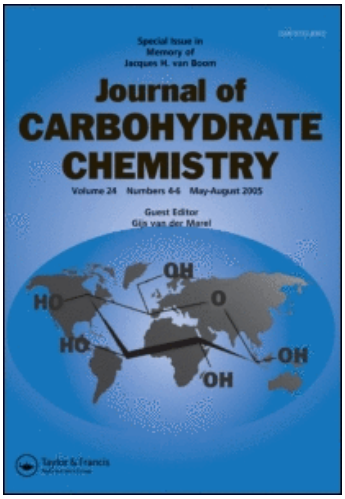

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SYNTHESIS AND HYDROGENOLYSIS OF DIOXOLANE-TYPE DIPHENYLMETHYLENE AND FLUOREN-9-YLIDENE CARBOHYDRATE ACETALS CONTAINING A NEIGHBOURING SUBSTITUTED HYDROXYL FUNCTION

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ABSTRACT

Series of dioxolane-type diphenylmethylene and fluoren-9-ylidene acetals of hexoses containing adjacent *O*-alkyl, deoxy or hydroxy functions were prepared and hydrogenolysed with the $LiAlH_4$-$AlCl_3$ reagent. The observed direction of ring-cleavage was discussed in terms of different influences, such as complex formation and orientation of the hydride reagent, the configurational arrangements of the free OH group to one of the oxygen atoms of the dioxolane ring, as well as the conformational relationship of the rings present in the 1,6-anhydro derivatives.

INTRODUCTION

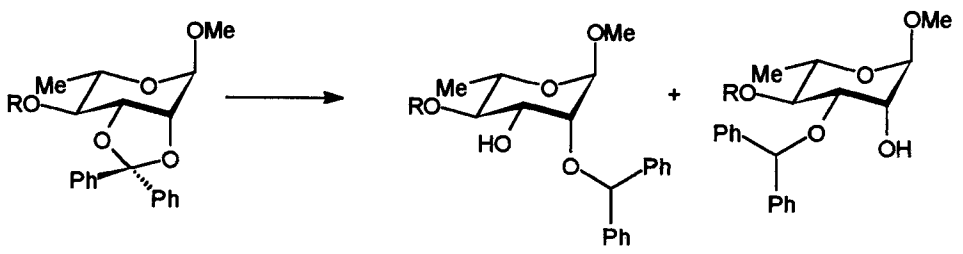
Our earlier studies on the hydrogenolysis of dioxolane-type benzylidene[1] or ethylidene[2] acetals of various pyranosides have demonstrated that the direction of the ring-

cleavage is essentially dependent on the steric arrangement of the 2'-aryl or -alkyl substituent of the dioxolane ring. However, sporadic experiments with dioxolane type ketals, such as methylene,[2] isopropylidene,[2] 2'-phenylethylidene[2] (acetophenone acetals) resulted, surprisingly, exclusively in *axial*-ether/*equatorial*-hydroxy derivatives. These observations initiated studies of the preparation and hydrogenolysis of dioxolane-type diphenylmethylene[3] and fluoren-9-ylidene[4] acetals. All of these symmetric ketals contained a free OH group in the vicinity of the dioxolane ring, and the OH groups were located in the neighbourhood of the *equatorial* oxygen atom of the dioxolane ring (thus being in a *gauche* arrangement). Hydrogenolysis of these ketals resulted exclusively in *axial* diphenylmethyl[3] or fluoren-9-yl[4] ethers with chloroalane (AlH_2Cl) as the reagent. It is to be noted that dichloroalane ($AlHCl_2$) split the diphenylmethyl and fluoren-9-yl ethers, as well, but under such conditions the benzyl and allyl ethers were stable. These properties of the diphenylmethylene acetals were successfully utilized in a practical synthesis of the immunodeterminant trisaccharide of *Mycobacterium leprae*.[5] To extend the synthetic efficacy of these easily transformable symmetric ketals we decided to investigate the fully protected derivatives of different diphenylmethylene and fluoren-9-ylidene acetals of hexopyranosides.

RESULTS AND DISCUSSION

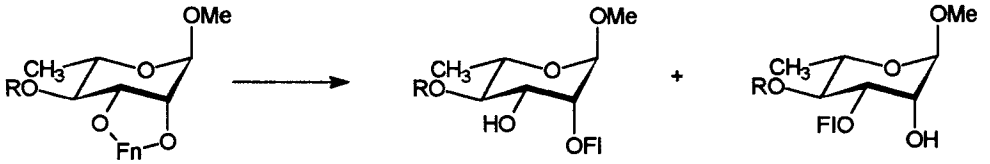
In order to study the applicability and versatility of dioxolane-type diphenylmethylene and fluoren-9-ylidene acetals as new protective groups we have assayed first the partial deprotection reactions on methyl 2,3-*O*-diphenylmethylene-α-L-rhamnopyranoside[3] (**1**) and methyl 2,3-*O*-fluoren-9-ylidene-α-L-rhamnopyranoside[4] (**17**) to give substituted benzyl derivatives. Benzyl and allyl ethers are among the most versatile carbohydrate derivatives easily prepared, and deprotected under various mild conditions.[6]

Thus, benyzlation or allylation of **1** resulted in the suitable model compounds **2** and **3**, respectively. Hydrogenolysis was not regiospecific in either case; a mixture of two structural isomers (**4**/**5** and **6**/**7**) were formed with the predominance of the *equatorial* diphenylmethyl ethers. The π-system of the allyl or benzyl groups cannot be responsible for the lack of selectivity since the 4-*O*-*n*-butyl (**8**), -ethyl (**9**) or -methyl (**10**) derivatives of **1** give a very similar cleavage pattern, although by the decrease of the bulkiness of these

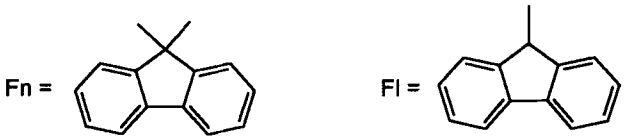


1	R = H		(1 : 0)	
2	Bn	**4**	(1 : 4.97)	**5**
3	All	**6**	(1 : 3.56)	**7**
8	*n*Bu	**11**	(1 : 4.68)	**12**
9	Et	**13**	(1 : 4.65)	**14**
10	Me	**15**	(1 : 2.27)	**16**

Scheme 1



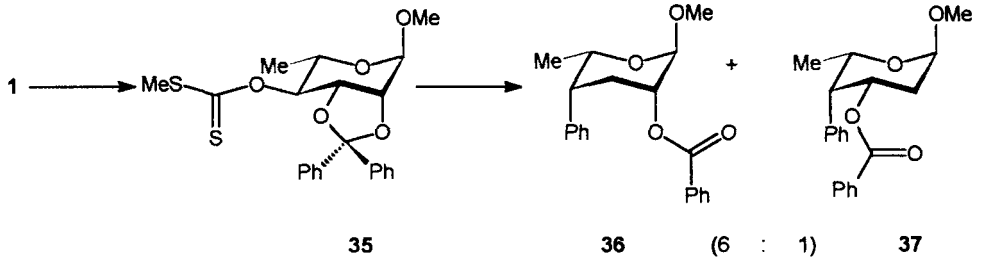
17	R = H		(1 : 0)	
18	Bn	**23**	(1 : 1.22)	**24**
19	All	**25**	(1 : 1.21)	**26**
20	*n*Bu	**27**	(1 : 0.97)	**28**
21	Et	**29**	(1 : 1.21)	**30**
22	Me	**31**	(1 : 0.87)	**32**



Scheme 2

substituents, the proportion of the *axial* ethers increased (Scheme 1). A very similar trend was also observed during the hydrogenolysis of the fluoren-9-ylidene derivatives **18-22** (Scheme 2).

