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Acetonation of L-Sorbose by Ketal Interchange[1,2]

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The acetonation reaction of L-sorbose with acetone dimethyl ketal was investigated. The products and the yields were greatly influenced by the reaction conditions. The reaction at 45°C gave 1, 3 : 4, 6-di-*O*-isopropylidene-*β*- (VIIa), 1, 2 : 4, 6-di-*O*-isopropylidene-*α*- (Va) and 2, 3 : 4, 6-di-*O*-isopropylidene-*α*-L-sorbofuranose (IVa) and the *β*-anomer of Va (VIa). At the refluxing temperature, the reaction afforded IVa and the 2-*O*-methyl derivative of VIIa (VIIe), while at room temperature it yielded 1, 2 : 3, 4-di-*O*-isopropylidene-*α*-L-sorbopyranose (VIIIa), 1, 2 : 4, 5-di-*O*-isopropylidene-*α*-L-sorbopyranose (IXa), and 5-*O*-*α*-methoxyisopropyl-1, 2 : 3, 4-di-*O*-isopropylidene-*α*-L-sorbopyranose (VIIIc).

In a previous communication,[3] it has been reported that the acetonation of L-sorbose with acetone diethyl ketal (2, 2-diethoxypropane)[4] produced 2, 3 : 4, 6-di-*O*-isopropylidene-*α*-L-sorbofuranose (IVa) and two new acetonated sugars, 1, 2 : 4, 6-di-*O*-isopropylidene-*α*-L-sorbofuranose (Va) and 1-*O*-*α*-ethoxy-isopropyl-2, 3 : 4, 6-di-*O*-isopropylidene-*α*-L-sorbofuranose (IVd), while the reaction with acetone gave exclusively IVa.[5] Furthermore, thin-layer chromatographic analyses of the reaction products with acetone dimethyl ketal (2, 2-dimethoxypropane)[6] indicated multiple spots. The relative concentrations of the spots varied with the reaction conditions employed. These facts suggest a complex mechanism for the acetonation reaction and prompted us to study the acetonation of L-sorbose with acetone dimethyl ketal in detail.

The acetonation of L-sorbose with acetone dimethyl ketal was performed in the presence of *p*-toluenesulfonic acid (TsOH) as a catalyst. The reaction at 45°C for 4 hr gave a semicrystalline syrup, the thin-layer chromatogram of which showed four major components (A, B, C, and D) and several minor ones. By filtration, the semicrystalline syrup was separated into two parts, a crystalline part and a syrupy part. From the latter part, B, C and D compounds were isolated in pure states by preparative thin-layer chromatography. The recrystallization of the crystalline part gave the A compound. Thin-layer chromatography of the mother liquor showed the presence of 1, 2-*O*-isopropylidene-*α*-L-sorbopyranose (IIa)[7] and 2, 3-*O*-isopropylidene-*α*-L-sorbofuranose (IIIa).[8] Reaction under reflux for several hours gave a syrupy mixture, from which two major products, C and E, were isolated. IIa was transformed into three other acetonated sugars, F, G, and H, under milder acetonation conditions. The acetonation of IIIa gave IVa, together with traces of the I and J compounds. The I and J compounds were also prepared in poor yields from the acetonation of IVa.

Among the above-obtained products (A–J), the B and C compounds were identical with Va and IVa respectively. The A, D, G, and H compounds were analyzed for a diacetonated sorbose, $C_{12}H_{20}O_6$, F and I, for a triacetonated one, $C_{16}H_{28}O_7$, and E, for $C_{13}H_{22}O_6$. The following chemical transformations were observed in these unknown derivatives. The methylation of the A product gave the E compound. On partial hydrolyses, the F compound gave IIa and H, while the I compound gave IVa.

Therefore, the structural elucidation of the four diacetonated sorboses, A, D, G, and H, became important. The possible structures were VIa, VIIa, VIIIa, IXa, and Xa (listed in Chart I) or their anomers. Barker and Stephens[9,10] reported that the compounds containing a furanose or tetrahydrofuranol ring exhibit infrared absorption bands of the A, B, C, and D types at 924±13, 879±7, 858±7, and 799±17 cm^{-1} respectively.

1) Sorboses. Part IX. For Part VIII, see K. Tokuyama and M. Katsuhara, This Bulletin, **39**, 2728 (1966).
2) Some of the results of this paper have appeared in a preliminary form: T. Maeda, M. Kiyokawa and K. Tokuyama, *ibid.*, **38**, 332 (1965).
3) K. Tokuyama and E. Honda, *ibid.*, **37**, 591 (1964).
4) C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, **60**, 1905 (1938).
5) T. Reichstein and A. Grussner, *Helv. Chim. Acta*, **17**, 311 (1934).
6) J. H. Brown, Jr., and N. B. Lorette, U. S. Pat. 2827494 (1958).
7) H. Ohle, *Ber.*, **71**, 762 (1938).
8) T. I. Temnikova and V. V. Sklyarava, *Zh. Prikl. Khim.*, **21**, 1131 (1954); *Chem. Abstr.*, **49**, 2952 (1955).
9) S. A. Barker and R. Stephens, *J. Chem. Soc.*, **1954**, 4550.
10) S. A. Barker, E. G. Bourne, M. Stacy and D. H. Wiffen, *ibid.*, **1954**, 171.

