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THE BEHAVIOR OF L-SORBOSE TOWARDS ANHYDROUS HYDROGEN FLUORIDE*

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ABSTRACT

L-Sorbose was converted into a mixture of L-sorbose dianhydrides by treatment with anhydrous hydrogen fluoride. Of the six dianhydrides isolated, two were known compounds. The structures have been established by n.m.r. spectroscopy. The relative amounts of dianhydrides obtained depended on the reaction conditions. By use of ^{13}C-n.m.r. spectroscopy, the reaction of L-sorbose with hydrogen fluoride was shown to involve L-sorbofuranosyl fluoride as an intermediate. Dianhydrides were also formed when L-sorbose was treated with methanol and sulfuric acid under Fischer glycosidation condition, or with trifluoroacetic acid.

INTRODUCTION

The reaction of D-fructose and of inulin with anhydrous fluoride was described in a previous paper[1], and it was shown that even brief treatment with hydrogen fluoride at low temperature resulted in a complete conversion into a mixture of D-fructose dianhydrides. Whereas the behavior of D-fructose towards mineral acids has been investigated rather extensively[1], the only previous study on L-sorbose has been reported by Wolfrom and Hilton[2] who found that treatment of L-sorbose with cold, concentrated hydrochloric acid gave a complex mixture of products from which two pure L-sorbose dianhydrides (**1** and **3**) were isolated.

RESULTS AND DISCUSSION

Storage of solutions of L-sorbose in liquid hydrogen fluoride under various conditions of temperature, time, and concentration gave a mixture of the L-sorbose

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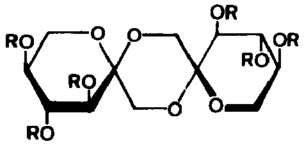

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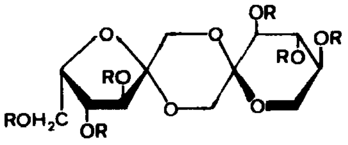

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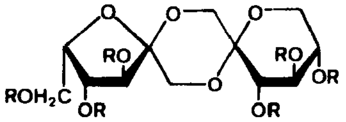

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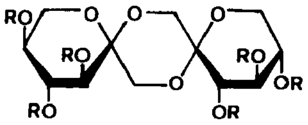

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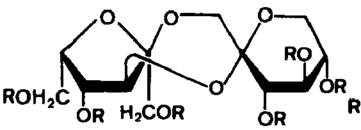

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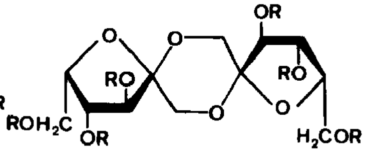


11 R=H
12 R=Ac

dianhydrides **1**, **3**, **5**, **7**, **9**, and **11** by precipitation with an excess of ether or evaporation of hydrogen fluoride. Either procedure gave identical product mixtures, as found previously for the corresponding reaction with D-fructose[1]. The composition of the mixture was, however, dependent on the initial concentration of the solution in hydrogen fluoride, the temperature, and the reaction time (Table I). Thus, at low temperature the difuranose dianhydride **11** was formed, especially when hydrogen fluoride was diluted with liquid sulfur dioxide. When the reaction was carried out at room temperature, **11** was not formed, but the proportion of **9** increased considerably. The variations in the other products (**1**, **3**, **5**, and **7**) were less consistent, **5** invariably being a minor product (Table I). When a low temperature was used, the crude product mixture was colorless and the yield was quantitative; the mixture obtained after a 4-h reaction time at 20° was black, indicating extensive decomposition.

