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HIGHLY STEREOSELECTIVE *C*-α-D-RIBOFURANOSYLATION. REACTIONS OF D-RIBOFURANOSYL FLUORIDE DERIVATIVES WITH ENOL TRIMETHYLSILYL ETHERS AND WITH ALLYLTRIMETHYLSILANE*

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ABSTRACT

2,3,5-Tri-*O*-methyl-D-ribofuranosyl fluoride (**6**), 2,3-di-*O*-benzyl-5-*O*-methyl-D-ribofuranosyl fluoride (**7**), and 5-*O*-benzyl-2,3-di-*O*-methyl-D-ribofuranosyl fluoride (**8**) were obtained in 57 (**6α**, 15; and **6β**, 42), 87 (**7α**, 22; and **7β**, 65), and 85.5 (**8α**, 35.5; and **8β**, 50%) yields, respectively, from the corresponding OH-1 derivatives by the reaction with *N,N*-diethyl-1,1,2,3,3,3-hexafluoropropylamine, adduct of hexafluoropropene with diethylamine. These fluorides and 2,3,5-tri-*O*-benzyl-D-ribofuranosyl fluoride (**5**) reacted with isopropenyl trimethylsilyl ether, (*Z*)-1-ethyl-1-propenyl trimethylsilyl ether, and allyltrimethylsilane, in the presence of boron trifluoride·diethyl etherate to give the corresponding 1-D-ribofuranosyl-2-propanones, 2-D-ribofuranosyl-3-pentanones, and 3-D-ribofuranosyl-1-propenes in good yields. *C*-Acetonylation was confirmed to afford the α-D anomer as the initial product, and the α-D anomer was isomerized into the corresponding β-D anomer to give a mixture. The *C*-allylation reaction gave only the α-D anomer. *C*-Pentanonylation, however, gave a mixture of diastereoisomers that could not be isolated. All reactions afforded almost the same results starting with either α- or β-D-ribofuranosyl fluoride. No reaction of the β anomer of **5** with 1-isopropyl-2-methyl-1-propenyl trimethylsilyl ether took place.

INTRODUCTION

Glycosyl fluorides have been shown to be excellent glycosyl donors[2,3] and subsequently have been used for glycosylation by several groups[4–11]. We have also reported the reactions of 2,3,5-tri-*O*-benzyl-β-D-ribofuranosyl fluoride with isopropenyl trimethylsilylether[12,13], allyltrimethylsilane[1], and cyanotrimethylsilane[1].

*Synthetic studies by the use of fluorinated intermediates. Part 3. For Part 2, see ref. 1.

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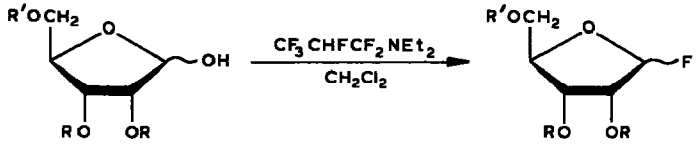
The first two reactions were shown to proceed with a remarkably high stereoselectivity to give preponderantly the α-D anomer. The last reaction, in contrast, afforded, as the initial products, isonitrile derivatives that were then subjected to isomerization into the corresponding cyanide derivatives, thus proceeding with low stereoselectivity. On the basis of the high stereoselectivity of the first two reactions, we investigated the reaction of some other D-ribofuranosyl fluoride derivatives with enol trimethylsilyl ethers and allyltrimethylsilane, and the results are described herein.

RESULTS AND DISCUSSION

Preparation of D-*ribofuranosyl fluoride derivatives.* — 2,3,5-Tri-*O*-benzyl-D-ribofuranosyl fluoride (**5**) was prepared by the treatment of 2,3,5-tri-*O*-benzyl-D-ribofuranose (**1**) with *N,N*-diethyl-1,1,2,3,3,3-hexafluoropropylamine (Ishikawa reagent; the adduct of hexafluoropropene with diethylamine) as previously reported[13,14]. 2,3,5-Tri-*O*-methyl- (**6**), 2,3-di-*O*-benzyl-5-*O*-methyl- (**7**), and 5-*O*-benzyl-2,3-di-*O*-methyl-D-ribofuranosyl fluoride (**8**) were prepared by treatment with



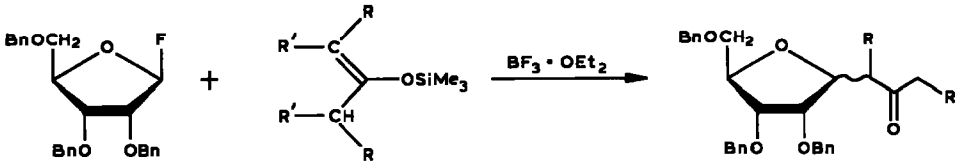
1 R = R′ = Bn
2 R = R′ = Me
3 R = Bn, R′ = Me
4 R = Me, R′ = Bn

5 R = R′ = Bn
6 R = R′ = Me
7 R = Bn, R′ = Me
8 R = Me, R′ = Bn

the Ishikawa reagent (1.5 mol. equiv.) with 2,3,5-tri-*O*-methyl-[15] (**2**), 2,3-di-*O*-benzyl-5-*O*-methyl- (**3**), and 5-*O*-benzyl-2,3-di-*O*-methyl-D-ribofuranose (**4**), respectively. All of these reactions, except that of **2**, proceeded smoothly in dichloromethane at room temperature to give **7** in 87% (22% of **7α** and 65% of **7β**) and **8** in 85% (35.5% of **8α** and 50% of **8β**) yield. The reaction of **2** was accompanied by undesirable discoloration to give **6** in ~40% yield. The yield was improved up to 57% (15% of **6α** and 42% of **6β**) by decreasing the proportion of the Ishikawa reagent to 1–1.1 mol. equiv. An attempt at permethylation of methyl β-D-ribofuranoside[16] by the Hakomori method[17] was unsuccessful, giving methyl 2,3,5-tri-*O*-methyl-β-D-ribofuranoside in ~10% yield only. The reaction with methyl iodide–pulverized sodium hydroxide in dimethyl sulfoxide[18] unexpectedly resulted in a 40% yield at most, in spite of several trials; this might be due to the preparation of pulverized sodium hydroxide on a preparative scale. The method of Wallenfelds *et al.*[19] using silver oxide–methyl iodide in *N,N*-dimethylformamide was approp-

riate, giving the permethylated β-D-ribofuranoside in ~80% yield. Compounds **3** and **4** were prepared from methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside[20] by methylation (methyl iodide–sodium hydride) or benzylation (benzyl bromide–sodium hydride), followed by *O*-deisopropylidenation with aqueous methanol–*p*-toluenesulfonic acid, benzylation or methylation, and hydrolysis with hydrochloric acid in aqueous 1,4-dioxane.

The structure of the D-ribofuranosyl fluoride derivatives, **6α**, **6β**, **7α**, **7β**, **8α**, and **8β** was confirmed by comparing the ^{1}H-n.m.r. and ^{19}F-n.m.r. spectra with those of **5** (α and β anomer)[13,14]. A characteristic difference was observed between the ^{19}F-n.m.r. spectra of the α and β anomers: the α anomers gave a quartet with larger splitting widths ($J_{1,F}$ 52–62, $J_{2,F}$ 19–22 Hz), and the β anomers a doublet ($J_{1,F}$ 51–58 Hz) with fine structures of small splitting width (3.5–4 Hz). These fine structures were apparently a quintet which might result from the overlapping of a doublet and a triplet ($J_{2,F}$, $J_{3,F}$, and $J_{4,F}$). This corresponds well to the difference observed between the ^{19}F-n.m.r. spectra of the 2,3,5-tri-*O*-acyl-D-ribofuranosyl fluoride anomers[21].



