R_t 4.5; ν_{max} 3425, 3344, 1718, 1709, 1300, 1271, 1244, 1195, 1174, 1081, 1031, 1003, 961, 948, 904, 857, 775 cm^{-1}.

Anal. Calcd for $C_{25}H_{40}O_5$: C, 71.39; H, 9.59. Found: C, 71.51; H, 9.68.

Wolff-Kishner Reduction of XVII.—By reduction of 50 mg of methyl 7-keto-3β,12α-dihydroxy-5α-cholanoate in a manner analogous to that described above a residue of 40 mg of 3β,12α-dihydroxy-5α-cholanoic acid was obtained. After methylation and crystallization of the ester from aqueous methanol, needles of methyl 3β,12α-dihydroxy-5α-cholanoate (XIX) were obtained:[18] mp 140–141°; $[\alpha]^{25}D$ +35.2 ± 1° (*c* 0.33); R_f 0.22 (solvent system B); R_t 1.16; ν_{max} 3413, 3344, 1718, 1214, 1043, 1027, 1010, 902 cm^{-1}.

Registry No.—II, 14772-92-0; II acetate, 15111-23-6; II oxime, 15073-84-4; III, 861-83-6; IIIa, 2464-18-8; IV, 14772-93-1; IVa, 15073-87-7; V, 15074-09-6; Va, 15073-88-8; VII, 15206-37-8; VIIa, 15073-89-9; VIII, 15073-90-2; VIIIa, 15073-91-3; IX, 15111-25-8; IXa, 15073-92-4; X, 15073-93-5; Xa, 15152-40-6; XI, 15073-94-6; XIa, 2464-18-8; XIV, 15073-95-7; XIVa, 15073-96-8; XV, 15074-10-9; XVI, 15073-97-9; XVII, 15180-34-4; XIX, 1912-56-7; ethyl ester of allocholic acid, 15073-99-1; methyl 3α,12α-dihydroxy-5α-cholanoate, 1912-65-8; methyl 3α-hydroxy-5α-cholanoate, 15074-01-8; methyl 3β-hydroxy-5α-cholanoate, 15074-02-9; methyl 3-keto-5α-cholanoate, 15074-03-0; methyl 3-keto-12α-hydroxy-5α-cholanoate, 14772-89-5; methyl 7-keto-5α-cholanoate, 15074-05-2; methyl 7β-hydroxy-5α-cholanoate, 15074-06-3; methyl 3-keto-7β,12α-dihydroxy-5α-cholanoate, 15074-07-4; methyl 3-keto-7β,12β-dihydroxy-5α-cholanoate, 15074-08-5; methyl 3-keto-7α,12β-dihydroxy-5α-cholanoate, 15093-95-5; methyl 3-keto-7β,12α-diacetoxy-5α-cholanoate, 15093-96-6; methyl 3-keto-7β,12β-diacetoxy-5α-cholanoate, 15206-38-9; methyl 3-keto-7α,12β-diacetoxy-5α-cholanoate, 15093-97-7; methyl 3-keto-7α,12α-dihydroxy-5α-cholanoate bistrimethylsilyl ether, 15093-98-8; methyl 3-keto-7α,12α-dihydroxy-5α-cholanoate bistrimethylsilyl ether, 15093-99-9.

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Synthesis of 1,4,5-Tri-*O*-benzoyl-2,3-dideoxy-D-*erythro*-hex-2-enulopyranose, Derivative of a Ketose-Related Glycal Having an Endocyclic Double Bond

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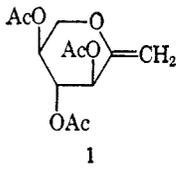
The benzoylation of 3-*O*-methylsulfonyl-D-fructose affords 1,2,4,5-tetra-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-fructopyranose (**6**) together with an isomer of **6** which is probably one of the anomeric 1,2,4,6-tetra-*O*-benzoyl-3-*O*-methylsulfonyl-D-fructofuranoses (**7**). With hydrogen bromide, the pyranose ester (**6**) gives crystalline 1,4,5-tri-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-fructopyranosyl bromide (**8**) and, with hydrogen chloride, the corresponding chloride (**9**). Treatment of **8** with silver benzoate gives **6**. The basis for the assignment of anomeric configurations to **6**, **8**, and **9** is discussed. Sodium iodide in acetone solution eliminates the bromine atom and the methylsulfonyloxy group from **8**, giving a crystalline unsaturated derivative which, upon hydrogenation over palladium, yields a mixture; from this mixture was isolated 1,5-anhydro-2,3,6-tri-*O*-benzoyl-4-deoxy-D-*lyxo*-hexitol (**11**). The isolation of **11** demonstrates that the unsaturated substance is 1,4,5-tri-*O*-benzoyl-2,3-dideoxy-D-*erythro*-hex-2-enulopyranose (**10**), a derivative of a ketose-related glycal with an endocyclic double bond.