All the products obtained contained some L-sorbose (Table I). A ^{13}C-n.m.r. spectrum (Fig. 1) of a solution of L-sorbose in hydrogen fluoride recorded at 0° showed that 29% of a sorbosyl fluoride was present, in addition to 22% of **1**, 25% of **3**, and 24% of **7**; the composition did not change with temperature. The fluoride

TABLE I

PRODUCTS FORMED BY THE ACTION OF ANHYDROUS HYDROGEN FLUORIDE ON L-SORBOSE

L-*Sorbose* (*g*)	*HF(mL)/* SO_2*(mL)*	*Reaction temp.* *(degrees)*	*Reaction time*	*Products*[a] *(%)*						
				1	**3**	**5**	**7**	**9**	**11**	L-*Sorbose*
10	20/0	20	4 h	22	15	4	18	35		6
10	20/0	20	1 h	24	13	3	9	47		5
				(29)	(8)		(16)	(47)		
10	20/0	−10	4 min	29	15	3	21	15	3	14
				(41)	(13)		(24)	(19)		
10	10/0	−10	1 min	34	18	3	18	10	4	13
				(42)	(10)	(10)	(24)	(9)		
10	10/10	−25	24 h	43	18	2	24	6		6
10	5/10	−25	24 h	29	14	12	8	4	20	12

[a] Values in parentheses were obtained by g.l.c. of the methylated products; the other values were estimated from ^{13}C-n.m.r. spectra (125 MHz) by use of integral of the signals of the secondary carbon atoms.

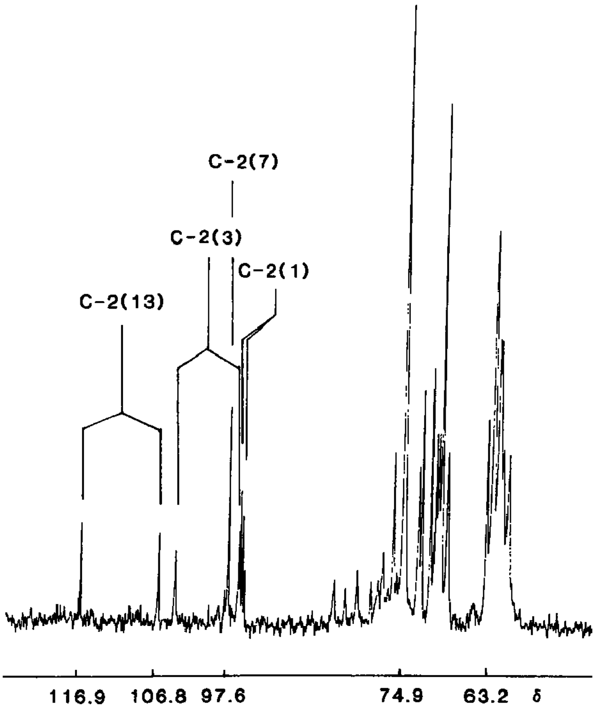


Fig. 1. ^{13}C-N.m.r. spectrum (22.63 MHz) of a solution of L-sorbose (0.5 g) in hydrogen fluoride (1.0 mL) containing ($^{2}H_6$)acetone (0.2 mL), prepared at −20°. The spectrum was recorded within 1 h at 0°.

observed in this solution is probably an L-sorbofuranosyl fluoride (C-2 at δ 111.8, $J_{C\text{-}2,F}$ 227 Hz)[3]; it was not found in the isolated products and, therefore, it must have undergone further reaction during the isolation procedure. Hydrolysis of some of this fluoride may explain the presence of L-sorbose in all the reaction mixtures.

The structures of the L-sorbose dianhydrides were determined through n.m.r. spectroscopy. Compounds **1**, **3**, **5**, **7**, and **9** all contain an α-L-sorbopyranose ring in the $^{2}C_5$(L) conformation as seen from the ^{1}H-n.m.r. spectra of their acetates ($J_{3,4} \simeq J_{4,5} \simeq J_{5,6a} \simeq$ 8–10 Hz). The ^{13}C-n.m.r. spectra (Table II) of **7** and **8** showed only six signals, hence they are di-α-L-sorbopyranose 1,2′:2,1′-dianhydride. A second product (**1**) contains two pyranose rings since the six ^{13}C-n.m.r. signals of the secondary carbon atoms were at δ 69–74; the ^{1}H-n.m.r. spectrum of the acetate **2** showed, in addition to the α-pyranose ring, a second ring with values of $J_{3,4}$, $J_{4,5}$, and $J_{5,6a}$ indicating a pyranose ring in the $^{5}C_2$(L) conformation. Therefore, it is assumed that **1** is α-L-sorbopyranose-β-L-sorbopyranose 1,2′:2,1′-dianhydride, analogous to the corresponding product obtained from D-fructose[1].