9 R = R′ = H
10 R = Me, R′ = H
11 R = R′ = Me

12 R = H
13 R = Me

Reactions of some D-*ribofuranosyl fluoride derivatives with trimethylsilyl compounds.* — These reactions were performed with isopropenyl trimethylsilyl ether[22] (**9**), (*Z*)-1-ethyl-1-propenyl trimethylsilyl ether[23] (**10**), 1-isopropyl-2-methyl-1-propenyl trimethylsilyl ether[24] (**11**), and allyltrimethylsilane (**15**). All reactions were induced by the catalysis of boron trifluoride·diethyl etherate, which has been effective[1,12,13] in the reactions of **5** with **9** or **15**, in diethyl ether and dichloromethane in the presence of molecular sieves at room temperature (see Table I). The reaction of the β anomer of **5** with **9** was complete within 5 min and gave 4,7-anhydro-5,6,8-tri-*O*-benzyl-1,3-dideoxy-D-*altro*-2-octulose [1-(2,3,5-tri-*O*-benzyl-α-D-ribofuranosyl)-2-propanone][12,13] **12α** (Table I). In view of the excellent reactivity of **5β**, this compound was treated with **10** and **11**. The reactivity of **10** was found to be lower compared with that of **9** (Table I). However, the reaction in dichloromethane was clearly improved to give 5,8-anhydro-6,7,9-tri-*O*-benzyl-1,2,4-trideoxy-4-*C*-methyl-D-3-nonulose [2-(2,3,5-tri-*O*-benzyl-D-ribofuranosyl)-3-pentanone] (**13**) in 92% yield (Table I). Compound **13** was a mixture of diastereoisomers, hardly separable, giving only a trace amount of isomerically pure compound. In this case, the

TABLE I

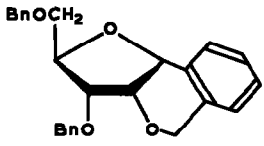
REACTION OF D-RIBOFURANOSYL FLUORIDES (**5, 6, 7,** AND **8**) WITH ENOL TRIMETHYLSILYL ETHERS (**9, 10,** AND **11**) AND WITH ALLYLTRIMETHYLSILANE (**15**)[a]

Fluoride	*Me_3Si cpd.*	*Solvent*	*Reaction time (min)*	*$BF_3 \cdot OEt_2$ (mol. equiv.)*	*Product yield (%) (α:β[b])*		*Recovery yield (%)*
5β[c]	**9**	Et_2O	5	0.05	**12**	94.6 (20:1)	
5β	**10**	Et_2O	30	0.05	**13**	52.1	39.7
5β	**10**	Et_2O	50	0.1	**13**	61.3	27
5β	**10**	CH_2Cl_2	50	0.05	**13**	91.9	6.7
5β	**11**	Et_2O	120	0.1		(no reaction)	
5β	**11**	Et_2O	120	1	**14**	23.4	38.5
5β	**11**	CH_2Cl_2	120	0.5		(no reaction[d])	
5β[e]	**15**	CH_2Cl_2	30	0.05	**16**	93.1 (100:0)	
5α[c]	**9**	Et_2O	20	0.05	**12**	89 (20:1)	
5α[e]	**15**	CH_2Cl_2	30	0.05	**17**	93.4 (100:0)	1.8
6β	**9**	Et_2O	5	0.05	**20**	90.2 (1.8:1)	
6β	**9**	Et_2O	15	0.025	**20**	39.0 (100:0)	42.0
6β	**10**	CH_2Cl_2	15	0.05	**21**	76.4	
6β	**15**	CH_2Cl_2	17	0.05	**16**	88.4 (100:0)	
7β	**9**	Et_2O	15	0.05	**22**	34.6 (100:0)	60.6[f]
7β	**9**	Et_2O	6	0.2	**22**	83.0 (100:0)	7.9[f]
7β	**10**	CH_2Cl_2	15	0.05	**23**	89.4	
7β	**15**	CH_2Cl_2	20	0.05	**18**	90.3 (100:0)	
7α	**9**	Et_2O	15	0.05	**22**	27.0 (100:0)	65.7[f]
7α	**15**	CH_2Cl_2	20	0.05	**18**	90.3 (100:0)	
8β	**9**	Et_2O	10	0.025	**24**	42.4 (100:0)	50.3
8β	**15**	CH_2Cl_2	10	0.05	**19**	84.2 (100:0)	
8α	**9**	Et_2O	15	0.05	**24**	58.5 (4.5:1)	35.7
8α,β[g]	**9**	Et_2O	7	0.2	**24**	85.6 (1.3:1)	6.5
8α,β[g]	**15**	CH_2Cl_2	10	0.05	**19**	75.2 (100:0)	

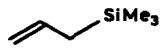
[a]All reactions were performed by the use of a D-ribofuranosyl fluoride derivative (100 mg) and a trimethylsilated compound (2 mol. equiv.) in a solvent (2 mL) in the presence of 4A molecular sieves (1 g) at room temperature. [b]The ratio was estimated by ^{1}H-n.m.r. spectra (–CH_2CO– and –$COCH_3$). [c]Data from refs. 12 and 13. [d]The formation of **14** was deduced on the basis of t.l.c. [e]Data from ref. 1. [f]Deterioration of $BF_3 \cdot OEt_2$ might have brought about extremely low yield, but stereoselectivity was clearly noticed. [g]~1:1 Mixture of **8α** and **8β**.

stereoselectivity was lowered considerably by an anomerization similar to that of **5β** with **9**, in which **12α** was isomerized into **12β** by extending the reaction time or performing the reaction in dichloromethane[12,13]. No reaction of **5β** with **11** took place, as the expected *C*-glycosyl compounds would bear a tertiary carbon atom, a stereochemically crowded structure, but compound **14**, which probably arose from an intramolecular Friedel–Crafts reaction, was obtained from the reaction mixture*. This compound was also obtained from the treatment of **5β** with less nucleophilic

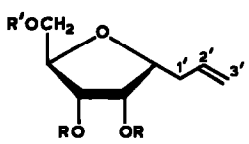
*The structure of compound **14** will be reported in a forthcoming publication.



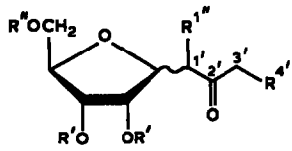
14



15



16 R = R′ = Bn
17 R = R′ = Me
18 R = Bn, R′ = Me
19 R = Me, R′ = Bn



20 R = H, R′ = R″ = Me
21 R = R′ = R″ = Me
22 R = H, R′ = Bn, R″ = Me
23 R = R″ = Me, R′ = Bn
24 R = H, R′ = Me, R″ = Bn

agents, such as trimethylsilylacetylene and ethyl trimethylsilylacetate[25], and by treatment[26] of **5β** with $BF_3 \cdot OEt_2$.

The reaction of **5α** with **9** also gave **12α** in a high yield with high stereoselectivity similarly to the reaction of **5β** with **9**. Moreover, both of the reactions of **5β** and **5α** with allyltrimethylsilane (**15**) gave the same product, *i.e.*, 4,7-anhydro-5,6,8-tri-*O*-benzyl-1,2,3-trideoxy-D-*altro*-oct-1-enitol [3-(2,3,5-tri-*O*-benzyl-α-D-ribofuranosyl)-1-propene][1] (**16**) (Table I); no β-D anomer was detected at all. Compound **16** was not susceptible to isomerization, in contrast to **12α** which was isomerized into **12β** in dichloromethane solution. Such preponderant formation of **12α** and **16** from either **5β** or **5α** led to the conclusion that these reactions proceeded *via* an SN1 mechanism by way of a D-ribofuranosyl cation[1,12,13].