TABLE 1. IR AND NMR SPECTRA OF SORBOFURANOSES

Compound	IR (cm^{-1}) Type A	Type B	Type C	Type D	Other Peaks	NMR (in $CDCl_3$) C_3-H (τ)	$J_{3,4}$ (cps)
IIIa	925	888	864	806	976, 907, 828, 750		
IIIb	931	880—920	858 851	808	987	5.58	0.5
IVa (C)	941	875 886	846 857	811	985, 979, 898, 835 769	5.48	0.5
IVb[a]	940—960	872	848 859	817	980, 834, 773	5.58	0.5
IVc (I)	953 932	883(sh) 872	854	814	993, 977, 843, 832 766	5.50	0.5
IVd	936	885	857	807	978, 896, 872, 771		
IVf	957	875	853	812	980, 933, 903, 966 898	5.50	0.5
Va (B)	945	880	850	817 788	776		
Vb	944 915	884	848 860	804 786	978, 824, 867	4.83	1.5
VIa (D)	936 916	867	848	796	980, 958, 842, 846		
VIb	914	869	848	790	983, 977, 948	4.77	0.3
VIIa (A)	931	888 873	850 862	808	983, 977, 948	5.82	1.2
VIIb	937	870 879	865	805	984, 968, 948, 892	5.30	$\leq$0.5
VIIe (E)	918	889	864	797	976, 899, 841, 837		
XI (J)	951 927—935	889 875	851	818(sh)	991, 975, 838(sh) 828, 833, 763		

a) K. Tokuyama, M. Kiyokawa and N. Hōki, This Bulletin, **36**, 1392 (1963).
sh) Observed as a shoulder

The infrared absorption spectra of the above sorboses are listed in Tables 1 and 2, as are those of other known sorboses. From the tables, the A and D compounds may be seen to have a furanose ring, and the G and H compounds, to have a pyranose ring. However, the F compound showed these four key bands in the infrared spectrum in spite of the formation of the pyranose, H, by its partial hydrolysis. In cases of such highly-acetonated derivatives as F, it is difficult to determine by infrared spectroscopy alone whether or not a sugar has a furanose ring, since ketals also show some absorption bands at similar frequencies.

The NMR spectra also provide evidence for their ring structures. The siganl due to a C-3 proton is expected to appear as either a signlet or a doublet, because the proton is able to couple only with the vicinal C-4 proton. The dihedral angles between the C-3 and C-4 protons of the possible pyranoses, VIIIa, IXa and Xa, would be about 180° in the stable 1 C conformation. Therefore, the spin-spin coupling constants ($J_{3,4}$) of the possible pyranoses should be considerably larger than those of the possible furanoses (VIa and VIIa) with any conformations. In accordance with these considerations, the signals due to the C-3 protons of A and D appeared as singlets, and those of F, G, and H, as doublets ($J_{3,4}$=9.5—10.4 cps), as Tables 1 and 2 show. Therefore, the A and D compounds were determined to be furanose, and F, G, and H, to be pyranose. The results of the NMR spectra were in good agreement with those obtained from infrared spectra, except for the cases of triacetonated sorboses.

Structures of the Furanoses. The A product was considered to have a tertiary hydroxyl group, because no acetylation occurred with acetic anhydride in pyridine at ordinary temperature and reduction was observed with a Fehling solution. These facts and the optical rotation supported the idea that the structure of the A product was 1, 3 : 4, 6-di-*O*-isopropylidene-β-L-sorbofuranose (VIIa). VIIa was easily hydrolyzed to L-sorbose when treated with 60% acetic acid, even at room temperature. The methylation of VIIa with diazomethane in methanol and dioxane or with methyl iodide

TABLE 2. IR AND NMR SPECTRA OF SORBOPYRANOSES

Compound	IR (cm^{-1}) Type A	Type B	Type C	Type D	Other Peaks	NMR (in $CDCl_3$) C_3-H (τ)[d]	$J_{3,4}$ (cps)
Sa[a]	936	—	—	787	946, 901	4.76	10.1
Sb[b]	939 936	886	—	780	975, 893 825		
Sc[c]	983 916	886	—	818	985, 905 895	4.93	9.8
IIa	922	878	—	812	970, 898 837, 790		
IIb	937	870 880	—	815 792	971, 906 830	4.98	9.5
VIIIa (H)	910	875	—	785	969, 898 830	6.69	9.5
VIIIb	913	—	—	782	972, 978 901, 895	6.58	9.6
VIIIc (F)	913	876	850 559	795	987, 906 822	6.71	10.0
IXa (G)	925	874	—	815 786	970, 894 837		
IXb	940 910	870	—	812 782	972, 899 834	4.84	10.4

