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Selective protonic activation of isomeric glycosylfructoses with pyridinium poly(hydrogen fluoride) and synthesis of spirodioxanyl oligosaccharides *

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ABSTRACT

Selective activation of the ketose unit in the isomeric glycosylfructoses, palatinose, leucrose, maltulose, turanose and lactulose, with pyridinium poly(hydrogen fluoride) resulted in the almost quantitative formation of glycosylated difructose dianhydrides. The reaction preferentially involves a reactive fructofuranosyl oxocarbenium ion and is subject to stereoelectronic control. The relative amounts of isomeric spirodioxanyl oligosaccharides obtained within a series was shown to depend on the reaction conditions, especially on the hydrogen fluoride–pyridine ratio. Using suitable concentrations of hydrogen fluoride in pyridine, the reaction was easily directed to the formation of the kinetic difuranosyl or thermodynamic pyranosyl derivatives. More rigorous conditions resulted in the specific hydrolysis of one glycosidic bond in the tetrasaccharides derived from palatinose, leucrose and turanose, to yield spirodioxanyl trisaccharides.

INTRODUCTION

D-Fructose dianhydrides were first obtained by the action of strong acids on D-fructose or inulin[3–6]. Alternative syntheses have been reported which involve fructosyltransferase enzymes acting on inulin or levan[7–10]. More efficient techniques are based on the use of anhydrous hydrogen fluoride (HF) as catalyst[11,12]. The reactivity of D-fructose in HF[11], which yields quantitatively difructose dianhydrides, has been extended to L-[13] and D,L-sorbose[1], and further rationalized on the

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basis of steric and electronic control in the formation of the spirodioxane system resulting from the reaction of transient oxocarbenium ions at the anomeric position in hexuloses.

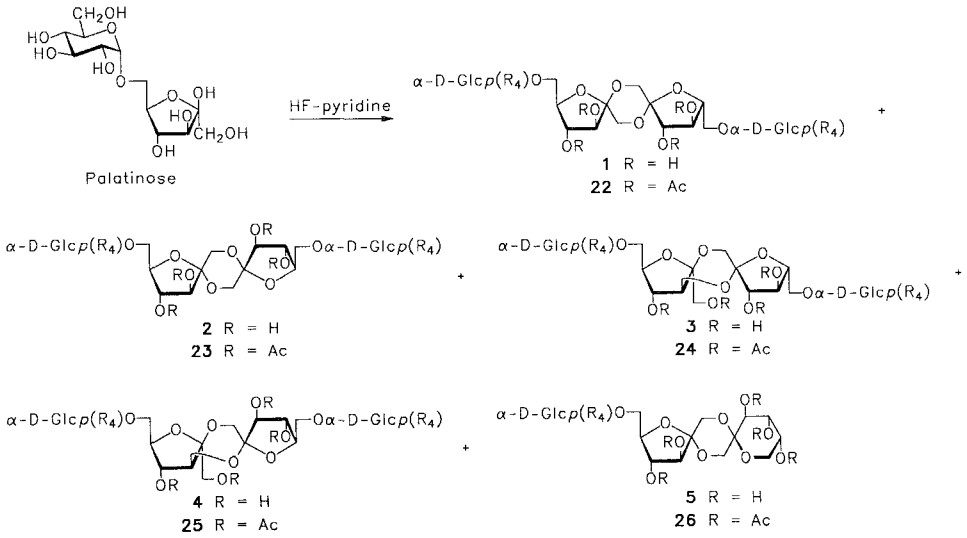
Hitherto, only two examples of glycosylated D-fructose dianhydrides have been reported in the literature, namely the 3- and 6-*O*-α-D-glucopyranosyl-α-D-fructofuranose β-D-fructofuranose 1,2′:2,3′-dianhydrides, which were obtained[10] by enzymic transglucosylation of α-D-fructofuranose β-D-fructofuranose 1,2′:2,3′-dianhydride with maltose. Furthermore, two diglucosyl difructose dianhydrides have been detected as components of the complex oligosaccharide mixture resulting from the action of citric acid on palatinose[14]. Glycosyl-D-fructose dianhydrides have now been readily prepared by treatment of various glycosylfructoses with pyridinium poly(hydrogen fluoride). The mechanism of the reaction and the relative stabilities of the products obtained are also discussed.

RESULTS AND DISCUSSION

Storage of solutions of palatinose (6-*O*-α-D-glucopyranosyl-D-fructofuranose, isomaltulose), leucrose (5-*O*-α-D-glucopyranosyl-D-fructopyranose), maltulose (4-*O*-α-D-glucopyranosyl-D-fructose), turanose (3-*O*-α-D-glucopyranosyl-D-fructose) and lactulose (4-*O*-β-D-galactopyranosyl-D-fructose) in pyridinium poly(hydrogen fluoride) resulted in the formation in high yield of mixtures of glycopyranosyl difructose dianhydrides which were recovered by quenching and precipitation with an excess of ether (Schemes 1–5 and Tables I–V). As previously found with hydrogen fluoride[11–13], the outcome of the reaction appeared to be strongly dependent upon variations in the strength of the protonic reagent, sugar concentration, temperature, and reaction time.

Commercial pyridinium poly(hydrogen fluoride), a stable complex which contains up to 70 wt% HF in pyridine is known to contain some "free" HF in equilibrium, thus acting as a reservoir for anhydrous HF[15]. We have found that a change in the HF:pyridine ratio significantly affects the relative amount of products obtained, presumably by modifying the concentration of free HF in the medium. Thus, under a low HF:pyridine ratio and a short reaction time, palatinose (Scheme 1 and Table I) gave mainly 6:6′-di-O-α-D-glucopyranosyl di-β-D-fructofuranose 1,2′:2,1′-dianhydride (**1**) and the α,β-difructofuranose anomer **2**. The percentage of **1** decreased very quickly when slightly stronger conditions were used, resulting in a concomitant increase of **2** in the mixture. Higher temperatures or reaction times resulted in the isomerization of **2** into the β,β-1,2′:2,3′-dianhydride **3**, which is believed to be a thermodynamic product in this reaction. The α,β anomer **4** of **3** was always found as a minor product in the final equilibrium. More drastic conditions caused selective hydrolysis of one glucosidic linkage to give the monoglucosylated α-furanose β-pyranose dianhydride **5**.

Leucrose (Scheme 2 and Table II) yielded, under mild reaction conditions, the 5:5′-di-*O*-α-D-glucopyranosyl di-α,β-D-fructopyranose dianhydride (**6**) as the major



Scheme 1. Products formed by the action of pyridinium poly(hydrogen fluoride) on palatinose.

product, which isomerized into the symmetrical di-β-D-fructopyranose dianhydride tetrasaccharide **7** under more rigorous conditions. When the relative proportion of HF in pyridine reached 12:3 (w/w), one of the glucosyl residues was partially cleaved resulting in the formation of the monoglucosylated, di-β-D-fructopyranose dianhydride (**8**).

The reactivity of maltulose (Scheme 3 and Table III) and lactulose (Scheme 5 and Table V) did not differ significantly on treatment with pyridinium poly(hydrogen fluoride). Three main products having, respectively, the di-α,β-D-fructofuranose (**9** and **19**), the α-D-fructofuranose β-D-fructopyranose (**10** and **20**), and di-α,β-D-fructopyranose 1,2′:2,1′-dianhydride (**11** and **21**) central structures were found. The relative amount of the 4:4′-di-α-D-glucopyranosyl fructofuranose fructopyranose dianhydride **10** and the corresponding 4:4′-di-β-D-galactopyranosyl derivative **20** increased at the expense of the difructofuranose (**9** and **19**) and difructopyranose (**11** and **21**) isomers when more rigorous conditions were used. Minor components could also be isolated (**12**) or detected (**13** and **14**) in the maltulose dianhydride mixtures, but they were not found in the case of lactulose.

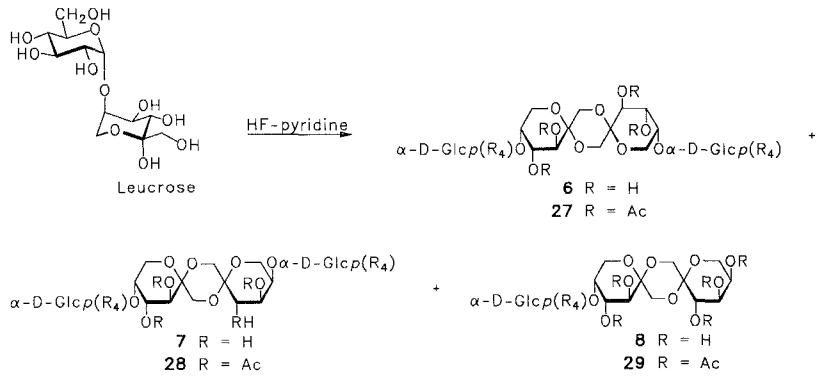
Turanose (Scheme 4 and Table IV) led exclusively to di-α-D-glucopyranosyl β,β- (**15**) and α,β- (**16**) difructofuranose 1,2′:2,1′-dianhydrides when the HF:pyridine ratio was 4:3. When higher proportions of HF in pyridine were used, di- (**17**) and mono- (**18**) glucosylated α-D-fructofuranose β-D-fructopyranose derivatives were also found in the final equilibrium. For a 12:3 ratio of HF in pyridine and longer reaction time, almost complete hydrolysis of one glycosidic bond occurred yielding the trisaccharide **18**.