It is very interesting that both of the fluorides **5β** and **5α** underwent an SN1-like reaction to give a *C*-glycosyl compound composed of an α-D anomer almost completely. The preferred formation of α-D-glycosyl compounds in the pyranose series is widely explained by the anomeric effect[27]. As the furanose ring tends to have a considerable flexibility due to pseudorotation, it has been difficult to explain the stereoselectivity of the furanosylation reaction by the anomeric effect[28]. The mutual stability of a pair of anomers has been discussed on the basis of such a steric effect as the 1,2- or 1,3-nonbonded group interaction. Generally, the 1,2-*trans* (β-D-*ribo*) is more stable energetically than the 1,2-*cis* relationship (α-D-*ribo*), although the difference may not be great[29]. As the proportion of α to β in **12** at equilibrium was ~1:2.5 (refs. 12, 13), the β-D anomer is a little more stable than the α-D anomer, and the steric factors are not controlling the attacking direction of

the nucleophile. A similar stereoselectivity was observed when the reaction was performed in dichloromethane (Table I) and, thus, a stereocontrol by solvent effect is difficult to take into consideration. The formation of **14** by the treatment of **5β** with **11** (23% yield) (Table I), and by the treatment of **5β** with $BF_3 \cdot OEt_2$ (0.5 and 1.5 mol. equiv.) in dichloromethane and ether (83 and 47%, respectively)[26] led to assumption of an anchimeric effect, by interaction of the phenyl group of the *O*-benzyl substituent toward a C-1 carbenium ion, as a potential factor of such stereocontrol. Participation of the phenyl group in synthetic organic chemistry is well known[30,31], although not in the field of carbohydrate chemistry. A study with Dreiding models demonstrated that both phenyl groups of the 2- and 5-*O*-benzyl substituents can participate in the interaction with the C-1 carbenium ion; these correspond to Ar-5 and Ar-7 participation[30]. Precise evaluation of the mutual strength of the interaction is, however, difficult. In order to confirm the participation of the 5-*O*-benzyl group in the α-D-ribofuranosylation, **7** (no benzyl group at O-5 but at O-2), **8** (no benzyl group at O-2 but at O-5), and **6** (no benzyl group at O-2, 3, and 5) were prepared and treated with **9**, **10**, and **15** (Table I). Compound **6β** with **9** gave 1-(2,3,5-tri-*O*-methyl-D-ribofuranosyl)-2-propanone (**20**) in a good yield, but with a low stereoselectivity (α:β, 1.8:1); one half the amount of $BF_3 \cdot OEt_2$ gave almost only the α anomer, but the reaction was not complete. Treatment of **20α** thus obtained with ~1 mol. equiv. of $BF_3 \cdot OEt_2$ showed the almost complete conversion into the β anomer after 10 min (^{1}H-n.m.r.), thus indicating that the reaction affords initially the α-D-glycosyl compounds and that the α anomer is isomerized into the β anomer at a rate higher than that of the isomerization of **12α** into **12β**. Treatment of **6β** with **10** gave 2-(2,3,5-tri-*O*-methyl-D-ribofuranosyl)-3-pentanone (**21**) also in a high yield (proportion of isomers not established), and with **15** gave 3-(2,3,5-tri-*O*-methyl-α-D-ribofuranosyl)-1-propene (**17**) as the sole product (Table I), similar to the stereoselectivity observed in the reaction of **5β** with **15**.

Treatment of **7β** with **9**, **10**, and **15** similarly gave 1-(2,3-di-*O*-benzyl-5-*O*-methyl-α-D-ribofuranosyl)-2-propanone (**22α**), 2-(2,3-di-*O*-benzyl-5-*O*-methyl-D-ribofuranosyl)-3-pentanone (**23**) (a mixture of isomers), and 3-(2,3-di-*O*-benzyl-5-*O*-methyl-α-D-ribofuranosyl)-1-propene (**18**), respectively, in good yield (Table I). The reaction of **8β** with **9** gave 1-(5-*O*-benzyl-2,3-di-*O*-methyl-α-D-ribofuranosyl)-2-propanone (**24α**) preponderantly in the initial stage, and that with **15** also gave 3-(5-*O*-benzyl-2,3-di-*O*-methyl-α-D-ribofuranosyl)-1-propene (**19**) in a high yield (Table I).

The α-D-ribofuranosyl fluoride derivative **7α** also gave the corresponding α-D-glycosyl compounds **22α** and **18** preponderantly in the treatment with **9** and **15**, respectively (Table I). Treatment of **8α** and **8α,β** (1:1 mixture of **8α** and **8β**) with **9** gave a mixture of **24α** and **24β** (Table I). The large amount of unchanged **8α** (nearer to the initial stage of the reaction) and of **24α** suggests also that the reaction gave the α-D-ribofuranosyl compound preponderantly. Treatment of **8α,β** with **15** also gave **19** as the sole product.

The structures of the 1-D-ribofuranosyl-2-propanones **20α**, **20β**, **22α**, **24α**,

and **24β** were determined by ^{1}H-n.m.r. spectroscopy by comparison with compounds[12,13] **12α** and **12β**, and those of the 3-D-ribofuranosyl-1-propenes **17**, **18**, and **19** by comparison[1] with **16***.

Since the change from *O*-benzyl to *O*-methyl groups made no difference, the participation of the phenyl group of *O*-benzyl substituents may be neglected as a potential factor of stereoselectivity. The BF_3-catalyzed reaction of D-ribofuranosyl fluorides with trimethylsilylated nucleophiles was confirmed to proceed very efficiently *via* an SN1-like mechanism with an almost 100% formation of α-D-ribofuranosyl compounds. An alternative stereocontrol by anchimeric effect may exist through the ether oxygen atom, since anchimeric participation by benzyloxy and methyloxy groups is well known[33].

EXPERIMENTAL

General methods. — The melting point was determined with a Yanagimoto Micro-Melting-point apparatus, and is uncorrected. Specific rotations were measured with a JASCO DIP-4 polarimeter. I.r. spectra were recorded with a Hitachi 285 spectrophotometer. ^{1}H-N.m.r. spectra were recorded with a JEOL JNM-FX 200 (200 MHz) and Nicolet NT-360 (360 MHz) spectrometer, and ^{13}C-n.m.r. spectra with a JEOL JNM-FX 200 (50 MHz) spectrometer, for solutions in $CDCl_3$ with tetramethylsilane as the internal standard. ^{19}F-N.m.r. spectra were recorded with a Hitachi R-24 F spectrometer for solutions in $CDCl_3$ with trifluoroacetic acid as an external standard. The Ishikawa reagent (commercial name; hexafluoropropylene–diethylamine) and allyltrimethylsilane were purchased from Tokyo Chemical Industry, Co., Ltd. and Aldrich Chem. Co., respectively. The solvents used were purified and dried according to the usual procedures. 2,3,5-Tri-*O*-benzyl-β-D-ribofuranosyl fluoride[13,14] (**5β**), 2,3,5-tri-*O*-methyl-D-ribofuranose[15] (**2**), methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside[20], 2-propenyl trimethylsilyl ether[22] (**9**), (*Z*)-1-ethyl-1-propenyl trimethylsilyl ether[23] (**10**), and 1-isopropyl-2-methyl-1-propenyl trimethylsilyl ether[24] (**11**) were respectively prepared according to the methods reported. Flowing column chromatography was performed on Kieselgel 60 (Merck, Art. 9385) in benzene–ethyl acetate or hexane–ethyl acetate.

