10,200). Lit.[3] m.p. 98–100°, λ_{max} 244 and 295 mμ (ε 16,300 and 11,700).

Several similar reactions were carried out for various periods ranging up to 4 hr., but in every case the total extractable (petroleum ether) material amounted to not more than *ca.* 15% of the original weight of starting material.

Preparation of 3,5-cyclo-6,8(14),9(11),22-ergostatetraene (VIII *from* III). A solution of 1.0 g. of *i*-dehydroergosterol (III) (m.p. 126–127°) and 1.0 ml. of trichloroacetyl chloride in 20 ml. of pyridine was allowed to stand overnight at room temperature. The resulting red solution was poured into a mixture of ice and aqueous potassium bicarbonate and the oily product was extracted into chloroform. The chloroform solution was washed, dried, and evaporated to dryness. Chromatography on 30 g. of alumina ("almost neutral") and elution with petroleum ether (b.p. 30–60°) yielded 0.4 g. of the hydrocarbon which after crystallization from acetone-water was still only 92% pure (λ_{max} 244 and 295 mμ, ε 15,000 and 11,000). The pure material was obtained by recrystallizing it twice further from acetone-methanol and gave VIII as colorless, long rods, m.p. 99–101°, λ_{max} 244 and 295 mμ (ε 16,100 and 12,100). Lit.[3] m.p. 98–100°, λ_{max} 244 and 295 mμ (ε 16,300 and 11,700). Elution of the chromatographic column with chloroform gave 88 mg. of dehydroergosterol (I), identified on the basis of its ultraviolet spectrum.

The hydrocarbon (VIII) was also obtained from the reaction of *i*-dehydroergosterol and 3,5-dinitrobenzoyl chloride in pyridine. However, both the reaction of *i*-dehydroergosterol with benzoyl chloride and with *p*-nitrobenzoyl chloride yielded products with ultraviolet spectra consistent with the corresponding 3,5-cyclo steroid ester and hydrolysis of these with hot potassium bicarbonate in aqueous acetone gave back the starting material.

An attempt to prepare and isolate the trichloroacetate of *i*-dehydroergosterol by the reaction (15 min. at room temp.) of *i*-dehydroergosterol in benzene containing 2 equivalents of pyridine and 1 equivalent of trichloroacetyl chloride followed by extraction with a cold aqueous potassium bicarbonate solution yielded an oil exhibiting maxima at 244, 295, 311, 324, and 340 mμ with approximately the same intensities at 244 and 324 mμ. On slow evaporation of the mixture from methanol-water crystals were obtained which showed substantially the same spectrum. The intensities of the maxima indicated a 40% content of I and a 40% content of VIII.

Acknowledgment. The interest, encouragement, and advice of Dr. Erich Mosettig throughout this investigation has been of a continuing help. The authors are also pleased to acknowledge a fruitful discussion with Dr. Alan H. Mehler.

BETHESDA 14, MD.

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH
PUBLIC HEALTH SERVICE, U. S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE]

Ribofuranose Derivatives from 3,5-Di-*O*-benzoyl-D-ribosyl Chloride. I. 1,3,5-Tri-*O*-benzoyl-β-D-ribose and 5-*O*-Benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose*[1]

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Received April 16, 1957

Condensation of the crystalline furanosyl halide, 3,5-di-*O*-benzoyl-D-ribosyl chloride (II), in ether solution with silver benzoate gives, in addition to the previously known 1,3,5-tri-*O*-benzoyl-α-D-ribose (I), a new D-ribofuranose tribenzoate which is shown to be 1,3,5-tri-*O*-benzoyl-β-D-ribose (III). Treatment of the same halide (II) in benzene solution with mercuric acetate gives a mono-*O*-benzoyl-*O*-benzylidyne-D-ribose which, by a series of reactions, has been converted to 1,2,3-tri-*O*-benzoyl-5-*O*-methanesulfonyl-β-D-ribose (XII). Synthesis of the latter substance from the known 2,3-*O*-benzylidene-β-D-ribofuranose (XIII) confirmed its structure and led to the conclusion that the orthoester is 5-*O*-benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose (VII).

The nature of the crystalline halide (II) is discussed with particular reference to the question of its anomeric configuration.