Compounds **3**, **5**, and **9** showed ^{13}C-n.m.r. signals at δ 80–84 and, therefore, contain a furanose ring. The ^{1}H-n.m.r. spectra of the acetates **4** and **6** have signals for H-3 and -4 of the furanose rings at δ 5.24–5.49, showing that O-3 and -4 are acetylated and, hence, that the furanose rings are 1,2-linked to the pyranose ring.

TABLE II

^{13}C-N.M.R. CHEMICAL SHIFTS (125 MHz) AND PHYSICAL CONSTANTS OF L-SORBOSE DIANHYDRIDES AND OF THEIR HEXAACETATES

Compound	*^{13}C-Chemical shifts*[a] *(δ)*			*M.p. (degrees)*	$[\alpha]_D^{20}$ *(degrees)*[a,b]
	C-2,2′	*C-3,4,5,3′,4′,5′*	*C-1,6,1′,6′*		
Dianhydrides					
α-L-Sorb*p*-β-L-sorb*p* 1,2′:2,1′ (**1**)	96.0	74.1;72.5;72.4;72.0	63.0;62.7;62.3;59.6	233–235	−11.5(2.6)
	95.9	70.0;69.1		249–250[c]	
β-L-Sorb*f*-α-L-sorb*p* 1,2′:2,1′ (**3**)	103.6	84.0;82.0;77.1;	72.7(2C);62.1;61.9	189–190	0.00(1)
	96.1	74.2;72.6;70.1		188–189[c]	
α-L-Sorb*f*-α-L-sorb*p* 1,2′:2,1′ (**5**)	102.3	80.6;79.0;77.1;	66.4;63.1;63.06;61.0	198–199	−118(0.5)
	96.6	74.3;73.8;70.0			
α-L-Sorb*p*-α-L-sorb*p* 1,2′:2,1′ (**7**)	97.5	75.9;74.3;70.1	63.9;63.5	239–241	−210(0.9)
α-L-Sorb*f*-α-L-sorb*p* 2,1′:3,2′ (**9**)	104.2	83.5;76.4;74.2	65.1;63.2;62.6;61.4	syrup	−21.5(2.6)
	95.2	74.0;72.9;70.1			
α-L-Sorb*f*-β-L-sorb*f* 1,2′:2,1′ (**11**)	103.9	83.6;81.9;78.9;	63.5;63.1;61.9;61.2	198–200	−11.0(1.3)
	99.3	78.7;77.0;76.0			
Hexaacetates					
α-L-Sorb*p*-β-L-sorb*p* 1,2′:2,1′ (**2**)	93.7	69.6(2C);68.9; 69.7;	61.1; 60.6;59.2;59.1	172–173	+3.7(3.3)
	92.4	67.2;66.5		168–169[c]	
β-L-Sorb*f*-α-L-sorb*p* 1,2′:2,1′ (**4**)	101.5	80.6;78.3;75.4;	62.5;61.6;61.1;59.2	171–172	−19(2.1)
	94.1	69.7(2C);69.0		177–179[c]	
α-L-Sorb*f*-α-L-sorb*p* 1,2′:2,1′ (**6**)	100.2	76.4;74.3(2C);72.1;	63.7;61.5;61.0;59.7	syrup	−106.6(0.44)
	96.5	69.5;69.1			
α-L-Sorb*p*-α-L-sorb*p* 1,2′:2,1′ (**8**)	96.0	72.5;68.9(2C)	62.4;59.6	183–184	−119(1.6)
α-L-Sorb*f*-α-L-sorb*p* 2,1′:3,2′ (**10**)	102.7	78.2;76.6;71.2	64.8;62.1;61.9;59.9	157–158	−52.9(1.4)
	93.6	70.2;69.8;69.0			
α-L-Sorb*f*-β-L-sorb*f* 1,2′:2,1′ (**12**)	98.5	81.0;78.0;76.2	62.9;62.6;62.2;61.5	155–156	−25.3(1.2)
	101.5	75.6;75.1;74.2			