Methyl 5-O-benzyl-2,3-di-O-methyl-β-D-ribofuranoside and 5-O-benzyl-2,3-di-O-methyl-D-ribofuranose (**4**). — To a solution of methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (5 g, 24 mmol) in oxolane (40 mL) under an N_2 atmosphere, was added NaH (1.3 g, 27 mmol; petroleum ether content, 55%). The solution was stirred until the evolution of H_2 ceased, and then was treated with tetrabutylammonium iodide (90 mg, 0.24 mmol) and benzyl bromide (6 mL, 50 mmol) for 3 h with stirring. The mixture was treated with silica gel (Wakogel C-300; 1.6 g), which was then filtered off and well washed with dichloromethane. The combined

*The structure of **16** has been identified with that of a known compound[32], but the citation in a previous paper[1] is incorrect.

filtrate and washings were dried ($MgSO_4$) and evaporated to give a syrup, which was then distributed between hexane (30 mL) and acetonitrile (30 mL). The acetonitrile layer was evaporated to a syrup which was subjected to chromatography separation in a 40:1 benzene–ethyl acetate system to give methyl 5-*O*-benzyl-2,3-*O*-isopropylidene-β-D-ribofuranoside (7.1 g, 98.6% yield). This (7 g, 24 mmol) was treated in 4:1 methanol–water (150 mL) with *p*-toluenesulfonic acid monohydrate (0.5 g, 2.6 mmol) for 2 h under reflux. After being cooled, the acidic solution was made neutral with Amberlite IRA-410 (OH) anion-exchange resin. After filtration, the solution was evaporated to a syrup which was chromatographed with ethyl acetate to give the starting material (1.6 g, 23% recovery yield) and methyl 5-*O*-benzyl-β-D-ribofuranoside (3.3 g, 50% yield). This (2.6 g, 10 mmol) was treated with methyl iodide (12.5 mL, 200 mmol) and Ag_2O (2.3 g, 100 mmol) in *N,N*-dimethylformamide (50 mL) in the dark with stirring at room temperature for 4 days. The mixture was filtered off, and the residue washed with methanol. The combined filtrate and washings were evaporated to a syrup which was again methylated as just described. The resulting syrup was chromatographed in 1:1 hexane–ethyl acetate to give methyl 5-*O*-benzyl-2,3-di-*O*-methyl-β-D-ribofuranoside (2.3 g, 80% yield), syrup, $[\alpha]_D^{28}$ +10.3° (*c* 1.3, chloroform); ^{1}H-n.m.r. (200 MHz): δ 3.36, 3.40, 3.49 (3 s, 9 H, 3 CH_3), 3.54 (dd, 1 H, $J_{4,5}$ 5.9, $J_{5,5'}$ 10.5 Hz, H-5), 3.65 (dd, 1 H, $J_{4,5'}$ 3.9 Hz, H-5'), 3.71 (d, 1 H, $J_{2,3}$ 4.9 Hz, H-2), 3.86 (dd, 1 H, $J_{3,4}$ 6.8 Hz, H-3), 4.21 (ddd, 1 H, H-4), 4.61 (s, 2 H, CH_2Ph), 4.92 (s, 1 H, H-1), and 7.24–7.32 (bs, 5 H, C_6H_5); ^{13}C-n.m.r. (50 MHz): δ 55.04 (OCH_3), 58.22 (2 OCH_3), 71.47, 73.16, 80.16, 80.48, 81.92 (C-2–5 and CH_2Ph), 105.42 (C-1), 127.45, 128.17, and 138.15 (C_6H_5).

Anal. Calc. for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.92; H, 7.80.

A solution of the aforementioned methyl β-D-ribofuranoside (2.3 g, 8.1 mmol) in 5:1 1,4-dioxane–M HCl was heated at reflux for 2 h. After being cooled, it was poured into a saturated $NaHCO_3$ aqueous solution to neutralize the acid. The solution was evaporated to give a solid which was extracted with acetone several times. The combined extracts were evaporated into a syrup which was chromatographed with 1:1 hexane–ethyl acetate to give **4** (1.7 g, 78% yield), syrup, $[\alpha]_D^{26}$ +44.6° (*c* 2.70, chloroform); ^{1}H-n.m.r. (200 MHz): δ 3.38, 3.42, 3.48, 3.49 (4 s, 6 H, 2 OCH_3 of two anomers), 3.38–3.72 (m, 3 H, H-5,5' and OH), 3.80–4.32 (m, 3 H, H-2,3,4), 4.48, 4.56 (AB type, *J* 11 Hz), 4.53, 4.62 (AB type, *J* 12 Hz) (2 H, CH_2Ph of two anomers), 5.24–5.34 (overlapped bs and bd, 1 H, H-1 of two anomers), and 7.27–7.33 (bs, 5 H, C_6H_5) (proportion of anomers ~3:2); ^{13}C-n.m.r. (50 MHz): δ 58.22, 58.40, 58.49 (OCH_3), 70.18, 73.34, 73.42, 79.72, 79.96, 80.04, 80.19, 80.25, 82.96 (C-2–5, CH_2Ph), 127.39, 127.65, 127.74, 128.32, 137.33, and 137.71 (C_6H_5).

Anal. Calc. for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.36; H, 7.42.

*Methyl 2,3-di-*O*-benzyl-5-*O*-methyl-β-*D*-ribofuranoside and 2,3-di-*O*-benzyl-5-*O*-methyl-*D*-ribofuranose* (**3**). — Treatment of methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (5 g, 24 mmol) with methyl iodide (3 mL, 48 mmol) in a similar way

to that described for **4** but without tetraethylammonium iodide gave methyl 2,3-*O*-isopropylidene-5-*O*-methyl-β-D-ribofuranoside (5.3 g, 100% yield). This (5 g, 23 mmol) was *O*-deisopropylidenated as described for **4** to give the starting material (1.6 g, 32% recovery yield) and methyl 5-*O*-methyl-β-D-ribofuranoside (1.7 g, 42% yield). This (1.6 g, 9 mmol) was treated with benzyl bromide (2.2 mL, 19 mmol) as described for **4** to give syrupy methyl 2,3-di-*O*-benzyl-5-*O*-methyl-β-D-ribofuranoside (2.8 g, 87% yield), $[\alpha]_D^{30}$ +21.1° (*c* 1.3, chloroform); ^{1}H-n.m.r. (200 MHz): δ 3.31 (s, 3 H, OCH_3), 3.35 (s, 3 H, OCH_3), 3.37 (dd, 1 H, $J_{5,5'}$ 10.3, $J_{4,5}$ 7.3 Hz, H-5), 3.52 (dd, 1 H, $J_{4,5'}$ 3.6 Hz, H-5'), 3.81 (d, 1 H, $J_{2,3}$ 4.9 Hz, H-2), 3.93 (dd, 1 H, $J_{3,4}$ 7.1 Hz, H-3), 4.30 (ddd, 1 H, H-4), 4.42, 4.58 (2 H, AB type, *J* 12 Hz, CH_2Ph), 4.57, 4.64 (2 H, AB type, *J* 11.5 Hz, CH_2Ph), 4.89 (s, 1 H, H-1), and 7.25–7.36 (bs, 5 H, C_6H_5); ^{13}C-n.m.r. (50 MHz): δ 50.44, 54.55 (2 OCH_3), 67.65, 67.76, 69.57, 73.77, 74.97, 75.55 (C-2–5 and CH_2Ph), 101.72 (C-1), 123.13, 123.24, 123.68, and 133.10 (C_6H_5).

Anal. Calc. for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.23; H, 7.26.

The compound (2.7 g, 7.5 mmol) just described was hydrolyzed as described for **4** to give syrupy **3** (2.1 g, 81% yield), $[\alpha]_D^{27}$ +54.8° (*c* 2.78, chloroform); ^{1}H-n.m.r. (200 MHz): δ 3.29, 3.31 (2 s, 3 H, OCH_3), 3.30–3.60 (m, 2 H, H-5,5'), 3.80–4.35 (m, 4 H, H-2,3,4 and OH), 4.38–4.75 (m, 4 H, 2 CH_2Ph), 5.27–5.35 (m, 1 H, H-1), and 7.24–7.32 (m, 10 H, 2 C_6H_5) (proportion of anomers, ~4:3); ^{13}C-n.m.r. (50 MHz): δ 58.98, 59.24 (2 OCH_3), 72.14, 72.43, 72.61, 72.78, 77.48, 77.59, 77.77, 80.30, 80.63, 80.74 (C-2–5 and 2 CH_2Ph), 96.09, 100.11 (2 C-1), 127.62, 127.77, 128.23, 128.29, 137.36, 137.45, 137.65, and 137.74 (C_6H_5).