a) 1, 2, 3, 4, 5-Penta-*O*-acetyl-α-L-sorbopyranose[e]
b) 1, 2, 3, 4, 5-Penta-*O*-acetyl-β-L-sorbopyranose[e]
c) 1, 3, 4, 5-Tetra-*O*-acetyl-α-L-sorbopyranose[e]
d) Observed as a doublet
e) H. H. Schlubach and G. Grafe, *Ann.*, **532**, 211 (1937); Y. Khonnine and G. Arragon, *Bull. Soc. Chim. France*, **1938**, 1404.

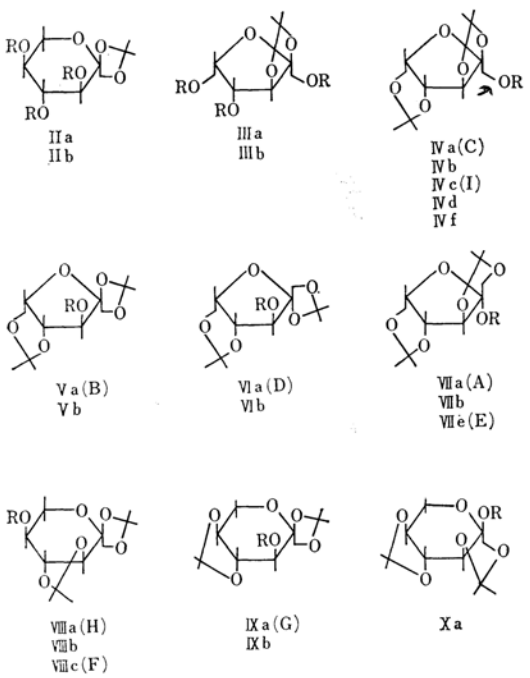

Chart 1

over silver oxide afforded methyl 1, 3 : 4, 6-di-*O*-isopropylidene-β-L-sorbofuranoside (VIIe), which was identical with the E product. On methylation with diazomethane in methanol, the yield of the expected VIIe was very low, but the major products were two isomeric compounds, K and L. They showed analytical data corresponding to $C_{13}H_{22}O_6$ and gave negative resorcinol tests.[1]

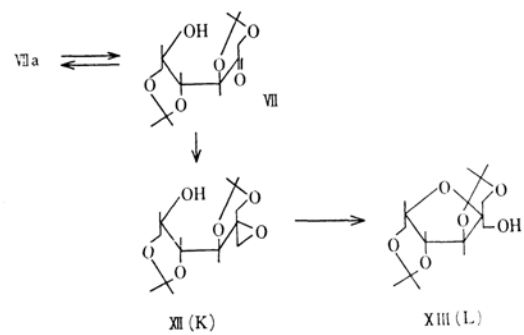

Chart II

The NMR spectrum of the K compound showed the presence of an epoxide group, as Figs. 1 and 2 show.[11] On being kept in methanol at room

11) The NMR spectra will be discussed in detail in a separate paper.

temperature for a long period, K gave L, in which the NMR signals due to the epoxide group disappeared, as is shown in Fig. 3. Therefore, the structures of the K and L compounds were determined to be XII and XIII[12] respectively. On the other hand, methylation with methyl iodide gave VIIe almost quantitatively. These data support the idea that VIIa exists in an equilibrium between the cyclic form, VIIa, and the acyclic keto-form (VIIa') in solutions. In other words, the predominant formation of XII and XIII in the reaction with diazomethane in methanol is due to a favorable equilibrium of the VIIa' form in polar protic solvents such as methanol, and the formation of VIIe is due to the favorable equilibrium of the VIIa form in aprotic solvents, such as dioxane or methyl iodide.

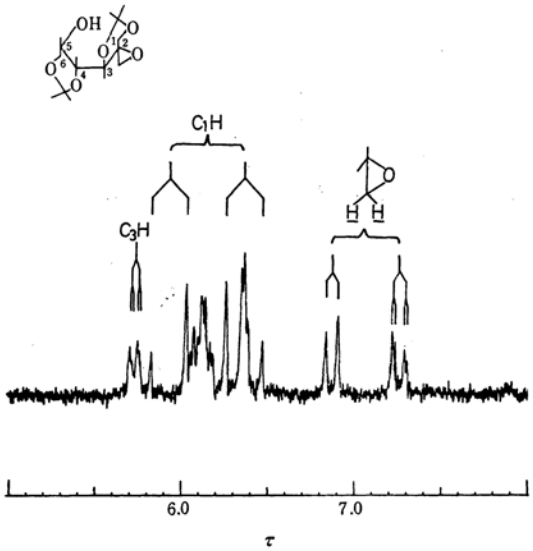

Fig. 1. Partial NMR spectrum of XII in deuteriochloroform at 60 Mc.