The structures of the glycosylated dianhydrides **1**, **2**, **4**–**11** and **13**–**21** were established by comparison of the ^{13}C NMR chemical shifts for carbon atoms of the

TABLE I

Products formed by the action of pyridinium poly(hydrogen fluoride) on palatinose

Experiment No.	Palatinose (g)	HF:py (mL)	Reaction temperature (°C)	Reaction time (h)	Products formed (%)					Residual palatinose (%)
					1	**2**	**3**	**4**	**5**	
1	0.2	4:3 (1.0)	20	0.3	25	45	5	5		20
2	0.2	7:3 (0.8)	0	0.3	< 2	75	9	4		10
3	0.1	7:3 (0.4)	20	0.3	< 2	55	28	6		9
4	0.1	7:3 (0.4)	20	1	< 2	45	37	6		5
5	0.1	7:3 (0.4)	0	2	< 2	48	35	5		7
6	0.2	7:3 (0.4)	20	1	< 2	67	20	5		2
7	0.3	7:3 (0.6)	20	2	< 2	65	25	5		2
8	0.1	7:3 (0.4)	20	6		40	30	5	10	5
9	0.1	9:3 (0.2)	20	6		45	25	5	10	5
10	0.1	12:3 (0.4)	20	1		43	34	5	8	5
11	0.1	12:3 (0.8)	20	2		30	20	5	25	7
12	0.1	12:3 (0.4)	20	5		4	10	4	15	5



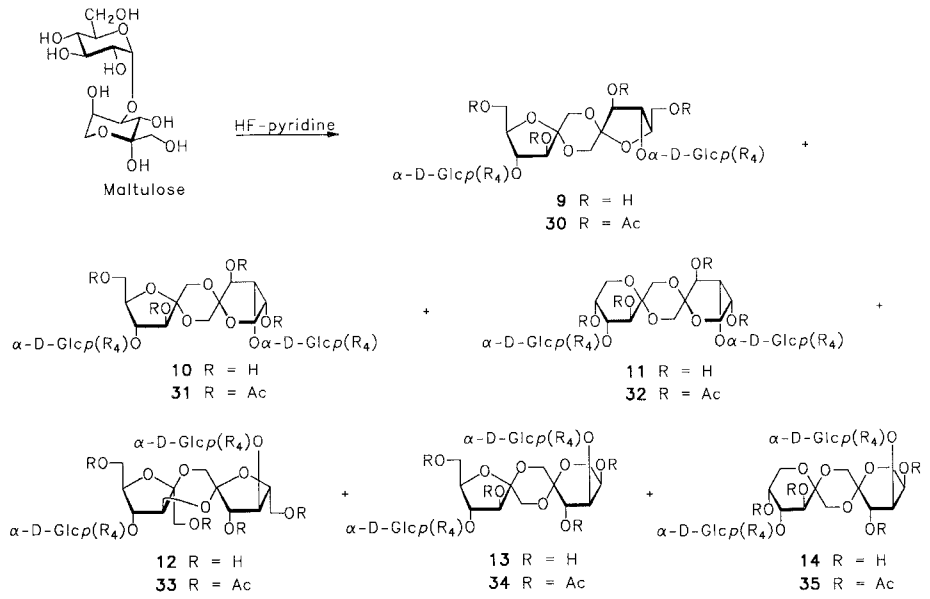
Scheme 2. Products formed by the action of pyridinium poly(hydrogen fluoride) on leucrose.

fructose moieties (Tables VII–XI) with those already partially assigned for the parent difructose dianhydrides (Table VI)[11,12,16]. Assignments in Table VI were completed taking into account substitution effects in ^{13}C NMR spectroscopy[17,18]. Thus, palatinose dianhydrides **1–5** (Table VII) showed signals at 67.7–70.1 ppm for *O*-glucosylated C-6(6′) in fructofuranose residues. In leucrose dianhydrides (Table VIII), the resonances for C-5(5′) were found to be shifted by 8.5 (α-D-fructopyranose residue) or ~ 10 ppm (β-D-fructopyranose residue) toward lower field as a result of the *O*-glucosylation as compared with the corresponding unsubstituted difructopyranose dianhydrides. Similarly, the resonances of the *O*-glucosylated carbon atoms in maltulose (Table IX) and turanose dianhydrides (Table X) were found to be shifted by 3.2–6.9 (fructofuranose rings) or 5.8–10.6 ppm (fructopyranose rings). In the case of lactulose dianhydrides (Table XI), the deshielding effect resulting from galactosylation at C-4(4′) at the fructofuranosyl rings is analogous to that observed in maltulose derivatives. However, for fructopyranose substitutions the deshielding effect was significantly larger (8.5–9.3 ppm) than had been previously observed for the disaccharide precursors[17].

TABLE II

Products formed by the action of pyridinium poly(hydrogen fluoride) on leucrose

Experiment No.	Leucrose (g)	HF:py (ML)	Reaction temperature (°C)	Reaction time (h)	Products formed (%)			Residual leucrose (%)
					6	**7**	**8**	
1	0.5	4:3 (2.0)	20	0.3	36			64
2	1.0	7:3 (1.5)	0	1	51	5		43
3	0.5	7:3 (1.0)	20	0.3	73	9		18
4	1.0	7:3 (2.0)	20	2	67	18		14
5	0.5	12:3 (1.0)	20	1.5	42	32	7	12
6	0.5	12:3 (1.0)	20	4	15	53	12	8
7	0.5	15:3 (1.0)	20	1	11	50	7	13
8	1.0	15:3 (2.0)	20	1.5	5	40	15	9



Scheme 3. Products formed by the action of pyridinium poly(hydrogen fluoride) on maltulose.

The deshielding effect resulting from the glycosylation at the difructose dianhydride moiety was also observed in the peracetylated derivatives **22**, **23**, **25–32**, and **36–42**, and, in agreement with results of Gagnaire and coworkers[19], was found to differ accordingly with the anomeric configuration of the linkage involved in the substitution. In α-D glucosylated derivatives **22**, **23**, **25–32**, and **36–39** (Schemes 1–4 and Tables VII–X), the resonance of the substituted carbon atom of the fructose residue was shifted by 4–6 ppm toward lower field as compared with the corresponding difructose dianhydride hexaacetates (Table VI). Likewise, the di-β-D-galactosylated dianhydrides **40–42** derived from lactulose (Scheme 5 and Table XI) showed signals for the C-4,4′ substituted carbon atoms at about 2 ppm lower field as compared with the corresponding maltulose dianhydrides **30–32** (Scheme 3 and Table IX). This behavior was, however, not found for the maltulose derivatives **31** and **32**, where the resonance of the α-D-glucosylated C-4,4′ carbon atoms in the fructopyranose moieties was found to be shifted by only 1–2.5 ppm, together with the adjacent C-3,3′ and C-5,5′ carbon atoms, as compared with the parent difructose dianhydride hexaacetates.

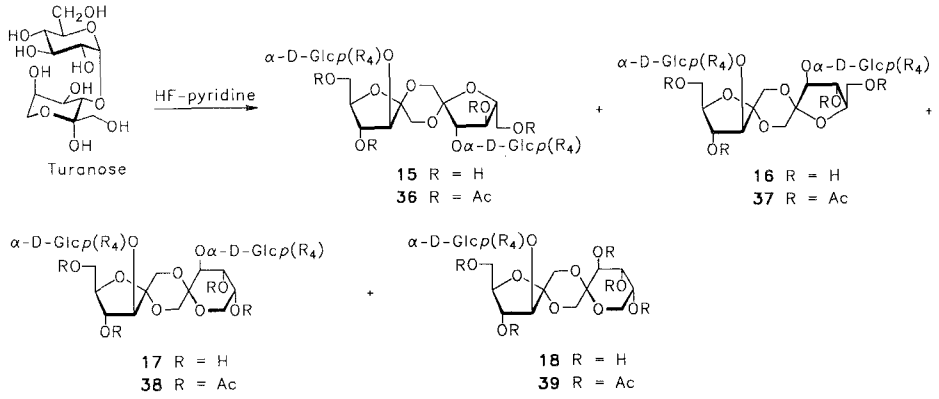
^{13}C NMR data for di-β-D-fructofuranose 1,2′:2,3′-dianhydrides do not appear to be available in the literature. The structures of the diglucosylated dianhydrides **3** and **12** have consequently been assigned by comparison of the resonances for the anomeric carbon atoms of the fructofuranosyl moieties (Tables VII and IX) with data for di-α-L-sorbofuranose 1,2′:2,3′-dianhydride (Table VI)[12]. The 1,2′:2,3′-dianhydride structure for compounds **3**, **4**, and **12** is furthermore supported by the shift (5–6 ppm) of the resonance for C-3′ toward lower field as compared with the

TABLE III

Products formed by the action of pyridinium poly(hydrogen fluoride) on maltulose

Experiment No.	Maltulose (g)	HF : py (mL)	Reaction temperature (°C)	Reaction time (h)	Products formed (%)						Residual maltulose (%)
					9	**10**	**11**	**12**	**13** [a]	**14** [a]	
1	0.3	4 : 3 (0.75)	20	0.3	25	18	12				45
2	0.5	7 : 3 (1.0)	0	0.3	41	20	18				20
3	0.1	7 : 3 (0.4)	0	0.6	20	36	23				21
4	0.5	7 : 3 (1.0)	20	0.5	12	54	12	7	3	2	8
5	2.0	7 : 3 (4.0)	20	1	10	70		7	3	3	3

[a] Detected (^{13}C NMR) but not isolated as pure products.



Scheme 4. Products formed by the action of pyridinium poly(hydrogen fluoride) on turanose.

corresponding α-D-fructofuranose β-D-fructofuranose 1,2′ : 2,1′-dianhydride derivatives **2** or **9**, in agreement with the involvement of C-3′ in the acetal linkage.

The anomeric configuration of the aldohexose substituent in the glycosylfructose dianhydrides **1–12** and **15–21** was confirmed by the ^{13}C NMR chemical shifts for the anomeric carbon atoms in the respective D-glucose (**1–12** and **15–18**) or D-galactose residues (**19–21**). Palatinose- (**1–5**), leucrose- (**6–8**) and maltulose-dianhydrides (**9–12**) showed δ-values of 101.5–98.8 (96.2–94.6 in peracetates **22–26**, **27–29**, and **30–33**, respectively) for C-1 (1′) of α-D-glucopyranosides, while the observed δ-values in the lactulose derivatives **19–21** (104.8–101.8; 102.0–99.8 in peracetates **40–42**) confirmed the β-D configuration of the galactopyranosyl substituent[17,18]. Turanose dianhydrides **15–18** showed δ-values of 97.1–96.7 for C-1(1′) of the glucopyranosyl unit linked to O-3(3′) of a fructofuranose ring and 102.5 when the linkage involved the fructopyranose structure **17**. Such values are slightly different from those reported for turanose (99.2–97.6 and 101.7 respectively)[17]. However, confirmation of the α-D configuration at the glucosidic linkage was obtained from the ^{13}C NMR chemical shifts for C-1(1′) of D-glucose in the peracetylated derivatives **36–39** (95.1–97.9 ppm).