The facts i) that the less bulky substituent gave the highest ratio of the *axial/equatorial* ethers, and ii) that the hydrogenolysis of the more flexible



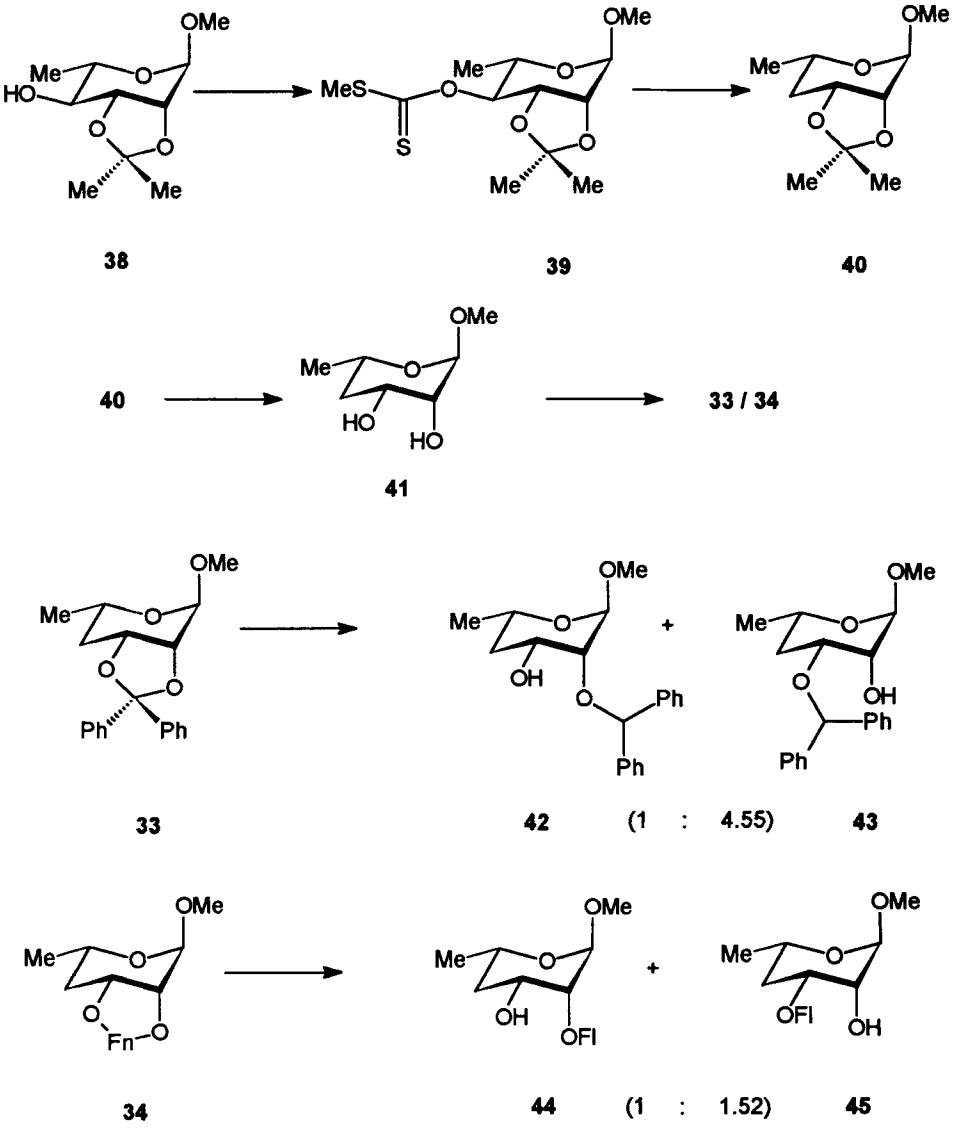
35 36 (6 : 1) 37

Scheme 3

diphenylmethylene acetals was shifted very strongly to the formation of the *equatorial* ethers suggested that the 4-*O*-substituents might prevent the attack of the reagent on the adjacent *equatorial* oxygen of the dioxolane ring. To test this assumption we decided to synthesize methyl 4,6-dideoxy-2,3-*O*-diphenylmethylene- (**33**) and methyl 4,6-dideoxy-2,3-*O*-fluoren-9-ylidene-α-L-*lyxo*-hexopyranoside (**34**). It is to be noted that the Barton-type deoxygenation[7] of the xanthate derivative (**35**) of methyl 2,3-*O*-diphenylmethylene-α-L-rhamnopyranoside (**1**) failed, and instead of the desired **33**, an inseparable 6:1 mixture of compounds **36** and **37** was obtained and whose structures were determined by high field NMR techniques (400 MHz) (Scheme 3).

On the other hand, reduction of the xanthate ester[8] **39** of methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside[9] (**38**) was successful, to give methyl 4,6-dideoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranoside[8] (**40**). Hydrolysis of the isopropylidene function resulted in the desired methyl 4,6-dideoxy-α-L-*lyxo*-hexopyranoside[8] (**41**). Treatment of compound **41** with dichlorodiphenylmethane or with 9,9-dichlorofluorene[10] gave acetals **33** and **34**, respectively. Their hydrogenolysis completely precluded the role of the substitution of OH-4 because, again, the 3-O-ethers dominated (**42**:**43**=1:4.55 and **44**:**45**=1:1.52) suggesting the essential role of the free OH group in all investigated ketals (Scheme 4).

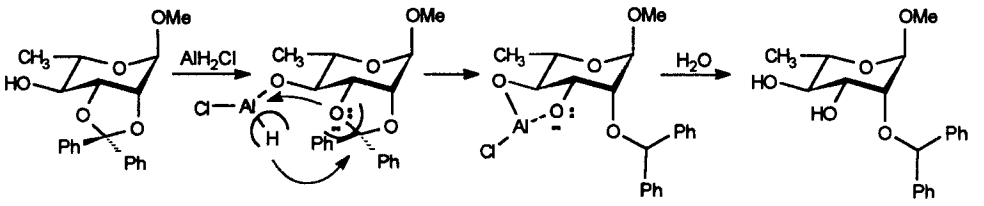
An acceptable explanation of the high stereoselectivity of the cleavage of the OH group-containing ketals is based on the proposed mechanism summarized on Scheme 5. Chlorohydrido-aluminate is formed in the first step of the reaction sequence, which is a



Scheme 4

strong Lewis acid and hydride donor. Thus the cleavage occurs through the intramolecular complexation of the adjacent oxygen of the acetal ring.

