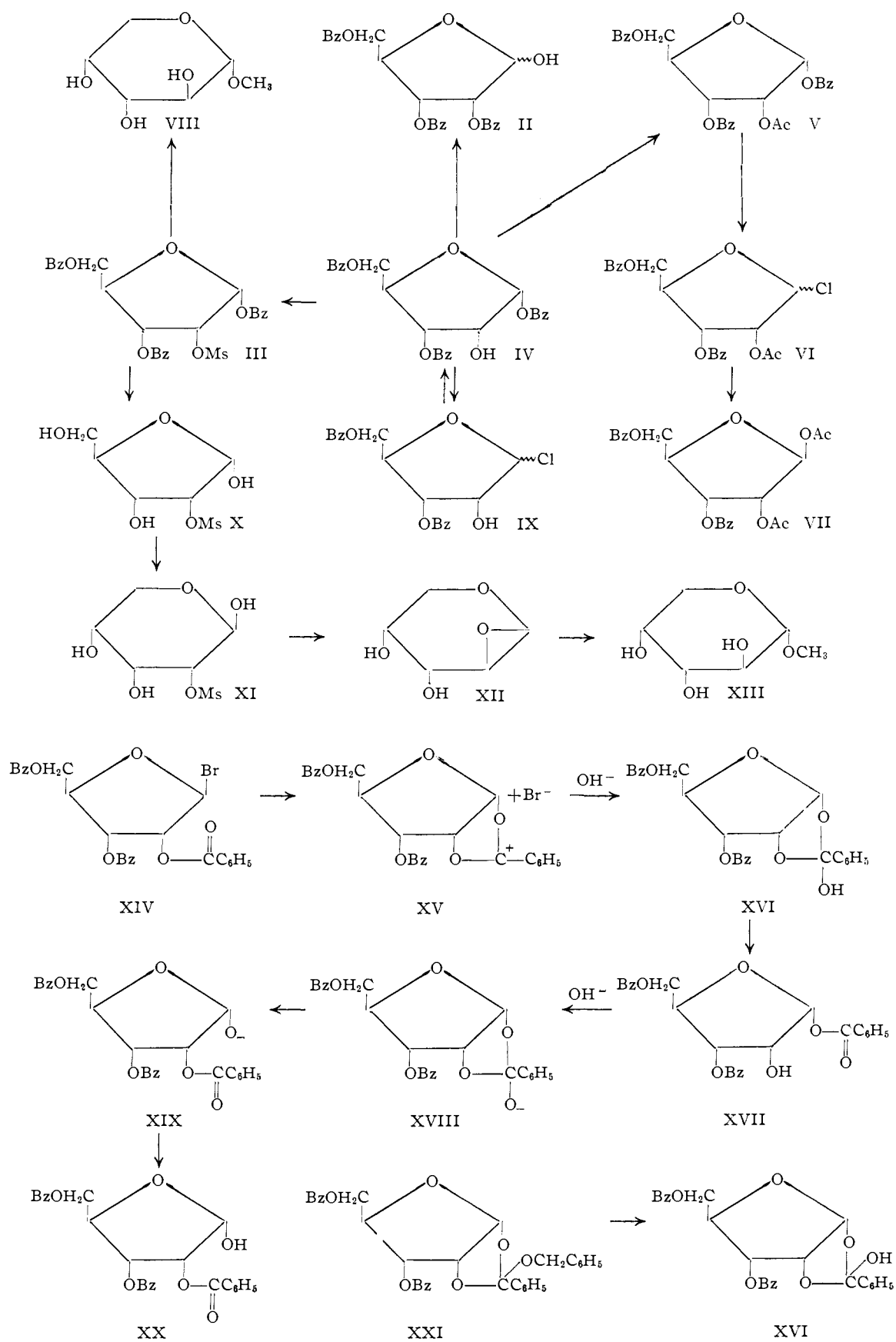
similar[20] we would predict that condensation of the chloride with silver benzoate would give one of the anomeric 1,3,5-tri-O-benzoyl-d-riboses. The α-anomer was actually obtained in this manner from the chloride in 35% yield.

