XXIX

5,6-di-O-isopropylidenehexofuranoses could easily be excluded also on the basis of the optical rotation of the hydrolysis product. The rotation of a solution of XXIX after hydrolysis with 0.1 N hydrochloric acid was in agreement only with the equilibrium value of D-galactose which is quite different from all other hexoses, the stereochemistry of which could permit the formation of a 1,2:5,6-di-O-isopropylidenehexofuranose. Furthermore, the melting point of XXIX differs from that of V and XXV. Thus the second di-O-isopropylidene-D-galactose has structure XXIX.

Experimental

Mass Spectra.—The spectra were determined with a CEC 21⁻ 103C mass spectrometer, equipped with a heated stainless steel inlet system operated at 170°; ionizing potential 70 e.v., ionizing current 50 μamp., temperature of the ion source 250°. The sample (~0.5–1.0 mg.) was sublimed from a glass tube into the reservoir (3 l.).

High resolution spectra were determined[13] with a CEC 21-110 double focusing mass spectrometer, equipped with a glass inlet system operated at 200°; ionizing current 250 μamp., ionizing potential 150 e.v.

1,2:4,5-Di-O-isopropylidene-d_{12}-D-fructopyranose (XIX).—D-Fructose (170 mg.) was dissolved in deuterium oxide to replace the hydroxyl protons with deuterium. After evaporation of the excess deuterium oxide, the residue was converted to the di-O-isopropylidene derivative[22] using acetone-d_6 in place of acetone. The product had m.p. 115–120° which was undepressed on admixture of authentic, nondeuterated material (lit.[22] 119.5°). The mass spectra of the product when purified either by recrystallization or by gas chromatography (3% SE-30, 165°) were identical, thus proving that no changes occur on gas chromatographic separation.

1,2:5,6-Di-O-isopropylidene-d_{12}-D-glucofuranose (V).—D-Glucose (100 mg.) was similarly converted to D-glucose-O-d_6; the

(22) H. O. L. Fischer and C. Taube, *Chem. Ber.*, **60B**, 485 (1927).

di-O-isopropylidene derivative was prepared[23] by treating this with acetone-d_6; m.p. 109–110° (reported[24] for unlabeled material, 109–110°).

1,2:3,4-Di-O-isopropylidene-D-galactopyranose (II), 1,2:5,6-Di-O-isopropylidene-D-galactofuranose (XXIX), and Their d_{12}-Analogs IIa and XXIXa.—A mixture of 10 mg. of D-galactose, 50 mg. of cupric sulfate, and 0.8 ml. of acetone was sealed in an ampoule and heated on a steam bath for 18 hr. The acetone layer was separated and made slightly basic with potassium carbonate. After evaporation of the excess acetone, the residue was shown by gas chromatography (Apiezon L, 200°) to consist of two components (ratio 4:1), in addition to traces of acetone and its self-condensation products. Both components were collected; the mass spectrum of the larger fraction was found to be identical with the spectrum of 1,2:3,4-di-O-isopropylidene-D-galactopyranose (II) prepared by the method of Levene and Meyer[21] (by this procedure only a trace, less than 3%, of the second component is detectable by gas chromatography). The smaller, slower-moving fraction was a solid, m.p. 97.5–98.5°; it has been assigned the structure 1,2:5,6-di-O-isopropylidene-D-galactofuranose (XXIV) for reasons discussed above.

Samples of both di-O-isopropylidene-D-galactoses (II and XXIX) were each dissolved in 1.00 ml. of 0.1 N hydrochloric acid and hydrolyzed for 2 hr. at 100°. The optical rotations of the resulting solutions were measured: D-galactose from derivative II, $[\alpha]^{32}$D +78° (0.1 N HCl, c 0.55) and D-galactose from derivative XXIX, $[\alpha]^{32}$D+75° (0.1 N HCl, c 0.19); lit. [25]$[\alpha]^{32}$D +77.4° (H$_2$O, c 11.4).