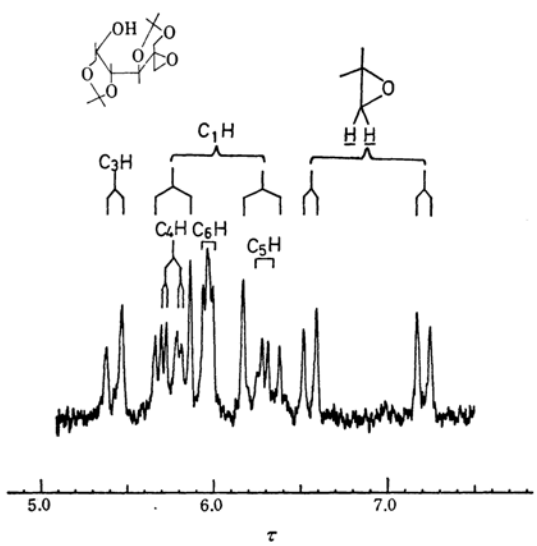

Fig. 2. Partial NMR spectrum of XII in pyridine-d_5 at 60 Mc.

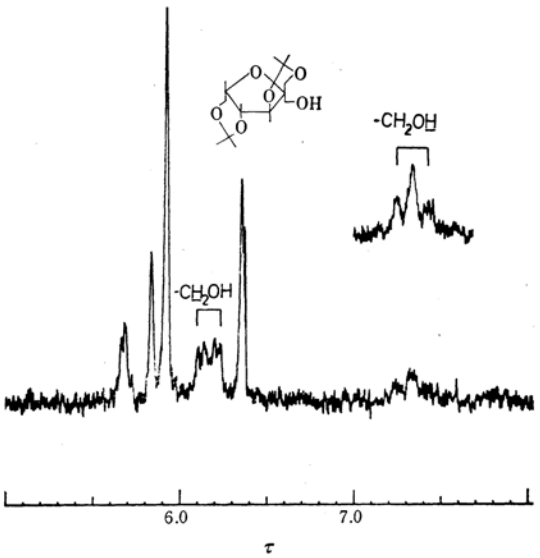

Fig. 3. Partial NMR spectrum of XIII in deuteriochloroform at 60 Mc.

The optical rotation suggested that the D compound had a β-configuration. The fact that the NMR spectrum of the acetate of D showed a sharp singlet (one proton) at τ 4.77 due to the AcOCH suggested for D the structure of 1, 2 : 4, 6-di-*O*-isopropylidene-β-L-sorbofuranose (VIa), the β-anomer of Va. The large difference between the R_f values of VIa and Va on thin-layer chromatography may be due to the hydrogen bonding in the latter.[13]

The I compound was almost identical with IVd in its infrared spectrum. It was partially hydrolyzed to IVa and derived by the acetonation of IVa. Therefore, the structure of the I compound was determined to be 1-*O*-α-methoxyisopropyl-2, 3 : 4,6 -di-*O*-isopropylidene-α-L-sorbofuranose (IVc), the methyl homolog of IVd. The J compound was detected between IVa and IVc on the thin-layer chromatograms, but the isolation of pure J was unsuccessful because it was limited in amount. On the other hand, a compound showing a R_f value similar to that of J in the thin-layer chromatogram was detected in the mother liquor obtained from the recrystallization of the crude IVa prepared by Reichstein's method.[5] The isolation of this component was achieved by the oxidative removal of the major IVa in the mother liquor with sodium hypochlorite in the

12) C. D. Gutsche, "Organic Reactions," Vol. VIII, John Wiley & Sons, New York, N. Y. (1954), p. 364.

13) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed., Methuen, London (1958), p. 95.

presence of nickel peroxide.[14-17] The colorless needles thus isolated were identical with J in the thin-layer chromatogram. This component showed analytical data corresponding to $C_{27}H_{44}O_{12}$ and afforded IVa or IIIa on paritial hydrolyses. Thus, the structure was determined to be 1, 1'-*O*-isopropylidene-bis-(2, 3 : 4, 6-di-*O*-isopropylidene-α-L-sorbofuranose) (XI). On distillation, XI was decomposed into two compounds: one was IVa, and the other was an unknown compound. The unknown product was analyzed for $C_{15}H_{24}O_6$ and showed the band characteristic of a double bond in its infrared spectrum. Therefore, the structure should be 1-*O*-isopropenyl-2, 3 : 4, 6-di-*O*-isopropylidene-α-L-sorbofuranose (IVf).