Discussion

The migration of the C_2-benzoyl of tri-O-benzoyl-d-ribofuranosyl bromide to C_1 on acidic or neutral hydrolysis and subsequent migration back to C_2 under alkaline conditions is an unusual and interesting phenomenon. One rationalization of these rearrangements is represented by XIV → XVII → XX.[21]

It should be noted that the cyclic orthoacid structure XVI is postulated as an unstable intermediate in this sequence. This view is supported by the fact, found earlier, that a deliberate attempt to synthesize this structure through the hydrogenolysis of 3,5-di-O-benzoyl-1,2-O-(1-benzyloxybenzylidene)-α-d-ribose (XXI) actually gave what we now have shown to be 1,3,5-tri-O-benzoyl-α-d-ribose.

It seems highly probable that other sequences of reactions analogous to XIV → XVII have been encountered. In our own work[2] the hydrolysis of 2-O-acetyl-3,5-di-O-benzoyl-d-ribosyl bromide (X–XII) was found to give a crystalline di-O-benzoyl-

XXII → XXIII
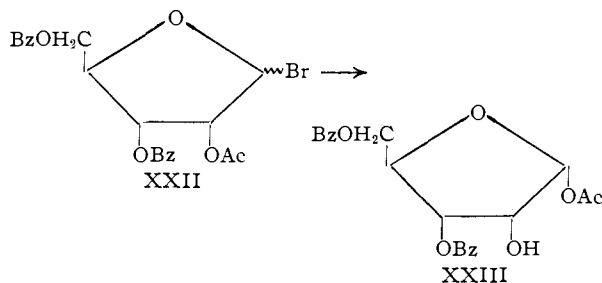
d-ribofuranose monoacetate which was stable in dilute acid solution but mutarotated in dilute pyri-

(20) These two highly reactive halides possess some unusual properties and are currently under investigation in this Laboratory.

(21) Tri-O-benzoyl-d-ribofuranosyl bromide has been obtained only in the form of a sirup and may well be a mixture of anomers. It is formulated as the β-anomer here, however, since this form only would be expected to hydrolyze through participation of the benzoyl group at C_2. In an earlier paper [H. G. Fletcher, Jr. and R. K. Ness, This Journal, **76**, 760 (1954), reference 7] we noted that, while the hydrolysis of tri-O-benzoyl-α-d-ribopyranosyl bromide in aqueous dioxane leads to a final rotation corresponding closely to the equilibrium rotation of 2,3,4-tri-O-benzoyl-d-ribose, its (*trans*) anomer gives a more dextrorotatory final rotation. A similar discrepancy was noted when aqueous acetone was used as a solvent. While preliminary observations carried out at that time seemed to indicate that the final rotation obtained on the hydrolysis of the β-halides was unaffected by the addition of pyridine, it now seems possible that $C_2 \to C_1$ migration of benzoyl had taken place in a small proportion of the material. The 1,3,4-tri-O-benzoyl-α-d-ribose thus formed might, as a pyranose

Tri-O-benzoyl-β-d-ribopyranosyl bromide   1,3,4-Tri-O-benzoyl-α-d-ribose
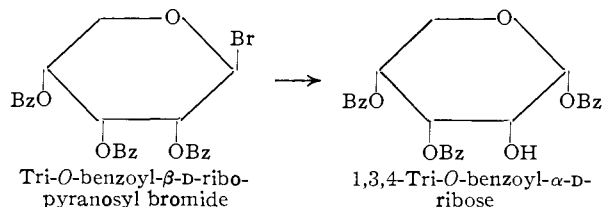
derivative, be more stable to $C_1 \to C_2$ acyl migration than its furanose analog which is the subject of the present paper.

dine. While this substance was earlier[2] assumed to have a 1,2-O-(1-hydroxyethylidene)-structure, the present work indicates that it is most probably 1-O-acetyl-3,5-di-O-benzoyl-α-d-ribose (XXIII).