1,2:3,4-Di-O-isopropylidene-L-arabinopyranose (VII) and its d_{12}-analog, m.p. 40.0° (reported[26] for nonlabeled material, 42°); **2,3:4,6-di-O-isopropylidene-L-sorbofuranose (XXII)** and its d_{12}-analog; **1,2:3,4-di-O-isopropylidene-L-fucopyranose (XXIV)**; **1,-2:3,5-di-O-isopropylidene-D-xylofuranose (X)** (prepared on 1 mg. of D-xylose) and its d_{12}-analog; **2,3-O-isopropylidene-D-ribofuranose (XIV)**, **2,3-O-isopropylidene-1,5-anhydro-D-ribofuranose (XV)** and their d_6-analogs; and **2,3-O-isopropylidene-α-D-lyxofuranose (XXVIII)** were prepared by the procedure described above for D-galactose and purified by gas chromatography (3% SE-30, 130–160°).

(23) D. J. Bell, *J. Chem. Soc.*, 1874 (1935).
(24) E. Fischer and C. Rund, *Chem. Ber.*, **49**, 88 (1916).
(25) Rindell, *Neue Ztschr. Rübenzuckerind.*, **4**, 166 (1880); *cf.* "Beilstein," Band 31, p. 298.
(26) P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, **115**, 731 (1936).

Formation and Hydroboration of an Olefinic Sugar[1]

By Henri Arzoumanian, Edward M. Acton,[2] and Leon Goodman

The tosylate VI of methyl 6-deoxy-2,3-O-isopropylidene-β-D-allofuranoside (IV) on base-catalyzed elimination afforded the furanose propenyl ether VII, rather than the desired terminal olefin VIII. Hydroboration of VII occurred from the less hindered side to form methyl 6-deoxy-2,3-O-isopropylidene-β-D-gulofuranoside (IX), identical with an authentic sample prepared by inverting the rhamnofuranoside tosylate (XI).

The D-ribofuranose moieties I in RNA are connected in this important polymer through a series of 3',5'-phosphate linkages. If the homologous 5-deoxy-D-allofuranose bases II could be incorporated into nucleic acids, these would probably be linked by 3',6'-phosphate bonds with attendant changes in the nucleic acid geometry. As a first step in the preparation of II, we were interested in devising a synthesis of hitherto unreported 5-deoxy-D-allose, and this paper reports some efforts in that direction.
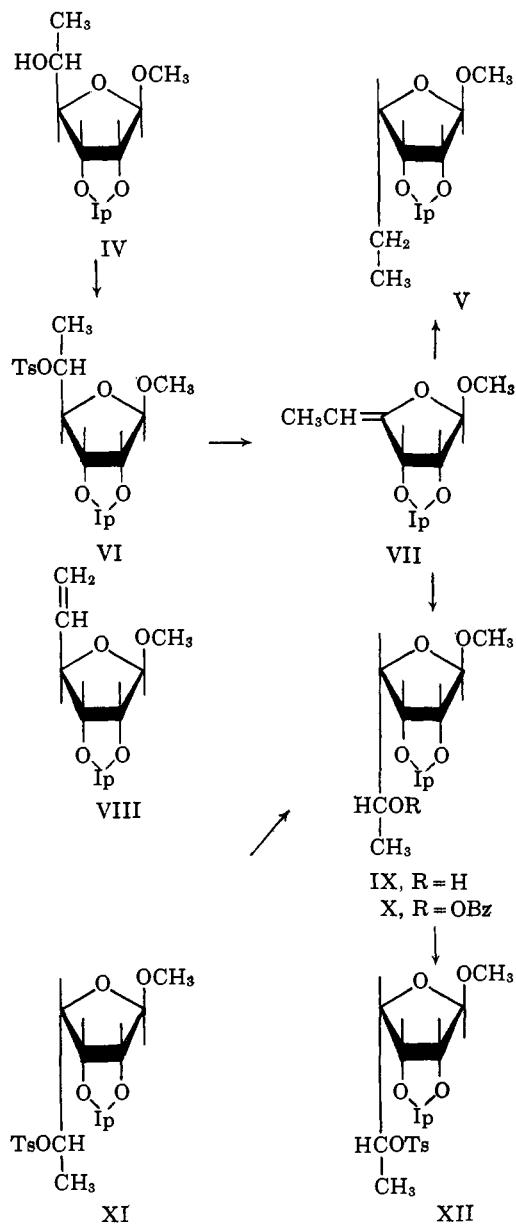
I