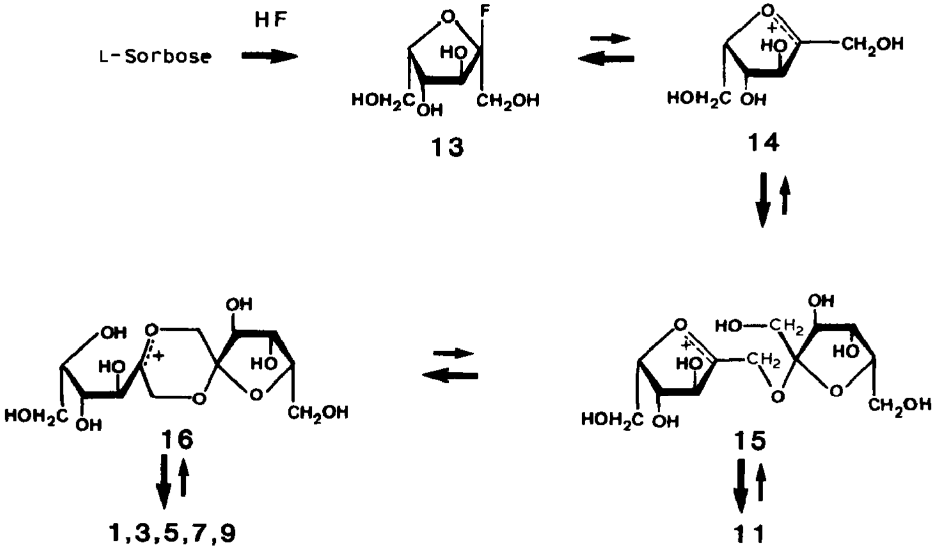
[a] For solution in water for the dianhydrides, in chloroform for the hexaacetates. [b] Concentration in parentheses. [c] Ref. 2.

In **10**, the signals for H-3 were shifted upfield, to δ 4.05 and 4.37. This indicated that **10** has the furanose ring 2,3-linked to the pyranose ring and that O-1 of the furanose residue is acetylated. The furanose ring of **9** obviously has the α-L configuration. The anomeric configuration at C-2 of the furanose rings in **3** and **5** have been assigned from the ^{13}C-n.m.r. chemical shifts of C-3, -4, and -5, compared to those of α- and β-L-sorbofuranose[4].

The last-named isomer (**11**) is obviously a difuranose dianhydride as seen from the ^{13}C-n.m.r. chemical shifts of the secondary carbon atoms and is, therefore, α-L-sorbofuranose-β-L-sorbofuranose 1,2′:2,1′-dianhydride. It may be noted that the proton–proton coupling constants in the α- and β-rings of **12** agree well with those of **6** and **4**, respectively.

The two dianhydrides (**1** and **3**), as well as their hexaacetates (**2** and **4**), have been described by Wolfrom and Hilton[2]. Recently, Hamada *et al.*[5] also described **1** and **3**, obtained by treatment of L-sorbose with hydrochloric acid; however, the optical rotations and some of the chemical shifts reported were different from those found by the present authors and by Wolfrom and Hilton[2].

The mechanism of the formation of the dianhydrides **1, 3, 5, 7, 9,** and **11** is undoubtedly analogous to that of the reaction of D-fructose with hydrogen fluoride, *i.e.*, involving as intermediates a glycosyl fluoride (**13**) and an oxocarbonium ion (**14**), and then subsequent formation of dimeric carbonium ions such as **15** (Scheme 1). An analogous mechanism was proposed by Wolfrom and Hilton[2]. The observation of the furanosyl fluoride **13** in hydrogen fluoride solution and the formation of the difuranose anhydride **11** by mild treatment with hydrogen fluoride indicate that **11** may be the first dianhydride formed in hydrogen fluoride, and that it subsequently rearranges to the other isomers *via* intermediates, such as **15** and **16**.