In view of the wealth of synthetic uses which have been found for the ordinary aldopyranose-related glycals, it is somewhat surprising that more attention has not been paid to the ketose-related glycals. Of the latter, apparently only one has been synthesized, 3,4,5-tri-*O*-acetyl-1,2-dideoxy-L-*xylo*-hex-1-enulopyranose (**1**).



1

This substance, recently described by Tokuyama, Tsujino, and Kiyokawa,[1] was prepared through the action of sodium iodide in acetone solution on 3,4,6-tri-*O*-acetyl-1-*O*-*p*-tolylsulfonyl-α-L-sorbopyranosyl bromide, a procedure analogous to that which we have used earlier for the synthesis of furanose-related glycals.[2,3] Two types of ketose-related glycals may be envisaged: those with an exocyclic double bond (exemplified by **1**) and those with an endocyclic double bond (as in **10**, Chart I). We have now turned our attention to the problem of the synthesis of an example of the latter type of glycal. In view of the possibility that the glycal might prove to be a highly reactive substance, the very mild conditions involved in eliminating a bromine atom and a sulfonyloxy group from adjacent carbon atoms recommended the synthetic method used earlier.[1-3] D-Fructose was therefore converted into its 1,2:5,6-di-*O*-isopropylidene derivative (**2**)[4] through the action of acetone in the presence of a strongly acidic ion-exchange resin[5] and the remaining free hydroxyl group (at C-3) esterified with methanesulfonyl chloride to give the known[6] 1,2:4,5-di-*O*-isopropylidene-3-*O*-methylsulfonyl-D-fructopyranose (**3**). The isopropylidene groups were removed from **3** by acidic hydrolysis to give 3-*O*-methylsulfonyl-D-fructose[6] which was not iso-

(1) K. Tokuyama, E. Tsujino, and M. Kiyokawa, *Bull. Chem. Soc. Japan*, **38**, 1344 (1965).

(2) R. K. Ness and H. G. Fletcher, Jr., *J. Org. Chem.*, **28**, 435 (1963).

(3) M. Haga and R. K. Ness, *ibid.*, **30**, 158 (1965).

(4) E. Fischer, *Ber.*, **28**, 1145 (1895).

(5) Ion-exchange resins have been used by J. E. Cadotte, F. Smith, and D. Spriestersbach [*J. Am. Chem. Soc.*, **74**, 1501 (1952)] and by K. Erne [*Acta Chem. Scand.*, **9**, 893 (1955)] for the preparation of **2**; a detailed description of an improved procedure is included in the Experimental Section.

(6) B. Helferich and H. Jochinke, *Ber.*, **73**, 1049 (1940).