Anal. Calc. for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.44; H, 7.06.

5-O-Benzyl-2,3-di-O-methyl-α- (**8α**) *and -β-*D*-ribofuranosyl fluoride* (**8β**). — To a solution of **4** (1.7 g, 6.3 mmol) in dichloromethane (80 mL), under an N_2 atmosphere in a three-necked, round-bottomed flask, was added the Ishikawa reagent (1.8 mL, 1.6 mol. equiv.) through a syringe and the mixture was stirred at room temperature for 45 min. The reaction was quenched with aqueous, saturated $NaHCO_3$ solution (20 mL) and the organic layer separated. The aqueous layer was extracted with dichloromethane (3 × 30 mL) which was combined with the organic layer and dried ($MgSO_4$). After filtration, the solution was evaporated to a syrup which was subjected to chromatography in 2:1 hexane–ethyl acetate to give **8β** (0.86 g, 50% yield) and **8α** (0.61 g, 35% yield).

Compound **8α**. Syrup, $[\alpha]_D^{28}$ +40.1° (*c* 2.73, chloroform); ^{1}H-n.m.r. (200 MHz): δ 3.43 (s, 3 H, OCH_3), 3.51 (s, 3 H, OCH_3), 3.57 (d, 2 H, H-5), 3.77–3.88 (m, 2 H, H-2,3), 4.45–4.60 (m, 3 H, H-4 and CH_2Ph), 5.79 (dd, 1 H, $J_{1,F}$ 66.2, $J_{1,2}$ 2.9 Hz, H-1), and 7.31–7.36 (m, 5 H, C_6H_5); ^{13}C-n.m.r. (50 MHz): 58.57, 58.63 (2 OCH_3), 70.07, 73.48, 77.33, 84.45 (C-3–5 and CH_2Ph), 81.25 (d, $J_{C\text{-}2,F}$ 22.0 Hz, C-2), 108.1 (d, $J_{C\text{-}1,F}$ 233 Hz, C-1), 127.72, 127.71, 128.35, and 137.60 (C_6H_5); ^{19}F-n.m.r.: δ 52.45 (dd, $J_{1,F}$ 53.1, $J_{2,F}$ 18.9 Hz).

Anal. Calc. for $C_{14}H_{19}FO_4$: C, 62.21; H, 7.08. Found: C, 61.90; H, 7.03.

Compound **8β**. Syrup, $[\alpha]_D^{27}$ +54.8° (*c* 2.78, chloroform); ^{1}H-n.m.r. (200

MHz): δ 3.41 (s, 3 H, OCH_3), 3.51 (s, 3 H, OCH_3), 3.61 (dd, 1 H, $J_{4,5}$ 5.4, $J_{5,5'}$ 11.0 Hz, H-5), 3.72 (dd, 1 H, $J_{4,5'}$ 3.4 Hz, H-5'), 3.88–4.00 (m, 2 H, H-2,3), 4.20–4.25 (m, 1 H, H-4), 4.57, 4.64 (2 H, AB type, *J* 12.2 Hz, CH_2Ph), 5.73 (d, 1 H, $J_{1,F}$ 62.6 Hz, H-1), and 7.26–7.35 (m, 5 H, C_6H_5); ^{13}C-n.m.r. (50 MHz): δ 58.46, 58.69, (2 OCH_3), 70.39, 73.33, 79.16, 82.20 (C-3–5 and CH_2Ph), 81.15 (d, $J_{C-2,F}$ 29.3 Hz, C-2), 111.79 (d, $J_{C-1,F}$ 224 Hz, C-1), 127.50, 128.23, and 137.97 (C_6H_5); ^{19}F-n.m.r.: δ 37 (d-quintet, $J_{1,F}$ 51.3 Hz, overlapped dt with spacing of 3.3 Hz).

Anal. Calc. for $C_{14}H_{19}FO_4$: C, 62.21; H, 7.08. Found: C, 62.38; H, 7.18.

*2,3,5-Tri-*O*-methyl-α-* (**6α**) *and -β-*D*-ribofuranosyl fluoride* (**6β**). — 2,3,5-Tri-*O*-methyl-D-ribofuranose (**2**; 2.31 g, 12 mmol) was treated with the Ishikawa reagent (2.3 mL, 1.1 mmol) as described for **8α,β** to give **6β** (0.78 g, 33.5% yield) and **6α** (0.24 g, 10.5% yield).

Compound **6α**. Syrup, $[\alpha]_D^{20}$ +49.0° (*c* 1.35, chloroform); ^{1}H-n.m.r. (200 MHz): δ 3.38 (s, 3 H, OCH_3), 3.46 (s, 3 H, OCH_3), 3.50 (d, 2 H, $J_{4,5}$ 3.7 Hz, H-5), 3.53 (s, 3 H, OCH_3), 3.7–3.9 (m, 2 H, H-2,3), 4.48 (bs, 1 H, H-4), and 5.79 (dd, 1 H, $J_{1,F}$ 66.2, $J_{1,2}$ 3.0 Hz, H-1); ^{13}C-n.m.r. (50 MHz): δ 58.57, 58.63, 59.36 (3 OCH_3), 72.69, 77.18, 84.39 (C-3–5), 81.24 (C-2, $J_{C-2,F}$ 20.5 Hz), and 108.12 (C-1, $J_{C-1,F}$ 233 Hz); ^{19}F-n.m.r.: δ 52.2 (dd, $J_{1,F}$ 61.6, $J_{2,F}$ 22.3 Hz).

Anal. Calc. for $C_8H_{15}FO_4$: C, 49.48; H, 7.78. Found: C, 49.27; H, 7.61.

Compound **6β**. Syrup, $[\alpha]_D^{20}$ +81.0° (*c* 1.68, chloroform); ^{1}H-n.m.r. (200 MHz): δ 3.42 (s, 3 H, OCH_3), 3.45 (s, 3 H, OCH_3), 3.52 (dd, 1 H, $J_{4,5}$ 5.6, $J_{5,5'}$ 10.8 Hz, H-5), 3.53 (s, 3 H, OCH_3), 3.63 (dd, 1 H, $J_{4,5'}$ 3.4 Hz, H-5'), 3.90–3.96 (m, 2 H, H-2,3), 4.15–4.30 (m, 1 H, H-4), and 5.71 (d, 1 H, $J_{1,F}$ 63.0 Hz, H-1); ^{13}C-n.m.r. (50 MHz): δ 58.46, 58.72; 59.33 (3 OCH_3), 73.22, 79.23, 82.00 (C-3–5), 81.11 (d, $J_{C-2,F}$ 30.8 Hz, C-2), and 111.80 (d, $J_{C-1,F}$ 224.2 Hz, C-1); ^{19}F-n.m.r.: δ 37 (d-quintet, $J_{1,F}$ 58.1 Hz, overlapped dt with a spacing of 3.6 Hz).

Anal. Calc. for $C_8H_{15}FO_4$: C, 49.48; H, 7.78. Found: C, 49.76; H, 7.59.

*2,3-Di-*O*-benzyl-5-*O*-methyl-α-* (**7α**) *and -β-*D*-ribofuranosyl fluoride* (**7β**). — Treatment of **3** (2.10 g, 6.1 mmol) with the Ishikawa reagent (1.58 mL, 1.5 mol. equiv.) as described for **8α,β** gave **7β** (1.374 g, 65.1% yield) and **7α** (0.463 g, 21.9% yield); the reaction time was 50 min in this case, and the chromatography was performed with 40:1 benzene–ethyl acetate.