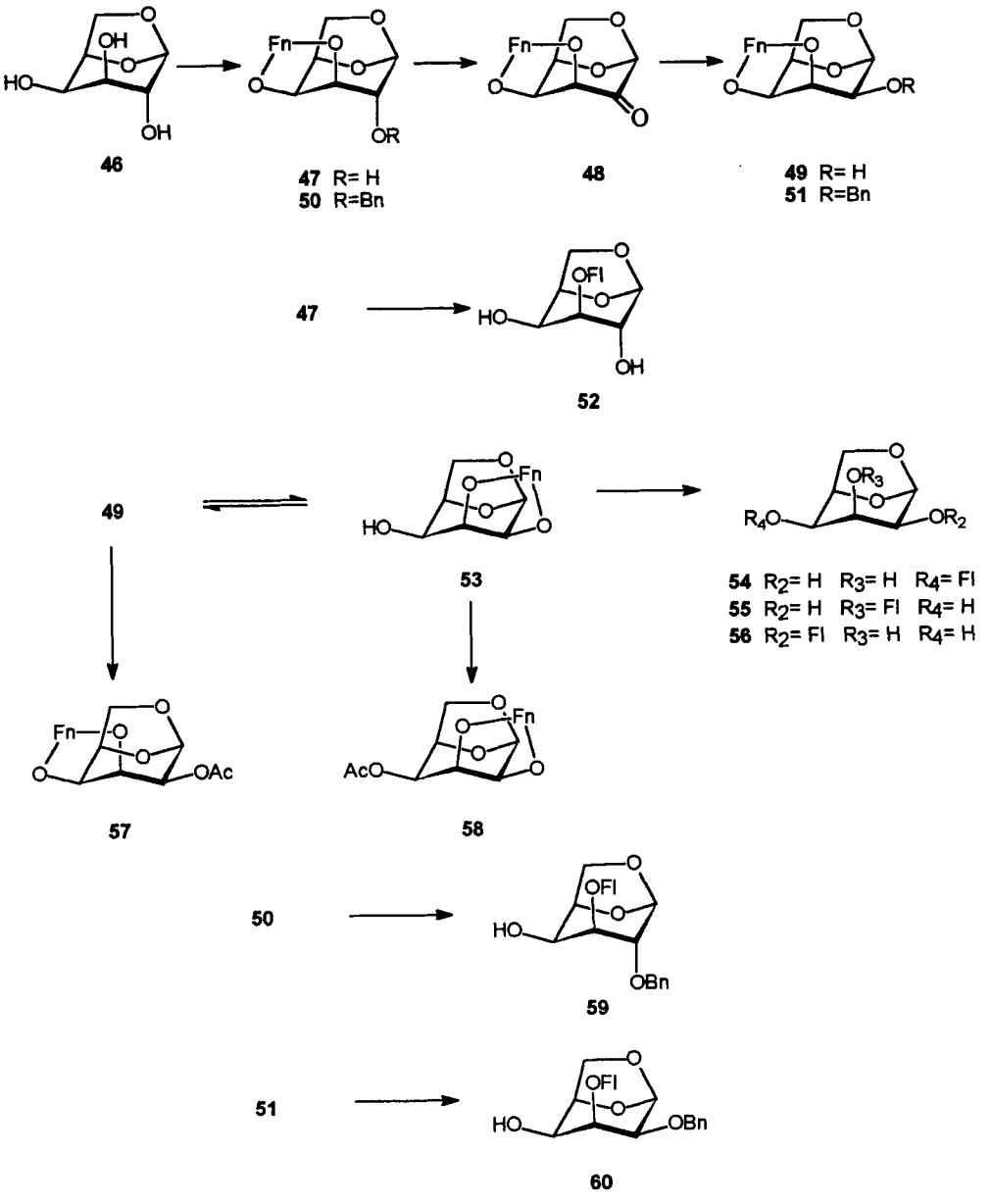
All ketals investigated up to now contained a free OH group located *gauche* to the *equatorial* oxygen of the dioxolane ring. The synthesis of 1,6-anhydro-3,4-*O*-fluoren-9-ylidene-β-D-talopyranose (**49**) has provided a new type of ketal in which the free OH-2 is



Scheme 5

in an *equatorial* position and is located in the vicinity of the *axial* oxygen of the dioxolane ring. Hydrogenolysis of compound **49** resulted, surprisingly, in all of three ether isomers (**54-56**) in a 18:62:20 ratio. The formation of the two *equatorial* ethers (**54** and **56**) is explained by migration of the ketal group; from **49**, 1,6-anhydro-2,3-*O*-fluoren-9-ylidene-β-D-talopyranose (**53**) was formed in this way. This migration was substantiated by treatment of **49** with a catalytic amount of $AlCl_3$ followed by acetylation to afford 2-*O*-acetyl-1,6-anhydro-3,4-*O*-fluoren-9-ylidene-β-D-talopyranose (**57**) and 4-*O*-acetyl-1,6-anhydro-2,3-*O*-fluoren-9-ylidene-β-D-talopyranose (**58**). Compound **54** was formed by hydrogenolysis of **49**, the 2-ether derivative (**56**) was produced from **53**, and the formation of **55** in a rather high yield can only be explained by the fact that the *axial O*-3 is extremely hindered, being in a 1,3-*cis-diaxial* arrangement with both *C*-6 and *O*-1, and thus in such cases an intramolecular delivery system does not work successfully. This assumption is strongly supported by the obtained cleavage patterns of 1,6-anhydro-3,4-*O*-fluoren-9-ylidene-β-D-galactopyranose (**47**), 1,6-anhydro-2-*O*-benzyl-3,4-*O*-fluoren-9-ylidene-β-D-galactopyranose (**50**), and 1,6-anhydro-2-*O*-benzyl-3,4-*O*-fluoren-9-ylidene-β-D-talopyranose (**51**) where the 3-*O*-fluorenyl ethers (**52**, **59** and **60**, respectively) were formed in nearly quantitative yield, showing that the *axial* oxygen of the dioxolane ring is unapproachable for the free chloroalane (Scheme 6).

These investigations clearly show the influences of different parameters[11] which determine the outcome of the ring cleavage reaction, such as complex formation and orientation of the hydride reagent, the configurational arrangements of the free OH group to one of the oxygen atoms of the dioxolane ring, as well as a very important role of the conformational relationship of the rings present in the 1,6-anhydro derivatives. The



Scheme 6

Table 1. ^{1}H NMR chemical shifts (ppm)

Comp.	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-9'*	*1-OCH$_3$*	*Other signals*[a]
2	5.02 s	4.06 dd	4.46 t	3.18 dd	3.66 m	1.18 d	---	3.34 s	4.47, 4.84 dd, OCH_2Ph
3	5.01 d	4.04 dd	4.37 t	3.09 dd	3.63 m	1.23 d	---	3.34 s	3.94, 4.29 m, H-1(All); 5.05, 5.07 m, H-3(All); 5.83 m, H-2(All)
4	4.56 d	3.79 dd	3.90 m	3.42 t	3.66 m	1.37 d	5.59 s	3.24 s	2.15 m, 3-OH; 4.68, 4.87 dd, OCH_2Ph
5	4.62 d	3.85 dd	3.90 dd	3.53 t	3.67 m	1.32 d	5.65 s	3.26 s	2.45 d, 2-OH; 4.64, 4.89 dd, OCH_2Ph
6	4.55 d	3.79 dd	3.84 ddd	3.31 t	3.61 m	1.35 d	5.60 s	3.24 s	2.13 d, 3-OH; 4.17, 4.32 m, H-1(All); 5.22 m, H-3(All); 5.83 m, H-2(All)
7	4.61 d	3.84 dd	3.82 dd	3.39 t	3.61 m	1.30 d	5.65 s	3.26 s	2.44 d, 2-OH; 4.13, 4.35 m, H-1(All); 5.15, 5.23 m, H-3(All); 5.90 m, H-2(All)
8	5.00 s	4.05 dd	4.33 t	2.99 dd	3.60 m	1.22 d	---	3.34 s	0.89 t, H-4(*n*Bu); 3.37, 3.78 dd, H-1(*n*Bu)
9	4.99 s	4.04 dd	4.34 t	3.01 dd	3.60 m	1.22 d	---	3.33 s	1.12 t, H-2(Et); 3.44, 3.83 m, H-1(Et)
10	5.00 s	4.05 dd	4.34 t	2.92 dd	3.58 m	1.23 d	---	3.34 s	3.45 s, 4-OCH_3
11	4.56 d	3.78 dd	3.81 m	3.21 t	3.58 m	1.34 d	5.60 s	3.24 s	0.92 t, H-4(*n*Bu); 2.12 d, 3-OH; 3.58, 3.80 dd, H-1(*n*Bu)
12	4.60 d	3.82 dd	3.79 dd	3.31 t	3.58 m	1.30 d	5.64 s	3.26 s	0.88 t, H-4(*n*Bu); 2.43 d, 2-OH; 3.54, 3.83 dd, H-1(*n*Bu)
13	4.56 d	3.78 dd	3.81 dd	3.23 t	3.58 m	1.34 d	5.60 s	3.24 s	1.23 t, H-2(Et); 2.12 d, 3-OH; 3.67, 3.83 dd, H-1(Et)
14	4.61 d	3.85 dd	3.78 dd	3.32 t	3.58 m	1.30 s	5.64 s	3.25 s	1.18 t, H-2(Et); 2.44 d, 2-OH; 3.65, 3.88 dd, H-1(Et)
15	4.55 d	3.78 dd	3.81 dd	3.13 t	3.56 m	1.35 d	5.59 s	3.25 s	2.16 d, 3-OH; 3.57 s, 4-OCH_3
16	4.61 d	3.82 dd	3.76 dd	3.22 t	3.55 m	1.30 d	5.66 s	3.26 s	2.45 d, 2-OH; 3.56 s, 4-OCH_3
18	4.96 s	4.76 d	4.75 t	3.62 m	3.86 m	1.42 d	---	3.41 s	4.65, 4.90 dd, OCH_2Ph
19	4.96 s	4.74 dd	4.65 t	3.56 dd	3.82 m	1.43 d	---	3.41 s	4.12, 4.35 m, H-1(All); 5.14, 5.22 m, H-3(All); 5.89 m, H-2(All)
20	4.96 s	4.72 dd	4.62 t	3.46 dd	3.79 m	1.42 d	---	3.40 s	0.87 t, H-4(*n*Bu); 3.52, 3.85 dd, H-1(*n*Bu)
21	4.96 s	4.73 dd	4.63 t	3.48 dd	3.79 m	1.42 d	---	3.40 s	1.17 t, H-2(Et); 3.61, 3.91 m, H-1(Et)
22	4.96 s	4.73 d	4.61 t	3.39 dd	3.78 m	1.42 d	---	3.41 s	3.54 s, 4-OCH_3
23	4.75 d	4.01 dd	3.95 ddd	3.32 t	3.66 m	1.35 d	5.63 s	3.28 s	2.31 m, 3-OH; 4.63, 4.88 dd, OCH_2Ph
24	4.72 d	4.03 dd	4.25 dd	3.46 t	3.76 m	1.33 d	5.61 s	3.34 s	2.69 m, 2-OH; 4.53, 4.80 dd, OCH_2Ph