The close similarity observed for the δ-values for the anomeric signals of the fructose residues in a homogeneous series of glycosylated and non-glycosylated difructose dianhydrides suggests that the overall conformations of the dianhydrides are not much distorted by the presence of the glycosyl substituents. Thus, the symmetry observed in the ^{13}C NMR spectra for the di-β-furanose dianhydrides **1** and **15**, as well as for the di-β-pyranose dianhydride **7**, indicates that the dioxane ring cannot adopt a chair conformation and that a boat conformation or a rapid interchange between two chairs, as has been reported for the corresponding di-β-D-fructofuranose[12] or di-β-D-fructopyranose 1,2′ : 2,1′-dianhydride[20,21], is expected. In compounds having a di-α,β-D-fructofuranose 1,2′ : 2,1′-dianhydride (**2**, **9**, **16**, and **19**), an α-D-fructofuranose β-D-fructopyranose 1,2′ : 2,1′-dianhydride (**5**,

TABLE IV

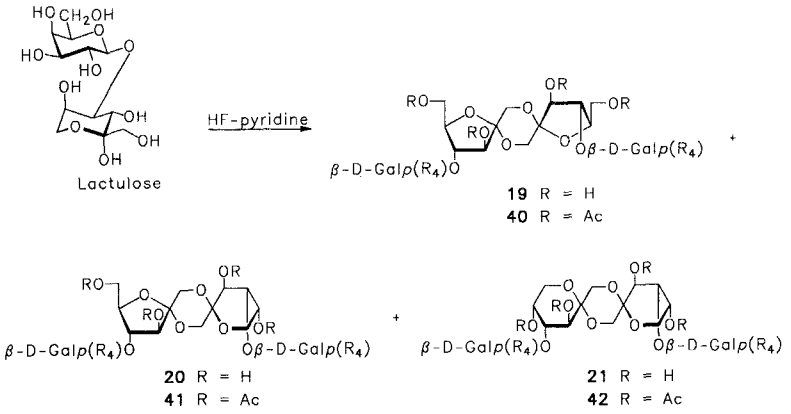
Products formed by the action of pyridinium poly(hydrogen fluoride) on turanose

Experiment No.	Turanose (g)	HF:py (mL)	Reaction temperature (°C)	Reaction time (h)	Products formed (%)				Residual turanose (%)
					15	**16**	**17**	**18**	
1	0.1	4:3 (0.5)	20	0.3	20	30			45
2	0.1	7:3 (0.2)	0	0.3	11	60	13		15
3	0.5	7:3 (1.0)	20	0.3	11	48	18	7	7
4	0.1	7:3 (0.4)	20	1	8	40	18	10	12
5	0.1	12:3 (0.4)	20	1	7	33	22	15	8
6	0.1	12:3 (0.4)	20	2.5	6	30	18	22	2
7	0.1	12:3 (0.4)	20	4.5	2	3	3	40	

TABLE V

Products formed by the action of pyridinium poly(hydrogen fluoride) on lactulose

Experiment No.	Lactulose (g)	HF:py (mL)	Reaction temperature (°C)	Reaction time (h)	Products formed			Residual lactulose (%)
					19	**20**	**21**	
1	0.5	4:3 (2.5)	20	0.3	15			85
2	0.5	7:3 (1.0)	0	0.3	34	21	15	23
3	0.5	7:3 (1.0)	20	0.3	29	45	13	13
4	0.5	12:3 (1.0)	20	1		60		10



Scheme 5. Products formed by the action of pyridinium poly(hydrogen fluoride) on lactulose.

10, **17**, **18** and **20**), a di-α,β-D-fructopyranose 1,2′:2,1′-dianhydride (**6**, **11**, and **21**), or a di-β-D-fructofuranose 1,2′:2,3′-dianhydride central structure (**3** and **22**), the dioxane ring presumably adopts a chair conformation in which the two oxygen substituents are axial and all carbon substituents are equatorial, which is in agreement with the anomeric effect, as found in the parent difructose dianhydrides[11,12,22,23]. Besides, the close similarity for the δ resonances of the α-D-fructofuranose carbon atoms in di-α,β-D-fructofuranose 1,2′:2,1′-dianhydride derivatives and their α-D-fructofuranose β-D-fructopyranose counterparts (i.e., **2** vs. **5**; **9** vs. **10**; **16** vs. **17** and **18**; **19** vs. **20**), for the 1,2-linked β-D-fructofuranose ring carbon atoms in di-α,β-D-fructofuranose 1,2′:2,1′- and di-β-D-fructofuranose 1,2′:2,3′-dianhydride derivatives (i.e., **2** vs. **3**; **9** vs. **12**), and for the β-D-fructopyranose ring carbon atoms in α-D-fructofuranose β-D-fructopyranose 1,2′:2,1′-dianhydride derivatives and their di-α,β-D-fructopyranose analogues (i.e., **10** vs. **11**; **22** vs. **23**), also support the idea that dianhydrides having the aforementioned structures have identical overall conformation. Finally, the dioxane ring in the palatinose dianhydride **4** must adopt a skew conformation to allow an axial orientation of the glycosidic groups that accomodates the anomeric effect, which keeps the C-3,1′,4′ carbon atoms in an equatorial orientation, as in the unsubstituted dianhydride[24].

A furanose oxocarbenium ion has been proposed as an intermediate in the formation of di-D-fructose or di-L-sorbose dianhydrides in HF[11,13]. This cannot evidently apply to leucrose since the furanose form is prevented by the glucopyranosyl substitution at C-5. In support of the latter hypothesis, leucrose was found to be the less reactive of the glycosylfructoses considered in the present study.

The changes in the relative proportions of the products found when going from kinetic to thermodynamic reaction conditions (from the top to the bottom in Tables I–V) is believed to reflect their relative stabilities. Results can be rationalized considering the conformations discussed above for the different structures. It is probable that transient di-β-D-fructofuranose dianhydrides are formed in the

TABLE VI

^{13}C NMR chemical shift assignments (ppm) for some di-D-fructose and di-L-sorbose dianhydrides, and their hexaacetates

Compound	Carbon											
	C-2	C-2′	C-3	C-4	C-5	C-3′	C-4′	C-5′	C-6	C-6′	C-1	C-1′
Dianhydrides [a]												
Di-β-D-Fru*f* 1,2′:2,1′	104.6 [c]		80.8	77.6	83.7				61.8		61.8	
α-D-Fru*f* β-D-Fru*f* 1,2′:2,1′	103.3 [d]	99.7 [d]	82.7	78.6	84.3	77.8	75.4	82.1	62.0	63.5	62.6	63.4
Di-α-L-Sor*f* 1,2′:2,3′	104.3 [c]	98.2 [c]										
α-D-Fru*f* β-D-Fru*f* 1,2′:2,3′	106.0 [e]	103.8 [e]	83.6	77.9	82.6	84.4	74.8	81.4	63.2	63.5	65.8	61.4
α-D-Fru*f* β-D-Fru*p* 1,2′:2,1′	103.1 [d]	96.5 [d]	82.8	78.6	84.3	69.4	69.9	69.9	62.1	62.1	62.3	64.3
α-D-Fru*p* β-D-Fru*p* 1,2′:2,1′	95.3 [d]	96.4 [d]	69.9 [d]	71.5 [d]	64.8 [d]	69.4 [d]	71.4 [d]	69.9 [d]	60.5 [d]	61.5 [d]	61.7 [d]	64.4 [d]
Di-β-D-Fru*p* 1,2′:2,1′	97.8 [d]		70.3	73.1	69.8				65.3		64.3	
β-D-Fru*f* βD-Fru*p* 1,2′:2,1′	101.5 [d]	97.6 [d]										
Hexaacetates [b]												
Di-β-D-Fru*f* 1,2′:2,1′	103.1 [c]		79.1	77.5	79.3				63.0		60.7	
α-D-Fru*f* β-D-Fru*f* 1,2′:2,1′	101.4 [d]	99.5 [d]	79.5	77.6	81.0	76.0	75.6	78.6	62.8	64.6	61.5	62.5
Di-α-L-Sor*f* 1,2′:2,3′	102.2 [c]	97.6 [c]										
α-D-Fru*f* β-D-Fru*p* 1,2′:2,1′	101.5 [d]	95.0 [d]	79.7	77.9	81.2	67.3	69.0	67.5	63.2	63.2	61.5	61.1
α-D-Fru*p* β-D-Fru*p* 1,2′:2,1′	92.8 [d]	94.7 [d]	67.2	69.2	64.8	67.1	68.9	67.5	57.8	61.4	61.2	60.9
Di-β-D-Fru*p* 1,2′:2,1′	97.8 [d]		70.3	73.1	69.8				65.3		64.3	
β-D-Fru*f* β-D-Fru*p* 1,2′:2,1′	101.4 [d]	96.6 [d]										

[a] In D_2O [internal acetone at 31.1 ppm except for α-D-Fru*f* β-D-Fru*f* 1,2′:2,3′-dianhydride where internal sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used. [b] In $CDCl_3$ (central peak 76.9 ppm). [c,d,e] Signals already assigned in refs. 12, 11, and 16, respectively.

