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Steric and electronic effects in the formation of dihexulose dianhydrides. Reaction of racemic sorbose in anhydrous hydrogen fluoride and a facile synthesis of D-sorbose*,†

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ABSTRACT

Treatment of DL-sorbose with anhydrous hydrogen fluoride gave a high yield of α-D-sorbopyranose α-L-sorbopyranose 1,2′:2,1′-dianhydride. Similarly, a mixture of D-fructose and D-sorbose gave a good yield of β-D-fructopyranose α-D-sorbopyranose 1,2′;2,1′-dianhydride. The formation of these products, compared to the more complicated mixtures of compounds obtained by treatment of L-sorbose or D-fructose with hydrogen fluoride, is discussed in terms of conformations, and steric and electronic factors.

INTRODUCTION

Treatment of L-sorbose with HF under various conditions yielded[2] the di(α-L-pyranose) dianhydride **1** (~20%), the α,β-dipyranose dianhydride **3** (20–40%), and β-L-sorbofuranose α-L-sorbopyranose 1,2′:2,1′-dianhydride (~15%). Likewise, D-fructose formed[3] the di(β-D-pyranose) dianhydride§ **4** (10–40%), the α,β-dipyranose dianhydride **5** (10–40%), and α-D-fructofuranose β-D-fructopyranose 1,2′;2,1′-dianhydride (30–40%). Minor amounts of other dianhydrides were also formed and, under more strenuous conditions, di(furanose) 2,1′:3,2′-dianhydrides were obtained. The relative proportions of the products probably reflect their relative stabilities and, in order to gain further information about this aspect, the reaction of DL-sorbose and of a mixture of D-fructose and D- or L-sorbose with HF has been studied.

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* Dedicated to Professor Grant Buchanan on the occasion of his 65th birthday.
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§ In ref. 3, the ^{1}H-n.m.r. spectrum for **4** was actually that of the α,β-dianhydride **6**.

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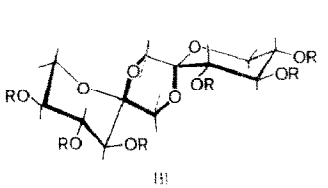
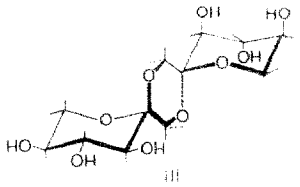
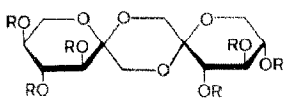