In recent communications we have described the preparation of 3,5-di-*O*-benzoyl-D-ribosyl bromide[4] and 3,5-di-*O*-benzoyl-D-ribosyl chloride (II).[5] These two substances are of unusual interest not only because they are the first ribofuranosyl halides to be obtained in crystalline form[6] but also because they are readily accessible from D-ribose[4] or from 2,3,5-tri-*O*-benzoyl-D-ribose[7] and, therefore, are of potential value for the synthesis of ribonucleosides. While both of these halides are relatively labile substances the chloride is, as might be expected, somewhat less reactive than the bromide and is, therefore, a more convenient object of study from the experimental point of view. The present paper will be devoted primarily to a description of the preparation, characterization, and proof of structure

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* This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

[1] In earlier papers (refs. 2 and 3) dealing with derivatives of orthobenzoic acid we have used the prefix "orthobenzoyl" to refer to the radical $C_6H_5C\equiv$. In the present and following papers we adopt the more accurate prefix "benzylidyne"; *cf. Chem. Abstr.*, **39**, 5963 (1945).

[2] H. G. Fletcher, Jr., and R. K. Ness, *J. Am. Chem. Soc.*, **77**, 5337 (1955).

[3] R. K. Ness and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **78**, 1001 (1956).

[4] R. K. Ness and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **76**, 1663 (1954).

[5] R. K. Ness and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **78**, 4710 (1956).

[6] One more crystalline di-*O*-benzoyl-D-ribofuranosyl halide is reported in the communication immediately following this one.

[7] R. K. Ness, H. W. Diehl, and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **76**, 763 (1954).

of the two products derived from 3,5-di-*O*-benzoyl-D-ribosyl chloride which are named in the title.

In an earlier study[5] we described the condensation of 3,5-di-*O*-benzoyl-D-ribosyl chloride (II) in benzene solution with silver benzoate as giving a precipitate from which 1,3,5-tri-*O*-benzoyl-α-D-ribose (I) could be isolated. Subsequent investigation has now shown that the benzene solution contains another D-ribose tribenzoate which is readily isolated in crystalline form. The new ester was not identical with any of the known D-ribose tribenzoates and did not exhibit mutarotation in chloroform solution. Benzoylation afforded the known β-D-ribofuranose tetrabenzoate[7] in good yield; the substance therefore appeared to be a 1,*x*,*x*-tri-*O*-benzoyl-β-D-ribofuranose. Since experiments with β-D-ribofuranose tetrabenzoate showed that its 1-*O*-benzoyl group was readily replaced through the action of boron trifluoride in acetic acid to give 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribose,[8] the new tribenzoate was acetylated and then acetolyzed in this selective manner. The product obtained proved to be the known[4,5] 1,2-di-*O*-acetyl-3,5-di-*O*-benzoyl-β-D-ribose (VI) and the tribenzoate from which it was derived is, therefore, 1,3,5-tri-*O*-benzoyl-β-D-ribose (III), the anomer of the substance (I) obtained earlier. Inspection of the optical rotatory values listed in Table I shows that these figures tend to support this conclusion, the 2*A*-values from the anomeric 1,3,5-tri-*O*-benzoyl-D-riboses agreeing roughly with those from the known anomeric D-ribofuranose tetrabenzoates.