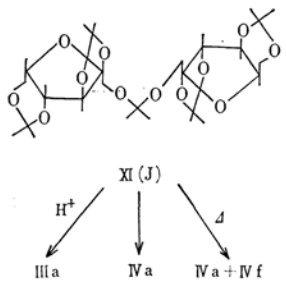

Chart III

Structures of the Pyranoses. Partial hydrolyses of the G and H compounds gave IIa. Since, in the course of the hydrolyses, no spots except those of G, H, and IIa were detected, it is quite natural to conclude that they contain a 1, 2-*O*-isopropylidene ring. Therefore, the structure of G and H must be either 1, 2 : 3, 4-di-*O*-isopropylidene-α-L-sorbopyranose (VIIIa) or 1, 2 : 4, 5-di-*O*-isopropylidene-α-L-sorbopyranose (IXa). The NMR spectra of the acetates of VIIIa (VIIIb) and IXa (IXb) were expected to show a multiplet and a doublet respectively corresponding to AcOCH at lower fields. The acetate of G showed a doublet at τ 4.84 (*J* 10.4 cps) and that of H, a sextet at τ 4.94.[18] From the spectra and optical rotations, the structures of G[19] and H were determined to be IXa and VIIIa respectively. The relatively large coupling constants indicated axial-axial trans arrangement between vicinal protons; these arrangements also supported the pyranose structures. The third pyranose, F, yielded IIa and VIIIa on partial hydrolysis. Thus the structure was determined to be 5-*O*-α-methoxyisopropyl-1, 2 : 3, 4-di-*O*-isopropylidene-α-L-sorbopyranose (VIIIc).

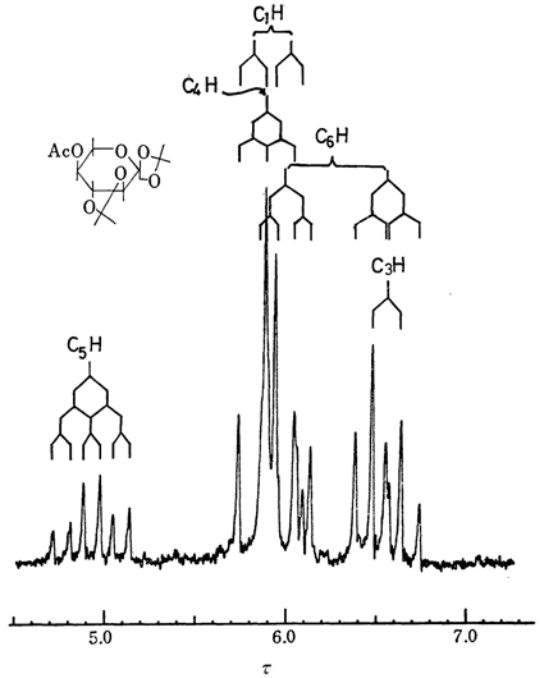

Fig. 4. Partial NMR spectrum of VIIIb in deuteriochloroform at 60 Mc.

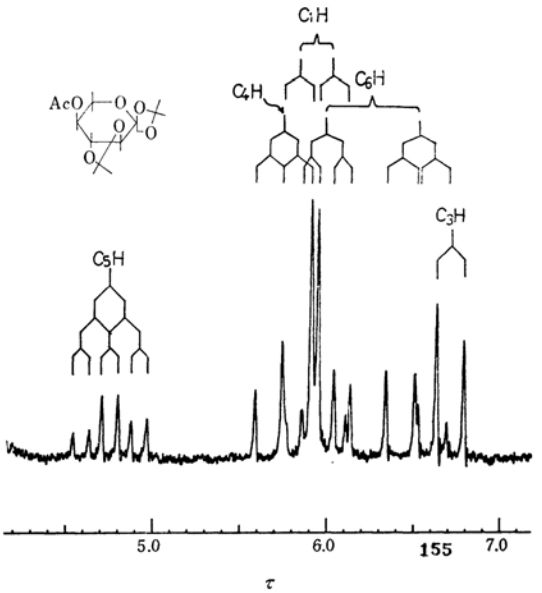

Fig. 5. Partial NMR spectrum of VIIIb in deuteriobenzene at 60 Mc.

As has been mentioned above, we have isolated many acetonated derivatives from the acetonation products of L-sorbose with acetone dimethyl ketal. The formations of the pyranose derivatives are of considerable interest in view of the fact that they are *O*-isopropylidene derivatives of

14) J. Weijland and J. B. Ziegler, U. S. Pat. 2367251.
15) J. Weijland, *J. Am. Chem. Soc.*, **67**, 1031 (1945).
16) K. Nakagawa, R. Konaka and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962).
17) A. Ujhidy, L. Mankó, B. Babos and B. Heil, *Veszpremi Vegyipari Egyetem Közleményei*, **8**, 49 (1964).
18) The NMR spectra of VIIIb are shown in Figs. 4 and 5. The spectra will be discussed in detail in another paper.
19) The G product was preliminarily reported as 1, 2 : 3, 4-di-*O*-isopropylidene-α-L-sorbofuranose.[2] The correct structure is IXa.

vicinal *trans*-glycols. The reaction mechanisms, which seem very complex, will be discussed in following papers.