TABLE VII

^{13}C NMR chemical shifts (ppm) for the fructose carbon atoms in palatinose dianhydrides and their peracetates

Compound	Carbon											
	C-2	C-2′	C-3	C-4	C-5	C-3′	C-4′	C-5′	C-6	C-6′	C-1	C-1′
Dianhydrides												
1	104.9		80.5	78.1	82.9				67.7		61.8	
2	103.5	100.8	82.6	78.6	83.1	77.6	75.7	80.3	67.6	70.1	62.7	63.3
3	104.7	98.9	77.7	75.3	80.1	83.4	77.0	74.1	69.6	69.3	63.0	64.3
4	104.9	102.6	81.6	77.2	79.8	82.3	73.5	79.7	67.6	67.6	64.1	59.7
5	103.3	96.6	82.7	78.8	83.3	69.5	69.9	69.9	67.7	62.0	62.4	64.4
Peracetates												
22	102.7		79.5	77.6	79.7				66.9		61.1	
23	101.5	99.5	80.6	78.0	81.2	76.1	75.8	78.2	67.5	69.5	61.5	62.6
24	102.6	99.1	76.3	76.3	78.5	80.3	77.9	71.8	69.5	67.6	62.3	63.9
25	102.6	101.5	79.3	78.0	79.9	79.1	76.5	75.3	67.1	68.9	64.2	59.4
26	101.5	94.9	80.7	78.0	81.4	67.4	68.9	67.8	67.3	61.5	61.5	61.1

TABLE VIII

^{13}C NMR chemical shifts (ppm) for the fructose carbon atoms in leucrose dianhydrides and their peracetates

Compound	Carbon											
	C-2	C-2′	C-3	C-4	C-5	C-3′	C-4′	C-5′	C-6	C-6′	C-1	C-1′
Dianhydrides												
6	95.2	96.3	70.0	71.5	72.3	69.7	70.0	79.9	59.6	61.5	61.9	63.2
7	97.9		70.7	73.5	79.5				64.4		64.1	
8	97.9	97.9	70.7	73.5	79.7	70.4	73.2	69.9	64.4	65.3	64.1	64.3
Peracetates												
27	94.6	92.5	68.6	69.3	69.9	67.1	69.0	73.4	58.9	62.4	61.2	60.7
28	96.9		68.6	70.3	73.2				62.9		63.2	
29	96.9	97.0	68.6	70.3	73.2	68.9	70.3	66.8	62.9	62.2	63.3	63.0

TABLE IX

^{13}C NMR chemical shifts for the fructose carbon atoms in maltulose dianhydrides and their peracetates

Compound	Carbon											
	C-2	C-2′	C-3	C-4	C-5	C-3′	C-4′	C-5′	C-6	C-6′	C-1	C-1′
Dianhydrides												
9	103.6	100.0	82.8	84.1	81.4	77.7	82.3	81.2	62.0	63.9	62.4	63.1
10	103.3	96.6	82.6	84.0	81.1	68.7	77.6	69.7	61.8	61.8	62.1	64.3
11	95.6	96.5	69.9	77.8	65.2	68.8	77.2	69.5	60.7	61.7	62.0	64.5
12	104.5	98.9	77.7	82.2	81.2	83.7	81.4	71.4	63.6	62.8	62.0	63.8
13	101.7	97.8										
14	98.1											
Peracetates												
30	101.3	99.2	79.4	83.8	82.0	76.9	79.4	77.5	62.7	64.4	61.4	62.3
31	101.3	95.0	79.7	83.8	81.8	69.0	70.0	69.9	63.0	61.3	61.0	60.9
32	92.5	94.6	69.7	71.7	65.8	69.0	70.2	69.9	56.6	61.5	61.3	60.3
33	102.8	98.6	76.6	80.5	79.0	80.1	79.7	70.6	64.0	64.0	62.0	63.9
34	101.3	96.5										
35	97.0											

TABLE X

^{13}C NMR chemical shifts for the fructose carbon atoms in turanose dianhydrides and their peracetates

Compound	Carbon											
	C-2	C-2′	C-3	C-4	C-5	C-3′	C-4′	C-5′	C-6	C-6′	C-1	C-1′
Dianhydrides												
15	105.4		86.6	76.1	83.1				61.8		62.3	
16	103.4	99.7	85.9	75.8	85.3	83.5	75.1	82.2	61.7	63.4	62.5	63.3
17	103.5	96.2	86.1	75.9	85.5	80.0	69.7	70.3	61.7	62.3	62.7	64.7
18	103.2	96.6	86.2	76.0	85.1	69.5	70.0	70.0	61.9	62.0	62.4	64.5
Peracetates												
36	105.3		83.1	78.0	79.5				63.5		59.4	
37	102.5	98.6	85.2	77.9	80.2	84.8	77.5	78.9	63.0	64.3	61.8	62.9
38	102.5	94.7	85.3	77.4	79.2	73.8	68.7	68.4	62.8	62.2	61.8	60.9
39	102.1	95.0	85.0	77.6	79.4	67.2	68.9	67.5	63.5	61.8	61.6	61.6

TABLE XI

^{13}C NMR chemical shifts for the fructose carbon atoms in lactulose dianhydrides and their peracetates

Compound	Carbon											
	C-2	C-2′	C-3	C-4	C-5	C-3′	C-4′	C-5′	C-6	C-6′	C-1	C-1′
Dianhydrides												
19	103.4	100.5	82.9	87.5	81.8	77.3	85.0	81.6	61.8	63.8	62.4	63.2
20	103.3	96.5	82.9	87.5	81.8	67.5	77.5	68.0	61.8	61.8	62.4	64.0
21	95.6	96.3	71.3	80.0	64.7	67.6	77.6	67.9	60.5	61.8	61.9	63.9
Peracetates												
40	101.6	99.9	79.4	85.5	81.4	76.3	82.4	78.5	62.8	64.2	61.4	62.5
41	101.3	94.8	79.4	85.3	81.2	68.7	73.1	67.5	62.8	61.2	61.1	60.6
42	92.5	94.8	70.4	73.4	66.2	68.7	73.2	67.7	56.6	61.8	61.3	60.5

kinetic step of the reaction, which readily rearrange to the α,β anomers, in agreement with the anomeric effect. Under thermodynamic conditions, these structures isomerize preferentially into α-D-fructofuranose β-D-fructopyranose 1,2′:2,1′-dianhydrides, in agreement with reported results on the relative stabilities of β-D-fructofuranose and β-D-fructopyranose derivatives[25]. The di-α,β-D-fructopyranose 1,2′:2,1′-dianhydrides are also kinetic products which rearrange into either α-D-fructofuranose β-D-fructopyranose or di-β-D-fructopyranose 1,2′:2,1′-dianhydride structures under thermodynamic conditions. Although, in the proposed conformations for the three types of structures, the oxygen substituents at the dioxane ring and the OCH_2 groups are oriented in response to the anomeric and exoanomeric effects[1], the α-pyranose ring in α-D, β-D-difructopyranose derivatives must adopt a $^1C_4$ conformation with HO-3 and HO-4 in the axial orientation, an unfavorable arrangement[11]. These results agree with the order of stability found for di-D-fructose and di-L-sorbose dianhydrides in anhydrous HF[11,13].

Some deviations from this general pattern have been observed for palatinose and turanose derivatives. Under nonhydrolytic conditions, palatinose dianhydride **2** isomerized into 6:6′-di-*O*-α-D-glucopyranosyl-di-β-D-fructofuranose 1,2′:2,3′-dianhydride **3** (Table I), although it could be expected[25] from steric and electronic considerations that **3** could have a higher free energy in comparison with **2**. Other types of interactions, such as solvent interactions, may explain the present results. In the case of turanose (Table IV), the 3:3′-diglucosylated di-β,β- and di-α,β-fructofuranose structures (**15** and **16**) appear to be much more stable than the corresponding 4:4′-diglycosylated analogs arising from maltulose or lactulose, or either the unsubstituted dianhydrides[11]. Furthermore, the 3′-*O*-α-D-glucopyranosyl linkage in **17** seems to be rather weak, since it was readily and selectively cleaved into the trisaccharide **18**. An anomalous destabilization of the fructopyranose in benefit of the furanose tautomer has also been observed in aqueous solutions of turanose, but not in pyridine solutions[26]. This peculiar behaviour of turanose and turanose derivatives is probably related with the rupture through solvation by HF, or water molecules, of the hydrogen bond between HO-4 of fructose and O-2 of glucose, which is known to stabilize the fructopyranose form in turanose crystals[27].

EXPERIMENTAL

Material and methods.—Turanose and lactulose were commercial products. Leucrose was kindly provided by Dr. D. Schwengers (Pfeifer and Langen, Dormagen, Germany). Palatinose was a gift from Dr. B. Thiriet (Béghin Say, Paris). Maltulose was prepared by boric acid-mediated isomerization of maltose in sodium hydroxide solutions following the method of Hicks et al.[28].

Anhydrous hydrogen fluoride (HF) was a commercial product obtained in steel cylinders. Prior to use, it was distilled and kept in polyethylene bottles at −25°C.

The stable complex of pyridinium poly(hydrogen fluoride) [(7:3 (w/w) hydrogen fluoride–pyridine] was prepared by careful addition of dried (KOH) pyridine into

anhyd HF in a dry ice-acetone bath. The complex was stored at −25°C in a polyethylene bottle kept inside a polyethylene bag and was used within two weeks. Different ratios of HF–pyridine were obtained by addition of anhyd pyridine or HF to the 7:3 complex.

^{13}C NMR spectra were recorded with a Bruker AC200 instrument. Spectra of unacetylated products were recorded for solutions in D_2O (internal acetone, 31.1 ppm). For acetylated compounds, solutions in $CDCl_3$ were used with the central peak of the triplet (76.9 ppm) as internal reference. FAB-mass spectra (Cs, acceleration potential 8 kV) were measured in the positive mode with a VG ZAB-SEQ instrument. Glycerol (unacetylated products) and *m*-nitrobenzyl alcohol (peracetylated derivatives) were used as the liquid matrices. Sodium iodide was usually added as cationizing agent.

Melting points were determined with a Büchi 535 apparatus and are corrected. Optical rotations were measured with a Jobin Yvon instrument.