Table 1. (continued)

Comp.	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-9'*	*1-OCH$_3$*	*Other signals*[a]
25	4.73 d	3.99 dd	3.87 ddd	3.20 t	3.61 m	1.32 d	5.63 s	3.28 s	2.29 d, 3-OH; 4.12, 4.32 m, H-1(All); 5.15, 5.26 m, H-3(All); 5.94 m, H-2(All)
26	4.69 d	3.97 m	4.14 dd	3.32 t	3.71 m	1.33 d	5.60 s	3.34 s	2.62 d, 2-OH; 4.04, 4.30 m, H-1(All); 5.13, 5.19 m, H-3(All); 5.87 m, H-2(All)
27	4.73 d	3.99 dd	3.84 m	3.12 t	3.58 m	1.32 d	5.62 s	3.27 s	0.90 t, H-4(*n*Bu); 2.27 d, 3-OH; 3.53, 3.80 dd, H-1(*n*Bu)
28	4.70 d	3.98 m	4.16 dd	3.26 t	3.69 m	1.33 d	5.61 s	3.35 s	0.85 t, H-2(*n*Bu); 2.59 d, 2-OH; 3.47, 3.78 m, H-1(*n*Bu)
29	4.74 d	3.99 dd	3.84 m	3.13 t	3.59 m	1.32 d	5.63 s	3.28 s	1.19 t, H-2(Et); 2.28 d, 3-OH; 3.62, 3.84 m, H-1(Et)
30	4.71 d	3.98 m	4.15 dd	3.26 t	3.69 m	1.34 d	5.60 s	3.34 s	1.14 t, H-2(Et); 2.61 d, 2-OH; 3.58, 3.81 m, H-1(Et)
31	4.74 d	3.99 dd	3.83 m	3.04 t	3.57 m	1.32 d	5.61 s	3.28 s	2.34 d, 3-OH; 3.54 s, 4-OCH$_3$
32	4.66 d	3.92 m	4.05 dd	3.16 t	3.63 m	1.33 d	5.60 s	3.32 s	2.65 d, 2-OH; 3.52 s, 4-OCH$_3$
33	5.06 s	3.86 d	4.49 m	1.46 m 1.89 ddd	3.79 m	1.18 d	---	3.36 s	---
34	5.01 s	4.51 d	4.83 m	1.87 m 2.20 m	3.96 m	1.38 d	---	3.44 s	---
35	5.05 s	4.14 d	4.52 t	5.81 dd	3.88 m	1.20 d	---	3.38 s	2.56 s, SCH$_3$
36	4.86 d	5.05 m	2.20 m 2.50 m	3.10 m	4.42 m	1.14 d	---	3.48 s	---
37	5.04 m	1.99 m 2.14 m	5.72 m	3.33 dd	4.44 m	1.15 d	---	3.42 s	---
42	4.64 s	--- 3.81-3.89 m ---		1.64 m 1.71 m	3.62 m	1.26 d	5.55 s	3.25 s	1.94 bs, 3-OH
43	4.75 s	--- 3.77-3.90 m ---		1.63 m 1.74 m	3.73 m	1.21 d	5.57 s	3.29 s	2.35 bs, 2-OH
44	4.85 s	3.85 m	3.85 m	1.60 m 1.71 m	3.80 m	1.24 d	5.63 s	3.29 s	2.09 d, 3-OH
45	4.68 s	---3.85-3.65 m ---		1.55 m 1.65 m	3.65 m	1.19 d	5.64 s	3.25 s	2.47 d, 2-OH

(continued)

Table 1. (continued)

Comp.	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-9'*	*1-OCH₃*	*Other signals*[a]
47	5.52 bs	4.00 d	4.79 d	5.01 dd	4.81 dd	3.75 dd 4.71 d	---	---	2.29 d, 2-OH
48	5.37 d	---	4.97 m	5.36 dd	5.08 m	3.84 dd 4.64 dd	---	---	---
49	5.45 d	4.00 ddd	5.16 t	4.96 m	4.71 m	3.82 dd 4.81 d	---	---	2.77 d, 2-OH
50	5.58 bs	3.74 s	4.80 d	5.05 dd	4.83 m	3.71 dd 4.62 dd	---	---	4.62, 4.74 dd, OCH_2Ph
51	5.44 d	3.77 dd	5.10 t	4.87 t	4.68 t	3.87 dd 4.92 d	---	---	4.60, 4.75 dd, OCH_2Ph
52	5.43 t	4.01 dt	4.17 ddd	4.08 m	4.40 m	3.65 m 4.21 dd	5.66 s	---	1.95 d, 2-OH; 3.05 d, 4-OH
53	5.57 d	4.55 dd	5.10 m	4.29 m	4.53 m	3.86 m 4.35 dd	---	---	2.62 d, 4-OH
54	5.15 t	3.31 dd	3.83 m	3.33 m	3.98 m	3.60 m 4.38 dd	5.73 s	---	---
55	5.30 d	3.81 ddd	4.73 m	4.10 m	4.34 m	3.64 m 4.29 d	5.78 s	---	2.48 d, 4-OH; 2.83 d, 2-OH
56	5.04 t	3.05 dd	3.72 m	3.57 m	4.22 m	3.60 m 4.30 d	5.77 s	---	---
59	5.36 t	3.60 dd	3.97 ddd	4.03 m	3.37 m	3.61 m 4.21 dd	5.53 s	---	3.03 d, 4-OH; 4.14, 4.22 dd, OCH_2Ph
60	5.57 t	3.66 dd	4.77 m	4.03 m	4.31 m	2.60 m 4.19 d	5.96 s	---	3.03 d, 4-OH; 4.74, 4.89 dd, OCH_2Ph

a. Abbrevations: $\overset{1}{\text{All}}$, $\overset{1}{OCH_2}\text{-}\overset{2}{CH}\text{=}\overset{3}{CH_2}$; $\overset{1}{n\text{Bu}}$, $\overset{1}{OCH_2}\text{-}\overset{2}{CH_2}\text{-}\overset{3}{CH_2}\text{-}\overset{4}{CH_3}$; $\overset{1}{\text{Et}}$, $\overset{1}{OCH_2}\text{-}\overset{2}{CH_3}$

Table 2. ^{13}C NMR chemical shifts (ppm)