II

III
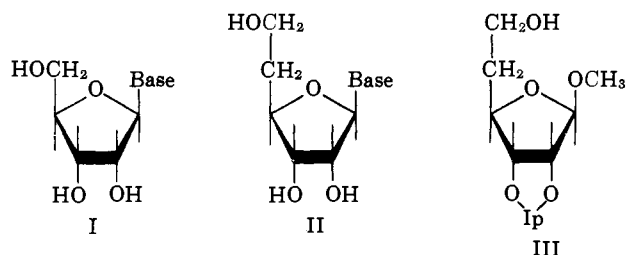
A logical point of departure for the work was the known[3,4] 6-deoxy-D-allose derivative IV, whose con-

(3) E. J. Reist, L. Goodman, R. R. Spencer, and B. R. Baker, *J. Am. Chem. Soc.*, **80**, 3962 (1958).
(4) P. A. Levene and J. Compton, *J. Biol. Chem.*, **116**, 169 (1936).

SCHEME I

version to the terminal olefin VIII followed by hydroboration might be expected to form the desired derivative III of 5-deoxy-D-allose; hydroboration is known generally to result in anti-Markovnikov addition of the elements of water to the olefinic bond.[5] When the 5-tosylate VI[3] of the 6-deoxyalloside IV was treated with one equivalent of potassium *t*-butoxide in refluxing *t*-butyl alcohol for 70 hr., the olefin formed (about 40% yield) was mainly the propenyl ether VII, rather than the desired terminal olefin VIII, and was accompanied by about 20% of the parent alcohol IV. Integration of the n.m.r. spectrum of the olefinic product suggested the presence of about 10% of VIII as judged by a deficiency in the C_6-methyl doublet of VII at 8.31 τ. Base treatment of VI in higher boiling solvents such as diethylene glycol dimethyl ether (diglyme), or in 2-methoxyethanol[6] containing sodium, afforded identical product in a shorter time, but separation of the olefinic product from the solvent was inconvenient and wasteful. Since allyl ethers rearrange to propenyl ethers[7] under conditions similar to those em-

ployed in the generation of VII, the possibility existed that the allyl ether VIII had been formed first, then isomerized to VII in the medium. However, when the tosylate VI was heated for 45 min. at 170° and 0.05 mm. with soda lime[8] and the distillate collected at −70°, conditions that permitted minimum contact between the base and the elimination product, the product was identical with that obtained previously, suggesting that VII was formed directly.

If the elimination[9] to form VII was a concerted process (E2) requiring *trans* orientation between the 5-tosyl group in VI and the C_4-proton, the resulting olefin VII should be the geometrical isomer shown in Scheme II,[10]

SCHEME II
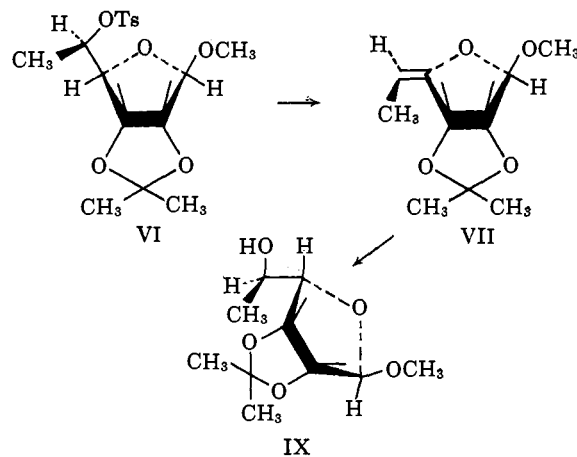
with the terminal methyl(C_6) extending forward from the plane of the paper. It is possible to obtain a primary alcohol from the hydroboration of an internal olefin by isomerizing[5] the intermediate borane in refluxing diglyme, whereupon the boron substituent moves to the least hindered position, generally the end of the carbon chain. The use of this procedure was considered for the possible conversion of VII to III, especially since there was precedent[11] in the hydroboration of vinyl ethyl ether to expect polarization of the olefinic bond under influence of the ether oxygen to give attack by the boron at C_5 rather than at C_4. The stereochemistry of hydroboration[5] is *cis* hydration from the less hindered side; in VII this means from the top (the isopropylidene group will hinder approach from beneath the furanose ring). Thus even if a borane from VII could be isomerized to a terminal borane, the final hydroboration product would have the wrong configuration at C_4. That these considerations were valid was demonstrated by hydroboration of VII in tetrahydrofuran with sodium borohydride and boron trifluoride etherate[12] to form methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-gulofuranoside (IX), having the allose configuration at C_5, but the rhamnose configuration at C_4. The product was a crystalline solid, further characterized as a crystalline tosylate XI. The identity of both these 6-deoxy-D-gulose derivatives was established

(5) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(6) E. Vis and H. G. Fletcher, Jr., *J. Org. Chem.*, **22**, 712 (1957).