LC of unacylated products was carried out using a Perkin–Elmer 250 pump fitted to a Perkin–Elmer LC-30 refractive index detector. LiChrosorb RP-18 5 μm (250 × 7.5 mm, eluent water) and LiChrosorb NH_2 7 μm (250 × 10 mm, eluent acetonitrile–water) columns were used under the following conditions: column temperature 20°C; flow rate 1–3 mL/min; injection amount, 50–100 μL of 1–5% (w/v) solutions of samples.

Acetylations were effected conventionally with 1:1 pyridine–acetic anhydride (10 mL for 1 g of sample). Deacetylations were carried out using the Zemplén technique. TLC of the peracetates was performed on Silica Gel 60 F_{254} plates (E. Merck), and detection was accomplished by charring with H_2SO_4. Flash and column chromatography were performed on Silica Gel 60 (230–240 mesh, E. Merck). Different mixtures of hexane–EtOAc, ether–hexane and CCl_4–acetone were used as eluents.

Microanalyses of unprotected dianhydrides were performed under Ar by the Service Central de Microanalyse du CNRS (Solaize), for samples prepared in sealed tubes after freeze-drying (−65°C, 1.36 Pa, 48 h). When water was retained, a further analysis was carried out after sample drying over P_2O_5 under reduced pressure (0.14 Pa) at 80°C for 6 h.

Reactions of glycosylfructoses in pyridinium poly(hydrogen fluoride).—All reactions were carried out in polyethylene bottles. The corresponding glycosylfructose was dissolved in the appropriate amount of HF–pyridine in various relative proportions as indicated, at 0°C and then kept at the indicated temperature (Tables I–V). The product was precipitated by addition of an excess of ether and triturated with acetone to give an amorphous powder which was collected and dried. The composition of the product mixtures (Tables I–V) was assessed by two complementary methods: (1) by ^{13}C NMR spectroscopy of solutions in D_2O using comparative intensities of the C-2,2′ resonances of fructosyl residues, and (2) using comparative integration of LC chromatograms of mixtures which were obtained under strictly reproducible conditions.

The dianhydrides were isolated and purified by semipreparative LC and/or column chromatography of their peracetates.

Separation of palatinose dianhydrides.—Solutions of crude product in water (5% w/v) were subjected to reversed-phase LC (LiChrosorb RP-18 5 μm). Complete separation was achieved under these conditions, the order of elution being **5**, **3**, **4**, **2**, and **1**.

Compounds **1**–**5**, obtained as white powders after freeze-drying, were also prepared by deacetylation of their peracetates **22**–**26**.

6:6′-Di-*O*-α-D-glucopyranosyl-di-β-D-fructofuranose 1,2′:2,1′-dianhydride (**1**) had $[\alpha]_D^{20}$ + 143° (*c* 0.6, H_2O). FABMS: *m/z* 671 (100%, $[M + Na]^+$), 649 (46, $[M + H]^+$). ^{13}C NMR (D_2O): Table VII and δ 99.5 (C-1 Glc), 73.9, 72.8, 72.2, 70.4 (C-2 to C-5 Glc), 61.4 (C-6 Glc). *Anal.* Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22. Found: C, 44.67; H, 6.06.

6-*O*-α-D-Glucopyranosyl-α-D-fructofuranose 6-*O*-α-D-glucopyranosyl-β-D-fructofuranose 1,2′:2,1′-dianhydride (**2**) had $[\alpha]_D^{20}$ + 109° (*c* 0.5, H_2O). FABMS: *m/z* 671 (100%, $[M + Na]^+$), 649 (63, $[M + H]^+$). ^{13}C NMR (D_2O): Table VII and δ 99.4, 99.3 (C-1,1′ Glc), 73.9, 73.8, 72.9 (2 C), 72.2 (2 C), 70.3 (2 C) (C-2 to C-5 and C-2′ to C-5′ Glc), 61.4, 61.3 (C-6,6′ Glc). *Anal.* Found after freeze-drying: C, 42.11; H, 6.35. Calcd for $C_{24}H_{40}O_{20} \cdot 2\,H_2O$: C, 42.11; H, 6.48. Found after drying over P_2O_5: C, 44.45; H, 6.04. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

6:6′-Di-*O*-α-D-glucopyranosyl-di-β-D-fructofuranose 1,2′:2,3′-dianhydride (**3**) had $[\alpha]_D^{20}$ + 148° (*c* 0.6, H_2O). FABMS: *m/z* 671 (100%, $[M + Na]^+$), 649 (49, $[M + H]^+$). ^{13}C NMR (D_2O): Table VII and δ 99.2 (2 C, C-1,1′ Glc), 73.7 (2 C), 73.0, 72.7, 72.2 (2 C), 70.5, 70.3 (C-2 to C-5 and C-2′ to C-5′ Glc), 61.5, 61.2 (C-6,6′ Glc). *Anal.* Found after freeze-drying: C, 43.01; H, 6.34. Calcd for $C_{24}H_{40}O_{20} \cdot H_2O$: C, 43.24; H, 6.35. Found after drying over P_2O_5: C, 44.64; H, 6.20. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

6-*O*-α-D-Glucopyranosyl-α-D-fructofuranose 6-*O*-α-D-glucopyranosyl-β-D-fructofuranose 1,2′:2,3′-dianhydride (**4**) had $[\alpha]_D^{20}$ + 133° (*c* 0.5, H_2O). FABMS: *m/z* 671 (47%, $[M + Na]^+$), 649 (100, $[M + H]^+$). ^{13}C NMR (D_2O): Table VII and δ 99.4, 99.2 (C-1,1′ Glc), 74.0, 73.9, 72.9 (2 C), 72.2 (2 C), 70.4 (2 C) (C-2 to C-5 and C-2′ to C-5′ Glc), 61.4 (2 C, C-6,6′ Glc). *Anal.* Found after freeze-drying: C, 43.06; H, 6.17. Calcd for $C_{24}H_{40}O_{20} \cdot H_2O$: C, 43.24; H, 6.35. Found after drying over P_2O_5: C, 44.77; H, 6.17. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

6-*O*-α-D-Glucopyranosyl-α-D-fructofuranose β-D-fructopyranose 1,2′:2,1′-dianhydride (**5**) had $[\alpha]_D^{20}$ + 36° (*c* 0.5, H_2O). FABMS: *m/z* 509 (100%, $[M + Na]^+$), 487 (65, $[M + H]^+$). ^{13}C NMR (D_2O): Table VII and δ 99.5 (C-1 Glc), 74.0, 72.9, 72.3, 70.5 (C-2 to C-5 Glc), 61.5 (C-6 Glc). *Anal.* Found after freeze-drying: C, 42.11; H, 6.35. Calcd for $C_{18}H_{30}O_{15} \cdot 2H_2O$: C, 41.38; H, 6.56. Found after drying over P_2O_5: C, 44.26; H, 6.38. Calcd for $C_{18}H_{30}O_{15}$: C, 44.45; H, 6.22.

Separation of leucrose dianhydrides.—Solutions of crude products in water (3% w/v) were subjected to reversed-phase LC (LiChrosorb RP-18 5 μm). Under these conditions, compound **8** could not be separated from unreacted leucrose, the

order of clution being **8**, **6**, and **7**. Separation of **8** was achieved on a LiChrosorb NH_2 (7 μm) column using 75 : 25 acetonitrile–water as eluant. Compounds **6** and **7** were not separated on this column, the order of elution being **8** and **6** + **7** (unresolved).

Compounds **6–8**, obtained as white powders after freeze-drying, were also prepared by deacylation of their peracetates **27–29**.

5-*O*-α-D-Glucopyranosyl-α-D-fructopyranose 5-*O*-D-glucopyranosyl-β-D-fructopyranose 1,2′ : 2,1′-dianhydride (**6**) had $[\alpha]_D^{20}$ + 18° (*c* 1, H_2O). FABMS: *m/z* 671 (100%, $[M + Na]^+$), 649 (35, $[M + H]^+$). ^{13}C NMR (D_2O): Table VIII and δ 101.5, 99.6 (C-1,1′ Glc), 73.7 (2 C), 73.1, 73.0, 72.9, 72.8, 70.5, 70.4 (C-2 to C-5 and C-2′ to C-5′ Glc), 61.5 (2 C, C-6,6′ Glc). *Anal.* Found after freeze-drying: C, 42.16; H, 6.47. Calcd for $C_{24}H_{40}O_{20} \cdot 2\ H_2O$: C, 42.11; H, 6.48. Found after drying over P_2O_5: C, 44.49; H, 6.14. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

5 : 5′-Di-*O*-α-D-glucopyranosyl-di-β-D-fructofuranose 1,2′ : 2,1′-dianhydride (**7**) had $[\alpha]_D^{20}$ −14° (*c* 1, H_2O). FABMS: *m/z* 671 (100%, $[M + Na]^+$), 649 (12, $[M + H]^+$). ^{13}C NMR (D_2O): Table VIII and δ 101.3, (C-1 Glc), 73.8, 73.0, 72.8, 70.4 (C-2 to C-5 Glc), 61.3 (C-6 Glc). *Anal.* Found after freeze-drying: C, 41.10; H, 6.61. Calcd for $C_{24}H_{40}O_{20} \cdot 3\ H_2O$: C, 41.03; H, 6.48. Found after drying over P_2O_5: C, 44.78; H, 5.99. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

5-*O*-α-D-glucopyranosyl-di-β-D-fructofuranose 1,2′ : 2,1′-dianhydride (**8**) had $[\alpha]_D^{20}$ −32° (*c* 1, H_2O). FABMS: *m/z* 509 (100%, $[M + Na]^+$), 487 (66, $[M + H]^+$). ^{13}C NMR (D_2O): Table VIII and δ 101.3 (C-1 Glc), 73.8, 73.0, 72.8, 70.4 (C-2 to C-5 Glc), 61.4 (C-6 Glc). *Anal.* Found after freeze-drying: C, 42.98; H, 6.36. Calcd for $C_{18}H_{30}O_{15} \cdot H_2O$: C, 42.86; H, 6.39. Found after drying over P_2O_5: C, 44.57; H, 5.98. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

Separation of maltulose dianhydrides.—Solutions of crude products in water (1% w/v) were subjected to reversed-phase LC [LiChrosorb RP-18 (5 μm)]. Three fractions were collected, the first, containing unreacted maltulose; the second, a mixture of dianhydrides **9** and **12–14**; and the third, **10** and **11**. Pure samples of **9** and **10** were obtained from fractions in which they were the only constituents (Table III, i.e., Experiments No. 1–3 for **9** and Experiment No. 5 for **10**). Purification of **11** and **12** was only possible after acetylation, column chromatography and deacetylation of their peracetates **32** and **33** as described later. Dianhydrides **13** and **14** were detected by ^{13}C NMR spectroscopy (signals at 101.7 and 97.8 for C-2,2′ of **13** and 98.1 ppm for C-2,2″ of **14**) but not isolated as pure products. Compounds **9–12** were isolated as white powders after freeze-drying.