Comp.	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-9'*	*1-OCH₃*	*Other signals*[a]
2	97.96	76.25	79.34	80.57	64.36	17.74	109.22	54.75	72.98, O<u>C</u>H₂Ph
3	97.97	76.24	79.20	80.47	64.48	17.76	109.15	54.76	72.04, C-1(All); 116.98, C-3(All); 134.74, C-2(All)
4	98.47	77.27	71.66	82.27	67.06	18.16	83.71	54.62	74.89, O<u>C</u>H₂Ph
5	99.94	68.72	78.35	80.10	67.18	17.90	82.37	54.62	75.42, O<u>C</u>H₂Ph
6	98.53	77.27	71.54	82.08	67.12	18.09	83.73	54.63	73.82, C-1(All); 116.96, C-3(All); 135.08, C-2(All)
7	99.95	68.78	78.03	79.85	67.17	17.84	82.31	54.62	74.24, C-1(All); 116.88, C-3(All); 134.80, C-2(All)
8	97.98	76.22	79.29	81.03	64.57	17.75	109.05	54.71	13.84, C-4(*n*Bu); 19.23, C-3(*n*Bu); 32.03, C-2(*n*Bu); 71.12, C-1(*n*Bu)
9	97.95	76.20	79.25	80.91	64.54	17.70	109.07	54.71	15.47, C-2(Et); 66.74, C-1(Et)
10	98.00	76.26	78.96	82.77	64.51	17.71	109.16	54.78	59.33, 4-OCH₃
11	98.51	77.14	71.50	82.46	67.19	18.07	83.64	54.58	13.94, C-4(*n*Bu); 19.29, C-3(*n*Bu); 32.48, C-2(*n*Bu); 72.79, C-1(*n*Bu)
12	99.93	68.80	78.02	80.30	67.27	17.80	82.36	54.57	13.99, C-4(*n*Bu); 19.32, C-3(*n*Bu); 32.51, C-2(*n*Bu); 73.42, C-1(*n*Bu)
13	98.53	77.18	71.46	82.34	67.22	18.03	83.70	54.59	15.79, C-2(Et); 68.33, C-1(Et)
14	99.93	68.71	77.95	80.09	67.25	17.77	82.24	54.56	15.71, C-2(Et); 68.76, C-1(Et)
15	98.46	77.22	71.38	84.02	67.09	18.07	83.69	54.67	60.72, 4-OCH₃
16	99.96	68.85	77.95	82.19	67.20	17.76	82.50	54.66	61.17, 4-OCH₃
18	98.13	77.16	78.93	81.59	64.20	18.13	112.98	54.92	72.54, O<u>C</u>H₂Ph
19	98.14	77.19	78.82	81.81	64.29	18.06	112.93	54.92	71.87, C-1(All); 117.25, C-3(All); 134.70, C-2(All)
20	98.15	77.07	78.86	82.78	64.43	18.04	112.87	54.87	13.91, C-4(*n*Bu); 19.27, C-3(*n*Bu); 32.16, C-2(*n*Bu); 71.23, C-1(*n*Bu)
21	98.13	77.10	78.84	82.62	64.39	17.98	112.88	54.88	15.50, C-2(Et); 66.90, C-1(Et)
22	98.19	77.07	78.57	84.29	64.33	18.02	112.92	54.95	59.28, 4-OCH₃
23	99.02	77.91	71.52	81.46	67.01	18.05	82.15	54.75	75.01, O<u>C</u>H₂Ph
24	99.99	69.40	79.80	80.30	67.36	17.94	80.97	54.77	75.66, O<u>C</u>H₂Ph
25	99.03	77.87	71.33	81.85	67.06	17.96	81.42	54.75	73.89, C-1(All); 116.84, C-3(All); 135.09, C-2(All)
26	100.00	69.61	80.22	79.54	67.35	17.91	81.32	54.76	74.49, C-1(All); 116.98, C-3(All); 134.77, C-2(All)
27	99.02	77.90	71.34	82.10	67.18	17.93	81.41	54.70	13.92, C-4(*n*Bu); 19.28, C-3(*n*Bu); 32.46, C-2(*n*Bu); 72.93, C-1(*n*Bu)
28	99.99	69.53	80.12	80.10	67.48	17.89	81.12	54.73	13.96, C-4(*n*Bu); 19.25, C-3(*n*Bu); 32.39, C-2(*n*Bu); 73.62, C-1(*n*Bu)

(continued)

Table 2. (continued)

Comp.	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-9'*	*1-OCH$_3$*	*Other signals*[a]
29	99.02	77.87	71.25	81.95	67.18	17.88	81.41	54.71	15.78, C-2(Et); 68.42, C-1(Et)
30	99.98	69.57	80.16	79.85	67.44	17.84	81.28	54.73	15.61, C-2(Et); 68.97, C-1(Et)
31	98.96	77.88	71.18	83.63	67.10	17.91	81.34	54.79	60.80, 4-OCH$_3$
32	100.00	69.73	79.92	81.88	67.40	17.86	81.52	54.76	61.52, 4-OCH$_3$
33	98.68	71.85	73.04	35.32	62.07	21.25	108.94	54.87	---
34	98.99	71.34	73.71	35.53	61.95	21.72	112.90	55.01	---
35	98.00	76.09	76.35	82.23	64.21	17.37	109.92	55.03	19.30, SCH$_3$
36	99.11	70.27	30.20	42.23	68.70	16.58	---	55.38	165.77, O<u>C</u>OPh
37	98.93	30.24	69.53	48.45	65.79	18.59	---	54.76	166.20, O<u>C</u>OPh
43	100.96	66.43	72.00	33.55	63.76	21.11	80.69	54.66	---
44	99.90	75.24	65.50	37.45	64.16	21.16	81.07	54.79	---
45	101.02	67.63	71.31	34.80	63.66	21.11	79.97	54.66	---
47	101.55	69.09	77.53	71.78	72.55	63.04	112.63	---	---
48	98.47	196.11	74.72	71.71	73.90	62.62	115.33	---	---
49	99.65	69.08	72.08	72.35	73.17	64.33	113.59	---	---
50	100.38	75.59	79.52	69.50	72.24	62.54	112.56	---	72.13, O<u>C</u>H$_2$Ph
51	98.63	74.66	71.69	72.50	73.31	64.52	114.06	---	71.58, O<u>C</u>H$_2$Ph
52	101.04	69.23	77.00	64.27	74.93	63.59	80.59	---	---
53	98.90	75.68	73.33	66.80	73.14	63.27	114.10	---	---
54	101.21	69.11	68.82	69.39	73.20	65.04	80.60	---	---
55	101.05	69.61	78.00	67.48	74.55	64.50	84.17	---	---
56	100.49	70.94	68.70	66.94	74.52	64.48	80.50	---	---
59	100.03	76.24	73.89	64.64	74.48	63.41	80.56	---	72.17, O<u>C</u>H$_2$Ph
60	98.64	78.31	77.32	66.83	74.89	64.84	83.29	---	72.46, O<u>C</u>H$_2$Ph

a. Abbrevations: *1 2 3* *1 2 3 4* *1 2*
All, OCH$_2$-CH=CH$_2$; *n*Bu, OCH$_2$-CH$_2$-CH$_2$-CH$_3$; Et, OCH$_2$-CH$_3$

balance of these influencing parameters has to be taken into account to predict the direction of the hydrogenolytic ring cleavage of the symmetric ketal derivatives.

EXPERIMENTAL

General methods. Solutions were concentrated at 40 °C (bath) under diminished pressure. Optical rotations were measured in $CHCl_3$ at room temperature with Perkin-Elmer 241 automatic polarimeter. The ^1H (200 and 400 MHz) and ^{13}C NMR (50.3 and 101 MHz) spectra for solutions in $CDCl_3$ were recorded with a Bruker WP-200 SY and Varian XLA-400 spectrometers (internal Me_4Si). Heteronuclear correlation spectroscopy was used to assign lines in the ^{13}C NMR spectra. Melting points were determined on a Kofler apparatus and are uncorrected. TLC was performed on Kieselgel 60 F_{254} (Merck) with A (9:1) B (85:15) C (8:2) D (7:3) hexane-ethyl acetate, E (99:1) F (98:2) G (95:5) and H (9:1) dichloromethane-acetone, with detection by spraying with 50% aq sulfuric acid followed by heating. For HPLC a Hewlett Packard 1090 series II Liquid Chromatograph equipped with a diode array detector, automatic sampler and ChemStation was used. Each sample was separated on a Hewlett Packard DIOL 10 μm (0.46x20 cm) column with different ratios of hexane-ethyl acetate as the mobile phases flowing at a rate of 1.0 mL/min at 40 °C. The quality of the hexane and ethyl acetate were HPLC grade. Effluent was monitored at 254 nm.