(7) T. J. Prosser, *J. Am. Chem. Soc.*, **83**, 1701 (1961); C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961).

(8) F. Weygand and H. Wolz, *Chem. Ber.*, **85**, 256 (1952); K. Antonakis, A. Dowgiallo, and L. Szabo, *Bull. soc. chim. France*, 1355 (1962).

(9) J. F. Bunnett, *Angew. Chem. Intern. Ed. Engl.*, 1, 225 (1962).

(10) The structures VI and IX in Scheme II are depicted as rotamers (at the C_4–C_5 bonds) of VI and IX in Scheme I; in accord with the usual Fischer convention, the configuration of C_5 in the formulas of Scheme I is portrayed with the functional groups at C_5 (OH, OTs, OBz) and the hydrogen at C_5 projecting out from the plane of the paper, and with C_6 lying behind the plane of the paper.

(11) B. M. Mikhailov and T. A. Shchegoleva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 546 (1959); ref. 5, p. 112.

(12) H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover, and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4233 (1960).

TABLE I

NUCLEAR MAGNETIC RESONANCE DATA[a]

Compound	C₁-H	C₂-H + C₃-H	C₄-H	C₅-H	C₆-H	OCH₃	C(CH₃)₂	J₂,₃	J₃,₄	J₄,₅	J₅,₆
		Proton chemical shifts, τ						Proton coupling constants, c.p.s.			
IV	5.01	5.11,[b] 5.41[b] (AB)	5.84[b]	6.1-6.2[c]	8.77[b]	6.55	8.51, 8.66	6.2	<0.5	3	6.5
IX	5.08	~5.3[c]	6.28[d]	5.85[e]	8.72[b]	6.67	8.53, 8.70		3.1	6.2	~6.2
VI	5.11		6.07[b]		8.70[b]	6.67	8.56, 8.74		<0.5	10.0	~6.2
XI	5.23		6.17[f]		8.50	6.74	8.75, 8.91			~8	6.2
XII	5.38		6.17[f]		8.56[b]	6.85	8.68, 8.75		3.0	9.0	~6.3
VII	4.98		. . .		8.31[b]	6.66	8.55, 8.65				7.1
V	5.16	5.45[c]	6.19[g]	8.25[c]	8.99[c]	6.72	8.54, 8.68		3.0	~6.8	6.8

[a] Spectra were determined in chloroform-d solutions (5-15% wt./wt.) containing 1% tetramethylsilane as internal reference, with Varian A-60 and HR-60 spectrometers. Signals are singlets unless otherwise designated; multiplets are measured from multiplet centers. Accuracy is ±0.02 p.p.m. for chemical shifts and ±0.5 c.p.s. for coupling constants; J₁,₂ was always <0.5. [b] Doublet [c] Multiplet, but not fully resolved. [d] Pair of doublets. [e] Quintet. [f] Quartet. [g] Triplet of doublets.

by comparison with authentic samples prepared from L-rhamnose. Inversion of methyl 2,3-O-isopropylidene-5-O-tosyl-α-L-rhamnoside (XI) by the useful displacement[13] with sodium benzoate in dimethylformamide afforded the 5-O-benzoate X of the 6-deoxyguloside; saponification afforded authentic free IX, which was further converted to the authentic 5-O-tosyl guloside XII. Comparison of these materials with IX and XII from the hydroboration revealed identical n.m.r. and infrared spectra within each pair, a good agreement in optical rotation, and absence of any mixture melting point depression. The fact that authentic IX melted some 10° higher than the 6-deoxyguloside IX from the hydroboration may reflect the presence of a little, difficultly removed, hydroboration product (possibly III) from the isomeric olefin VIII[14] suspected in VII; the much better agreement in melting points of the two samples of the tosylate XII suggests that purification of the derivative is easier. Mixture melting point depressions with the epimeric rhamnoside and deoxyalloside tosylates (XI and VI, respectively) were striking. The absolute configurations at C₅ of the epimeric tosylates XI and XII could be predicted[15] by comparing the n.m.r. spectra, data for which are compiled in Table I, along with data for the other compounds prepared during this study. The abnormal chemical shifts of the acetonide methyls in the spectrum of XI can be accounted for by the shielding of those methyls by the tosyl moiety; similarly, the abnormal chemical shifts of the C₁-proton and methoxyl in XII can be accounted for by shielding by the tosyl group. Assuming that the most stable conformation for either XI or XII is the rotamer with the C₅-proton pointed under the furanose ring, then, as in Scheme III, the tosyl group in XI lies in front of the plane of the paper, and in XII the tosyl group lies behind the plane of the paper. Molecular models show that the aromatic