4-*O*-α-D-Glucopyranosyl-α-D-fructofuranose 4-*O*-α-D-glucopyranosyl-β-D-fructofuranose 1,2′ : 2,1′-dianhydride (**9**) had $[\alpha]_D^{20}$ + 115° (*c* 0.7, H_2O). FABMS: *m/z* 671 (100%, $[M + Na]^+$), 649 (33, $[M + H]^+$). ^{13}C NMR (D_2O): Table IX and δ 99.4, 99.8 (C-1,1′ Glc), 73.6 (2C), 73.3 (2 C), 72.0 (2 C), 70.3 (2 C) (C-2 to C-5 and C-2′ to C-5′ Glc), 61.3 (2C, C-6,6′ Glc). *Anal.* Found after freeze-drying: C, 42.52; H, 6.54. Calcd for $C_{24}H_{40}O_{20} \cdot 2\ H_2O$: C, 42.11; H, 6.48. Found after drying over P_2O_5: C, 44.43; H, 6.20. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

4-*O*-α-D-Glucopyranosyl-α-D-fructofuranose 4-*O*-α-D-glucopyranosyl-β-D-fructopyranose 1,2′:2,1′-dianhydride (**10**) had $[\alpha]_D^{20}$ + 89° (*c* 0.8, H_2O). FABMS: *m/z* 671 (70%, $[M + Na]^+$), 649 (100, $[M + H]^+$). ^{13}C NMR (D_2O): Table IX and δ 101.2, 100.4 (C-1,1′ Glc), 73.5, 73.4, 73.2, 73.1, 72.4, 71.9, 70.3, 70.1 (C-2 to C-5 and C-2′ to C-5′ Glc), 61.3, 61.2 (C-6,6′ Glc). *Anal.* Found after freeze-drying: C, 42.13; H, 6.48. Calcd for $C_{24}H_{40}O_{20} \cdot 2\ H_2O$: C, 42.11; H, 6.48. Found after drying over P_2O_5: C, 44.56; H, 6.30. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

4-*O*-α-D-Glucopyranosyl-α-D-fructopyranose 4-*O*-α-D-glucopyranosyl-β-D-fructopyranose 1,2′:2,1′-dianhydride (**11**) had $[\alpha]_D^{20}$ + 47° (*c* 0.8, H_2O). FABMS: *m/z* 671 (100%, $[M + Na]^+$), 649 (48, $[M + H]^+$). ^{13}C NMR (D_2O): Table IX and δ 101.4, 98.5 (C-1,1′ Glc), 74.5, 73.2 (2 C), 72.6 (3 C), 70.5, 70.3 (C-2 to C-5 and C-2′ to C-5′ Glc), 61.5, 61.4 (C-6,6′ Glc). *Anal.* Found after freeze-drying: C, 43.07; H, 6.37. Calcd for $C_{24}H_{40}O_{20} \cdot H_2O$: C, 43.24; H, 6.35. Found after drying over P_2O_5: C, 44.50; H, 6.22. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

4:4′-Di-*O*-α-D-glucopyranosyl-di-β-D-fructofuranose 1,2′:2,3′-dianhydride (**12**) had $[\alpha]_D^{20}$ + 68° (*c* 1, H_2O). FABMS: *m/z* 671 (100%, $[M + Na]^+$), 649 (75, $[M + H]^+$). ^{13}C NMR (D_2O): Table IX and δ 99.2, 98.9 (C-1,1′ Glc), 73.5 (3 C), 73.2, 72.0, 71.8, 70.3 (2 C) (C-2 to C-5 and C-2′ to C-5′ Glc), 61.2 (2 C, C-6,6′ Glc). *Anal.* Found after freeze-drying: C, 41.04; H, 6.52. Calcd for $C_{24}H_{40}O_{20} \cdot 3\ H_2O$: C, 41.03; H, 6.60. Found after drying over P_2O_5: C, 44.18; H, 6.50. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

Separation of turanose dianhydrides.—Solutions of crude products in water (1% w/v) were subjected to reversed-phase LC [LiChrosorb RP-18 (5 μm)]. Two fractions were collected, the first containing unreacted turanose together with dianhydrides **15**, **17**, and **18**, and the second containing pure **16**. After a second LC of the unresolved fraction (LiChrosorb NH_2, 7 μm, 78:22 acetonitrile–water), pure **15**, **17**, and **18** were obtained, the order of elution being **18**, **15**, and **17**. Compounds **15** and **16** were not resolved under these conditions.

Dianhydrides **15**–**18**, isolated as white powders after freeze-drying, were also prepared by deacylation of their peracetates **36**–**39**.

3:3′-Di-*O*-α-D-glucopyranosyl-di-β-D-fructofuranose 1,2′:2,1′-dianhydride (**15**) had $[\alpha]_D^{20}$ + 118° (*c* 1.1, H_2O). FABMS: *m/z* 671 (15%, $[M + Na]^+$), 649 (100, $[M + H]^+$). ^{13}C NMR (D_2O): Table X and δ 97.1 (C-1 Glc), 73.9, 73.7, 72.0, 70.2 (C-2 to C-5 Glc), 61.4 (C-6 Glc). *Anal.* Found after freeze-drying: C, 42.22; H, 6.27. Calcd for $C_{24}H_{40}O_{20} \cdot 2\ H_2O$: C, 42.11; H, 6.48. Found after drying over P_2O_5: C, 44.31; H, 6.12. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

3-*O*-α-D-Glucopyranosyl-α-D-fructofuranose 3-*O*-α-D-glucopyranosyl-β-D-fructofuranose 1,2′:2,1′-dianhydride (**16**) had $[\alpha]_D^{20}$ + 117° (*c* 1, H_2O). FABMS: *m/z* 671 (90%, $[M + Na]^+$), 649 (100, $[M + H]^+$). ^{13}C NMR (D_2O): Table X and δ 100.1, 96.7 (C-1,1′ Glc), 73.6, 73.5, 73.2 (2 C), 72.1, 71.7, 70.1 (2 C) (C-2 to C-5 and C-2′ to C-5′ Glc), 61.2, 61.1 (C-6,6′ Glc). *Anal.* Found after freeze-drying: C, 41.04; H, 6.54. Calcd for $C_{24}H_{40}O_{20} \cdot 3\ H_2O$: C, 41.03; H, 6.60. Found after drying over P_2O_5: C, 44.38; H, 6.34. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

3-*O*-α-D-Glucopyranosyl-α-D-fructofuranose 3-*O*-α-D-glucopyranosyl-β-D-fructopyranose 1,2′:2,1′-dianhydride (**17**) had $[\alpha]_D^{20}$ + 61° (*c* 0.9, H_2O). FABMS: *m/z* 671 (100%, $[M + Na]^+$), 649 (20, $[M + H]^+$). ^{13}C NMR (D_2O): Table X and δ 102.5, 96.8 (C-1,1′ Glc), 73.8 (2 C), 73.7 (2 C), 72.9, 71.9, 70.2 (2 C) (C-2 to C-5 and C-2′ to C-5′ Glc), 61.3 (2 C, C-6,6′ Glc). *Anal.* Found after freeze-drying: C, 40.88; H, 6.67. Calcd for $C_{24}H_{40}O_{20} \cdot 3\ H_2O$: C, 41.03; H, 6.60. Found after drying over P_2O_5: C, 44.60; H, 6.35. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

3-*O*-α-D-Glucopyranosyl-α-D-fructofuranose β-D-fructopyranose 1,2′ : 2,1′-dianhydride (**18**) had $[\alpha]_D^{20}$ +51° (*c* 0.8, H_2O). FABMS: *m/z* 509 (100%, $[M + Na]^+$), 487 (25, $[M + H]^+$). ^{13}C NMR (D_2O): Table X and δ 96.8 (C-1 Glc), 73.8, 73.7, 71.9, 70.2 (C-2 to C-5 Glc), 61.3 (C-6 Glc). *Anal.* Found after freeze-drying: C, 41.22; H, 6.49. Calcd for $C_{18}H_{30}O_{15} \cdot 2\ H_2O$: C, 41.38; H, 6.56. Found after drying over P_2O_5: C, 44.67; H, 6.06. Calcd for $C_{18}H_{30}O_{15}$: C, 44.35; H, 6.22.

Separation of lactulose dianhydrides.—Solutions of the crude products in water (1% w/v) were subjected to reversed-phase LC [LiChrosorb RP-18 (5 μm)]. Dianhydrides **19–21** were separated under these conditions, the order of elution being **19**, **20**, and **21**. Minor products having slower retention times could not be identified.

Compounds **19–21**, isolated as white powders after freeze-drying, were also prepared by deacylation of their peracetates **40–42**.