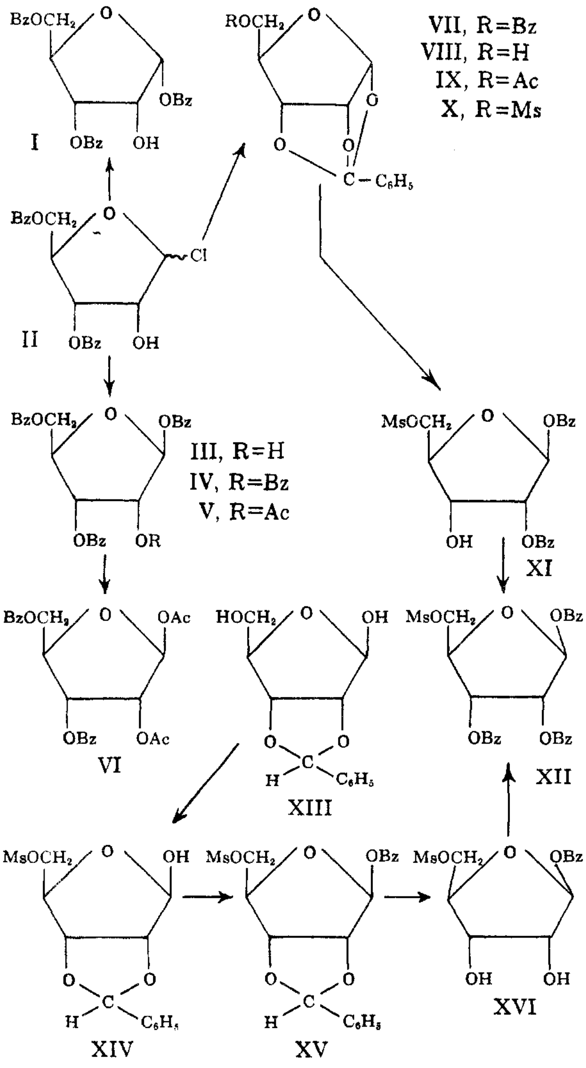

TABLE I
RIBOFURANOSE BENZOATES

	[α]$^{20}_{D}$ (CHCl$_3$)	[*M*]$^{20}_{D}$	Difference 2*A*
α-D-Ribofuranose tetrabenzoate	+90.4°[a]	+51,300	41,700
β-D-Ribofuranose tetrabenzoate	+17.0°[b]	+ 9,600	
1,3,5-Tri-*O*-benzoyl-α-D-ribose	+85.3°[c]	+39,400	37,700
1,3,5-Tri-*O*-benzoyl-β-D-ribose	+ 3.6°[d]	+ 1,700	

[a] Ref. 5. [b] Ref. 7. [c] Ref. 4. [d] Present work.

When an attempt was made to condense 3,5-di-*O*-benzoyl-D-ribosyl chloride (II) in benzene solution with mercuric acetate a product was obtained which showed no hydroxyl absorption in the infrared and gave analytical values corresponding to a benzoylbenzylidynepentose. Both this substance and the crystalline derivative obtained through barium methoxide-catalyzed debenzoylation showed marked lability, particularly toward acidic reagents, further suggesting a benzylidyne structure. The alkali-debenzoylated product was further characterized through the preparation of its acetate. Mesylation of the orthobenzoate gave a crystalline mesyl ester which was treated in methylene chloride solution at room temperature with benzoic acid to yield a crystalline di-*O*-benzoyl-*O*-methylsulfonylpentose; further benzoylation gave a tri-*O*-benzoyl-*O*-methylsulfonylpentose. The structure of the latter substance was demonstrated unequivocally by the following independent synthesis. 2,3-*O*-Benzylidene-β-D-ribofuranose[9] (XIII) was converted to the 5-*O*-methylsulfonyl derivative (XIV)[10] and thence to 1-*O*-benzoyl-2,3-*O*-benzylidene-5-*O*-methylsulfonyl-β-D-ribose (XV). Mild acid hydrolysis to cleave the cyclic acetal gave 1-*O*-benzoyl-5-*O*-methylsulfonyl-β-D-ribose (XVI) which, on further benzoylation, gave 1,2,3-tri-*O*-benzoyl-5-*O*-

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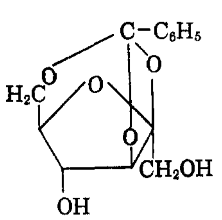
(8) In earlier work (ref. 4) anhydrous zinc chloride, a less convenient reagent, had been used to carry out this transformation.

(9) H. B. Wood, Jr., H. W. Diehl, and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **78**, 4715 (1956). See also G. R. Barker and J. W. Spoors, *J. Chem. Soc.*, 1192 (1956).

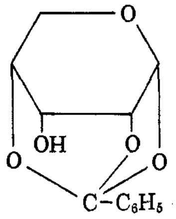
(10) The analogous *p*-tolylsulfonyl derivative has recently been described as an intermediate in the synthesis of 1,5-anhydro-β-D-ribofuranose: E. Vis and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **79**, 1182 (1957).

methylsulfonyl-β-D-ribose (XII), identical with the substance derived from the orthoester (VIII). Since this sequence of reactions demonstrates that the normal benzoyl group in the benzoylbenzylidynepentose is located at C5,[11] the orthoester may be written as VII, 5-*O*-benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose, the assignment of anomeric configuration appearing to be mandatory on steric grounds.