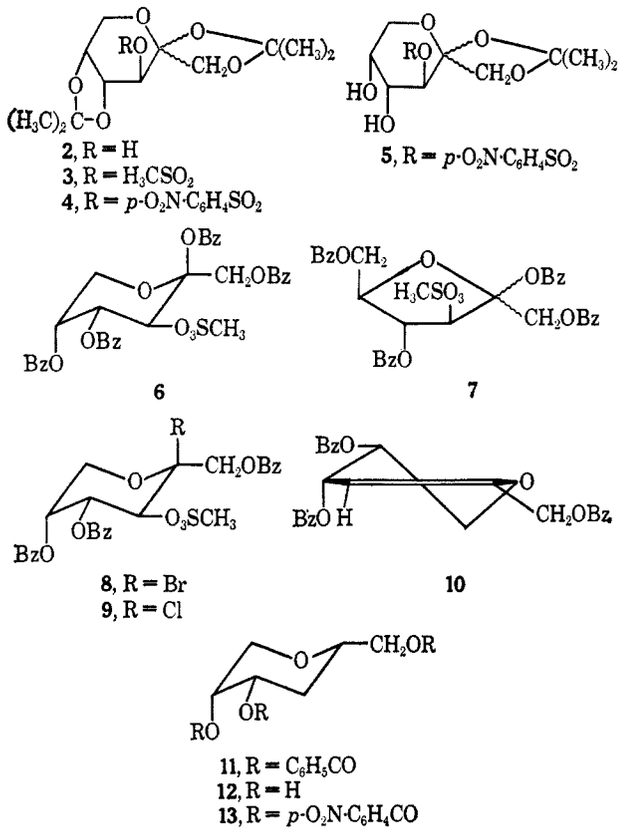
TABLE I

OPTICAL ROTATIONS OF SOME D-FRUCTOPYRANOSE AND D-ARABINOPYRANOSE DERIVATIVES

Compounds	$[\alpha]^{20}D$, deg	$[M]^{20}D$
1,2,4,5-Tetra-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-fructopyranose (6)	−143 ($CHCl_3$)	−96,500
1,4,5-Tri-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-fructopyranosyl bromide (8)	−207 (CH_2Cl_2)	−131,000
1,4,5-Tri-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-fructopyranosyl chloride (9)	−178 (CH_2Cl_2)	−105,000
1,3,4-Tri-*O*-benzoyl-2-*O*-methylsulfonyl-α-D-arabinopyranose	−127 ($CHCl_3$)[a]	−68,600
1,3,4-Tri-*O*-benzoyl-2-*O*-methylsulfonyl-β-D-arabinopyranose	−238 ($CHCl_3$)[a]	−129,000
3,4-Di-*O*-benzoyl-2-*O*-methylsulfonyl-β-D-arabinopyranosyl bromide	−351 (CH_2Cl_2)[a]	−175,000

[a] H. B. Wood, Jr., and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **80**, 5242 (1958).

CHART I



lated but benzoylated directly. Two crystalline tetra-*O*-benzoyl-3-*O*-methylsulfonyl-D-fructoses were thus obtained;[7] one of these was dextrorotatory ($[\alpha]^{20}D$ +40.4° in chloroform) while the other was levorotatory ($[\alpha]^{20}D$ −143° in chloroform). With hydrogen bromide, the levorotatory isomer gave a crystalline tri-*O*-benzoyl-3-*O*-methylsulfonyl-D-fructosyl bromide which was strongly levorotatory ($[\alpha]^{20}D$ −207° in dichloromethane); the dextrorotatory isomer, on the other hand, gave an amorphous bromide. It is, therefore, evident that the two tetra-*O*-benzoyl-3-*O*-methylsulfonyl-D-fructoses are not anomers. A crystalline chloride was prepared from the levorotatory ester and this was found to have $[\alpha]^{20}D$ −178° in dichloromethane. On the basis of evidence which will appear later in this paper, the crystalline tri-*O*-benzoyl-3-*O*-methylsulfonyl-D-fructosyl bromide (and, consequently, the corresponding chloride as well as the levorotatory tetra-*O*-benzoyl-3-*O*-methylsulfonyl-D-fructose) has a pyranose structure. Undoubtedly the anomeric configuration of the bromide and of the chloride is the same; that the bromide is more levorotatory than the chloride (Table I) indicates that both halides have the β-D configuration.[8]

As one might expect, the D-fructopyranose series bears a close resemblance to the D-arabinopyranose series. In the latter, the *1C* conformation predominates and the stable D-arabinopyranosyl halides have the β-D configuration, the halogen atoms being in axial positions as would be expected from the anomeric effect. The stable D-fructopyranosyl halides also have the β-D configuration[8-10] since here the *1C* conformation of the D-arabinopyranose series is further stabilized by the presence of an equatorial acyloxymethyl group. The close resemblance between 3-*O*-methylsulfonyl-D-fructopyranose derivatives and those of 2-*O*-methylsulfonyl-D-arabinopyranose may be seen by comparison of the rotations listed in Table I. The methylsulfonyl group does not, of course, participate in displacements of halogen atoms from adjacent carbon atoms but the benzoyl group at C-1 in 1,4,5-tri-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-fructopyranosyl bromide (**8**) should ensure the formation of a β-D derivative when the halide reacts with silver benzoate. In fact, **8** gave the original, strongly levorotatory ester which may now be designated as 1,2,4,5-tetra-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-fructopyranose (**6**). The structure of the dextrorotatory isomer of this substance will be discussed later in this paper.