Compound **7α**. Syrup, $[\alpha]_D^{27}$ +39.5° (*c* 1.33, chloroform); ^{1}H-n.m.r. (200 MHz): δ 3.27 (s, 3 H, OCH_3), 3.28 (dd, 1 H, $J_{4,5}$ 3.9, $J_{5,5'}$ 10.7 Hz, H-5), 3.36 (dd, 1 H, $J_{4,5'}$ 3.9 Hz, H-5'), 3.74–3.94 (bd, 1 H, H-2), 3.91 (bs, 1 H, H-3), 4.46 (bs, 1 H, H-4), 4.61, 4.74 (2 H, AB type, *J* 12.2 Hz, CH_2Ph), 4.61, 4.70 (2 H, AB type, *J* 12.2 Hz, CH_2Ph), 5.68 (dd, 1 H, $J_{1,F}$ 65.4, $J_{1,2}$ 3.3 Hz, H-1), and 7.30–7.35 (bs, 10 H, 2 C_6H_5); ^{13}C-n.m.r. (50 MHz): δ 59.27 (OCH_3), 72.17, 72.49, 72.69, 74.19, 84.80 (C-3–5 and 2 CH_2Ph), 78.67 (d, $J_{C-2,F}$ 20.5 Hz, C-2), 108.41 (d, $J_{C-1,F}$ 233 Hz, C-1), 127.65, 127.77, 127.85, 128.00, 128.23, 128.32, 137.28, and 137.83 (2 C_6H_5); ^{19}F-n.m.r.: δ 52.0 (dd, $J_{1,F}$ 55.4, $J_{2,F}$ 18.9 Hz).

Anal. Calc. for $C_{20}H_{23}FO_4$: C, 69.35; H, 6.69. Found: C, 69.45; H, 6.81.

Compound **7β**. M.p. 43.9–44.0° (pentane), $[\alpha]_D^{26}$ +67.9° (*c* 2.01,

chloroform); ^{1}H-n.m.r. (200 MHz): δ 3.36 (s, 3 H, OCH_3), 3.46 (dd, 1 H, $J_{4,5}$ 5.4, $J_{5,5'}$ 11.0 Hz, H-5), 3.59 (dd, 1 H, $J_{4,5'}$ 3.2 Hz, H-5'), 3.97 (t, 1 H, $J_{2,3}$ 4.4, $J_{2,F}$ 4.2 Hz, H-2), 4.07 (ddd, 1 H, $J_{3,4}$ 8.3, $J_{3,F}$ 2.7 Hz, H-3), 4.40 (ddt, 1 H, $J_{4,F}$ 4.3 Hz, H-4), 4.46, 4.57 (2 H, AB type, *J* 12 Hz, C*H*$_2$Ph), 4.64 (s, 2 H, C*H*$_2$Ph), 5.65 (d, 1 H, $J_{1,F}$ 63.2 Hz, H-1), and 7.21–7.37 (m, 10 H, 2 C_6H_5); ^{13}C-n.m.r. (50 MHz): δ 59.24 (OCH_3), 72.69, 72.81, 76.92, 82.00, 82.06 (C-3–5 and 2 CH_2Ph), 78.75 (d, $J_{C\text{-}2,F}$ 30.8 Hz, C-2), 112.35 (d, $J_{C\text{-}1,F}$ 224 Hz, C-1), 127.77, 127.82, 128.12, 128.23, 128.32, 128.38, 137.19, and 137.30 (2 C_6H_5); ^{19}F-n.m.r.: δ 35.7 (d-quintet, $J_{1,F}$ 51.3 Hz, overlapped dt with a spacing of 3.4 Hz).

Anal. Calc. for $C_{20}H_{23}FO_4$: C, 69.35; H, 6.69. Found: C, 69.52; H, 6.78.

1-[2,3,5-Tri-O-methyl-α- (**20α**) *and -β-*D*-ribofuranosyl]-2-propanone* (**20β**). — To **6β** (100 mg, 0.52 mmol) and molecular sieves 4A (1 g) in a 30-mL, two-necked, round-bottomed flask under an N_2 atmosphere were added in turn, through a syringe, diethyl ether (2 mL) and isopropenyl trimethylsilyl ether (**9**, 0.163 mL, 1.03 mmol) and, through a microsyringe, $BF_3 \cdot OEt_2$ (3.2 μL, 25.8 μmol). After stirring for 5 min at room temperature, the reaction was quenched with aqueous saturated $NaHCO_3$ solution (2 mL). The solids were filtered off and well washed with acetone. The combined filtrate and washings were evaporated to dryness, and the residue was crushed and extracted with acetone. The extract was evaporated to a syrup which was chromatographed in 2:1 hexane–ethyl acetate to give **20** (110 mg, 90% yield; α:β, 1.8:1). Further chromatography gave **20α** (first fraction) and **20β** (5–10 mg).

Compound **20α**. Syrup, $[\alpha]_D^{23}$ +13.5° (*c* 0.93, chloroform); ν_{max}^{NaCl} 1715 (C=O) cm^{-1}; ^{1}H-n.m.r. (200 MHz): δ 2.18 (s, 3 H, H-3'), 2.79 (dd, 1 H, $J_{1,1'}$ 6.3, $J_{1',1''}$ 17 Hz, H-1'), 2.90 (dd, 1 H, $J_{1,1''}$ 6.8 Hz, H-1''), 3.39 (s, 3 H, OCH_3), 3.43 (dd, 1 H, $J_{4,5}$ 4.6, $J_{5,5'}$ 10.5 Hz, H-5), 3.46 (s, 6 H, 2 OCH_3), 3.54 (dd, 1 H, $J_{4,5'}$ 3.4 Hz, H-5'), 3.78 (dd, 1 H, $J_{2,3}$ 4.6, $J_{3,4}$ 6.6 Hz, H-3), 3.93 (t, 1 H, $J_{1,2}$ 4.6 Hz, H-2), 4.02 (ddd, 1 H, H-4), and 4.50 (dt, 1 H, H-1); ^{13}C-n.m.r. (50 MHz): δ 30.66 (C-3'), 43.64 (C-1'), 58.54, 59.33, 59.68 (3 OCH_3), 73.01, 75.81, 78.91, 79.43, 82.00 (C-1–5), and 207.17 (C-2').

Anal. Calc. for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 57.15; H, 8.55.

Compound **20β**. Syrup, $[\alpha]_D^{22}$ −12.9° (*c* 0.85, chloroform), ν_{max}^{NaCl} 1715 (C=O) cm^{-1}; ^{1}H-n.m.r. (200 MHz): δ 2.17 (s, 3 H, H-3'), 2.67 (d, 2 H, $J_{1,1'}$ 6.3 Hz, H-1'), 3.36 (s, 3 H, OCH_3), 3.40 (s, 3 H, OCH_3), 3.43 (s, 3 H, OCH_3), 3.38–3.53 (m, 3 H, H-2,5,5'), 3.73 (t, 1 H, $J_{2,3}$ 4.9, $J_{3,4}$ 4.7 Hz, H-3), 4.08 (q, 1 H, $J_{4,5}$ 4.6 Hz, H-4), and 4.31 (q, 1 H, $J_{1,2}$ 6.1 Hz, H-1); ^{13}C-n.m.r. (50 MHz): δ 30.54 (C-3'), 47.66 (C-1'), 57.76, 58.00, 59.36 (3 OCH_3), 72.96, 76.54, 79.31, 80.80, 82.87 (C-1–5), and 206.38 (C-2').

Anal. Calc. for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 56.45; H, 8.50.

The conditions used for other *C*-ribofuranosylation reactions are shown in Table I. In the cases of reactions involving **5**, **7**, and **8**, the work-up after the reaction was different; the combined filtrate and washings were separated in a separatory funnel instead of being evaporated, and the extraction was performed with

dichloromethane. The aqueous layer was further extracted 5 times with dichloromethane.