Several substances closely related to, but probably less strained than, 1,2,3-*O*-benzylidyne-α-D-ribose (VIII) have recently been reported. Helferich and his coworkers,[12,13] for instance, have described a 2,3,6-*O*-benzylidyne-β-D-fructofuranose (XVII) while the present authors[14] have obtained a pyranose analog of VIII, 1,2,4-*O*-benzylidyne-α-D-ribose (XVIII). It should be noted, however, that both these substances were derived from 1-benzyloxybenzylidene derivatives through the acid catalyzed loss of benzyl alcohol. The formation of 1,2,3-*O*-benzylidyne-α-D-ribose (VII) through dehydrohalogenation of II as described here represents a wholly different approach to this type of compound.



XVII



XVIII

The anomeric configurations of compounds XI, XII and XIV to XVI. These five compounds almost certainly have the same configuration at C1 and have all been assigned the β-configuration on the basis of two different lines of evidence. 2,3-*O*-Benzylidene-β-D-ribofuranose (XIII), $[\alpha]_D^{20}$ −22.4°[9] was earlier shown to be a β-isomer; the rotation of its 5-*O*-mesyl derivative (XIV), $[\alpha]_D^{20}$ −4°, suggests that this also is a β-isomer. The rotation of monobenzoate XV, $[\alpha]_D^{20}$ −47.3°, further supports this view. On the other hand, let us consider the probable mechanism of the scission of the benzylidyne cage by benzoic acid in going from X to XI. This transformation may be rationalized by assuming protonation of X followed by nucleophilic attack with inversion at C1. Obviously, the potential benzoyl group in X may give rise to a normal benzoyl at C2 or C3, retention of configuration being expected at both positions in either case. All question of mechanism aside, we will show in the succeeding paper[15] that benzoic acid alone converts VII to 1,2,5-tri-*O*-benzoyl-β-D-ribose, a transformation which may be construed as supporting the β configurations in the present case and also as favoring by analogy XI rather than its 1,3-di-*O*-benzoyl isomer which *a priori* seems equally plausible.

In passing, attention is drawn to the somewhat unusual circumstance that each of the three benzoyl groups in XII was introduced by a different method when the substance was prepared from 1,2,3-*O*-benzylidyne-α-D-ribose (VIII).

*Anomeric configuration of 3,5-di-O-benzoyl-*D*-ribosyl chloride* (II). The anomeric configurations of the fully acylated glycosyl halides are usually indicated quite clearly by their rotations. The aldosyl halides having C2 unsubstituted present a peculiar problem, however, since in contrast to the above class, they often mutarotate in inert solvents. Thus 3,4,6-tri-*O*-acetyl-β-D-glucosyl chloride ($[\alpha]_D$ +28.7°[16]) readily isomerizes to the α-anomer ($[\alpha]_D^{20}$+ 185°) in acetone solution.[16] Matters are further complicated in the case of the 3,5-di-*O*-benzoyl-D-ribosyl halides by the fact that spontaneous loss of halogen acid accompanies mutarotation. Thus, while the bromide shows $[\alpha]_D^{20}$ +96° (3 min.) → +27° (60 min., constant)[4] in absolute chloroform and the chloride shows $[\alpha]_D^{20}$ +1.2° (5 min.) → +50.7° (500 hrs.)[5] in methylene chloride we cannot safely conclude therefore that the bromide is an α-anomer and the chloride a β-anomer. The initial rotations, however, rule out the possibility that both are β-anomers since such a relationship would require the bromide to be more negative than the chloride.[17]

The steric and structural features of replacement products are often a reliable key to the configuration of fully acylated glycosyl halides because the reactions of these substances are dominated by neighboring group effects when an acyloxy group is adjacent and *trans* to the halogen. While C2 bears no acyl group in the present case, it should be pointed out that the conversion of II to I and to VII can easily be rationalized if we assume that the halide is the α-anomer and that the displacement proceeds through participation of the benzoyloxy group at C5.[18] The

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[11] Rebenzoylation of VIII afforded VII, showing that catalytic debenzoylation had not affected the orthobenzoate group.

[12] B. Helferich and L. Bottenbruch, *Chem. Ber.*, **86**, 651 (1953).

[13] B. Helferich and W. Schulte-Hürmann, *Chem. Ber.*, **87**, 977 (1954).

[14] Reference 2. The statement made in this paper that "no orthobenzoylribofuranose appeared possible" emphasizes the inadequacy of rigid mechanical models for portraying many of these cage structures.

[15] R. K. Ness and H. G. Fletcher, Jr., *J. Org. Chem.*, **22**, 1470 (1957).