4-*O*-β-D-Galactopyranosyl-α-D-fructofuranose 4-*O*-β-D-galactopyranosyl-β-D-fructofuranose 1,2′:2,1′-dianhydride (**19**) had $[\alpha]_D^{20}$ + 18° (*c* 1, H_2O). FABMS: *m/z* 671 (100%, $[M + Na]^+$), 649 (80, $[M + H]^+$). ^{13}C NMR (D_2O): Table XI and δ 104.5, 103.6 (C-1,1′ Gal), 76.1 (2 C), 73.4 (2 C), 71.5 (2 C), 69.3 (2 C) (C-2 to C-5 and C-5′ to C-5′ Gal), 61.8 (2 C, C-6,6′ Gal). *Anal.* Found after freeze-drying: C, 40.91; H, 6.42. Calcd for $C_{24}H_{40}O_{20} \cdot 3\ H_2O$: C, 41.03; H, 6.60. Found after drying over P_2O_5: C, 44.06; H, 6.17. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

4-*O*-β-D-Galactopyranosyl-α-D-fructofuranose 4-*O*-β-D-galactopyranosyl-β-D-fructopyranose 1,2′:2,1′-dianhydride (**20**) had $[\alpha]_D^{20}$ −14° (*c* 1, H_2O). FABMS: *m/z* 671 (80, $[M + Na]^+$), 649 (100, $[M + H]^+$). ^{13}C NMR (D_2O): Table XI and δ 104.5, 101.8 (C-1,1′ Gal), 76.2, 76.1, 73.5 (2 C), 71.6, 71.5, 69.5, 69.4 (C-2 to C-5 and C-2′ to C-5′ Gal), 61.8 (2 C, C-6,6′ Gal). *Anal.* Found after freeze-drying: C, 41.77; H, 6.54. Calcd. for $C_{24}H_{40}O_{20} \cdot 2\ H_2O$: C, 42.11; H, 6.48. Found after drying over P_2O_5: C, 44.35; H, 6.29. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

4-*O*-β-D-Galactopyranosyl-α-D-fructopyranose 4-*O*-β-D-galactopyranosyl-β-D-fructopyranose 1,2′:2,1′-dianhydride (**21**) had $[\alpha]_D^{20}$ −32° (*c* 1, H_2O). FABMS: *m/z* 671 (90, $[M + Na]^+$), 649 (100, $[M + H]^+$). ^{13}C NMR (D_2O): Table XI and δ 104.8, 101.8 (C-1,1′ Gal), 76.3, 76.1, 73.5 (2 C), 71.9, 71.6, 69.5 (2 C) (C-2 to C-5 and C-2′ to C-5′ Gal), 61.9 (2 C, C-6,6′ Gal). *Anal.* Found after freeze-drying: C, 42.02; H, 6.14. Calcd for $C_{24}H_{40}O_{20} \cdot 2\ H_2O$: C, 42.11; H, 6.48. Found after drying over P_2O_5: C, 44.71; H, 6.35. Calcd for $C_{24}H_{40}O_{20}$: C, 44.45; H, 6.22.

Separation of palatinose dianhydride peracetates.—Crude product mixtures resulting from the action of pyridinium poly(hydrogen fluoride) on palatinose (Table

I, Experiments No. 1, 2, 7, and 11) were acetylated. The product, which contained at least two main components (TLC, 1:1 hexane–EtOAc), was processed as follows: for Experiment No. 1, column chromatography (1:1 hexane–EtOAc) yielded **23** (0.13 g, 36%) and impure **22** (80 mg, 23%). Further column chromatography (5:1 ether–hexane) gave pure, syrupy **22** (50 mg, 14%). For Experiment No. 2, column chromatography (1:1 hexane–EtOAc) yielded **23** (0.21 g, 60%) and a mixture of **24** and **25** (2:1, 20 mg, 9%). For Experiment No. 7, the mixture of peracetates was dissolved in hot EtOH and stored for 48 h at room temperature to yield crystalline **23** (0.15 g, 28%). The mother liquor was concentrated, and the residue was subjected to column chromatography (1:1 hexane–EtOAc)) to give additional **23** (0.13 g, 25%) and a mixture of **24** and **25** (5:1, 0.13 g, 25%). Further column chromatography (5:1 ether–hexane) was necessary to obtain pure, syrupy **25** (16 mg, 3%) and **24** (80 mg, 15%). For Experiment No. 11, column chromatography (1:1 hexane–EtOAc) gave syrupy **26** (25 mg, 14%) and **25** (30 mg, 17%).

3,4 : 3′,4′-Tetra-*O*-acetyl-6 : 6′-di-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-di-β-D-fructofuranose 1,2′:2,1′-dianhydride (**22**) had $[\alpha]_D^{20}$ +118° (*c* 0.5, $CHCl_3$). FABMS: *m/z* 1175 (100%, $[M + Na]^+$), 1153 (79, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table VII and δ 95.6 (C-1 Glc), 70.8, 70.0, 68.2, 67.3, (C-2 to C-5 Glc), 61.6 (C-6 Glc). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 49.93; H, 5.59.

3,4-Di-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-fructofuranose 3,4-di-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-fructofuranose 1,2′:2,1′-dianhydride (**23**) had mp 187–188°C (from EtOH or ether); $[\alpha]_D^{20}$ +96° (*c* 0.5, $CHCl_3$). FABMS: *m/z* 1175 (100%, $[M + Na]^+$), 1153 (17, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table VII and δ 95.8 (2 C, C-1,1′ Glc), 70.8, 70.6, 70.0, 69.8, 68.2, 68.1, 67.4, 67.3 (C-2 to C-5 and C-2′ to C-5′ Glc), 61.6 (2 C, C-6,6′ Glc). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 50.00; H, 5.41.

3,4 : 1′,4′-Tetra-*O*-acetyl-6 : 6′-di-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-di-β-D-fructofuranose 1,2′:2,3′-dianhydride (**24**) had $[\alpha]_D^{20}$ + 85° (*c* 0.5, $CHCl_3$). FABMS: *m/z* 1175 (10%, $[M + Na]^+$), 1153 (100, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table VII and δ 96.0, 95.5 (C-1,1′ Glc), 70.6 (2 C), 69.8, 69.6, 68.1 (2 C), 67.4 (2 C) (C-2–C-5 and C-2′–C-5′ Glc), 61.4, 61.3, (C-6,6′ Glc). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 49.73; H, 5.43.

3,4-Di-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-fructofuranose 1,4-di-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-fructofuranose 1,2′:2,3′-dianhydride (**25**) had $[\alpha]_D^{20}$ +112° (*c* 1.1, $CHCl_3$). FABMS: *m/z* 1175 (100%, $[M + Na]^+$), 1153 (17, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table VII and δ 95.9 (2 C, C-1,1′ Glc), 70.9 (2 C), 70.3 (2 C), 68.4 (2 C), 67.5 (2 C) (C-2 to C-5 and C-2′ to C-5′ Glc), 61.7 (2 C, C-6,6′ Glc). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 50.10; H, 5.42.

3,4-Di-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-fructofuranose 3,4,5-tri-*O*-acetyl-β-D-fructopyranose 1,2′:2,1′-dianhydride (**26**) had $[\alpha]_D^{20}$ +60° (*c* 1.2, $CHCl_3$). FABMS: *m/z* 887 (100%, $[M + Na]^+$), 865 (59, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table VII and δ 96.0 (C-1 Glc), 70.8, 70.0, 68.3, 67.4, (C-2 to

C-5 Glc), 61.6 (C-6 Glc). *Anal.* Calcd for $C_{36}H_{48}O_{24}$: C, 50.00; H, 5.59. Found: C, 50.09; H, 5.61.

Separation of leucrose dianhydride peracetates.—Crude product mixtures arising from the action of pyridinium poly(hydrogen fluoride) on leucrose (Table II, Experiments No. 3, 6, and 8) were acetylated, and the product was subjected to column chromatography (3:2 hexane–EtOAc) to give: for Experiment No. 3, **27** (585 mg, 60%) and **28** (55 mg, 6%); for Experiment No. 6, **27** (70 mg, 8%), **28** (415 mg, 46%), and **29** (60 mg, 7%); for Experiment No. 8, **28** (630 mg, 35%) and **29** (200 mg, 10%). The order of elution was **29**, **28**, and **27**.

3,4-Di-*O*-acetyl-5-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-fructopyranose 3,4-di-*O*-acetyl-5-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-fructopyranose 1,2′:2,1′-dianhydride (**27**) had mp 136–139°C (from EtOH); $[\alpha]_D^{20}$ +72° (*c* 1, $CHCl_3$). FABMS: *m/z* 1175 (100%, $[M + Na]^+$), 1153 (25, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table VIII and δ 96.2, 95.1 (C-1,1′ Glc), 70.6, 70.0, 69.6 (2 C), 68.6, 68.4, 67.8, 67.7 (C-2 to C-5 and C-2′ to C-5′ Glc), 61.9, 61.8 (C-6,6′ Glc). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 49.96; H, 5.63.

3,4 : 3′,4′-Tetra-*O*-acetyl-5 : 5′-di-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-di-β-D-fructopyranose 1,2′:2,1′-dianhydride (**28**) had mp 137–141°C (from EtOH); $[\alpha]_D^{20}$ +8° (*c* 0.5, $CHCl_3$). FABMS: *m/z* 1175 (100%, $[M + Na]^+$), 1153 (30, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table VIII and δ 95.6 (C-1 Glc), 70.3 (2 C), 68.6, 67.5, (C-2 to C-5 Glc), 61.8 (C-6 Glc). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 49.67; H, 5.71.

3,4 : 3′,4′,5′-Penta-*O*-acetyl-5-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-di-β-D-fructopyranose 1,2′:2,1′-dianhydride (**29**), isolated as a syrup, had $[\alpha]_D^{20}$ −20° (*c* 1, $CHCl_3$). FABMS: *m/z* 887 (100%, $[M + Na]^+$), 865 (16, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table VIII and δ 96.1 (C-1 Glc), 70.3 (2 C), 68.7, 67.5, (C-2 to C-5 Glc), 61.8 (C-6 Glc). *Anal.* Calcd for $C_{36}H_{48}O_{24}$: C, 50.00; H, 5.59. Found: C, 49.61; H, 5.67.