Another example is evident in the work of Richtmyer and Hudson[5] who obtained three celtrobiose heptaacetates from the hydrolysis of acetochloroceltrobiose (XXIV). Two of these (XXV and XXVI) mutarotate in chloroform in opposite

XXIV   XXV, $[\alpha]^{20}D$ +22.3 → +15.1°

XXVI, $[\alpha]^{20}D$ +3.9 → +15.1°   XXVII, $[\alpha]^{20}D$ +1.0°
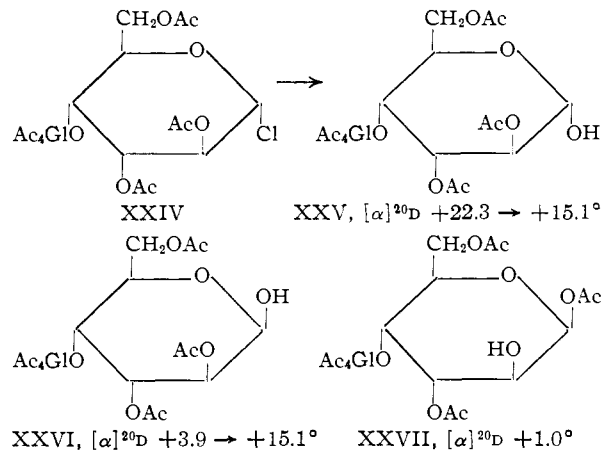
directions to the same end value and obviously form an anomeric pair. The third did not mutarotate in chloroform although cautious acetylation converted it quantitatively to β-celtrobiose octaacetate. While the earlier authors suggested two alternative cyclic orthoacid structures for this heptaacetate, it now seems likely that the substance has structure XXVII. Indeed, the fact that acetylation converted the substance quantitatively to the β-octaacetate (rather than a mixture of anomers) may be taken as evidence in support of this view.

To the authors' best knowledge there remains no good evidence for the existence of cyclic orthoacid structures in the sugar series.

Experimental[3]

Comparative Infrared Studies of 1,2,3,5-Tetra-O-benzoyl-β-d-ribose, 2,3,5-Tri-O-benzoyl-β-d-ribose (II) and 1,3,5-Tri-O-benzoyl-α-d-ribose (IV).—The compounds were studied at various concentrations in chloroform solution employing a Perkin–Elmer recording infrared spectrophotometer (model 21) with a slit width of 50 μ, absorbances (Table I) being determined for the maximum at *ca.* 5.78–

TABLE I

1,2,3,5-Tetra-O-benzoyl-β-d-ribose

Concn., g./l.	10.04	8.35	4.02	2.06	1.36
log I_0/I	1.51	1.15	0.59	0.31	0.21

2,3,5-Tri-O-benzoyl-β-d-ribose

Concn., g./l.	12.09	6.93	3.53	2.57	1.17
log I_0/I	1.56	0.92	0.48	0.32	0.16

1,3,5-Tri-O-benzoyl-α-d-ribose

Concn., g./l.	8.58	4.53	2.91	1.26	1.00
log I_0/I	1.10	0.62	0.41	0.18	0.13

5.79 μ. Since the carbonyl absorption band in each of these compounds was practically completely resolved, the maximum transmission was taken as the transmission of a blank. A plot of log I_0/I against concentration for each of the three cases was used to obtain the following values for (log I_0/I)/c (= slope) for the compounds in the order given: 0.1427, 0.1316 and 0.1335. Since the same cell thickness (d =

0.0495 cm.) was used throughout and $\epsilon = (M \log I_0/I)/cd$ where ϵ is the molecular extinction coefficient and M the molecular weight, we may calculate ϵ for the three compounds as 1633, 1229 and 1247. For comparison purposes each extinction coefficient may be divided by the number of carbonyl groups present to give 408, 410 and 416, values which are seen to be reasonably concordant.

Amorphous 1,2,3,5-Tetra-O-benzoyl-α-D-ribose.—To a mixture of 7 ml. of dry pyridine and 0.20 ml. of benzoyl chloride which had been cooled to 0° was added 572.1 mg. of 1,3,5-tri-O-benzoyl-α-D-ribose. After standing at 0° for 1.3 hr. and 20° for 1 hr., the mixture was treated with one drop of water and 10 min. later with a large volume of ice-water. The brittle gum thus precipitated was separated and washed repeatedly with cold water. Attempts to obtain the product in crystalline form failed. The dried sirup showed a rotation in chloroform (c 2.3) of +90.7°. Chromatography on alumina showed only one major component present, $[\alpha]^{20}$D +90.4° (CHCl$_3$, c 2.17).