Treatment of the bromide **8** with sodium iodide in acetone solution at room temperature afforded a crystalline, unsaturated derivative in 79% yield. The elemental composition of the product corresponded to that of a six-carbon glycal tribenzoate; on reduction with hydrogen in the presence of a palladium catalyst, this material gave a mixture of products from which 1,5-anhydro-2,3,6-tri-*O*-benzoyl-4-deoxy-D-*lyxo*-hexitol (**11**) was isolated; this substance has been described recently by Rosenthal and Koch.[11] The identity of the reduction product was confirmed through the preparation of 1,5-anhydro-4-deoxy-D-*lyxo*-hexitol (**12**) and of its tri-*p*-nitrobenzoate (**13**), substances which have been described by Gorin.[12] The isolation of **11** after the reduction of the glycal tribenzoate establishes the pyranose ring structure and the position of the double bond in the substance which may be designated as 1,4,5-tri-*O*-benzoyl-2,3-dideoxy-D-*erythro*-hex-2-enulopyranose (**10**). It may be noted that the optical rotation and chromatographic analysis of the reduction

(7) In passing, it is interesting to note that attempts to introduce a benzoyl group at C-2 in either 1,3,4,5-tetra-*O*-benzoyl-D-fructopyranose or 1,3,4,6-tetra-*O*-benzoyl-D-fructofuranose have been unsuccessful [P. Brigl and R. Schinle, *Ber.*, **66**, 325 (1933); *ibid.*, **67**, 127 (1934)]. The methylsulfonyl group at C-3 may offer less hindrance to the introduction of a benzoyl group at C-2 and may, perhaps, facilitate the benzoylation by rendering the hydroxyl group at C-2 more acidic.

(8) C. S. Hudson, *J. Am. Chem. Soc.*, **46**, 477 (1924).
(9) D. H. Brauns, *ibid.*, **45**, 2381 (1923).
(10) R. K. Ness and H. G. Fletcher, Jr., *ibid.*, **75**, 2619 (1953).
(11) A. Rosenthal and H. J. Koch, *Can. J. Chem.*, **42**, 2025 (1964).
(12) P. A. J. Gorin, *ibid.*, **38**, 641 (1960).

product from **10** showed that **11** was the predominant product. The *cis* addition of hydrogen to the less hindered side of **10** (the upper side, as depicted) would give **11**; a *cis* addition of hydrogen to the more hindered side of **10** would give 1,5-anhydro-4-deoxy-L-*ribo*-hexitol.[12] Further studies of some of the chemical properties of **10** are in progress.

As mentioned earlier, the dextrorotatory tetra-*O*-benzoyl-3-*O*-methylsulfonyl-D-fructose, obtained on benzoylation of 3-*O*-methylsulfonyl-D-fructose, did not give **8** when treated with hydrogen bromide. That it gave an amorphous bromide different from **8** strongly suggests that it has a furanose (rather than acyclic) structure. With sodium iodide in acetone solution, the crude amorphous bromide reacted much more rapidly than did **8**; the product thus formed decolorized permanganate but was not further investigated.

At an early stage of the investigation described here we thought it possible that a leaving group more effective than the methylsulfonyloxy group might be required for the synthesis of **10** and, therefore, undertook a simultaneous investigation of the preparation of some 3-*O*-*p*-nitrophenylsulfonyl-D-fructose derivatives. Two of these, 1,2:4,5-di-*O*-isopropylidene-3-*O*-*p*-nitrophenylsulfonyl-D-fructopyranose (**4**) and 1,2-isopropylidene-3-*O*-*p*-nitrophenylsulfonyl-D-fructopyranose (**5**), are described in the Experimental Section.