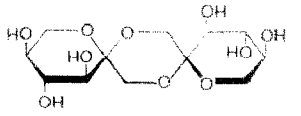




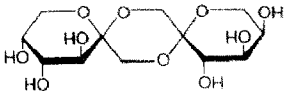
α-L-Sor*p*-α-L-Sor*p*

1 R=H

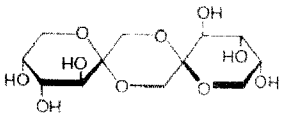
2 R=CH_3CO



3 α-L-Sor*p*-β-L-Sor*p*



4 β-D-Fru*p*-β-D-Fru*p*



5 α-D-Fru*p*-β-D-Fru*p*

RESULTS AND DISCUSSION

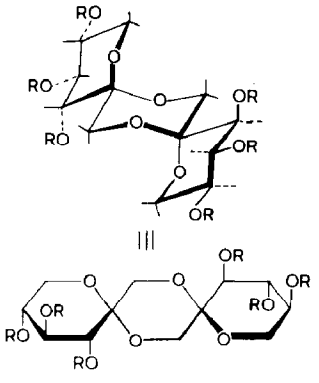
In the crystal, the di-β-D-fructopyranose dianhydride **4** has two pyranose rings each in a $^2C_5$(D) conformation, and the dioxane ring adopts a distorted boat conformation[4]. A strontium complex of **4** had the same conformation[5]. The corresponding di-α-L-sorbopyranose dianhydride **1** had the two pyranose rings each in the $^2C_5$(L) conformation[2], and a boat conformation would be expected for its dioxane ring by analogy with **4**. This expectation has been confirmed in solution by n.O.e. measurements on the hexa-acetate **2**. Thus, irradiation of H-3 strongly enhanced the signal from H-1,1-*exo*, whereas H-1,1-*endo* were unaffected (Table I). If the dioxane ring of **1** or **2** adopted a rigid chair conformation, the two pyranose rings would give different signals. An equilibrium between two chair conformations would result in equal n.O.e. of all H-1 signals on irradiation of H-3. The fact that the dioxane ring of **4** adopts a boat form instead of the generally more stable chair form has been discussed[6]. Molecular models show, however, that, if the dioxane ring of **1** or **4** had a chair conformation, one of its two oxygen substituents would be equatorial, *i.e.*, counter to the anomeric effect. Futhermore, in one of the two pyranose rings, the aglyconic OCH_2 group cannot be oriented in response to the exo-anomeric effect[7]. These factors may explain the preference for a boat conformation in the dioxane rings of **1** and **4**.

The α-D,β-D-difructopyranose dianhydride **5** has the dioxane ring in a rigid chair conformation[3]. The α-L,β-L-disorbopyranose dianhydride **3** undoubtedly has a similar conformation, as this allows an orientation of the glycosidic groups that accommodates both the anomeric and the exo-anomeric effect. This structure requires, however, the β-L-pyranose ring to adopt the $^5C_2$(L) conformation with the three hydroxyl groups axial, as found from the ^{1}H-n.m.r. spectrum of the corresponding octa-acetate[2].

The structure of α-D-fructofuranose β-D-fructopyranose 1,2′:2,1′-dianhydride has been established by X-ray crystallography[6]. The corresponding β-L-sorbofuranose α-L-sorbopyranose 1,2′:2,1′-dianhydride probably has a similar conformation in which the dioxane ring has a chair conformation and both the five- and six-membered rings are arranged to accommodate the anomeric and exo-anomeric effects.

Thus, the structures and conformations of the six products discussed here seem to be determined by the anomeric and exo-anomeric effects, even when this leads to such instability factors as a dioxane ring in a boat conformation or the presence of three axial hydroxyl groups on a pyranose ring.

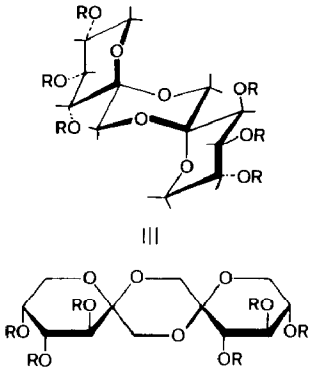
Inspection of molecular models showed that racemic sorbose could form the α-D,α-L-disorbopyranose 1,2′:2,1′-dianhydride (**6**) with the three six-membered rings in chair conformations, thus accommodating the anomeric and exo-anomeric effects, and with all the substituents equatorial. Such a product would be expected to be more stable than any of the compounds just discussed and might therefore be obtained in better yield.



α-D-Sor*p*-α-L-Sor*p*

6 R=H

7 R=CH_3CO



β-D-Fru*p*-α-D-Sor*p*

8 R=H

9 R=CH_3CO

In order to carry out this experiment, D-sorbose was required. It has been prepared in low yield by base-catalyzed rearrangement of D-galactose and of D-gulose[8]. On the other hand, idose is readily rearranged to sorbose, as described in both the D and the L series[9,10]. As D-idopyranose penta-acetate is conveniently prepared by the method of Paulsen *et al.*[11], this product appeared to be a suitable precursor for the preparation of D-sorbose, and in fact, Zemplén deacetylation followed by deionization gave crystalline D-sorbose (60–70%).