Scheme 1. Proposed mechanism for the formation of disorbose dianhydrides by the action of HF on L-sorbose.

Reaction of L-sorbose with trifluoroacetic acid for several days gave a mixture of dianhydrides and a large proportion of unreacted sorbose. After acetylation, the acetate **12** crystallized in low yield. On treatment with boiling methanolic sulfuric acid, dianhydrides were also obtained, analogous to the result found with D-fructose[1].

EXPERIMENTAL

General methods. — ^{13}C-N.m.r. spectra were recorded with Bruker WH-90, WP-100, WM-400, and WM-500 instruments. For other general methods, see ref. 1.

Reactions with HF. — These reactions were carried out as described previously for D-fructose[1]. The composition of the crude product mixtures (Table I) were assessed by ^{13}C-n.m.r. spectroscopy, at 125 MHz, of solutions in D_2O using the integrated signals of secondary carbon atoms. Some analyses were also carried out by methylation followed by g.l.c.[1]. Of the six dianhydrides obtained, only the α,β-dipyranose **1** could be crystallized directly from the crude mixture as described later. The other dianhydrides were all isolated as their hexaacetates after a series of chromatographic separation of the acetylated reaction mixtures. The pure dianhydrides **3**, **5**, **7**, **9**, and **11** were subsequently prepared by deacetylation of the corresponding acetates. Some detailed examples of the procedures used are presented in the following paragraphs.

Reactions of L-*sorbose with HF in liquid SO_2.* — To L-sorbose (10 g) in a 250-mL polyethylene bottle at −78° was added liquid SO_2 (10 mL) followed by HF (10 mL). The mixture was shaken while the temperature rose to ~ −10° (the boiling point of SO_2). After a few min, a homogeneous solution was obtained which was kept at −25° for 20 h, cooled to −78°, and stirred with ether (~150 mL). The supernatant solution was removed by decantation, and the precipitate was washed several times with ether, stirred with ether until a powder was obtained, filtered, and dried *in vacuo*. A 125-MHz ^{13}C-n.m.r. spectrum gave the composition shown in Table I. A solution of the product (~9.5 g) in methanol (30 mL) was seeded with **1** and kept overnight at room temperature. The crystals were collected, washed with methanol, and dried to give crude **1** (3.4 g, 38%), m.p. 230°. Two recrystallizations from water–ethanol gave 2.5 g of **1** having the physical data listed in Table II.

Acetylation of the material in the main mother liquors with acetic anhydride–pyridine gave a product (9.1 g), which was separated into four fractions by chromatography on a column of silica gel using ether as eluant.

The first-eluted fraction (3.0 g) crystallized from ether to give **8** (1.6 g), m.p. 180°. Rechromatography of the mother liquor material with ether as eluant and crystallization from ether gave an additional 0.7 g of **8**. The combined portions of **8** were recrystallized twice from ethanol to give 1.8 g (11%) of **8** with the physical data listed in Table II; ^{1}H-n.m.r. ($CDCl_3$, 400 MHz): δ 5.42 (H-4), 4.95 (H-3), 4.88 (H-5), 3.88 (H-1 or 1′), 3.78 (H-6*e*), 3.58 (H-6*a*), 3.47 (H-1 or 1′), and 2.12, 1.96, 1.95 (OAc); $J_{1,1'}$ 12.8, $J_{3,4}$ 10.4, $J_{4,5}$ 9.9, $J_{5,6a}$ 10.9, $J_{5,6e}$ 6.0, and $J_{6,6}$ 10.0 Hz.

Anal. Calc. for $C_{24}H_{32}O_{16}$: C, 50.00; H, 5.60. Found: C, 49.93; H, 5.80.