Experimental Section[13]

1,2:4,5-Di-*O*-isopropylidene-D-fructopyranose (2).—To a suspension of dry Dowex 50W-X8 (H^+) ion-exchange resin[14] (10 g) in acetone (1 l.) which had been cooled to −5° was added finely powdered D-fructose (50.0 g). Protected from atmospheric moisture, the mixture was stirred at −5° for 48 hr and the solution was then decanted from the resin which was washed several times with acetone. The solvent was removed from the combined decantate and washings to give a crystalline residue from which absolute ethanol (50 ml) was distilled *in vacuo*. The residue was then dissolved in warm absolute ethanol (60 ml) and the solution, diluted with ether (25 ml), stored at −5° overnight to give 39.3 g (54%) of 1,2:4,5-di-*O*-isopropylidene-D-fructopyranose (**2**): mp 117–118°; $[\alpha]^{20}D$ −161.5° (*c* 1.22, water) (lit.[4] mp 119–120°; $[\alpha]^{20}D$ −161.4° (water)). Solvent was removed from the mother liquor and the syrup dissolved in ethanol–pentane to give two further crops (8.8 g, 12%) of slightly less pure material: mp 117–118°; $[\alpha]^{20}D$ −160.4° (*c* 1.23, water).

1,2:4,5-Di-*O*-isopropylidene-3-*O*-methylsulfonyl-D-fructopyranose (3) was prepared in the conventional manner from **2** in 92% yield; it was recrystallized successively from aqueous ethanol, from methanol, and from ether and dried *in vacuo*: mp 102–104°; $[\alpha]^{20}D$ −159° (*c* 0.99, chloroform) (lit.[6] mp 104–105°; $[\alpha]^{22}D$ −161.4° (chloroform)).

1,2:4,5-Di-*O*-isopropylidene-3-*O*-*p*-nitrophenylsulfonyl-D-fructopyranose (4).—The diacetal (**2**, 10.0 g) was treated with *p*-nitrobenzenesulfonyl chloride in pyridine solution in conventional fashion to yield a crystalline product upon the addition of water; it was recrystallized from ether: 14.1 g (82%), mp 136–137° dec (in bath at 123°, 8°/min). Recrystallized from ethanol, the substance had mp 133–134° dec (in bath at 123°, 8°/min) and $[\alpha]^{20}D$ −158° (*c* 1.06, chloroform).

Anal. Calcd for $C_{18}H_{23}NO_{10}S$ (445.46): C, 48.53; H, 5.20; N, 3.14; S, 7.20. Found: C, 48.61; H, 4.97; N, 3.16; S, 7.13.

1,2-*O*-Isopropylidene-3-*O*-*p*-nitrophenylsulfonyl-D-fructose (5).—A portion (5.00 g) of **4** was suspended in a mixture of methanol (45 ml) and water (25 ml) and the solution was boiled under reflux while 1 *N* sulfuric acid (20 ml) was added. Refluxing was continued, the mixture becoming homogeneous after 13 min and then precipitating a mass of crystalline material. After a total of 15 min, the mixture was cooled and the crystals were collected and dried *in vacuo*, yield, 4.02 g (88%). The product was twice recrystallized from methanol and once from acetone: mp 132–133° dec (in bath at 120°, 8°/min); $[\alpha]^{20}D$ −110° (*c* 1.03, acetone).

Anal. Calcd for $C_{15}H_{19}NO_{10}S$ (405.40): C, 44.44; H, 4.72; N, 3.46; S, 7.91. Found: C, 44.52; H, 4.98; N, 3.49; S, 7.99.

The structure of **5** is assigned by analogy with 1,2-*O*-isopropylidene-D-fructopyranose.[5]