Treatment of equal parts of D- and L-sorbose with HF in liquid sulfur dioxide at −25°, followed by precipitation with ether, gave 95% of a crude product, the ^{13}C-n.m.r. spectrum (Fig. 1B) of which revealed mainly one component. Extraction with water left 61% of the rather insoluble and high-melting α-D,α-L-sorbopyranose dianhydride **6**, the ^{13}C-n.m.r. spectrum (large signals in Fig. 1B) of which was similar to, but not identical

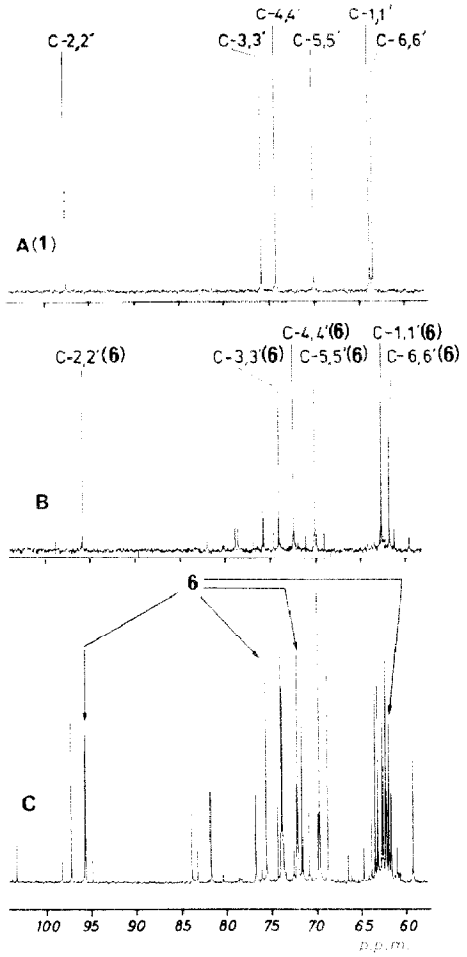


Fig. 1. ^{13}C-N.m.r. spectra (125 MHz) of solutions in D_2O: A, di-α-L-sorbopyranose 1,2':2,1'-dianhydride (**1**); B, crude mixture resulting from treatment of DL-sorbose with HF; C, crude mixture from treatment of L-sorbose with HF.

with, that of the di(α-L) dianhydride **1** (Fig. 1A). A comparison of the ^{13}C-n.m.r. spectra of the crude products resulting from treatment of racemic sorbose (Fig. 1B) and L-sorbose (Fig. 1C) with HF under identical conditions demonstrated the preference for the formation of **6**. The ^{1}H-n.m.r. spectra of **6** and of its hexa-acetate **7** showed that both pyranose rings adopt the stable chair conformation in which H-3,4,5 are axial. The structure was further substantiated by performing a n.O.e. experiment. Saturation of H-3 enhanced the signals of H-1 (3.1%) and H-1′ (1.3%) in addition to that of H-4 (3.9%). Similarly, saturation of H-1 and H-1′ enhanced the signals of H-3 by 4.8 and 3.3%, respectively (Table I). Thus, the signals showing large n.O.e.'s arise from equatorial protons that are close to H-3 in the proposed structure having a chair conformation for the dioxane ring.

One of the possible products from the treatment of a mixture of D-fructose and

TABLE I

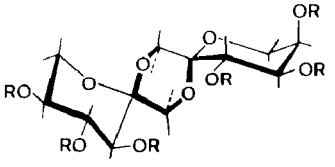
Nuclear Overhauser enhancement experiments[a] on the hexa-acetates **2**, **7**, and **11**

Compound	*Proton-Saturated*[b]	*Observed n.O.e.* (%)	
2	H-3	H-1′ (6.9)	H-1 (−0.6), H-4 (5.4)
	H-1′	H-3 (12.9)	H-1 (25.8)
	H-1	H-1′ (30.7)	H-3 (−1.1)
7	H-3	H-1 (3.1)	H-1′ (1.3), H-4 (3.9)
	H-1	H-1′ (14.3)	H-3 (4.8)
	H-1′	H-1 (16.5)	H-3 (3.3)
11 β-fructose unit	H-3	H-1 (3.8)	H-1′ (1.6)
	H-1	H-1′ (21.8)	H-3 (6.8)
	H-1′	H-1 (22.5)	H-3 (4.0)