The third fraction (4.0 g) was crystallized from ether to give **4** (2.2 g) which, after two recrystallizations from ethanol, gave 1.4 g (9%) of a product having the physical data listed in Table II; ^{1}H-n.m.r. ($CDCl_3$, 400 MHz): δ 5.50 (H-4′), 5.32 (H-4), 5.24 (H-3), 5.00 (H-5′), 4.84 (H-3′), 4.66 (H-5), 4.20 (2H-6), 3.94 (H-1*e*), 3.91 (H-6′*e*), 3.82 (H-1′*e*), 3.66 (H-1*a*), 3.51 (H-6′*a*), 3.46 (H-1′*a*), and 2.09, 2.06, 2.05, 2.01, 1.99, 1.96 (OAc); $J_{1,1} = J_{1',1'}$ 11.8, $J_{3,4}$ 1.8, $J_{4,5}$ 6.0, $J_{5,6}$ 6.4, $J_{6,6}$ ~0, $J_{3',4'}$ 9.8, $J_{4',5'}$ 9.8, $J_{5',6'a}$ 10.8, $J_{5',6e}$ 6.0, and $J_{6',6'}$ 10.8 Hz.

Anal. Calc. for $C_{24}H_{32}O_{16}$: C, 50.00; H, 5.60. Found: C, 49.98; H, 5.75.

Repeated rechromatography of the second fraction gave small quantities of impure **6** (see below).

In a similar experiment, L-sorbose (5 g), liquid SO_2 (5 mL), and HF (2.5 mL) were kept for 22 h at −25° and processed as described above to give 4.5 g of crude product. A 125-MHz, ^{13}C-n.m.r. spectrum gave the composition shown in Table I.

The material was acetylated to give a product (7.9 g) which was separated into four fractions by chromatography on a column of silica gel using ether as eluant. The two fast-moving fractions (~2 g) were twice rechromatographed to give 500 mg of impure **6**.

The two slow-moving fractions crystallized from ether; recrystallization from ethanol gave **12** (550 mg, 7%), m.p. 151–153°. Two additional recrystallizations from ethanol gave a product having the physical data listed in Table II; ^{1}H-n.m.r. ($CDCl_3$, 500 MHz): δ 5.60 (H-4), 5.40 (H-4′), 5.34 (H-3′), 5.10 (H-3), 4.73 (H-5′), 4.56 (H-5), 4.31 (H-6*e*), 4.30 (H-1 or 1′, H-6*e*), 4.23 (H-1 or 1′), 4.22 (H-6′*a*), 4.18 (H-6*a*), 3.69 (H-1 or 1′), 3.63 (H-1 or 1′), and 2.16, 2.11, 2.09, 2.08 (6 H, OAc); $J_{1,1} = J_{1',1'}$ 11.5, $J_{3,4}$ 5.7, $J_{4,5}$ 5.7, $J_{5,6a}$ 5.0, $J_{5,6b}$ 5.8, $J_{6a,6b}$ 11, $J_{3',4'}$ 2.0, $J_{4',5'}$ 6.9, $J_{5',6'a}$ 7.3, $J_{5',6'b}$ 6.0, and $J_{6'a,6'b}$ 11.2 Hz.

Anal. Calc. for $C_{24}H_{32}O_{16}$: C, 50.00; H, 5.60. Found: C, 49.82; H, 5.60.

Reaction of L-*sorbose with HF for 1 h at 20°.* — To L-sorbose (10 g), cooled in ice was added HF (20 mL) and the solution was kept at 20° for 1 h. Most of the HF was then evaporated in a stream of air, and the dark residue was stirred with ether to give a sticky precipitate which was stirred several times with ether to give a black powder that could be filtered off and dried. The product (8.9 g) had the composition shown in Table I as seen from a ^{13}C-n.m.r. spectrum. Acetylation of this product with 2:3 acetic anhydride–pyridine (50 mL) gave a material (16 g) which was dissolved in ether (~150 mL), and the solution filtered through carbon. The filtrate crystallized overnight. The product (3.4 g) was recrystallized from ethanol to give **10** (2.7 g, 17%), m.p. 157–158°; additional recrystallization did not change the m.p.; physical data are listed in Table II; ^{1}H-n.m.r. ($CDCl_3$, 400 MHz): δ 5.50 (H-4′), 5.35 (H-4), 4.98 (H-5′), 4.88 (H-3′), 4.73 (H-5), 4.37 (H-1*e*), 4.24 (H-6*e*), 4.17 (H-6*a*), 4.06 (H-3), 4.05 (H-1*a*), 3.95 (H-6′*e*), 3.79 (H-1′*e*), 3.61 (H-6′*a*), 3.55 (H-1′*a*), and 2.11, 2.06, 2.05 (6 H), 2.01, 1.99 (OAc); $J_{1,1}$ 11.6, $J_{3,4}$ ~0.6, $J_{4,5}$ 3.6, $J_{5,6a}$ 5.6, $J_{5,6b}$ 6.8, $J_{6a,6b}$ 11.6, $J_{1',1'}$ 12.4, $J_{3',4'}$ 9.6, $J_{4',5'}$ 9.6, $J_{5',6'a}$ 10.8, $J_{5',6'e}$ 6.0, and $J_{6'a,6'e}$ 10.8 Hz.