SCHEME III

XI   XII
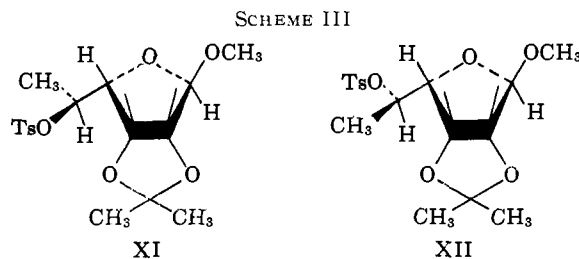
ring of the tosylate XI can approach the acetonide methyls, and in XII the aromatic ring can approach the C₁-substituents. In general, except for XI, chemical shifts of the acetonide methyl resonances in Table I

(13) E. J. Reist, L. Goodman, and B. R. Baker, J. Am. Chem. Soc., 80, 5775 (1958).

(14) The desired terminal olefin VIII has recently been prepared; its synthesis and hydroboration will be the subject of a separate paper.

(15) S. A. Fuqua, personal communication.

resemble those recorded[16] for a series of isopropylidene glucofuranosides; and except for XII, chemical shifts for the C₁-protons and methoxyls resemble those recorded[17] for a methyl β-D-ribofuranoside.

The formation of the olefin VII can be compared to the reaction described[18,19] between the rhamnose 5-tosylate XI and aqueous methanolic potassium hydroxide, which also formed an olefin along with a little free 5-hydroxyl sugar (XI, Ts = H). The olefin was not completely identified, and was assumed[19] to be the terminal olefin (anomeric with VIII at C₄). The conversion of VI to VII makes it very likely (especially if electronic influences are decisive) that the product from X was also a 4,5-olefin, in fact the same geometrical isomer VII. The optical rotation[19] and refractive index[18,19] reported for the olefin from XI agree with data for VII. A striking property of VII, also noted by Muskat,[19] is the instantaneous consumption of bromine in large excess in chloroform or carbon tetrachloride solutions; easy loss of hydrogen bromide such as was found with the bromine adduct of a pyranoside vinyl ether[20] similar to VII can give rise to a series of degradation products requiring the excess bromine.

The double bond in VII was easily saturated by hydrogenation at one atmosphere with a 5% palladium-carbon catalyst. The same steric considerations which predicted hydroboration by attack from the topside of the molecule VII also predicted topside attack in the reduction, so that in the product V the ethyl side chain (C₅ and C₆) extends downward.

Experimental[21]

Gas chromatography (g.l.p.c.) was used to determine purity of the volatile compounds prepared, both when crude and when purified, and in some cases was used preparatively. A 1.5-m. column, 3/8 in. diam., packed with 20% butanediol succinate supported on acid-washed, 80-100 mesh Chromosorb W, was used at 200° with helium as carrier gas at 200 ml./min. in an Aerograph Autoprep A-700 (Wilkens Instrument and Research Inc., Walnut Creek, Calif.), with an injection temperature of 210°. The olefin VII had a retention time (r.t.) of 1.8 min. and the dideoxy compound V had r.t. 1.3 min.; under the same conditions, the two 5-hydroxyl compounds IV and IX were resolved, r.t. 5.2 and 4.5 min., respectively. Lower temperatures or flow rates, if used are mentioned under each compound; otherwise all g.l.p.c. data are for these conditions.

Methyl 5,6-Dideoxy-2,3-O-isopropylidene-β-D-allofuranoside-4-ene (VII).—A solution of 11.5 g. (0.0309 mole) of methyl 6-

(16) R. J. Abraham, L. D. Hall, L. Hough, and K. A. McLauchlan, J. Chem. Soc., 3699 (1962).

(17) L. D. Hall, Chem. Ind. (London), 950 (1963).