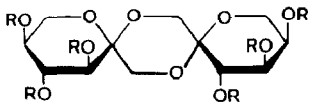
[a] Measured in the difference mode; accuracy, ±10%. [b] H-1, Upfield signal from H-1 protons. H-1′, Downfield signal from H-1 protons.

D-sorbose with HF is β-D-fructopyranose α-D-sorbopyranose 1,2′:2,1′-dianhydride (**8**), with a structure similar to that of **6**, with only one axial hydroxyl group (HO-5 of the fructose unit). Therefore, **8** would be expected to have a high stability and to be formed readily; in fact, reaction of D-fructose and D-sorbose with HF gave mainly **8**, which crystallized readily from the mixture in 57% yield. Its structure and that of the hexa-acetate (**9**) were evident from the ^{1}H-n.m.r. spectra.

Finally, a mixture of D-fructose and L-sorbose was treated with HF. Inspection of molecular models showed that none of the mixed dipyranose dianhydrides would be very stable, and a complex mixture of products would be expected as confirmed by the complexity of the ^{13}C-n.m.r. spectrum of the crude product. Acetylation, followed by chromatography, gave a crystalline hexa-acetate in low yield. The n.m.r. spectra of this product showed it to be β-D-fructopyranose α-L-sorbopyranose 1,2′:2,1′-dianhydride hexa-acetate (**11**), with a structure similar to that of **2** except that the configuration at



11



α-L-Sor*p*-β-D-Fru*p*

10 R=H
11 R=CH_3CO

C-5 inverted. Therefore, it may be assumed that **11** has a conformation similar to that of **2** with the dioxane ring in a boat form, and this was confirmed by a n.O.e. experiment (Table I), analogous to that performed on **2**. Deacetylation of **11** yielded the crystalline dianhydride **10**.

Whereas there is much experimental evidence for the anomeric effect, information on the stabilization arising from the exo-anomeric effect has been more difficult to obtain[12,13]. From the present work, it is concluded that all of the dipyranose 1,2':2,1'-dianhydrides discussed adopt conformations in which both the anomeric and exo-anomeric effects are accommodated for both the pyranose and the dioxane rings. The combined effect of these stability factors, apparently, can force the dioxane ring to adopt a boat conformation (**1**, **4**, and **10**) or cause the pyranose rings to adopt conformations with three axial hydroxyl groups (**3** and **5**). However, it should be noted that the conformations adopted by the dianhydrides are all determined by a combination of the anomeric and exo-anomeric effects and, therefore, it is difficult to obtain specific information about the latter effect.

EXPERIMENTAL

General methods. — Melting points are uncorrected. N.m.r. spectra were obtained on a Bruker AM-500 instrument: ^1H spectra (500 MHz) of solutions in $CDCl_3$ (internal Me_4Si) and D_2O at 27° (DOH δ 4.75, acetone = 2.25 p.p.m.); ^{13}C spectra (125 MHz) of solutions in D_2O (internal 1,4-dioxane, 67.40 p.p.m.) and $CDCl_3$ (central signal of the $CDCl_3$ triplet, 76.91 p.p.m.). Optical rotations were measured on a Perkin–Elmer 241 instrument.