1,2,4,5-Tetra-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-fructopyranose (6) and 1,2,4,6-Tetra-*O*-benzoyl-3-*O*-methylsulfonyl-D-fructofuranose (7).—To a well-stirred suspension of **3** (70.0 g) in hot water (315 ml, 93°) was added 1 *N* sulfuric acid (35 ml) and the mixture was stirred and held at 93–96°. The **3** dissolved almost completely but, after *ca.* 4 min, 1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-D-fructopyranose[6] crystallized in part. In 10 min, the solution was again clear and, after 40 min, it was cooled in an ice bath and neutralized with barium carbonate.[15] The filtered solution was concentrated *in vacuo* at less than 50° and pyridine (200 ml) added to the resulting syrup. After reconcentration *in vacuo* and distillation of a second batch of pyridine (200 ml) from the syrup, the crude 3-*O*-methylsulfonyl-D-fructose was dissolved in a mixture of dry pyridine (150 ml) and dichloromethane (300 ml). The solution was cooled to −10° and stirred while a mixture of benzoyl chloride (100 ml) and dichloromethane (100 ml) was added dropwise over the course of 2 hr. Additional benzoyl chloride (47 ml) was then added directly and, 15 min later, the reaction mixture was allowed to warm to room temperature; it was stirred for 16 hr, cooled in ice, and treated with 15 ml of finely chopped ice. Two hours later, the reaction mixture was poured into a large volume of water and decanted from the resulting gum which was washed with four 500-ml portions of fresh water. The aqueous washings were extracted with dichloromethane and the extract was used to dissolve the gum; the resulting solution was washed successively with water, cold 3 *N* sulfuric acid, and saturated aqueous sodium bicarbonate. Moisture was removed with magnesium sulfate and the solution was concentrated *in vacuo* to give a syrup from which ethyl acetate (200 ml) was evaporated *in vacuo*. Dissolved in a mixture of ethyl acetate (200 ml) and pentane (*ca.* 200 ml), the mixture crystallized spontaneously to give **6**, containing 3.6% of ethyl acetate of solvation (identified by nmr): yield, 60.25 g (42% on a solvent-free basis); mp 134–140°. The substance can be recrystallized from dichloromethane–pentane, from absolute ethanol (after prior solution in dichloromethane and removal of this solvent), and from ethyl acetate–pentane. In each case, however, the crystalline material was found to contain solvent. Recrystallized from absolute ethanol, the substance had mp 138–141° dec (in bath at 130°, 10°/min), 149–150° dec (in bath below 90°, 10°/min) with sintering at 138°; $[\alpha]^{20}D$ −143° (solvent-free basis, *c* 1.10, chloroform). Dried *in vacuo* at 100°, that material lost 2.57% of its weight; an additional hour under these conditions caused no further loss.

Anal. Calcd for $C_{35}H_{30}O_{12}S$ (674.70): C, 62.31; H, 4.48; S, 4.75. Found: C, 61.99; H, 4.32; S, 5.06.

The original ethyl acetate–pentane mother liquor was concentrated *in vacuo* to dryness and the residue dissolved in a mixture of ether (200 ml) and pentane (50 ml). On seeding,[16] **7** crystallized: yield, 19.15 g (14%); mp 146–147° dec. The product was dissolved in dichloromethane, the solvent removed *in vacuo*, and the syrup crystallized from ether: mp 146–147° dec (in bath at 130°, 15°/min); $[\alpha]^{20}D$ +40.4° (*c* 1.00, chloroform).

(13) Melting points were determined with a Hershberg-type apparatus using Pyrex capillaries. As many of the substances described are thermally unstable, precise details for the determination of their melting points are given. Thin layer chromatography was conducted on silica gel G or GF_{254} (E. Merck AG, Darmstadt) while column chromatography was conducted on silica gel (0.05–0.20 mm) of the same manufacturer. Chloroform used for column chromatography was of USP grade. Nmr spectra were obtained in $CDCl_3$ solution using a Varian A-60 spectrometer and tetramethylsilane as an internal standard.

(14) For the initial run, the resin was washed several times with acetone and dried *in vacuo* overnight. At the conclusion of the reaction, the acetone-wet resin can be reused immediately for a second preparation or stored under acetone until needed. A single batch of the resin has been used in five successive runs with no appreciable change in yield.

(15) Neutralization at an elevated temperature gives rise to extensive decomposition.

(16) Seed crystals were originally obtained subsequent to chromatography of a sample of the mixture on silica gel using chloroform for elution; in this system **6** moves slightly faster than **7**. A chromatographically pure sample of **7** crystallized from its solution in absolute ethanol.

Anal. Calcd for $C_{35}H_{30}O_{12}S$ (674.70): C, 62.31; H, 4.48. Found: C, 62.10; H, 4.49.

1,4,5-Tri-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-fructopyranosyl Bromide (8).—1,2,4,5-Tetra-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-fructopyranose (**6**, 13.85 g, solvent-free basis) was dissolved in dichloromethane (20 ml) and 32% hydrogen bromide in glacial acetic acid (16 ml) was added to the solution. After 2 hr at room temperature, the reaction mixture was diluted with additional dichloromethane and slowly poured into a well-stirred mixture of ice, water, and an excess of sodium bicarbonate. When neutralization was complete, the organic layer was separated, dried with magnesium sulfate, and concentrated *in vacuo* to a syrup which was dissolved in ether (50 ml). The ether was removed *in vacuo* and, when the syrup was again dissolved in ether (50 ml), crystallization occurred. Pentane (50 ml) was added and crystallization allowed to proceed: yield, 11.7 g (90%); mp 157–158° dec (in bath at 145°, 10°/min) (recrystallization from ether–pentane failed to change the melting point); $[\alpha]^{20}D$ −207° (*c* 0.96, dry dichloromethane).