Anal. Calc. for $C_{24}H_{32}O_{16}$: C, 50.00; H, 5.60. Found: C, 49.95; H, 5.83.

Column chromatography of the main mother-liquor and crystallization from ether gave 1.2 g (7%) of **8**, m.p. 183–184°, and mixtures of **2** and **4**.

3,4,5,3',4',5'-Hexa-O-acetyl-α-L-sorbopyranose-β-L-sorbopyranose 1,2':2,1'-dianhydride (**2**). — Treatment of **1** (700 mg) with acetic anhydride–pyridine for 4 h at 20°, processing in the usual manner, and crystallization from ether gave **2** (1.0 g, 90%), m.p. 170–172°. Two recrystallizations from ethanol gave a product having the physical data listed in Table II; ^{1}H-n.m.r. ($CDCl_3$, 400 MHz); δ 5.51 (H-4), 5.00 (H-5), 4.91 (H-5'), 4.90 (H-3'), 4.84 (H-3), 4.75 (H-4'), 4.05 (H-6'*a*), 3.91 (H-6'*a*), 3.82 (H-6'*e*), 3.76, 3.70, 3.67 (H-1, H-1'), 3.52 (H-6*a*), 3.46 (H-1, H-1'), and 2.09, 2.08, 2.06, 2.01, 1.99 (OAc); $J_{1,1} = J_{1',1'}$ 11.9, $J_{3,4}$ 9.8, $J_{4,5}$ 9.5, $J_{5,6e}$ 6.0, $J_{5,6a}$ 10.7, $J_{6,6}$ 10.7, $J_{3',4'}$ 2.1, $J_{4',5'}$ 2.8, $J_{5',6'e}$ 2.7, $J_{5',6'a}$ 2.8, $J_{4',6'e}$ 0.7, and $J_{6',6'}$ 12.6 Hz.

α-L-Sorbofuranose-α-L-sorbopyranose 1,2':2,1'-dianhydride (**5**). — The impure acetate **6** (320 mg) (see above) was treated with sodium methoxide in methanol for 18 h at 20°. The solution was then de-ionized with Amberlite IR-120 (H^+) cation-exchange resin, filtered through carbon, and evaporated to give a product (140 mg) which crystallized partially. Two recrystallizations from ethanol gave **5** (30 mg) having the physical data listed in Table II.

Anal. Calc. for $C_{12}H_{20}O_{10}$: C, 44.44; H, 6.22. Found: C, 44.39; H, 6.27.

3,4,5,3',4',5'-Hexa-O-acetyl-α-L-sorbofuranose-α-L-sorbopyranose 1,2':2,1'-dianhydride (**6**). — Acetylation of **5** (80 mg) with acetic anhydride–pyridine and purification by column chromatography using ether as eluant gave **6** as a colorless syrup having the physical data listed in Table II; ^{1}H-n.m.r. ($CDCl_3$, 400 MHz): δ 5.49 (H-4), 5.47 (H-4'), 5.32 (H-3), 4.96 (H-3'), 4.90 (H-5'), 4.52 (H-5), 4.18 (H-6a), 4.07 (H-6b), 3.93, 3.77, 3.74, 3.66 (H-1,1'), 3.87 (H-6'*e*), 3.62 (H-6'*a*), and 2.15, 2.10, 2.07, 2.05, 2.00, 1.98 (OAc); $J_{1,1} = J_{1,1'}$ 12.4, $J_{3,4}$ 6.6, $J_{4,5}$ 6.7, $J_{5,6a}$ 5.2, $J_{5,6b}$ 4.4, $J_{6a,6b}$ 12.0, $J_{3',4'}$ 10.2, $J_{4',5'}$ 10.0, $J_{5',6'e}$ 5.5, $J_{5',6'a}$ 10.9, and $J_{6',6'}$ 10.8 Hz.