General method for alkylation of Methyl 2,3-*O*-Diphenylmethylene-α-L-rhamnopyranoside (1) and Methyl 2,3-*O*-Fluoren-9-ylidene-α-L-rhamnopyranoside (17). To a stirred solution of **1**[3] (1.0 g, 2.92 mmol) or **17**[4] (1.0 g, 2.94 mmol) in dry *N,N*-dimethylformamide (1.0 mL) was added NaH (105 mg, 1.5 equiv) and the alkylating agent (2 equiv). The mixture was stirred for 1-2 h at room temperature, then diluted with EtOAc, washed with water until neutral, dried (Na_2SO_4), and concentrated. The resulting crude syrup was purified by column chromatography and/or crystallized from appropriate solvent.

Methyl 4-*O*-Benzyl-2,3-*O*-diphenylmethylene-α-L-rhamnopyranoside (2). From **1**, eluted with solvent A; yield: 1.11 g (88%); $[\alpha]_D$ -94.0° (*c* 0.45); R_f 0.51 (solvent B).

Anal. Calcd for $C_{27}H_{28}O_5$ (432.515): C, 74.98; H, 6.52. Found: C, 75.17; H, 6.50.

Methyl 4-*O*-Allyl-2,3-*O*-diphenylmethylene-α-L-rhamnopyranoside (3). From **1**, eluted with solvent A; yield: 1.03 g (92%); $[\alpha]_D$ -95.4° (*c* 1.10); R_f 0.52 (solvent A).

Anal. Calcd for $C_{23}H_{26}O_5$ (382.455): C, 72.23; H, 6.85. Found: C, 72.03; H, 6.87.

Methyl 4-*O*-*n*-Butyl-2,3-*O*-diphenylmethylene-α-L-rhamnopyranoside (8). From **1**, eluted with solvent A; yield: 1.01 g (87%); $[\alpha]_D$ -82.0° (*c* 0.58); R_f 0.44 (solvent A).

Anal. Calcd for $C_{24}H_{30}O_5$ (398.498): C, 72.34; H, 7.59. Found: C, 72.21; H, 7.56.

Methyl 2,3-*O*-Diphenylmethylene-4-*O*-ethyl-α-L-rhamnopyranoside (9). From **1**, eluted with solvent A; yield: 0.83 g (77%); $[\alpha]_D$ -90.7° (*c* 1.28); R_f 0.38 (solvent A); the product crystallized upon standing, mp 46 °C (after recrystallization from EtOH).

Anal. Calcd for $C_{22}H_{26}O_5$ (370.344): C, 71.33; H, 7.08. Found: C, 71.45; H, 7.04.

Methyl 2,3-*O*-Diphenylmethylene-4-*O*-methyl-α-L-rhamnopyranoside (10). From **1**, eluted with solvent A; yield: 0.95 g (91%); $[\alpha]_D$ -101.2° (*c* 0.66); R_f 0.41 (solvent A); the product crystallized upon standing, mp 66 °C (after recrystallization from hexane).

Anal. Calcd for $C_{21}H_{24}O_5$ (356.418): C, 70.77; H, 6.79. Found: C, 70.88; H, 6.82.

Methyl 4-*O*-Benzyl-2,3-*O*-fluoren-9-ylidene-α-L-rhamnopyranoside (18). From **17**, crystallized from hexane; yield: 1.08 g (85%); mp 102-103 °C; $[\alpha]_D$ -4.2° (*c* 0.73); R_f 0.56 (solvent C).

Anal. Calcd for $C_{27}H_{26}O_5$ (430.499): C, 75.33; H, 6.09. Found: C, 75.20; H, 6.14.

Methyl 4-*O*-Allyl-2,3-*O*-fluoren-9-ylidene-α-L-rhamnopyranoside (19). From **17**, eluted with solvent A; yield: 1.01 g (90%); $[\alpha]_D$ +31.2° (*c* 0.95); R_f 0.25 (solvent A).

Anal. Calcd for $C_{23}H_{24}O_5$ (380.440): C, 72.61; H, 6.36. Found: C, 72.80; H, 6.40.

Methyl 4-*O*-*n*-Butyl-2,3-*O*-fluoren-9-ylidene-α-L-rhamnopyranoside (20). From **17**, crystallized from EtOH; yield: 1.03 g (88%); mp 92-94 °C; $[\alpha]_D$ +14.2° (*c* 0.88); R_f 0.36 (solvent A).

Anal. Calcd for $C_{24}H_{28}O_5$ (396.482): C, 72.71; H, 7.12. Found: C, 72.81; H, 7.10.

Methyl 4-*O*-Ethyl-2,3-*O*-fluoren-9-ylidene-α-L-rhamnopyranoside (21). From **17**, crystallized from EtOH; yield: 0.93 g (86%); mp 139-140 °C; $[\alpha]_D$ +18.5° (*c* 0.83); R_f 0.35 (solvent A).

Anal. Calcd for $C_{22}H_{24}O_5$ (368.429): C, 71.72; H, 6.57. Found: C, 71.63; H, 6.55.

Methyl 2,3-*O*-Fluoren-9-ylidene-4-*O*-methyl-α-L-rhamnopyranoside (22). From **17**, crystallized from hexane-EtOAc; yield: 0.93 g (86%); mp 114 °C; $[\alpha]_D$ +22.0° (*c* 0.69); R_f 0.54 (solvent D).

Anal. Calcd for $C_{21}H_{22}O_5$ (354.402): C, 71.17; H, 6.26. Found: C, 71.30; H, 6.25.

Preparation of diphenylmethyl (4-7, 11-16) and fluoren-9-yl ethers (23-32). To a stirred solution of acetals (**2,3**, **8-10**, **18-22**) in dry 1:1 dichloromethane-ether was added $LiAlH_4$ (4.5 equiv/1 equiv of substrate) and $AlCl_3$ (1.5 equiv/1 equiv of substrate). The solution was heated under reflux and the reaction was monitored by TLC. When the conversion of the starting material was complete (1-2 h) the mixture was diluted with ether, the excess of $LiAlH_4$ was decomposed by successive addition of EtOAc and water, the organic layer was washed twice with water, dried (Na_2SO_4), and concentrated. The resulting crude syrup was purified by column chromatography.

Methyl 4-*O*-Benzyl-2-*O*-diphenylmethyl-α-L-rhamnopyranoside (4) and Methyl 4-*O*-Benzyl-3-*O*-diphenylmethyl-α-L-rhamnopyranoside (5). From **2**, eluted with solvent C. Compound **4**: 9%; $[\alpha]_D$ -1.4° (*c* 0.37); R_f 0.39 (solvent C).

Anal. Calcd for $C_{27}H_{30}O_5$ (434.531): C, 74.63; H, 6.96. Found: C, 74.80; H, 6.93. Compound **5**: 40%; $[\alpha]_D$ -77.6° (*c* 0.15); R_f 0.19 (solvent C).

Anal. Calcd for $C_{27}H_{30}O_5$ (434.531): C, 74.63; H, 6.96. Found: C, 74.77; H, 7.00.

Methyl 4-*O*-Allyl-2-*O*-diphenylmethyl-α-L-rhamnopyranoside (6) and Methyl 4-*O*-Allyl-3-*O*-diphenylmethyl-α-L-rhamnopyranoside (7). From **3**, eluted with solvent C. Compound **6**: 15%; $[\alpha]_D$ +3.0° (*c* 0.33); R_f 0.35 (solvent C).

Anal. Calcd for $C_{23}H_{28}O_5$ (384.471): C, 71.85; H, 7.34. Found: C, 71.76; H, 7.38. Compound 7:51%; $[\alpha]_D$ -81.2° (*c* 0.55); R_f 0.17 (solvent C).