Experimental

Thin-layer chromatography was performed on a silica gel plate using either acetone - chloroform (10 : 90 v/v) (Solvent A) or *n*-hexane - ether (2 : 1 v/v) (Solvent B) as the solvent for both detection and preparation. The

Table 3. R_f-values of diacetonated sorboses

Compound	Solvent A	Solvent B
VIIIc	0.80—0.93	0.90—0.98
VIIe	0.80—0.88	0.77—0.89
IVc	0.73—0.87	0.72—0.88
VIIa	0.59—0.77	0.54—0.63
Va	0.37—0.41	0.48—0.52
VIIIa	0.26—0.29	0.60—0.63
IXa	0.37—0.41	0.60—0.63
IVa	0.26—0.29	0.48—0.52
VIa	0.24—0.30	0.31—0.38
XI	0.43—0.46	0.48—0.52

separated materials were developed with either iodine vapor or 0.2% resorcinol in 10% ethanolic phosphoric acid, and then heated in an oven. The R_f values are shown in Table 3. In the cases of preparative thin-layer chromatography, the developed zones were extracted with acetone. The evaporation of the acetone *in vacuo* gave the materials.

The NMR spectra were measured on Varian A-60 spectrometer at 60 Mc in deuteriochloroform at room temperature, using tetramethyl silane as an internal reference. All the melting points were measured on a Kofler block and corrected. The solvents used were removed under reduced pressure below 40°C.

Acetonation of L-Sorbose with Acetone Dimethyl Ketal. (i) To a mixture of dry, finely-powdered L-sorbose (82 g, through 200 mesh) and acetone dimethyl ketal (144 g), dioxane (100 m*l*) containing TsOH (300 mg) was added. The suspended solution was vigorously stirred for 4 hr at 45°C, and then neutralized with a slight excess of methanolic sodium methoxide. After the removal of the unreacted L-sorbose (25.2 g) by filtration, the filtrate was concentrated to a thick syrup; this syrup was dissolved in chloroform (200 m*l*), washed with water, and dried over anhydrous magnesium sulfate. The evaporation of the solvent, followed by the addition of ether (70 m*l*) to the residual syrup, gave crystals; recrystallization of these crystals gave VIIa (A) as white plates (5.0 g). The evaporation of the ether gave a syrup (37 g). From this syrup (15.78 g), Va (B), IVa (C), and VIa (D) were obtained by preparative thin-layer chromatography in the ratio of Va, 1.563 g, IVa, 1.920 g, and VIa, 1.470 g.

(ii) A mixture of L-sorbose (8.0 g) and acetone dimethyl ketal (40 m*l*) was heated under reflux in the presence of TsOH (300 mg) for 5.5 hr, and then neutralized with a slight excess of methanolic sodium methoxide. The solvent was removed to give a syrup, which was then dissolved in chloroform, washed with water, and dried. The chloroform was then evaporated to give another syrup (12.0 g). From the syrup (6.61 g), IVa (C) and VIIe (E) were isolated in pure states by repeated preparative thin-layer chromatography. The yield of IVa was 440 mg, and that of VIIe, 541 mg.

The analytical data are summarized below. VIIa (A): mp 159—160°C, $[\alpha]_D^{24.5}$ +43.4 (*c* 1.139, acetone). Found: C, 55.56; H, 7.78%, mol wt, 278. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75%, mol wt, 260. VIa (D): syrup, $[\alpha]_D^{23.0}$ +58.6 (*c* 0.432 acetone). Found: C, 55.56; H, 8.09%. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75%.

VIIe (E): mp 46—47°C, $[\alpha]_D^{25.0}$ +25.4 (*c* 1.087, acetone). Found: C, 57.14; H, 8.07%. Calcd for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08%; CH_3O: NMR at 60 Mc: τ 6.60 (singlet).

Reaction of IIa with Acetone Dimethyl Ketal. Acetone dimethyl ketal (20 m*l*) was added to a mixture of IIa (6.0 g) and TsOH (10 mg). After it had been stirred at room temperature for 1 hr, the solution was neutralized with pyridine. After the removal of the solvent, the residue was extracted with warm *n*-hexane (3×50 m*l*). The concentration of the *n*-hexane to *ca.* 20 m*l* yielded VIIIa (H) (540 mg) as colorless needles. From the mother liquor, VIIIc (F) (574 mg) and IXa (G) (66 mg) were isolated by preparative thin-layer chromatography.

VIIIa (H): mp 103—105°C (recrystallized from *n*-hexane), $[\alpha]_D^{27.5}$ −91.2 (*c* 1.051, acetone). Found: C, 55.17; H, 7.87%. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75%.

VIIIc (F): mp 133—135°C, $[\alpha]_D^{24.0}$ −82.2 (*c* 1.017, chloroform). Found: C, 57.77; H, 8.38; CH_3O; 9.03%. Calcd for $C_{16}H_{28}O_7$: C, 57.81; H, 8.49; CH_3O, 9.33%.