Anal. Calcd for $C_{28}H_{25}BrO_{10}S$ (633.49): C, 53.09; H, 3.98; Br, 12.61; S, 5.06. Found: C, 53.17; H, 4.10; Br, 12.78; S, 5.05.

1,4,5-Tri-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-fructopyranosyl Chloride (9).—1,2,4,5-Tetra-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-fructopyranose (**6**, 1.00 g, solvent-free basis) was dissolved in dry dichloromethane and the solution concentrated *in vacuo* to give a syrup which was dissolved in glacial acetic acid (3 ml) and sufficient dichloromethane to prevent the crystallization of **6**. Hydrogen chloride was passed into the solution for 60 min and the reaction mixture was then stirred in a stoppered flask for 2.5 hr. The reaction mixture was concentrated *in vacuo* at room temperature and the residual acetic acid solution of the product was stored at +5° overnight. Brought to room temperature, the acetic acid melted, leaving crystals of **9** which grew rapidly upon the addition of pentane: yield, 0.44 g (50%); mp 160–162° dec (in bath at 150°, 12°/min). The chloride (**9**) was recrystallized twice from ether–pentane (after initial solution in dichloromethane and removal of this solvent): mp 161–163° dec (in bath at 150°, 10°/min); $[\alpha]^{20}D$ −178° (*c* 0.98, dry dichoromethane).

Anal. Calcd for $C_{28}H_{25}ClO_{10}S$ (589.03): C, 57.09; H, 4.28; Cl, 6.02; S, 5.44. Found: C, 56.86; H, 4.36; Cl, 6.04; S, 5.48.

1,2,4,5-Tetra-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-fructopyranose (6) from 1,4,5-Tri-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-fructopyranosyl Bromide (8).—A mixture of **8** (130 mg) and silver benzoate (130 mg) in dry dichloromethane (1 ml) was stirred for 17 hr and then filtered through a bed of Celite, the residue being washed thoroughly with dichloromethane. Removal of the solvent from the combined filtrate and washings gave a crystalline residue which was recrystallized from a mixture of ether (1 ml) and pentane: yield, 149 mg (theory, 138 mg); mp 139–143° (gas evolution, in bath at 130°, 10°/min, decomposed at 150°). Recrystallized from ethanol, the material had mp 134–144° (in bath at 130°, 10°/min, decomposed at 164°); the infrared spectrum of the substance was identical with that of a specimen of **6** which had been prepared from 3-*O*-methylsulfonyl-D-fructose and crystallized from ethanol.

1,4,5-Tri-*O*-benzoyl-2,3-dideoxy-D-*erythro*-hex-2-enulopyranose (10).—To a solution of anhydrous sodium iodide (10 g) in acetone (100 ml, dried over Molecular Sieve 4A[17]) was added **8** (10.00 g). Almost immediately, the color of free iodine was visible and, within a few minutes, a precipitate formed. The course of the reaction was monitored by tlc using carbon tetrachloride–ether (1:1) and silica gel GF_{254}; the product was detected by spraying with 0.5% aqueous potassium permanganate or with 10% sulfuric acid and heating. After 41 hr, **8** was barely detectable and the reaction mixture was concentrated *in vacuo* to dryness. The residue was extracted with dichloromethane and the combined extracts were washed successively with aqueous sodium bicarbonate, aqueous sodium thiosulfate, and water. Moisture was removed with magnesium sulfate and the solution was concentrated *in vacuo;* a solution of the residue in absolute ethanol (30 ml) was seeded[18] and crystallization allowed to proceed: yield 5.73 g (79%). After two recrystallizations from absolute ethanol, the product had mp 74–76° and $[\alpha]^{20}D$ +163° (*c* 1.09, chloroform).

Anal. Calcd for $C_{27}H_{22}O_7$ (458.48): C, 70.73; H, 4.84. Found: C, 70.78; H, 4.83.