Anal. Calc. for $C_{24}H_{32}O_{16}$: C, 50.00; H, 5.60. Found: C, 50.30; H, 5.83.

β-L-Sorborfuranose-α-L-sorbopyranose 1,2':2,1'-dianhydride (**3**). — Deacetylation of acetate **4** (1.0 g) as described above and crystallization from methanol–ethanol gave **3** (430 mg, 77%), m.p. 188–190°. Two recrystallizations gave a product showing the data listed in Table II.

Di-α-L-sorbopyranose 1,2':2,1'-dianhydride (**7**). — Deacetylation of acetate **8** (1 g) and crystallization from methanol–ethanol gave **7** (350 mg, 62%) having the data listed in Table II.

Anal. Calc. for $C_{12}H_{20}O_{10}$: C, 44.44; H, 6.22. Found: C, 44.03; H, 6.34.

α-L-Sorbofuranose-α-L-sorbopyranose 3,2':2,1'-dianhydride (**9**). — Deacetylation of acetate **10** gave a syrup showing the physical data given in Table II.

Anal. Calc. for $C_{12}H_{20}O_{10}$: C, 44.44; H, 6.22. Found: C, 44.08; H, 6.50.

α-L-Sorbofuranose-β-L-sorbofuranose 1,2':2,1'-dianhydride (**11**). — Deacetylation of acetate **12** and crystallization from ethanol gave **11** (200 mg, 71%), m.p. 195–197°. Two additional recrystallizations gave the product having the physical data shown in Table II.

Anal. Calc. for $C_{12}H_{20}O_{10}$: C, 44.44; H, 6.22. Found: C, 44.35; H, 6.27.

Reaction of L-*sorbose with trifluoroacetic acid.* — A mixture of L-sorbose (5 g) and trifluoroacetic acid (50 mL) was kept for 4 days at 20° and then concentrated *in vacuo*, and water was distilled from the residue three times. The remaining product was dissolved in ethanol (~20 mL) and left to crystallize for several days, depositing unreacted L-sorbose (0.94 g). A ^{13}C-n.m.r. spectrum (125 MHz, D_2O) showed that the material in the mother liquor contained **1** (7%), **3** (19%), **5** (6%), **11** (39%), and sorbose (29%). The product was acetylated and the resulting mixture of acetates (4.4 g) crystallized from ether to give 300 mg (~4%) of **12**, m.p. 156–157°.

When L-sorbose was boiled in trifluoroacetic acid, extensive decomposition took place.

Reaction of L-*sorbose with methanolic* H_2SO_4. — A mixture of L-sorbose (5 g), methanol (10 mL), and H_2SO_4 (sp.gr. 1.83, 0.2 mL) was boiled for 20 h, neutralized ($CaCO_3$), filtered, and evaporated. The residue contained (integrals of ^{13}C-n.m.r. signals at 125 MHz for secondary carbon atoms) **1** (3%), **3** (19%), **5** (5%), **7** (6%), **9** (6%), L-sorbose (22%), and methyl α-L-sorbopyranoside[6] (20%).

An experiment carried out in the same manner with 50 mL of methanol gave **1** (14%), **3** (17%), **5** (7%), **7** (3%), **9** (4%), L-sorbose (8%), and methyl α-L-sorbopyranoside (48%).

Finally, when the same experiment was performed with 500 mL of methanol, the product contained mainly methyl α-L-sorbopyranoside, ~10% of L-sorbose, and a small proportion (~5%) of a mixture of dianhydrides.

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