[16] R. U. Lemieux and G. Huber, *Can. J. Chem.*, **31**, 1040 (1953).

[17] C. S. Hudson, *J. Am. Chem. Soc.*, **46**, 462 (1924).

[18] Participation of an acyloxy group at C5 in displacement reactions at C1 in a pentofuranose derivative does not seem wholly unreasonable when one recalls that 2,3-*O*-benzylidene-5-*O*-*p*-toluenesulfonyl-β-D-ribofuranose readily gives 1,5-anhydro-β-D-ribofuranose when treated with alkali (Vis and Fletcher, ref. 10) and that derivatives of 1,5-*O*-benzylidene-β-D-ribofuranose have recently been prepared (Barker and Spoors, ref. 9). Such C5 to C1 interaction has not, to our knowledge, been demonstrated, however.

cyclic intermediate thus formed could react with a benzoate ion to give I or with itself to form a second cyclic intermediate ion involving the benzoyloxy group at C3; the latter could stabilize itself through loss of a proton from the hydroxyl group at C2 with the formation of VII.

EXPERIMENTAL[19]

1,3,5-Tri-O-benzoyl-β-D-ribose (III) *from 3,5-di-O-ribosyl chloride* (II). One gram of 3,5-di-*O*-benzoyl-D-ribosyl chloride[6] was added to an actively stirred suspension of 1.0 g. of silver benzoate in 10 ml. of dry benzene. After 1.5 hr. at room temperature the solid material[20] was removed and washed with benzene. The combined washings and filtrate were concentrated to a sirup; from 10 ml. of ether crystallization was spontaneous: 0.22 g., (18%), m.p. 137–139°. One recrystallization from 2:1 methylene chloride–pentane gave 0.143 g. of pure *1,3,5-tri-O-benzoyl-β-D-ribose* (III), m.p. 144–145°,[21] $[\alpha]^{20}_{D}$ +3.6° in chloroform (*c* 2.2).

Anal. Calcd. for $C_{26}H_{22}O_8$: C, 67.52; H, 4.80. Found: C, 67.66; H, 4.88.

β-D-Ribofuranose tetrabenzoate (IV) *from 1,3,5-tri-O-benzoyl-β-D-ribose* (III). 1,3,5-Tri-*O*-benzoyl-β-D-ribose (43.6 mg.) was treated with a cold mixture of 0.5 ml. of pyridine and 0.02 ml. of benzoyl chloride for 1 hr. After the usual workup there was obtained from absolute alcohol a total of 41.9 mg. (79%) of crystalline product melting at 120–121°. Mixed with authentic β-D-ribofuranose tetrabenzoate[7] it melted at 120–121°.

1-O-Acetyl-2,3,5-tri-O-benzoyl-β-D-ribose from β-D-ribofuranose tetrabenzoate (IV). A solution of β-D-ribofuranose tetrabenzoate (115.8 mg.) in 4.0 ml. of acetic anhydride was observed to rotate +0.38° in a 1-dm. tube at 20°. The addition of 0.20 ml. of 7.0*M* boron trifluoride in ether caused a rapid mutarotation: +0.89° (45 sec.), +1.05° (85 sec. and 8 min.). Fourteen minutes after the addition of the catalyst the mixture was worked up to yield 47.4 mg. (46%) of crystalline product melting at 129–130°. Mixed with authentic 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribose it melted at 129–131°.

1,2-Di-O-acetyl-3,5-di-O-benzoyl-β-D-ribose (VI) *from 1,3,5-tri-O-benzoyl-β-D-ribose* (III). 1,3,5-Tri-*O*-benzoyl-β-D-ribose (100.9 mg.) was acetylated at −5° with an excess of acetic anhydride in pyridine solution; excess reactants were removed in conventional fashion to give 114.5 mg. of a solvent-free sirup which was treated with 4 ml. of a mixture made from 20 ml. of acetic anhydride and 1 ml. of 7*M* boron trifluoride in ether. After 13 min. the material was worked up to yield 49.8 mg. (51%) of crystalline material melting at 126–127°. Mixed with authentic 1,2-di-*O*-acetyl-3,5-di-*O*-benzoyl-β-D-ribose[4] the product melted at 126–127°.