Separation of maltulose dianhydride peracetates.—Crude product mixtures resulting from the action of HF–pyridine on maltulose (Table III, Experiments No. 2 and 5) were acetylated, and the resulting material was processed as follows: for Experiment No. 2, column chromatography (1:2 hexane–EtOAc) yielded pure **30** (0.27 g, 30%), **32** (0.1 g, 11%), and **31** (80 mg, 9%). For Experiment No. 5, flash chromatography (2:5 hexane–EtOAc) gave a first fraction (0.7 g, 19%) consisting of a mixture of diglucosyl dianhydrides (*m/z* 1175, $[M + Na]^+$, in the FABMS), and then pure **31** (2.12 g, 59%). The fastest running fraction showed three spots on TLC using 3:1 CCl_4–acetone as eluent after several elutions. Column chromatography using a 4:1 → 3:1 → 2:1 gradient of CCl_4–acetone gave a first fraction (0.19 g, 5%) consisting apparently of a mixture of compounds **34** and **35** (signals at 101.3 and 96.5 for C-2,2′ of **34** and 97.0 ppm for C-2,2′ of **35** in the ^{13}C NMR spectrum), and then pure **33** (0.21 g, 6%) and **30** (0.11 g, 3%).

3,6-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-fructofuranose 3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glycopyranosyl)-β-D-fruc-

tofuranose 1,2′:2,1′-dianhydride (**30**) had mp 163–165°C (from EtOH); $[\alpha]_D^{20}$ +102° (*c* 1.1, $CHCl_3$). FABMS: *m/z* 1175 (100%, $[M + Na]^+$), 1153 (25, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table IX and δ 95.7, 95.3 (C-1,1′ Glc), 70.4, 70.0, 69.6, 69.2, 68.3, 68.1, 67.8 (2 C) (C-2 to C-5 and C-2′ to C-5′ Glc), 61.8, 61.6 (C-6,6′ Glc). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 50.01; H, 5.61.

3,6-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-fructofuranose 3,5-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-fructopyranose 1,2′:2,1′-dianhydride (**31**) had mp 119–121°C (from EtOH); $[\alpha]_D^{20}$ +74° (*c* 1, $CHCl_3$). FABMS: *m/z* 1175 (100%, $[M + Na]^+$), 1153 (22, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table IX and δ 96.0, 95.5 (C-1,1′ Glc), 70.6, 70.3, 69.5, 69.3, 68.3 68.0, 67.9, 67.8 (C-2 to C-5 and C-2′ to C-5′ Glc), 61.8, 61.7 (C-6,6′ Glc). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 49.73; H, 5.63.

3,5-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-fructopyranose 3,5-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-fructopyranose 1,2′:2,1′-dianhydride (**32**), isolated as a syrup, had $[\alpha]_D^{20}$ +70° (*c* 1, $CHCl_3$). FABMS: *m/z* 1175 (100%, $[M + Na]^+$), 1153 (35, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table IX and δ 96.0, 94.6 (C-1,1′ Glc), 70.6 (2 C), 69.5, 69.3, 68.3 68.0 (2 C) 67.4 (C-2 to C-5 and C-2′ to C-5′ Glc), 61.7, 61.5 (C-6,6′ Glc). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 49.76; H, 5.57.

3,6 : 1′,6′-Tetra-*O*-acetyl-4 : 4′-di-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-di-β-D-fructofuranose 1,2′:2,3′-dianhydride (**33**), isolated as a syrup, had $[\alpha]_D^{20}$ +68° (*c* 1, $CHCl_3$). FABMS: *m/z* 1175 (100%, $[M + Na]^+$), 1153 (10, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table IX and δ 95.5, 94.6 (C-1,1′ Glc), 70.4, 69.7 (2 C), 69.1, 68.0 (4 C) 67.4 (C-2 to C-5 and C-2′ to C-5′ Glc), 61.6, 61.4 (C-6,6′ Glc). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 50.11; H, 5.62.

Separation of turanose dianhydride peracetates.—Crude product mixtures resulting from the action of pyridinium poly(hydrogen fluoride) on turanose (Table IV, Experiments No. 2, 3, and 7) were acetylated. The product, which contained at least two main components (TLC), was subjected to column chromatography (1 : 1 hexane–EtOAc) yielding: for Experiment No. 2, **36** (10 mg, 5%) and **37** (88 mg, 49%); for Experiment No. 3, **36** (60 mg, 6%), **37** (340 mg, 37%), **39** (30 mg, 3%), and impure **38** (90 mg, 10%); for Experiment No. 7, **39** (63 mg, 31%). A second column chromatography with the same solvent was required to obtain pure **38** (Experiment No. 3, 70 mg, 7%). The order of elution was **39**, **36**, **38** and **37**. Compounds **36–39** were isolated as white foams after evaporation from ether–hexane.

4,6 : 4′,6′-Tetra-*O*-acetyl-3 : 3′-di-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-di-β-D-fructofuranose 1,2′:2,1′-dianhydride (**36**) had $[\alpha]_D^{20}$ +124° (*c* 1, $CHCl_3$). FABMS: *m/z* 1175 (100%, $[M + Na]^+$), 1153 (13, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table X and δ 95.3 (C-1 Glc), 69.8 (2 C), 68.4, 68.0 (C-2 to C-5 Glc), 61.2 (C-6 Glc). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 49.77; H, 5.58.

4,6-Di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-fructofuranose 4,6-di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-fruc-

tofuranose 1,2′:2,1′-dianhydride (**37**) had $[\alpha]_D^{20}$ +95° (*c* 1, $CHCl_3$). FABMS: *m/z* 1175 (100%, $[M + Na]^+$), 1153 (12, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table X and δ 97.9, 95.3 (C-1,1′ Glc), 70.8, 69.7 (2 C), 68.4 (2 C), 68.0, 67.9 (C-2 to C-5 and C-2′ to C-5′ Glc), 61.5 (2 C, C-6,6′ Glc). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 49.79; H, 5.62.

4,6-Di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-fructofuranose 4,5-di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-fructopyranose 1,2′:2,1′-dianhydride (**38**) had $[\alpha]_D^{20}$ +76° (*c* 0.9, $CHCl_3$). FABMS: *m/z* 1175 (100, $[M + Na]^+$), 1153 (12, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table X and δ 96.8, 95.5 (C-1,1′ Glc), 70.8, 70.0, 69.8, 69.7, 68.4 (2 C), 68.2 (2 C) (C-2 to C-5 and C-2′ to C-5′ Glc), 61.9, 61.2 (C-6,6′ Glc). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 49.93; H, 5.74.

4,6-Di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-fructofuranose 3,4,5-tri-*O*-acetyl-β-D-fructopyranose 1,2′:2,1′-dianhydride (**39**) had $[\alpha]_D^{20}$ +36° (*c* 0.9, $CHCl_3$). FABMS: *m/z* 887 (100%, $[M + Na]^+$), 865 (14, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table X and δ 95.1 (C-1 Glc), 69.8, 69.5, 68.4 (2 C), (C-2 to C-5 Glc), 61.6 (C-6 Glc). *Anal.* Calcd for $C_{36}H_{48}O_{24}$: C, 50.00; H, 5.59. Found: C, 49.97; H, 5.69.

Separation of lactulose dianhydrides peracetates.—Crude product mixtures arising from the action of pyridinium poly(hydrogen fluoride) on lactulose (Table V, Experiments No. 2 and 4) were acetylated and the resulting material processed as follows: for Experiment No. 2, flash chromatography (1:3 hexane–EtOAc) gave a first fraction (0.19 g, 20%) identified as peracetylated lactulose by deacylation and comparison of its ^{13}C NMR spectrum with that of a known sample, and then a fraction (0.54 g, 60%) which showed three spots on TLC using 2:1 CCl_4–acetone as eluent and several elutions.

Column chromatography using a 3:1 → 2:1 gradient of CCl_4–acetone yielded pure, sirupy **40** (0.18 g, 20%), **41** (0.135 g, 15%), and **42** (60 mg, 7%). For Experiment No. 4, flash chromatography (1:2 hexane–EtOAc) yielded **41** (0.415 g, 50%).

3,6-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-fructofuranose 3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-fructofuranose 1,2′:2,1′-dianhydride (**40**) had $[\alpha]_D^{20}$ −8° (*c* 1, $CHCl_3$). FABMS: *m/z* 1175 (100%, $[M + Na]^+$), 1153 (95, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table XI and δ 101.3, 100.9 (C-1,1′ Gal), 70.8, 70.7, 70.6 (2 C), 68.4, 68.3, 66.7, 66.5 (C-2 to C-5 and C-2′ to C-5′ Gal), 60.8, 60.7 (C-6,6′ Gal). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 49.97; H, 5.53.

3,6-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-fructofuranose 3,5-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-fructopyranose 1,2′:2,1′-dianhydride (**41**) had $[\alpha]_D^{20}$ −28° (*c* 1, $CHCl_3$). FABMS: *m/z* 1175 (100%, $[M + Na]^+$), 1153 (30, $[M + H]^+$). ^{13}C NMR ($CDCl_3$): Table XI and δ 101.0, 99.8 (C-1,1′ Gal), 70.7 (2 C), 70.5, 70.2, 68.7, 68.0, 66.5, 66.4 (C-2 to

C-5 and C-2′ to C-5′ Gal), 60.6 (2 C, C-6,6′ Gal). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 49.99; H, 5.59.

3,5-Di-*O*-acetyl-4-*O*-(2,3,4-6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-fructopyranose 3,5-di-*O*-acetyl-4-*O*-acetyl-β-D-galactopyranosyl)-β-D-fructopyranose 1,2′:2,1′-dianhydride (**42**) had $[\alpha]_D^{20}$ −70° (*c* 1, $CHCl_3$). FABMS: *m/z* 1175 (100%, $[M+Na]^+$), 1153 (28, $[M+H]^+$). ^{13}C NMR ($CDCl_3$): Table XI and δ 102.0, 100.1 (C-1,1′ Gal), 71.2, 70.9, 70.6 (2 C), 68.8, 68.7, 66.8, 66.6 (C-2 to C-5 and C-2′ to C-5′ Gal), 61.1, 60.7 (C-6,6′ Gal). *Anal.* Calcd for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 49.92; H, 5.55.

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