1-(2,3-Di-O-benzyl-5-O-methyl-α-D-ribofuranosyl)-2-propanone (**22α**). — Syrup, $[\alpha]_D^{22}$ +35.7° (*c* 0.98, chloroform); ν_{max}^{NaCl} 1715 (C=O) cm^{-1}; ^{1}H-n.m.r. (200 MHz): δ 2.05 (s, 3 H, H-3′), 2.80 (dd, 1 H, $J_{1,1'}$ 6.1, $J_{1',1''}$ 17.1 Hz, H-1′), 2.93 (dd, 1 H, $J_{1,1''}$ 7.6 Hz, H-1″), 3.32 (s, 3 H, OCH_3), 3.37 (dd, 1 H, $J_{4,5}$ 4.6, $J_{5,5'}$ 10.5 Hz, H-5), 3.47 (dd, 1 H, $J_{4,5'}$ 3.2 Hz, H-5′), 3.96–4.14 (m, 3 H, H-2,3,4), 4.44, 4.78 (2 H, AB type, *J* 11.3 Hz, CH_2Ph), 4.55, 4.68 (2 H, AB type, *J* 11.8 Hz, CH_2Ph), 4.35–4.55 (m, 1 H, H-1), and 7.25–7.34 (bd, 10 H, 2 C_6H_5); ^{13}C-n.m.r.: δ 30.63 (C-3′), 43.90 (C-1′), 59.24 (OCH_3), 72.69, 73.54, 76.02, 77.65, 79.05, 79.69 (C-1–5 and 2 CH_2Ph), 127.56, 127.71, 127.94, 128.20, 128.32, 137.77, 138.15 (2 C_6H_5), and 207.23 (C-2′).

Anal. Calc. for $C_{23}H_{28}O_5$: C, 71.85; H, 7.34. Found: C, 71.65; H, 7.55.

1-(5-O-Benzyl-2,3-di-O-methyl-α-D-ribofuranosyl)-2-propanone (**24α**). — Syrup, $[\alpha]_D^{22}$ +5.3° (*c* 1.51, chloroform); ν_{max}^{NaCl} 1705 (C=O) cm^{-1}; ^{1}H-n.m.r. (200 MHz): δ 2.17 (s, 3 H, H-3′), 2.76 (dd, 1 H, $J_{1,1'}$ 6.8, $J_{1',1''}$ 17.6 Hz, H-1′), 2.89 (dd, 1 H, $J_{1,1''}$ 6.8 Hz, H-1″), 3.41 (s, 3 H, OCH_3), 3.44 (s, 3 H, OCH_3), 3.52 (dd, 1 H, $J_{4,5}$ 4.0, $J_{5,5'}$ 11.0 Hz, H-5), 3.60 (dd, 1 H, $J_{4,5'}$ 3.7 Hz, H-5′), 3.82 (dd, 1 H, $J_{2,3}$ 4.6, $J_{3,4}$ 5.8 Hz, H-3), 3.92 (t, 1 H, $J_{1,2}$ 4.6 Hz, H-2), 4.05 (dt, 1 H, H-4), 4.49 (dt, 1 H, H-1), 4.51, 4.61 (2 H, AB type, *J* 12.5 Hz, CH_2Ph), and 7.24–7.44 (bs, 5 H, C_6H_5); ^{13}C-n.m.r. (50 MHz): δ 30.63 (C-3′), 43.70 (C-1′), 58.49, 59.60 (2 OCH_3), 70.36, 73.37, 75.81, 79.23, 79.55, 82.06 (C-1–5 and CH_2Ph), 127.45, 128.20, 138.06 (C_6H_5), and 207.02 (C-2′).

Anal. Calc. for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 66.45; H, 7.76.

1-(5-O-Benzyl-2,3-di-O-methyl-β-D-ribofuranosyl)-2-propanone (**24β**). — Syrup, $[\alpha]_D^{22}$ −3.2° (*c* 0.95, chloroform), ν_{max}^{NaCl} 1705 (C=O) cm^{-1}; ^{1}H-n.m.r. (200 MHz): δ 2.17 (s, 3 H, H-3′), 2.68 (d, 2 H, $J_{1,1'}$ 6.4 Hz, H-1′), 3.41 (s, 3 H, OCH_3), 3.46 (s, 3 H, OCH_3), 3.54 (d, 2 H, $J_{4,5}$ 4.0 Hz, H-5), 3.47–3.56 (1 H, overlapped with H-5,H-2), 3.78 (t, 1 H, $J_{2,3}$ 4.0, $J_{3,4}$ 4.0 Hz, H-3), 4.11 (q, 1 H, H-4), 4.32 (q, 1 H, $J_{1,2}$ 6.4 Hz, H-1), 4.56 (bs, 2 H, CH_2Ph), and 7.32 (s, 5 H, C_6H_5); ^{13}C-n.m.r. (50 MHz): δ 30.48 (C-3′), 47.72 (C-1′), 57.70, 57.93 (2 OCH_3), 70.33, 73.36, 76.46, 79.37, 80.95, 82.96 (C-1–5 and CH_2Ph), 127.39, 127.50, 128.23, 138.00 (C_6H_5), and 206.29 (C-2′).

Anal. Calc. for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 66.16; H, 7.63.

3-(2,3,5-Tri-O-methyl-α-D-ribofuranosyl)-1-propene (**17**). — Syrup, $[\alpha]_D^{22}$ +49.2° (*c* 1.22, chloroform); ^{1}H-n.m.r. (200 MHz): δ 2.44 (t, 2 H, $J_{1,1'}$ 7.1, $J_{1',2'}$ 6.9 Hz, H-1′), 3.39 (s, 3 H, OCH_3), 3.45 (s, 3 H, OCH_3), 3.47 (dd, 1 H, $J_{4,5}$ 4.3, $J_{5,5'}$ 10.6 Hz, H-5), 3.53 (s, 3 H, OCH_3), 3.56 (dd, 1 H, $J_{4,5'}$ 3.1 Hz, H-5′), 3.78 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 4.5 Hz, H-2), 3.81 (dd, 1 H, $J_{3,4}$ 6.5 Hz, H-3), 4.05 (2 H, overlapped dt and ddd, H-1 and -4, respectively), 5.06 (dd, 1 H, $J_{2',3'}$ 10.2, $J_{3',3''}$ 1.9 Hz, H-3′), 5.13 (dd, 1 H, $J_{2',3''}$ 17.1 Hz, H-3″), and 5.82 (ddt, 1 H, H-2′); ^{13}C-n.m.r. (50 MHz): δ 33.87 (C-1′), 58.40, 59.24, 59.71 (3 OCH_3), 72.90, 78.91, 79.55, 79.75, 82.03 (C-1–5), 116.62 (C-3′), and 134.68 (C-2′).

Anal. Calc. for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 59.63; H, 9.06.