(18) P. A. Levene and J. Compton, J. Am. Chem. Soc., 57, 2306 (1935).

(19) I. E. Muskat, ibid., 56, 2653 (1934).

(20) B. Helferich and E. Himmen, Ber., 61B, 1825 (1928).

(21) Melting points were determined on a Fisher-Johns block and are corrected. Infrared spectra were determined on all compounds reported, either as pure liquids, or in Nujol null for solids. Optical rotations were determined on 1% solutions (except for XI, as noted) in 1-dm. tubes with a Rudolf photoelectric polarimeter, the error reported represents an estimation of maximum possible weighing and volumetric errors, plus a constant instrument error at this concentration of ±1.2°

deoxy-2,3-O-isopropylidene-5-O-tosyl-β-D-allofuranoside[3] (VI) in 250 ml. of redistilled t-butyl alcohol was treated with 3.47 g. (0.0309 mole) of potassium t-butoxide, and the mixture was refluxed for 70 hr. while a white precipitate was formed. Most of the solvent was removed by concentration at 17 mm. (at or below 30°, to minimize volatilization of VII), and the residue was dissolved in 25 ml. of water. The product was extracted with four 5-ml. portions of dichloromethane. The combined, dried extracts upon concentration at 30° and 17 mm. afforded 4.74 g. (76% yield) of colorless oil, which showed some hydroxyl absorption in the infrared but complete absence of tosyl bands at 6.24 (weak) and 8.48 (strong) μ. The only infrared absorption band in the 5.5 to 6.5 μ region was of moderate intensity at 5.87 μ and was assigned to C=C stretching, although the wave length was shorter than expected; a weak band at 10.9 μ was tentatively assigned to the single olefinic C–H. Gas chromatography showed that the olefin contained 28% 5-hydroxyl compound IV as a by-product. The olefin was distilled (50–60% recovery) at 40–42° (0.1 mm.), $[\alpha]^{25}$D +12.5 ± 1.7° (chloroform), $[\alpha]^{24}$D +13.0 ± 1.7° (methanol; lit.[19] $[\alpha]^{25}$D +14° in methanol for the olefin obtained from XI), $n^{24.5}$D 1.4500 (lit. n^{24}D 1.4491,[18] n^{25}D 1.4485,[19] for the olefin from XI); however, the olefin VII still contained 5% of the alcohol IV.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.0; H, 8.05; O, 32.0. Found: C, 59.7; H, 8.22; O, 32.2.

Removal of the remaining IV by alumina chromatography in petroleum ether afforded a sample of VII which gradually polymerized on standing. There were indications of increased oxygen content in other purified samples of VII, suggestive of an oxidative polymerization.

Methyl 5,6-Dideoxy-2,3-O-isopropylidene-β-D-gulofuranoside (V).—A stirred solution of 0.750 g. (3.75 mmoles) of VII in 50 ml. of absolute ethanol was hydrogenated at 1 atmosphere with 0.075 g. of 5% palladium–charcoal. After 25 min., hydrogen consumption was complete, the catalyst was collected by filtration through Celite, and the filtrate was evaporated at 40° (20 mm.) to form a colorless liquid residue (67%), $[\alpha]^{24}$D −77.2 ± 3.6° (chloroform). The infrared spectrum disclosed the loss of absorption bands in VII at 5.8 and 10.9 μ. Gas chromatography indicated 8% of a second component (r.t. 1.65 min.) closely following the main peak, and 2% of IV, which had been present in the starting material VII. Integration of the n.m.r. spectrum indicated the terminal C_6-methyl signal was deficient by just the amount of the second component present.

Anal. Calcd. for $C_{10}H_{18}O_4$: C, 59.4; H, 8.97. Found: C, 59.4; H, 8.96.

A sample of the major component V for the n.m.r. spectrum was collected by preparative gas chromatography at 125° with a flow rate of 50 ml./min. (r.t. 14 min.). A small amount of the second component (r.t. 19 min.) was also collected; both components upon infrared comparison showed absence of hydroxyl and presence of methyl isopropylidene furanoside (7.25, 8.27, 8.61, and 11.4–11.5 μ) bands.