D-*Sorbose.* — To a suspension of penta-*O*-acetyl-α-D-idopyranose[11] (40 g) in MeOH (200 mL) was added sodium methoxide [from Na (800 mg) and MeOH (100 mL)], and the mixture was kept for 20 h at room temperature, then deionized with a mixture of Amberlite IR-120 (H^+) and IRA-400 (OH^-) resins, filtered through charcoal, and concentrated. The residue (~17 g) crystallized from EtOH to give D-sorbose (10.4 g, 56%), m.p. 161–163°. The material in the mother liquor was treated with NaOMe in MeOH, deionized, and crystallized from EtOH to give more product (2.7 g, total yield of 71%). In a series of preparations, the yield of D-sorbose varied from 55–70%.

A sample, recrystallized from EtOH–water, had m.p. 164–165°, $[\alpha]_D^{20}$ +43° (*c* 2.9, water), lit.[14] m.p. 160–162°, $[\alpha]_D^{23}$ +43° (water).

α-D-*Sorbopyranose* α-L-*sorbopyranose 1,2':2,1'-dianhydride* (**6**). — A mixture of D (4 g) and L-sorbose (4 g) in a polyethylene bottle was cooled in solid CO_2–acetone whilst liquid SO_2 (8 mL) and anhydrous HF (8 mL) were added. The mixture was stirred for ~2 min until a homogeneous solution was obtained, then kept for 20 h at −25°. The solution was then cooled in solid CO_2–acetone, cold ether (~60 mL) was added, and the precipitate was washed several times with ether by decantation, filtered off, and dried to give a colourless powder (6.88 g, 95%). The ^{13}C-n.m.r. spectrum (Fig. 1B) revealed mainly **6** and small proportions of other products. Extraction with boiling water (50

mL) removed the minor products and left **6** (4.21 g, 58%) which was pure as seen from a ^{13}C-n.m.r. spectrum of a saturated aqueous solution. The product was almost insoluble in cold water. A sample, recrystallized from a large amount of boiling water, had m.p. >320°. N.m.r. data (D_2O): ^1H, δ 3.99 (H-1), 3.66 (H-6*eq*), 3.54 (H-4), 3.52 (H-5), 3.37 (H-1′), 3.34 (H-6*ax*), 3.15 (H-3); $J_{1,1}$ 12, $J_{3,4}$ 9, $J_{4,5}$ ~9, $J_{5,6ax}$ 5, $J_{5,6eq}$ ~10, $J_{6,6}$ 11 Hz; ^{13}C, 95.8 (C-2), 74.2, 72.5, 70.1 (C-3,4,5), 62.6, 61.8 p.p.m. (C-1,6).

Anal. Calc. for $C_{12}H_{20}O_{10}$: C, 44.24; H, 6.22. Found: C, 44.37; H, 6.27.

A ^{13}C-n.m.r. spectrum of the water-soluble products in the aqueous extract revealed a complex mixture similar to that obtained[2] by treatment of L-sorbose with HF. When DL-sorbose was treated with HF at room temperature for 1 h, the crude product was dark-coloured, but **6** was still the main product (^{13}C-n.m.r. spectrum).

*3,4,5-Tri-*O*-acetyl-α-*D*-sorbopyranose 3,4,5-tri-*O*-acetyl-α-*L*-sorbopyranose 1,2′:2,1′-dianhydride* (**7**). — Crude **6** (1.0 g) was acetylated with Ac_2O in pyridine to give, after conventional processing, a product (1.77 g), which was recrystallized from CH_2Cl_2–ether to yield **7** (1.2 g, 60%), m.p. 280–282°, $[\alpha]_D^{20}$ ~0° (*c* 1.2, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.55 (H-4), 5.05 (H-5), 4.88 (H-3), 3.97 (H-6*eq*), 3.67 (H-1*ax*), 3.57 (H-1*eq*), 3.52 (H-6*ax*), 2.00, 2.04, 2.10 (OAc); $J_{1,1}$ 11.8, $J_{3,4}$ 10.0, $J_{4,5}$ 10.0, $J_{5,6ax}$ 10.7, $J_{5,6eq}$ 6.1, $J_{6,6}$ 10.7 Hz; ^{13}C, 93.9 (C-2), 70-0 (C-3), 69.9 (C-4), 69.1 (C-5), 61.1 (C-1), 59.3 p.p.m. (C-6) (assigned through a C,H-correlated n.m.r. spectrum).