*3-(2,3-Di-*O*-benzyl-5-*O*-methyl-α-*D*-ribofuranosyl)-1-propene* (**18**). — Syrup, $[\alpha]_D^{21}$ +48.5° (*c* 1.18, chloroform); ^{1}H-n.m.r. (360 MHz): δ 2.51 (t, 2 H, $J_{1,1'}$ 7.0, $J_{1',2'}$ 6.9 Hz, H-1'), 3.33 (s, 3 H, OCH_3), 3.39 (dd, 1 H, $J_{4,5}$ 4.2, $J_{5,5'}$ 10.7 Hz, H-5), 3.54 (dd, 1 H, $J_{4,5'}$ 2.9 Hz, H-5'), 3.97 (t, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 4.3 Hz, H-3), 4.05 (2 H, completely overlapped dt and dd, H-1 and -3, respectively), 4.17 (ddd, 1 H, $J_{3,4}$ 7.3 Hz, H-4), 4.53, 4.67 (2 H , AB type, *J* 12 Hz, CH_2Ph), 4.59, 4.82 (2 H, AB type, *J* 11.5 Hz, CH_2Ph), 5.03 (bd, 1 H, $J_{2',3'}$ 10.2 Hz, H-3'), 5.09 (bd, 1 H, $J_{2',3''}$ 17.2 Hz, H-3''), 5.78 (ddt, 1 H, H-2'), and 7.22–7.35 (bs, 10 H, 2 C_6H_5); ^{13}C-n.m.r. (50 MHz): δ 34.16 (C-1'), 59.22 (OCH_3), 72.49, 72.58, 73.25, 77.51, 79.05, 79.81, 79.99 (C-1–5 and CH_2Ph), 116.68 (C-3'), 127.42, 127.53, 127.59, 128.15, 128.26, 137.86, 138.33 (2 C_6H_5), and 134.80 (C-2').

Anal. Calc. for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66. Found: C, 75.21; H, 7.55.

*3-(5-*O*-Benzyl-2,3-di-*O*-methyl-α-*D*-ribofuranosyl)-1-propene* (**19**). — Syrup, $[\alpha]_D^{22}$ +34.2° (*c* 1.52, chloroform); ^{1}H-n.m.r. (200 MHz): δ 2.44 (t, 2 H, $J_{1,1'}$ 7.1, $J_{1',2'}$ 7.1 Hz, H-1'), 3.40 (s, 3 H, OCH_3), 3.52 (s, 3 H, OCH_3), 3.54 (dd, 1 H, $J_{4,5}$ 4.2, $J_{5,5'}$ 10.5 Hz, H-5), 3.64 (dd, 1 H, $J_{4,5'}$ 3.4 Hz, H-5'), 3.77 (t, 1 H, $J_{1,2}$ 4.3, $J_{2,3}$ 4.4 Hz, H-2), 3.86 (dd, 1 H, $J_{3,4}$ 6.6 Hz, H-3), 4.06 (dt, 1 H, H-1), 4.08 (dt, 1 H, H-4), 4.53, 4.63 (2 H, AB type, *J* 12.2 Hz, CH_2Ph), 5.06 (bd, 1 H, $J_{2',3'}$ 10.4 Hz, H-3'), 5.13 (bd, 1 H, $J_{2',3''}$ 17.0 Hz, H-3''), 5.83 (ddt, 1 H, H-2'), and 7.26–7.33 (bs, 5 H, C_6H_5); ^{13}C-n.m.r. (50 MHz): δ 35.92 (C-1'), 60.40, 61.68 (2 OCH_3), 72.33, 75.609, 81.23, 82.78, 81.84, 84.143 (C-1–5 and CH_2Ph), 118.60 (C-3'), 129.39, 130.14, 140.15 (C_6H_5), and 136.80 (C-2').

Anal. Calc. for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 70.00; H, 8.25.

*2-(2,3,5-Tri-*O*-benzyl-*D*-ribofuranosyl)-3-pentanone* (**13**), *2-(2,3,5-tri-*O*-methyl-*D*-ribofuranosyl)-3-pentanone* (**21**), *and 2-(2,3-di-*O*-benzyl-5-*O*-methyl-*D*-ribofuranosyl)-3-pentanone* (**23**). — Repeated chromatography on a column of silica gel afforded only a trace amount (5–10 mg) of each pure compound. It was not possible to establish the configuration of these compounds.

Compound **13**. Syrup, ν_{max}^{NaCl} 1720 (C=O) cm^{-1}; ^{1}H-n.m.r. (360 MHz): δ 0.76 (t, 3 H, $J_{3',4'}$ 7.2, $J_{3'',4'}$ 7.2 Hz, H-4'), 1.09 (d, 3 H, $J_{1'',1'}$ 7.1 Hz, H-1''), 2.14 (dq, 1 H, $J_{3',3''}$ 18.4 Hz, H-3'), 2.35 (dq, 1 H, H-3''), 2.99 (dq, 1 H, $J_{1,1'}$ 9.2 Hz, H-1'), 3.44 (dd, 1 H, $J_{4,5}$ 4.2, $J_{5,5'}$ 10.7 Hz, H-5), 3.53 (dd, 1 H, $J_{4,5'}$ 3.3 Hz, H-5'), 3.93 (dd, 1 H, $J_{2,3}$ 5.0, $J_{3,4}$ 5.0 Hz, H-3), 4.03 (dd, 1 H, $J_{1,2}$ 4.8 Hz, H-2), 4.05 (ddd, 1 H, H-4), 4.19 (dd, 1 H, H-1), 4.22, 4.41–4.67 (1 H and 5 H, 3 AB type, 3 CH_2Ph), and 7.18–7.26 (m, 15 H, 3 C_6H_5).

Anal. Calc. for $C_{31}H_{36}O_5$: C, 76.20; H, 7.43. Found: C, 75.91; H, 7.47.

Compound **21**. Syrup, ν_{max}^{NaCl} 1735 (C=O) cm^{-1}; ^{1}H-n.m.r. (360 MHz): δ 1.01 (t, 3 H, $J_{3',4'}$ 7.3 Hz, H-4'), 1.18 (d, 3 H, $J_{1'',1'}$ 7.1 Hz, H-1''), 2.55 (q, 2 H, H-3'), 2.98 (dq, 1 H, $J_{1,1'}$ 9.6 Hz, H-1'), 3.32, 3.37, 3.43 (s, 3 × 3 H, 3 OCH_3), 3.44 (dd, 1 H, $J_{4,5}$ 4.3, $J_{5,5'}$ 10.7 Hz, H-5), 3.54 (dd, 1 H, $J_{4,5'}$ 3.0 Hz, H-5'), 3.69 (dd, 1 H, $J_{2,3}$ 4.8, $J_{3,4}$ 7.2 Hz, H-3), 3.80 (t, 1 H, $J_{1,2}$ 4.8 Hz, H-2), 3.90 (ddd, 1 H, H-4), and 4.18 (dd, 1 H, H-1).

Anal. Calc. for $C_{13}H_{24}O_5$: C, 59.98; H, 9.29. Found: C, 60.03; H, 9.07.

Compound **23**. Syrup, ν_{max}^{NaCl} 1725 (C=O) cm^{-1}; ^{1}H-n.m.r. (360 MHz): δ 0.83 (t, 3 H, $J_{3',4'}$ 7.2, $J_{3'',4'}$ 7.2 Hz, H-4'), 1.10 (d, 3 H, $J_{1'',1''}$ 9.8 Hz, H-1''), 2.21 (dd, 1 H, $J_{3',3''}$ 18.3 Hz, H-3'), 2.41 (dd, 1 H, H-3''), 3.05 (dq, 1 H, $J_{1'',1''}$ 9.8 Hz, H-1'), 3.34 (s, 3 H, OCH_3), 3.40 (dd, 1 H, $J_{4,5}$ 4.5, $J_{5,5'}$ 10.6 Hz, H-5), 3.53 (dd, 1 H, $J_{4,5'}$ 3.1 Hz, H-5'), 3.96 (dd, 1 H, $J_{2,3}$ 4.6, $J_{3,4}$ 4.7 Hz, H-3), 4.09 (ddd, 1 H, H-4), 4.10 (t, 1 H, $J_{1,2}$ 4.6 Hz, H-2), 4.25 (dd, 1 H, H-1), 4.28, 4.75 (2 H, AB type, J 11.6 Hz, CH_2Ph), 4.58, 4.70 (2 H, AB type, J 12 Hz, CH_2Ph), and 7.26–7.35 (m, 10 H, 2 C_6H_5).

Anal. Calc. for $C_{25}H_{32}O_5$: C, 72.79; H, 7.82. Found: C, 72.25; H, 7.57 (susceptible to decomposition).

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