Methyl 6-Deoxy-2,3-O-isopropylidene-β-D-gulofuranoside (IX). (1) From VII.—Sodium borohydride (0.134 g., 3.54 mmoles) was added to a solution under nitrogen of 2.21 g. (11.0 mmoles) of olefin VII in 20 ml. of anhydrous tetrahydrofuran, and the stirred mixture was treated dropwise during a 30-min. period with a solution of 0.660 g. (4.65 mmoles) of freshly distilled boron trifluoride etherate in 10 ml. of anhydrous tetrahydrofuran. Stirring of the mixture was continued at room temperature under nitrogen for 1.5 hr., and the excess reagent was decomposed by dropwise addition of water until the moderate effervescence sub-

sided; 2 ml. of 2 M sodium hydroxide and 1.5 ml. of 30% hydrogen peroxide were added, the mixture was stirred at room temperature for 1.25 hr., and the tetrahydrofuran was removed under reduced pressure. The aqueous residue was extracted with ether, and the extracts were dried and freed of ether at reduced pressure. The residual product was a colorless sirup (1.41 g., 59%) that crystallized on standing. Infrared bands characteristic of VII at 5.85 and 10.9 μ were absent, and a strong –OH band appeared at 2.87 μ. A flame test showed the absence of boron compounds. Gas chromatography indicated a purity of 96% (r.t. 12.2 min. at 60 ml./min. flow rate) with a single contaminant (r.t. 7.7 min. at 60 ml./min.). Preparative g.l.p.c. afforded an analytical sample, m.p. 65–68°, $[\alpha]^{24}$D −88.5 ± 5.7° (methanol).

Anal. Calcd. for $C_{10}H_{18}O_5$: C, 55.0; H, 8.31; O, 36.7. Found: C, 54.9; H, 8.26; O, 36.5.

The 5-O-tosylate XII was prepared by treating 1.41 g. (6.45 mmoles) of IX in 50 ml. of pyridine with 2.45 g. (12.9 mmoles) of tosyl chloride in 10 ml. of chloroform, as described[3] for the analogous alloside. The sirupy product (1.60 g., 67%) retained only a weak absorption at 2.80 μ in the infrared (unreacted –OH) and was crystallized from ethyl acetate–petroleum ether (b.p. 30–60°). The resultant large prisms (34% yield) were collected in several crops and recrystallized from methanol (5 ml./g., 85% recovery); m.p. 68–69°, $[\alpha]^{23}$D −74.4 ± 3.0° (methanol). The melting point on admixture with the 6-deoxyalloside 5-tosylate VI, m.p. 96–97° (lit.[3,4] 91–92°, 93–94°), was 54–55°. With the 5-tosyl rhamnoside[4] XI, the mixture melting point was 48–54°.

Anal. Calcd. for $C_{17}H_{24}O_7S$: C, 54.8; H, 6.50; O, 30.1; S, 8.61. Found: C, 54.9; H, 6.75; O, 29.8; S, 8.41.

(2) **From XI.**—Inversion of the rhamnose tosylate XI (see below) with sodium benzoate in refluxing dimethylformamide[13] and debenzoylation of the resulting ester with anhydrous methanolic sodium methoxide was carried out as described[13] for preparation of the corresponding talosides. The product was separated from methyl benzoate by saponification with potassium hydroxide in methanol–water (5:1) at room temperature; the methanol was removed *in vacuo*, and the sugar was extracted from potassium salts with dichloromethane and obtained fom the extracts as a residual white solid. A contaminant (10%) with r.t. the same as the olefin VII was revealed by g.l.p.c. Recrystallization from Skelly B (25 ml./g., 68% recovery) afforded white needles, $[\alpha]^{23}$D −85.3 ±3.4° (methanol), m.p. 78–78.5°, m.p. 73–76° on admixture with the product from (1). The two materials were identical in infrared and n.m.r. spectra, and in r.t.

The 5-O-tosylate XII was prepared as in 1 above. The sirupy product (81%) crystallized on seeding with XII from (1), and was recrystallized from methanol, $[\alpha]^{24}$D −73.1 ± 3.0° (methanol), m.p. 70–71.5°. The mixture m.p. on admixture with XII from (1) was 69–70°, and the infrared and n.m.r. spectra of the two samples were identical.

Methyl 2,3-O-isopropylidene-5-O-tosyl-α-L-rhamnofuranoside XI, m.p. 83.5–84°, $[\alpha]^{25}$D −14.7 ± 0.8° (c 3 in methanol), was prepared[4] from L-rhamnose (lit.[4] m.p. 82–83°, $[\alpha]$D −14.3°).