Reduction of 1,4,5-Tri-*O*-benzoyl-2,3-dideoxy-D-*erythro*-hex-2-enulopyranose (10).—A solution of **10** (1.132 g) in glacial acetic acid (10 ml) was treated with 10% palladium on charcoal (0.5 g) and the suspension was shaken with hydrogen at room temperature and pressure until absorption of the gas had ceased (6 hr). After removal of the catalyst, the solution was concentrated *in vacuo* and the resulting syrup freed of residual acetic acid by distilling therefrom (*in vacuo*) toluene and absolute ethanol: $[\alpha]^{20}D$ −62.1° (*c* 2.97, 95% ethanol), 75.3° (*c* 2.05, chloroform). The crude product was chromatographed on silica gel (150 g) using chloroform–ether (5:1, 600 ml), followed by chloroform–ether (5:2, 600 ml), 10-ml fractions being collected and examined by tlc (carbon tetrachloride–ether, 1:1). Three components were encountered. The first and second appeared in fraction 34 in trace amounts. Fraction 35 (180 mg) contained the third component contaminated with the second. Fractions 36–42 contained the third and major component in pure form: yield, 700 mg; $[\alpha]^{20}D$ −79.0° (*c* 2.90, 95% ethanol), −102° (*c* 1.70, chloroform).

Anal. Calcd for $C_{27}H_{24}O_7$ (460.46): C, 70.42; H, 5.25. Found: C, 70.42; H, 5.35.

Rosenthal and Koch[11] reported $[\alpha]^{21}D$ +79° (*c* 1.58, chloroform) for 1,5-anhydro-2,3,6-tri-*O*-benzoyl-4-deoxy-L-*ribo*-hexitol and $[\alpha]^{21}D$ −63° (*c* 3, ethanol) for its diastereoisomer, 1,5-anhydro-2,3-6-tri-*O*-benzoyl-4-deoxy-D-*lyxo*-hexitol (**11**); the nmr spectrum of the latter compound, kindly provided by Dr. Rosenthal, proved to be identical with that of the major product isolated here.

1,5-Anhydro-4-deoxy-D-*lyxo*-hexitol (12).—A sample (630 mg) of the tribenzoate **11** was deacylated with methanolic barium methoxide in conventional fashion to give a crystalline magma (160 mg) which was recrystallized from a mixture of absolute ethanol (0.5 ml) and ethyl acetate (0.25 ml) to give 87 mg (43%) of nearly pure product, mp 76–79°. The compound was dissolved in methanol and the solution filtered through a layer of decolorizing carbon and then concentrated *in vacuo* to a syrup which was crystallized from ethyl acetate: yield, 60.8 mg; mp 78–81°; $[\alpha]^{20}D$ −45.1° (*c* 1.02, water). For 1,5-anhydro-4-deoxy-D-*lyxo*-hexitol (**12**), mp 85–87°,[11] 80–81°,[12] and $[\alpha]D$ −50° (water)[11,12] have been reported. Gorin[12] has calculated that, of all the diastereoisomeric 1,5-anhydro-4-deoxy-D-hexitols, only that with the *lyxo* configuration should be levorotatory. *p*-Nitrobenzoylation of our product gave an ester which was successively recrystallized from aqueous pyridine and absolute ethanol: mp 114–115; $[\alpha]^{20}D$ −111° (*c* 0.80, chloroform). Gorin[12] reported mp 113–115° and $[\alpha]D$ −83° (chloroform) for 1,5-anhydro-4-deoxy-2,3,6-tri-*O*-*p*-nitrobenzoyl-D-*lyxo*-hexitol (**13**).

Registry No.—**2**, 15080-25-8; **3**, 15080-26-9; **4**, 15156-65-7; **5**, 15156-64-6; **6**, 15080-04-3; **7**, 15180-32-2; **8**, 15080-05-4; **9**, 15080-06-5; **10**, 15080-09-8; **11**, 15080-07-6; **12**, 15080-08-7.

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(17) Fisher Scientific Co.

(18) Seed crystals were originally obtained subsequent to column chromatography of the crude preparation from a similar experiment, ether–carbon tetrachloride (1:4) being used for elution. Solvent was removed from a chromatographically homogeneous fraction; the resulting syrup crystallized spontaneously after 1.5 months.