IXa (G): mp 80—83°C, $[\alpha]_D^{24.0}$ −69.2 (*c* 1.090, chloroform). Found: C, 55.18; H, 7.72%. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75%.

Reaction of IVa with Acetone Dimethyl Ketal. A mixture of IVa (10 g), acetone dimethyl ketal (30 m*l*), and TsOH (10 mg) was allowed to stand at room temperature. After 1 hr, the solution was neutralized with methanolic sodium, methoxide. The evaporation of the solvent gave a syrup, the thin-layer chromatography of which indicated unreacted IVa, IVc (I), and a trace of XI (J). The syrup was dissolved in *n*-hexane (50 m*l*), washed with water (10×50 m*l*), dried and evaporated to give IVc (I) (0.5 g). $[\alpha]_D^{26.0}$ −10.9 (*c*, 1.118, acetone).

Found: C, 57.54; H, 8.43; CH_3O, 9.35%. Calcd for $C_{16}H_{28}O_7$: C, 57.81; H, 8.49; CH_3O, 9.33%.

Acetylation of VIIa. (i) A mixture of VIIa (500 mg), acetic anhydride (5 m*l*) and pyridine (5 m*l*) was allowed to stand in a refrigerator for 16 hr. No reaction was observed.

(ii) The same mixture was heated on a steam bath for 30 min. The evaporation of the excess reagents and the recrystallization of the residue from ethanol and water gave VIIb (67 mg), mp 67—69°C, $[\alpha]_D^{25.0}$ +1.3 (*c* 1.001, acetone).

Found: C, 55.74; H, 7.46%, mol wt, 314. Calcd for $C_{14}H_{22}O_7$: C, 55.62; H, 7.34%; mol wt, 302.

Methylation of VIIa. (i) To a solution of VIIa (3.0 g) in methanol (10 m*l*) and dioxane (20 m*l*), was there added an ether solution of diazomethane, prepared from 20.6 g of nitrosomethyl urea.[20] After

20) F. Arndt, "Organic Syntheses," Coll. Vol. II, p. 165 (1948).

10 days in a refrigerator, the solvents were removed. The extraction of the residue with cold *n*-hexane and the subsequent evaporation of the solvent gave a syrup (616 mg). By preparative thin-layer chromatography, VIIe (25 mg) was obtained, mp 46—47°C.

(ii) VIIa (1.0 g) in 40 m*l* of methanol was treated with an ether solution of diazomethane for 48 hr in a refrigerator. After the syrupy mixture (1.10 g) thus obtained had been worked up, it was purified by repeated preparative thin-layer chromatography with ether, followed by recrystallization from *n*-hexane, to afford XII (52 mg, R_f 0.4—0.6) and XIII (100 mg, R_f 0.65—0.7).

For XII, mp 113—114°C, $[\alpha]_D^{24.5}$ −38.4 (*c* 0.784, acetone). Found: C, 57.12; H, 8.34%. Calcd for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08%.

For XIII, mp 127—128°C, $[\alpha]_D^{24.5}$ +15.6 (*c* 0.949, acetone). Found: C, 56.93; H, 8.18%. Calcd for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08%.

(iii) A mixture of VIIa (1.2 g), methyl iodide (95 g), and silver oxide (4.6 g) was refluxed for 24 hr and then kept at room temperature. After 88 hr, the precipitates were removed by filtration and washed with ether, and the washings were combined with the filtrate. The combined solution was then concentrated to give VIIe as colorless needles, mp 46—47°C.

Hydrolysis of VIIa to L-Sorbose. VIIa (200 mg) was treated with 60% aqueous acetic acid at 20°C. After 15 min, the solvent was evaporated to dryness, giving L-sorbose in almost a quantitative yield.

Acetylation of VIa. VIa (100 mg) was treated with acetic anhydride (5 m*l*) and pyridine (5 m*l*) at room temperature. After 16 hr, the solution was evaporated to give a syrup (VIb) in almost a quantitative yield.

VIb: syrup, $[\alpha]_D^{23.0}$ +58.0 (*c* 0.226, acetone). Found: C, 55.79; H, 7.40%; mol wt, 331. Calcd for $C_{14}H_{22}O_7$: C, 55.62; H, 7.34%, mol wt, 302.

Hydrolysis of IVc. A mixture of IVc (100 mg) and 60% acetic acid (1.5 m*l*) was warmed at 40°C for 1 hr. After cooling, the solution was made alkaline with sodium carbonate, and then the solvent was evaporated. The residue was extracted with acetone, after which the acetone was distilled off to yield a syrup. Crystallization of the syrup from *n*-hexane gave IVa (50 mg), mp 76—77°C.