Anal. Calc. for $C_{24}H_{32}O_{16}$: C, 50.00; H, 5.60. Found: C, 49.80; H, 5.54.

*β-*D*-Fructopyranose α-*D*-sorbopyranose 1,2′:2,1′-dianhydride* (**8**). — A mixture of D-sorbose (2 g) and D-fructose (2 g) was treated with HF (4 mL) and SO_2 (4 mL) as described above. The crude product (3.7 g) was crystallized from water–ethanol to give **8** (2.1 g, 57%), m.p. 210° (dec.), $[\alpha]_D^{20}$ −43° (*c* 1.4, water). N.m.r. data (D_2O): ^1H, δ 3.35, 3.39, 3.97, 3.99 (H-1,1′), 3.83 (H-6′*eq*), 3.53 (H-4′), 3.50 (H-5′), 3.32 (H-6′*ax*), 3.12 (H-3′); $J_{1',1'}$ 12 Hz, $J_{3',4'} = J_{4',5'}$ = 9.2, $J_{5',6'ax}$ 10.5, $J_{5',6'eq}$ 5.3, $J_{6',6'}$ 10.8 Hz; δ 3.85 (H-5), 3.75 (H-4), 3.70 (H-6*eq*), 3.60 (H-6*ax*), 3.41 (H-3); $J_{3,4}$ 10.4, $J_{4,5}$ 3.5, $J_{5,6ax}$ 2.0, $J_{5,6eq}$ 1.2, $J_{6,6}$ 11.5 Hz; ^{13}C, δ 62.0, 61.6 (C-1,1′), 96.2, 95.8 (C-2,2′), 72.5 (C-3′), 74.1 (C-4′), 70.1 (C-5′), 62.6 (C-6′), 69.3 (C-3), 69.79 (C-4), 69.84 (C-5), 64.3 p.p.m. (C-6) (assigned through a C,H-correlated spectrum).

Anal. Calc. for $C_{12}H_{20}O_{10}$: C, 44.24; H, 6.22. Found: C, 44.17; H, 6.18.

*3,4,5-Tri-*O*-acetyl-β-*D*-fructopyranose 3,4,5-tri-*O*-acetyl-α-*D*-sorbopyranose 1,2′:2,1′-dianhydride* (**9**). — Crude **8** (1.0 g) was acetylated conventionally with Ac_2O in pyridine, and the product was crystallized from ether to give **9** (1.3 g, 73%), m.p. 238°. Recrystallization from CH_2Cl_2–EtOH gave a product with m.p. 236–238°, $[\alpha]_D^{20}$ −42° (*c* 2.2, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.49 (H-4′), 4.95 (H-5′), 4.83 (H-3′), 3.91 (H-6′*eq*), 3.61, 3.66 (H-1,1,1′,1′), 3.51 (H-6′*ax*); $J_{1,1} = J_{1',1'}$ = 11.7, $J_{3',4'} = J_{4',5'}$ = 10.0, $J_{5',6'ax}$ 10.6, $J_{5',6'eq}$ 6.0, $J_{6',6'}$ 11.0 Hz; δ 5.35 (H-4), 5.31 (H-5), 5.16 (H-3), 3.82 (H-6*eq*), 3.81 (H-6*ax*); $J_{3,4}$ 10.3, $J_{4,5}$ 3.4, $J_{5,6ax}$ 1.8, $J_{5,6eq}$ 1.5, $J_{6,6}$ 12.0 Hz; ^{13}C, δ 61.2, 61.3 (C-1,1′), 93.9, 94.5 (C-2,2′), 69.82 (C-3′), 69.78 (C-4′), 69.1 (C-5′), 68.8 (C-5), 67.4 (C-4), 67.2 (C-3), 61.25 (C-6), 59.2 p.p.m. (C-6′) (assigned through a C,H-correlated spectrum).