Anal. Calcd for $C_{23}H_{28}O_5$ (384.471): C, 71.85; H, 7.34. Found: C, 71.70; H, 7.30.

Methyl 4-*O*-*n*-Butyl-2-*O*-diphenylmethyl-α-L-rhamnopyranoside (11) and Methyl 4-*O*-*n*-Butyl-3-*O*-diphenylmethyl-α-L-rhamnopyranoside (12). From **8**, eluted with solvent C. Compound **11**: 17%; $[\alpha]_D$ +3.3° (*c* 0.60); R_f 0.39 (solvent C).

Anal. Calcd for $C_{24}H_{32}O_5$ (400.514): C, 71.97; H, 8.05. Found: C, 72.14; H, 8.00. Compound **12**: 65%; $[\alpha]_D$ -78.5° (*c* 0.83); R_f 0.22 (solvent C).

Anal. Calcd for $C_{24}H_{32}O_5$ (400.514): C, 71.97; H, 8.05. Found: C, 72.11; H, 8.10.

Methyl 4-*O*-Ethyl-2-*O*-diphenylmethyl-α-L-rhamnopyranoside (13) and Methyl 4-*O*-Ethyl-3-*O*-diphenylmethyl-α-L-rhamnopyranoside (14). From **9**, eluted with solvent C. Compound **13**: 11%; $[\alpha]_D$ -3.0° (*c* 0.23); R_f 0.35 (solvent C); the product crystallized upon standing, mp 116 °C (after recrystallization from EtOH).

Anal. Calcd for $C_{22}H_{28}O_5$ (372.360): C, 70.96; H, 7.58. Found: C, 71.13; H, 7.60. Compound **14**: 40%; $[\alpha]_D$ -74.1° (*c* 0.52); R_f 0.18 (solvent C).

Anal. Calcd for $C_{22}H_{28}O_5$ (372.360): C, 70.96; H, 7.58. Found: C, 70.75; H, 7.62.

Methyl 2-*O*-Diphenylmethyl-4-*O*-methyl-α-L-rhamnopyranoside (15) and Methyl 3-*O*-Diphenylmethyl-4-*O*-methyl-α-L-rhamnopyranoside (16). From **10**, eluted with solvent F. Compound **16**: 45%; $[\alpha]_D$ -71.5° (*c* 0.56); R_f 0.37 (solvent F).

Anal. Calcd for $C_{21}H_{26}O_5$ (358.434): C, 70.37; H, 7.31. Found: C, 70.59; H, 7.28. Compound **15**: 25%; $[\alpha]_D$ +3.0° (*c* 0.33); R_f 0.27 (solvent F).

Anal. Calcd for $C_{21}H_{26}O_5$ (358.434): C, 70.37; H, 7.31. Found: C, 70.21; H, 7.30.

Methyl 4-*O*-Benzyl-2-*O*-fluoren-9-yl-α-L-rhamnopyranoside (23) and Methyl 4-*O*-Benzyl-3-*O*-fluoren-9-yl-α-L-rhamnopyranoside (24). From **18**, eluted with solvent C. Compound **23**: 38%; $[\alpha]_D$ -15.9° (*c* 0.58); R_f 0.36 (solvent C); the product crystallized upon standing, mp 113-114 °C.

Anal. Calcd for $C_{27}H_{28}O_5$ (432.515): C, 74.98; H, 6.52. Found: C, 75.10; H, 6.53. Compound **24**: 37%; $[\alpha]_D$ -63.7° (*c* 0.61); R_f 0.18 (solvent C).

Anal. Calcd for $C_{27}H_{28}O_5$ (432.515): C, 74.98; H, 6.52. Found: C, 75.15; H, 6.57.

Methyl 4-*O*-Allyl-2-*O*-fluoren-9-yl-α-L-rhamnopyranoside (25) and Methyl 4-*O*-Allyl-3-*O*-fluoren-9-yl-α-L-rhamnopyranoside (26). From **19**, eluted with solvent C. Compound **25**: 43%; $[\alpha]_D$ -27.0° (*c* 0.71); R_f 0.34 (solvent C); the product crystallized upon standing, mp 88 °C.

Anal. Calcd for $C_{23}H_{26}O_5$ (382.455): C, 72.23; H, 6.85. Found: C, 72.37; H, 6.86.

Compound **26**: 45%; $[\alpha]_D$ -85.0° (*c* 0.56); R_f 0.22 (solvent C); the product crystallized upon standing, mp 72 °C.

Anal. Calcd for $C_{23}H_{26}O_5$ (382.455): C, 72.23; H, 6.85. Found: C, 72.11; H, 6.87.

Methyl 4-*O*-*n*-Butyl-2-*O*-fluoren-9-yl-α-L-rhamnopyranoside (27) and Methyl 4-*O*-*n*-Butyl-3-*O*-fluoren-9-yl-α-L-rhamnopyranoside (28). From **20**, eluted with

solvent C. Compound **27**: 50%; $[\alpha]_D$ -21.3° (*c* 0.85); R_f 0.37 (solvent C); the product crystallized upon standing, mp 80 °C (after recrystallization from EtOH).

Anal. Calcd for $C_{24}H_{30}O_5$ (398.498): C, 72.34; H, 7.59. Found: C, 72.45; H, 7.61. Compound **28**: 30%; $[\alpha]_D$ -70.2° (*c* 0.22); R_f 0.22 (solvent C); the product crystallized upon standing, mp 109-110 °C (after recrystallization from EtOH).

Anal. Calcd for $C_{24}H_{30}O_5$ (398.498): C, 72.34; H, 7.59. Found: C, 72.52; H, 7.62.

Methyl 4-*O*-Ethyl-2-*O*-fluoren-9-yl-α-L-rhamnopyranoside (29) and Methyl 4-*O*-Ethyl-3-*O*-fluoren-9-yl-α-L-rhamnopyranoside (30). From **21**, eluted with solvent C. Compound **29**: 48%; $[\alpha]_D$ -23.0° (*c* 0.48); R_f 0.56 (solvent D); the product crystallized upon standing, mp 122 °C (after recrystallization from EtOH).

Anal. Calcd for $C_{22}H_{26}O_5$ (370.344): C, 71.33; H, 7.08. Found: C, 71.55; H, 7.03. Compound **30**: 40%; $[\alpha]_D$ -73.4° (*c* 0.57); R_f 0.47 (solvent D).

Anal. Calcd for $C_{22}H_{26}O_5$ (370.344): C, 71.33; H, 7.08. Found: C, 71.09; H, 7.13.

Methyl 2-*O*-Fluoren-9-yl-4-*O*-methyl-α-L-rhamnopyranoside (31) and Methyl 3-*O*-Fluoren-9-yl-4-*O*-methyl-α-L-rhamnopyranoside (32). From **22**, eluted with solvent D. Compound **31**: 52%; $[\alpha]_D$ -25.6° (*c* 0.59); R_f 0.30 (solvent D); the product crystallized upon standing, mp 104 °C (after recrystallization from hexane).

Anal. Calcd for $C_{21}H_{24}O_5$ (356.418): C, 70.77; H, 6.79. Found: C, 70.95; H, 6.83. Compound **32** did not exsist in pure form, because the mother liquor was an inseparable mixture of **31** and **32**. Having obtained the ^{13}C NMR spectrum of pure **31** it was possible to unambigously assign the signals due to **32** in a mixture of the two isomers.

Methyl 4,6-Dideoxy-2,3-*O*-diphenylmethylene-α-L-*lyxo*-hexopyranoside (33). To a stirred solution of **41**[8] (0.50 g, 3.1 mmol) in dry pyridine (2 mL) was added dichlorodiphenylmethane (1.18 ml, 2 equiv). The mixture was stirred overnight at 100 °C. The dark-red solution was poured onto crushed ice and, after 1 h, the mixture was partitioned between dichloromethane and 0.1 M sulfuric acid. The organic phase was washed with water until neutral, dried (Na_2SO_4), and concentrated. The dark-red residue was passed through a short column of silica gel (solvent E). The resulting crude syrup was purified by column chromatography (solvent A) to give **33** (0.48 g, 47%); $[\alpha]_D$ -51.0° (*c* 1.78); R_f 0.39 (solvent A).