2-O-Acetyl-1,3,5-tri-O-benzoyl-β-D-ribose (V). 1,3,5-Tri-*O*-benzoyl-β-D-ribose (58.6 mg.) was acetylated at a low temperature with acetic anhydride in pyridine solution following the customary procedure. The addition of water precipitated a sirup which was washed with water and then dissolved in 1 ml. of alcohol. The crystals (36.7 mg., 57%, m.p. 98–100°) which formed were twice recrystallized from absolute ethanol to give a pure product melting at 99–101° and rotating $[\alpha]^{20}_{D}$ −17° in chloroform (*c* 1.0).

Anal. Calcd. for $C_{28}H_{24}O_9$: C, 66.66; H, 4.80. Found: C, 66.38; H, 4.93.

5-O-Benzoyl-1,2,3-O-benzylidyne-α-D-ribose (VII) *from 3,5-di-O-benzoyl-D-ribosyl chloride* (II). 3,5-Di-*O*-benzoyl-D-ribosyl chloride (1.00 g.) was added over a 6-min. period to a vigorously stirred suspension of 1 g. of mercuric acetate in 10 ml. of dry benzene. After 15 min. from the beginning of the reaction, 30 ml. of saturated sodium chloride solution was added along with methylene chloride. The organic layer was successively washed with water and sodium bicarbonate solution; moisture was removed with sodium sulfate and the solution concentrated *in vacuo* to a crystalline residue. From methylene chloride–ether practically pure 5-*O*-benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose (VII) (0.43 g., 47%) was obtained: m.p. 181–183°. Repetition of the preparation employing 13 g. of the chloride gave the same product in 45% yield. Recrystallization from methylene chloride–pentane afforded a pure product melting at 182–183°, $[\alpha]^{20}_{D}$ +43.4° in chloroform (*c* 2.62).

Anal. Calcd. for $C_{19}H_{16}O_6$: C, 67.05; H, 4.75; mol. wt., 340. Found: 67.13; H, 4.98; mol. wt., 339 (Rast and cryoscopic in C_6H_6), 350 (signer, CH_2Cl_2).

Infrared absorption measurements in a potassium bromide pellet showed no hydroxyl absorption.

1,2,3-O-Benzylidyne-α-D-ribofuranose (VIII). A solution of 218.4 mg. of 5-*O*-benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose in 5 ml. of methylene chloride was diluted with 5 ml. of methanol and treated with 0.07 ml. of 1.5*N* barium methoxide at room temperature. Part of the starting material precipitated but soon redissolved; polarimetric observations showed the reaction to be complete after a total of 12 min. The mixture was treated with carbon dioxide and then concentrated to a dry mass which was dissolved in methylene chloride and filtered. Concentration of the filtrate followed by dissolution of the residue in *ca.* 1 ml. of ether and *ca.* 1 ml. of pentane gave 0.1194 g. (79%) of crystalline product melting at 102–103°. After two recrystallizations from ether-pentane, one from carbon tetrachloride and another from ether-pentane, pure 1,2,3-*O*-benzylidyne-α-D-ribofuranose, m.p. 106–108°, $[\alpha]^{20}_{D}$ +41.0° ($CHCl_3$, *c* 1.3, no mutarotation after 3 hr.), was obtained. The substance showed no carbonyl absorption in the infrared (5.6–5.9 μ).

Anal. Calcd. for $C_{12}H_{12}O_5$: C, 61.02; H, 5.12. Found: C, 60.96; H, 5.19.

Rebenzoylation of a sample of the above product with benzoyl chloride in pyridine at 0° for 5 min. gave crystalline 5-*O*-benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose in 96% yield.

5-O-Acetyl-1,2,3-O-benzylidyne-α-D-ribose (IX). 1,2,3-*O*-Benzylidyne-α-D-ribofuranose (103.0 mg.) was added to a cold (0°), stirred mixture of 2.0 ml. of dry pyridine and 0.2 ml. of acetyl chloride. Five minutes later, 10 ml. of saturated aqueous sodium bicarbonate was added and, after cooling, the product was removed by filtration. It was dissolved in ethanol which was then removed *in vacuo:* solution of the residue in 1 ml. of ethanol and addition of 3 ml. of pentane gave 17.9 mg. of crystalline material melting at 114–115°. Two further crops of crude product were recovered from the mother liquor to make a total of 66.0 mg. (54%). Two recrystallizations from hexane gave pure 5-*O*-acetyl-1,2,3-*O*-benzylidyne-α-D-ribose, m.p. 117–118°, $[\alpha]^{20}_{D}$ +42° in chloroform (*c* 0.67).