2-O-Acetyl-1,3,5-tri-O-benzoyl-α-D-ribose (V).—1,3,5-Tri-O-benzoyl-α-D-ribose (5.00 g.) was added slowly to a well-stirred mixture of 3.2 ml. of acetic anhydride and 7.0 ml. of pyridine which was cooled in an ice-bath. The reaction mixture was held at 0° for 30 minutes, at room temperature 15 minutes and then diluted with a mixture of water and methylene chloride. The organic layer, after successive washing with cold water, cold 3 N sulfuric acid and cold aqueous sodium bicarbonate, was dried with sodium sulfate and concentrated *in vacuo* to yield 5.59 g. of sirupy monoacetate. This product rotated +77° (c 5.5, abs. EtOH); chromatography on alumina showed it to be essentially homogeneous. A chromatographed sample rotating +76.8° (c 1.01, CHCl$_3$) was submitted for analysis.

Anal. Calcd. for C$_{28}$H$_{24}$O$_9$: C, 66.66; H, 4.80. Found: C, 66.37; H, 4.62.

1,2-Di-O-acetyl-3,5-di-O-benzoyl-D-ribose (VII) from 2-O-Acetyl-1,3,5-tri-O-benzoyl-α-D-ribose (V) via Amorphous 2-O-Acetyl-3,5-di-O-benzoyl-D-ribosyl Chloride (VI).—A solution of 5.48 g. of amorphous 2-O-acetyl-1,3,5-tri-O-benzoyl-α-D-ribose in 10 ml. of dry benzene was treated at 20° with a solution of 1.4 ml. of titanium tetrachloride in 50 ml. of dry benzene. Twenty minutes later methylene chloride was added and the solution washed, first with cold water and then with cold aqueous sodium bicarbonate. Moisture was removed with sodium sulfate and the solution concentrated under reduced pressure. The sirupy product, dissolved in 100 ml. of dry benzene, was treated with 15 g. of silver acetate and the resulting suspension stirred at room temperature for 50 minutes. The silver salts and solvent were then removed to give a residue which, from ether-pentane, afforded 2.13 g. (45% calculated on the original tribenzoate) of product melting at 125–127°. Recrystallization from absolute ethanol gave material rotating −3.0° in chloroform (c 1.67) and melting at 126–127° either alone or in admixture with 1,2-di-O-acetyl-3,5-di-O-benzoyl-D-ribose.[2]

1,3,5-Tri-O-benzoyl-2-O-methylsulfonyl-α-D-ribose (III).—To a well-stirred mixture of 10 ml. of pyridine and 1 ml. of methanesulfonyl chloride cooled in an ice-bath was added, over a period of 13 minutes, 5.00 g. of 1,3,5-tri-O-benzoyl-α-D-ribose. Fifty minutes after the addition was complete two drops of water was added and, some 10 minutes later, the product was precipitated by the addition of an excess of water. Rubbed successively with water and aqueous sodium bicarbonate, the substance crystallized; after drying it was recrystallized from methylene chloride–pentane: 4.15 g. (71%), m.p. 140–142°. Further recrystallization from the same mixture of solvents and then from absolute ethanol gave pure 1,3,5-tri-O-benzoyl-2-O-methylsulfonyl-α-D-ribose as stout needles melting at 141–142° and rotating +72.8° in chloroform (c 2.93).

Anal. Calcd. for C$_{27}$H$_{24}$O$_{10}$S: C, 59.99; H, 4.48; S, 5.93. Found: C, 60.08; H, 4.49; S, 5.98.

Conversion of 1,3,5-Tri-O-benzoyl-2-O-methylsulfonyl-α-D-ribose (III) to Methyl α-D-Arabinopyranoside (VIII).—A solution of 2.00 g. of the mesyl ester in a mixture of 20 ml. of methylene chloride and 20 ml. of absolute methanol was treated with 7.0 ml. of 1.3 N sodium methoxide at room temperature. Within 2 minutes sodium mesylate was observed to precipitate; after 24 hours excess alkali was neutralized with carbon dioxide, the precipitate (0.45 g., 103%) removed and the filtrate concentrated *in vacuo*.