Preparation of XI (J). Crude IVa prepared from L-sorbose (1 kg) by the Reichstein's method[5] was recrystallized from cyclohexane. From the mother liquor, the solvent was removed. The residue (*ca.* 100 g) was oxidized with sodium hypochlorite in the presence of nickel peroxide, according to Nakagawa's procedure.[15] After the reaction was over, a solid syrup (*ca.* 1 g) was obtained from the cooled solution by decantation. Recrystallizations from *n*-hexane and then from ether gave XI (J) (0.30 g) as colorless needles, mp 110—111°C, $[\alpha]_D^{23.5}$ −8.2 (*c* 0.998, acetone).

Found: C, 57.86; H, 7.91%; mol wt, 566. Calcd for $C_{27}H_{44}O_{12}$: C, 57.85; H, 7.96%, mol wt, 560.

Hydrolysis of XI to IVa. XI (1.0 g) was added to 0.5% w/w aqueous acetone (10 m*l*) containing TsOH (50 mg). After 100 min, the solution was neutralized with a slight excess of ethanolic sodium ethoxide. The solution was then evaporated completely. The residue was dissolved in chloroform (50 m*l*), washed with water (20 m*l*), dried, and evaporated. The recrystallization of the residue (879 mg) from *n*-hexane gave IVa (720 mg), mp 78°C.

Hydrolysis of XI to IIIa. XI (100 mg) was dissolved in 60% aqueous acetic acid (1 m*l*), and the solution was heated at 70°C for 35 min. After neutralization with ethanolic sodium ethoxide, the solvent was evaporated and the residue was extracted with ethyl acetate. Concentration, followed by recrystallization from ethyl acetate gave IIIa (52 mg).

Pyrolysis of XI. XI (9.0 g) was distilled under reduced pressure (10 mmHg) at 200°C. The distillate (5.1 g) consisted of three components, as was shown by thin-layer chromatography (R_f 0.85 (IVf), 0.50 (XI) and 0.40 (IVa)). XI, IVa and IVf (0.2 g) were isolated by preparative thin-layer chromatography (alumina-chloroform) from the distillate (0.7 g).

IVf: syrup, $[\alpha]_D^{24.5}$ +15.6 (*c* 0.694, acetone). Found: C, 59.84; H, 8.16%. Calcd for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05%.

IR 1656 cm^{-1} (liquid film).

Acetylation of IXa. IXa (100 mg) was acetylated with acetic anhydride (5 m*l*) in pyridine (5 m*l*) at 0°C. After 16 hr, the evaporation of the solvent gave syrup (IXb). $[\alpha]_D^{24.0}$ −78.5 (*c* 0.581 acetone).

Found: C, 55.83; H, 7.44%. Calcd for $C_{14}H_{22}O_7$: C, 55.62; H, 7.34%.

Preparations of IIb, IIIb, Vb, and VIIIb Acetates. The IIb, IIIb, Vb, and VIIIb acetates were prepared from IIa, IIIa, Va, and VIIIa respectively in a way similar to the above.

IIb: mp 77—78°C, $[\alpha]_D^{28.0}$ −72.0 (*c* 1.016, chloroform). Found: C, 52.18; H, 6.67%. Calcd for $C_{15}H_{22}O_9$: C, 52.02; H, 6.40%.

IIIb: syrup, $[\alpha]_D^{23.5}$ +2.6 (*c* 1.072, chloroform). Found: C, 51.93; H, 6.39%. Calcd for $C_{15}H_{22}O_9$: C, 52.02; H, 6.40%.

Vb: mp 44—46°C, $[\alpha]_D^{23}$ −61.4 (*c* 1.086, acetone). Found: C, 55.73; H, 7.41%. Calcd for $C_{14}H_{22}O_7$: C, 55.62; H, 7.34%.

VIIIb: mp 129—130°C, $[\alpha]_D^{28.0}$ −55.6 (*c* 1.255, acetone). Found: C, 55.82; H, 7.49%. Calcd for $C_{14}H_{22}O_7$: C, 55.62; H, 7.34%.

Hydrolysis of VIIIa. VIIIa (100 mg) was treated with 60% aqueous acetic acid (7.0 m*l*) at 50°C for 3 hr. Evaporation, followed by recrystallization, gave IIa (64 mg), mp 144—145°C.

Hydrolysis of IX. IXa (41.1 mg) was treated with 3.4 m*l* of 60% aqueous acetic acid at 30°C for 4 hr. IIa (36.9 mg) was then obtained in a way similar to the above.

Hydrolysis of VIIIc. (i) VIIIc (100 mg) was hydrolyzed with water (0.4 m*l*) and acetic acid (0.6 m*l*) at 15°C. After 10 min, the solution was neutralized with a sodium bicarbonate solution and extracted with chloroform (3×50 m*l*). The solution was then washed, dried, and evaporated. The recrystallization of the residue from *n*-hexane gave VIIIa (37 mg).

(ii) The same mixture was treated at room temperature for 2.5 hr. Evaporation followed by recrystallization from ethyl acetate, gave IIa (18 mg).

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