Anal. Calcd. for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found: C, 60.59; H, 4.96.

1,2(?)-Di-O-benzoyl-5-O-methylsulfonyl-β-D-ribose (XI) *from 1,2,3-O-Benzylidyne-α-D-ribofuranose* (VIII) *via 5-O-methylsulfonyl-1,2,3-O-benzylidyne-α-D-ribose* (X). 1,2,3-Benzylidyne-α-D-ribofuranose (149 mg.) was added to a cooled mixture of 0.5 ml. of dry pyridine and 0.10 ml. of methanesulfonyl chloride. After 15 min. at room temperature the reaction mixture was cooled and diluted with 5 ml. of saturated aqueous sodium bicarbonate. Five minutes later the crystalline precipitate was filtered off and dissolved in methylene chloride. The solution was dried with sodium

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[19] Melting points are corrected.

[20] As described previously (ref. 5), extraction of this solid with methylene chloride afforded 1,3,5-tri-*O*-benzoyl-α-D-ribose. However, our earlier description erred in stating that the extracts were combined with the original filtrate which was not the case. See the correction *J. Am. Chem. Soc.*, **78**, 6427 (1956).

[21] As described in the succeeding paper (ref. 15) 1,3,5-tri-*O*-benzoyl-β-D-ribose may exhibit a double melting point.

sulfate, filtered through decolorizing carbon, and concentrated *in vacuo* to give a crystalline mass of crude 5-*O*-methylsulfonyl-1,2,3-*O*-benzylidyne-α-D-ribose: 141.8 mg., m.p. 119–124°. Dissolved in 5 ml. of methylene chloride and observed in a 1.5-dm. tube, this product showed α^{20}_{D} +1.80° ($[\alpha]^{20}_{\mathrm{D}}$ *ca.* +42°). Benzoic acid (498 mg.) was dissolved in the solution and the rotation observed: +1.65° (3 min.), +1.52° (36 min.), +1.32° (112 min.), −0.24° (26 hr.), −0.44° (42 hr.), and −0.47° (49 hr.). The reaction mixture was then washed with sodium bicarbonate, dried with sodium sulfate and concentrated *in vacuo* at 25° to give a crystalline residue melting at 148–151° (dec.). Recrystallized from ethanol, the 1,2(?)-di-*O*-benzoyl-5-*O*-methylsulfonyl-β-D-ribose was obtained as slightly elongated prisms (96 mg., 35% based on X) melting with decomposition at 170–171° (in bath at 160°; 10°/min.). A second recrystallization failed to change this value. In acetone (*c* 0.94) the substance showed $[\alpha]^{20}_{\mathrm{D}}$ −29.0°.

Anal. Calcd. for $C_{20}H_{20}O_9S$: C, 55.04; H, 4.62. Found: C, 54.99; H, 4.76.

1,2,3-Tri-O-benzoyl-5-O-methylsulfonyl-β-D-ribose (XII) *from 1,2(?)-di-O-benzoyl-5-O-methylsulfonyl-β-D-ribose* (XI). 1,2(?)-Di-*O*-benzoyl-5-*O*-methylsulfonyl-β-D-ribose (20.8 mg.) was treated with a cold mixture of 0.10 ml. of benzoyl chloride and 1.0 ml. of dry pyridine and left at room temperature for 20 min. Aqueous sodium bicarbonate (*ca.* 4 ml.) was then added and the precipitated sirup separated. From 1 ml. of ethanol the product (19.1 mg., 74%) separated as clusters of needles m.p. 103–105°, $[\alpha]^{20}_{\mathrm{D}}$ −1.8° in chloroform (*c* 1.1). A second crystallization from ethanol afforded material melting at 104–105°. Mixed with authentic 1,2,3-tri-*O*-benzoyl-5-*O*-methylsulfonyl-β-D-ribose, prepared as described below, the product melted at 104–106°.