The residue was dissolved in 40 ml. of water and, after the methyl benzoate had been removed through extraction with methylene chloride, the solution was deionized by successive treatments with Amberlite IR-120 and Duolite A-4. Evaporation *in vacuo* gave a sirup which, dissolved in methanol–ether, afforded 0.2207 g. (36%) of crude methyl α-D-arabinopyranoside melting at 120–128°. After two recrystallizations from ethyl acetate and one from ethanol the product rotated −21° in water (c 0.96) and melted at 131–133° either alone or in admixture with authentic material. Methyl α-D-arabinopyranoside has been reported to melt at 132–133° and rotate −18.1° in water.[22]

The identity of the glycoside was confirmed through conversion to the tribenzoate *via* conventional benzoylation. From methanol the product could be obtained either as prisms having a double m.p. 133–134°, 146–147° or as needles of m.p. 145–147°, the former being the more stable in methanol. This dimorphism, hitherto unobserved, was then found to be shown by authentic methyl α-D-arabinopyranoside tribenzoate. Mixed melting points were undepressed. The prismatic form of the product was found to rotate in chloroform (c 1.55) −203° and gave acceptable analytical data. Fletcher and Hudson[22] reported a rotation in chloroform (c 1.27) of −202° for the needle form.

3,5-Di-O-benzoyl-D-ribofuranosyl Chloride (IX).—A solution of 10.00 g. of 1,3,5-tri-O-benzoyl-α-D-ribose in a mixture of 30 ml. of methylene chloride and 100 ml. of carbon tetrachloride was cooled in an ice-bath and treated with hydrogen chloride gas for 2–3 minutes. Seeds of the chloride[23] were added and the stream of gas continued for 8 minutes more. The mixture was kept cold for about 5 minutes, diluted with 100 ml. of pentane and, finally, filtered: 7.27 g. (89%). Recrystallized several times from 20 parts of methylene chloride–carbon tetrachloride–pentane (1:1:1) and twice from ether the product melted with decomposition at 123–124° (sample introduced at 122°, rate of heating 10° per minute) or 116–122° (sample introduced at 111°, rate of heating 10° per minute).

Anal. Calcd. for C$_{19}$H$_{17}$O$_6$Cl: C, 60.56; H, 4.55; Cl, 9.41. Found: C, 60.45; H, 4.64; Cl, 9.84.

A sample of the halide (1.0452 g.), made up to 25.00 ml. with dry methylene chloride, was observed at 20° in a 2-dm. tube: +0.10° (5 min.), +1.11° (91.5 hr.), +2.39° (192 hr.), +3.51° (307 hr.), +4.09° (429 hr.) and +4.23° (500 hr.). After the mutarotation the solution contained free hydrogen chloride and attempts to obtain a crystalline product therefrom failed.

1,3,5-Tri-O-benzoyl-α-D-ribose (IV) from 3,5-Di-O-benzoyl-D-ribofuranosyl Chloride (IX).—To an actively stirred suspension of 1.0 g. of silver benzoate in 10 ml. of dry benzene was added 1.00 g. of 3,5-di-O-benzoyl-D-ribofuranosyl chloride. After 1.5 hr. during which the mixture was stirred at room temperature the solid was removed and extracted with methylene chloride. The combined extracts and filtrate were concentrated to a sirup which gave, from a mixture of 1 ml. of methylene chloride and 9 ml. of ether, 429 mg. (35%) of product melting at 139–142° either alone or in admixture with 1,3,5-tri-O-benzoyl-α-D-ribose prepared through the hydrolysis of tri-O-benzoyl-D-ribofuranosyl bromide.

(22) H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, 72, 4173 (1950).

(23) Seeds of 3,5-di-O-benzoyl-D-ribofuranosyl chloride were initially and readily obtained through a similar, smaller-scale reaction which was continued to constant rotation and then concentrated *in vacuo*.