Anal. Calc. for $C_{24}H_{32}O_{16}$: C, 50.00; H, 5.60. Found: C, 49.97; H, 5.68.

*3,4,5-Tri-*O*-acetyl-β-*D*-fructopyranose* *3,4,5-tri-*O*-acetyl-α-*L*-sorbopyranose*

1,2':2,1'-dianhydride (**11**). — A mixture of D-fructose (5 g) and L-sorbose (5 g) was treated with liquid SO_2 (10 mL) and HF (10 mL) for 20 h at −25° as described above, and the product was then precipitated with ether and dried to give a crude colourless powder (9.7 g). A ^{13}C-n.m.r. spectrum revealed a complex mixture of compounds.

Acetylation of this product (5 g) with Ac_2O and pyridine gave a mixture (8.0 g) of acetates, which was subjected to column chromatography on silica gel using ether. The product (1.4 g) eluted first, crystallized from ether to give material (500 mg, 6%), with m.p. ~220°. Recrystallization from CH_2Cl_2–ether gave **11**, m.p. 229–231°, $[\alpha]_D^{20}$ −157° (*c* 1.1, chloroform). N.m.r. ($CDCl_3$): ^1H, δ 5.40 (H-4), 5.37 (H-3), 5.26 (H-5), 3.53, 4.04 (H-1), 4.01 (H-6*eq*), 3.70 (H-6*ax*); $J_{1,1'}$ 12.5, $J_{3,4}$ 10.5, $J_{4,5}$ 3.0, $J_{5,6eq}$ 1.7, $J_{5,6ax}$ 1.9, $J_{6,6'}$ 13.0 Hz; δ 5.48 (H-4'), 5.01 (H-3'), 4.95 (H-5'), 3.54, 3.91 (H-1'), 3.85 (H-6'*eq*), 3.65 (H-6'*ax*); $J_{1,1'}$ 12.5, $J_{3,4}$ 10.3, $J_{4,5}$ 9.6, $J_{5,6'ax}$ 10.7, $J_{5,6'eq}$ 6.1, $J_{6,6'}$ 10.8 Hz; ^{13}C, δ 96.8, 96.2 (C-2,2'), 72.6 (C-3'), 70.2 (C-3), 69.0 (C-4',5'), 68.8 (C-5), 66.7 (C-4), 62.9 (C-1), 62.5 (C-6'), 62.2 (C-6), 59.7 p.p.m. (C-1') (assigned through a CH-correlated spectrum).

Anal. Calc. for $C_{12}H_{20}O_{10}$: C, 50.00; H, 5.60. Found: C, 49.90; H, 5.61.

β-D-Fructopyranose α-L-sorbopyranose 1,2':2,1'-dianhydride (**10**). — To a suspension of **11** (1.4 g) in MeOH (25 mL) was added methanolic M NaOMe (1 mL). Dissolution occurred within a few minutes and the product precipitated. After 2 h, water (~25 mL) was added to obtain a homogeneous solution which was stirred for 2 h with excess of Amberlite IR-120 (H^+) resin, filtered through carbon, and concentrated to give **10** (600 mg, 76%), which was pure as seen from a ^{13}C-n.m.r. spectrum. Recrystallization from methanol–ethanol gave **10** with m.p. 194–196°, $[\alpha]_D^{20}$ −272° (*c* 0.6, water). ^{13}C-N.m.r. data (D_2O): 97.8, 97.5 (C-2,2'), 76.0, 74.5, 73.1, 70.3, 70.1, 69.8 (C-3 to C-5 and C-3' to C-5'), 65.3, 64.2, 64.0, 63.6 p.p.m. (C-1,6,1',6').

Anal. Calc. for $C_{12}H_{20}O_{10}$: C, 44.24; H, 6.22. Found: C, 44.14; H, 6.24.

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