2,3-O-Benzylidene-5-O-methylsulfonyl-β-D-ribose (XIV). 2,3-*O*-Benzylidene-β-D-ribofuranose (XIII, 0.5 g.), prepared as described by Wood, Diehl, and Fletcher,[9] was added to a cold mixture of 1.0 ml. of dry pyridine and 0.19 ml. of methanesulfonyl chloride. After 30 min. saturated aqueous sodium bicarbonate was added and, upon cooling, the solidified mass was removed by filtration. From ethanolic solution this solid gave 0.4683 g. (71%) of crystalline material melting at 139–141° (in bath at 125°, 8°/min.) and decomposing visibly at 150°. Successive recrystallizations from ethanol, from acetone-pentane and from ethanol failed to change this melting point. In chloroform (*c* 0.3) the compound showed $[\alpha]^{20}_{\mathrm{D}}$ −4° (constant over 1 hr.).

Anal. Calcd. for $C_{13}H_{16}O_7S$: C, 49.36; H, 5.10. Found: C, 49.51; H, 5.26.

1-O-Benzoyl-2,3-O-benzylidene-5-O-methylsulfonyl-β-D-ribose (XV). 2,3-*O*-Benzylidene-5-*O*-methylsulfonyl-β-D-ribose (XIV, 381 mg.) was added to a cold (0°) mixture of 1.00 ml. of dry pyridine and 0.20 ml. of benzoyl chloride. After 40 min. at 0° and 80 min. at 25°, 4 drops of aqueous sodium bicarbonate solution was added. Upon the addition of several milliliters of water and cooling, a solid was formed. Crystallization from 5 ml. of ethanol yielded 415.4 mg. (82%) of a product melting at 109–111°; two further crystallizations from ethanol gave pure material melting at 112–114° and rotating $[\alpha]^{20}_{\mathrm{D}}$ −47.3° in chloroform (*c* 2.2).

Anal. Calcd. for $C_{20}H_{20}O_8S$: C, 57.13; H, 4.80; S, 7.63. Found: C, 57.05; H, 5.04; S, 7.54.

1-O-Benzoyl-5-O-methylsulfonyl-β-D-ribose (XVI). 1-*O*-Benzoyl-2,3-*O*-benzylidene-5-*O*-methylsulfonyl-β-D-ribose (XV, 697 mg.) was dissolved in a mixture of 21 ml. of dioxane and 14 ml. of 0.1*N* sulfuric acid and the solution heated at 85° for 3 hr. The cooled reaction mixture was diluted with methylene chloride, washed with saturated aqueous sodium bicarbonate, and dried with magnesium sulfate. Solvent was removed *in vacuo;* the residue, dissolved in methylene chloride–pentane, gave 260 mg. (47%) of product melting at 113–117° (10°/min.). $[\alpha]^{20}_{\mathrm{D}}$ −6.8° in chloroform (*c* 0.4). Two recrystallizations from chloroform afforded material melting at 115–118° (in bath at 108°, 10°/min.),[22] $[\alpha]^{20}_{\mathrm{D}}$ −6.5° in chloroform (*c* 0.6). A third recrystallization from ethanol-pentane failed to change the melting point.

Anal. Calcd. for $C_{13}H_{16}O_8S$: C, 46.98; H, 4.85. Found: C, 46.84; H, 4.98.

1,2,3-Tri-O-benzoyl-5-O-methylsulfonyl-β-D-ribose (XII) *from 1-O-benzoyl-5-O-methylsulfonyl-β-D-ribose* (XVI). 1-*O*-Benzoyl-5-*O*-methylsulfonyl-β-D-ribose (XVI, 76.5 mg.) was added to a mixture of 0.1 ml. of benzoyl chloride and 0.5 ml. of dry pyridine. After 25 min. at 25°, the reaction mixture was diluted with a few drops of aqueous sodium bicarbonate solution and then with 8 ml. of water. The crystalline material thus precipitated was washed and recrystallized from ethanol: 107.8 mg. (87%), m.p. 103–107°. After two more recrystallizations from ethanol the product melted at 104–106° and showed a rotation in chloroform (*c* 1.08) of $[\alpha]^{20}_{\mathrm{D}}$ −7.0°.

Anal. Calcd. for $C_{27}H_{24}O_{10}S$: C, 59.99; H, 4.48; S, 5.93. Found: C, 60.09; H, 4.70; S, 5.90.

Acknowledgments. We wish to thank Mr. William M. Jones for infrared measurements. Combustion analyses were performed in the Institutes' Microanalytical Laboratory under the direction of Dr. William C. Alford.

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(22) The molten material decomposes visibly at 145°. A sample held at 100° and 0.1 mm. was almost completely fused after 20 min., decomposing with the evolution of benzoic acid.