Anal. Calcd for $C_{20}H_{22}O_4$ (326.391): C, 73.60; H, 6.79. Found: C, 73.86; H, 6.75.

Methyl 4,6-Dideoxy-2,3-*O*-fluoren-9-ylidene-α-L-*lyxo*-hexopyranoside (34). To a stirred solution of **41**[8] (0.50 g, 3.1 mmol) in dry pyridine (2 mL) was added 9,9-dichlorofluorene[10] (1.48 g, 2 equiv). The mixture was stirred for 2 days at 100 °C. The method used for the isolation and purification of **33** was applied to give **34** (0.45 g, 45%); $[\alpha]_D$ -5.40° (*c* 1.79); R_f 0.31 (solvent A).

Anal. Calcd for $C_{20}H_{20}O_4$ (324.376): C, 74.06; H, 6.21. Found: C, 73.81; H, 6.25.

Methyl 2,3-*O*-Diphenylmethylene-4-*O*-(methylthio)thiocarbonyl-α-L-rhamnopyranoside (35). To a stirred suspension of **1**[3] (1.0 g, 2.92 mmol) and 80% NaH (0.175 g, 2 equiv) in dry tetrahydrofuran (10 mL) was added imidazole (4 mg, 0.02 equiv). The mixture was stirred for 15 min at room temperature, then CS_2 (1.32 mL, 7.5 equiv) and, after 1 h, CH_3I (0.4 mL, 2 equiv) were added to this mixture. The stirring was continued for an additional 1.5 h. The mixture was then diluted with dichloromethane, and the organic layer was washed with water until neutral, dried (Na_2SO_4), and concentrated. Column chromatography (eluant C) of the crude product yielded amorphous **35** (1.17 g, 93%); $[\alpha]_D$ -81.4° (*c* 0.81); R_f 0.64 (solvent D).

Anal. Calcd for $C_{22}H_{24}O_5S_2$ (432.557): C, 61.09; H, 5.59; S, 14.83. Found: C, 61.30; H, 5.61; S, 14.94.

Methyl 2-*O*-Benzoyl 3,4,6-trideoxy-4-*C*-phenyl-α-L-*lyxo*-hexopyranoside (36) and Methyl 3-*O*-Benzoyl 2,4,6-trideoxy-4-*C*-phenyl-α-L-*lyxo*-hexopyranoside (37). To a solution of **35** (1.1 g, 2.54 mmol) in dry toluene (10 mL) was added a catalytic amount of AIBN and then Bu_3SnH (0.82 mL, 1.2 equiv) was added dropwise. The mixture was stirred under Ar at reflux temperature for 1 h, then concentrated. The column chromatography of the crude product gave a 6:1 mixture of **36** and **37**. The ratio of products was determined by NMR.

Methyl 4,6-Dideoxy-2-*O*-diphenylmethyl-α-L-*lyxo*-hexopyranoside (42) and Methyl 4,6-Dideoxy-3-*O*-diphenylmethyl-α-L-*lyxo*-hexopyranoside (43). The method used for the preparation of diphenylmethyl ethers (**4-7, 11-16**) was applied to **33** to give a 1:4.55 mixture of **42** and **43**. The ratio of products was determined by HPLC.

Methyl 4,6-Dideoxy-2-*O*-fluoren-9-yl-α-L-*lyxo*-hexopyranoside (44) and Methyl 4,6-Dideoxy-3-*O*-fluoren-9-yl-α-L-*lyxo*-hexopyranoside (45). The method used

for the preparation of fluoren-9-yl ethers (**23-32**) was applied to **34** to give a 1:1.52 mixture of **44** and **45**. The ratio of products was determined by HPLC.

1,6-Anhydro-3,4-*O*-fluoren-9-ylidene-β-D-galactopyranose (47). To a stirred solution of **46**[12] (2.38 g, 14.7 mmol) in dry pyridine (10 mL) was added 9,9-dichlorofluorene[10] (1.48 g, 2 equiv). The mixture was stirred for 4 days at 100 °C. The method used for the isolation of **33** was applied to give **47**. The resulting crude syrup was purified by column chromatography (eluant G) to give **47** (2.0 g, 42%); $[\alpha]_D$ -77.0° (*c* 0.72); R_f 0.27 (solvent G). The product crystallized upon standing, mp 186-188 °C (after recrystallization from EtOH).

Anal. Calcd for $C_{19}H_{16}O_5$ (324.332): C, 70.36; H, 4.97. Found: C, 70.30; H, 4.98.

1,6-Anhydro-3,4-*O*-fluoren-9-ylidene-β-D-*lyxo*-hexopyranos-2-ulose (48). To a stirred solution of **47** (1.43 g, 4.4 mmol) in dry dichloromethane were added powdered molecular sieves 4 Å (1.50 g) and pyridinium chlorochromate (6.0 g). The mixture was stirred in the dark at room temperature overnight, then diluted with ether, filtered through a short column of silica gel (eluant G, R_f 0.50), and concentrated. The yellow residue was used for the next step without any purification.

1,6-Anhydro-3,4-*O*-fluoren-9-ylidene-β-D-talopyranose (49). To a solution of **48** (0.78 g, 2.4 mmol) in dry methanol (15 mL) was added $NaBH_4$ (0.18 g, 2 equiv) and the solution was stirred for 1 h at room temperature. The excess of $NaBH_4$ was decomposed with 60% aqueous acetic acid. The mixture was diluted with dichloromethane, washed with water, dried (Na_2SO_4), and concentrated. The residue was crystallized from dichloromethane-hexane to give **49** (0.63 g, 80%); mp 222-224 °C; $[\alpha]_D$ -105.6° (*c* 0.97); R_f 0.43 (solvent G).

Anal. Calcd for $C_{19}H_{16}O_5$ (324.332): C, 70.36; H, 4.97. Found: C, 70.28; H, 4.96.

1,6-Anhydro-2-*O*-benzyl-3,4-*O*-fluoren-9-ylidene-β-D-galactopyranose (50). The method used for the conversion of **17** into **18** was applied to **47** to give **50**. The purification of the crude product by column chromatography (eluant E) gave pure **50** (88%); $[\alpha]_D$ -8.4° (*c* 1.21); R_f 0.53 (solvent F). The product crystallized upon standing, mp 166-168 °C (after recrystallization from EtOH).

Anal. Calcd for $C_{26}H_{22}O_5$ (414.457): C, 73.35; H, 5.35. Found: C, 73.14; H, 5.40.

1,6-Anhydro-2-*O*-benzyl-3,4-*O*-fluoren-9-ylidene-β-D-talopyranose (51). The method used for the conversion of **17** into **18** was applied to **49** to give **51**. The

purification of the crude product by crystallization from dichloromethane-EtOH gave pure **51** (89%); mp 201-203 °C; $[\alpha]_D$ -22.1° (*c* 0.27); R_f 0.38 (solvent D).

Anal. Calcd for $C_{26}H_{22}O_5$ (414.457): C, 73.35; H, 5.35. Found: C, 73.57; H, 5.31.

1,6-Anhydro-3-*O*-fluoren-9-yl-β-D-galactopyranose (52). To a stirred solution of **47** (100 mg, 0.31 mmol) in dry 1:1 dichloromethane-ether were added $LiAlH_4$ (23 mg, 2 equiv) and $AlCl_3$ (82 mg, 2 equiv). The stirring was continued for additional 30 min at room temperature, then the mixture was diluted with ether, the excess of $LiAlH_4$ was decomposed by successive addition of EtOAc and water, the organic layer was washed twice with water, dried (Na_2SO_4), and concentrated. The resulting crude syrup was purified by column chromatography (eluant H) to give **52** (79 mg, 79%); the product crystallized upon standing, mp 176-180 °C; $[\alpha]_D$ -28.5° (*c* 0.24); R_f 0.27 (solvent H).

Anal. Calcd for $C_{19}H_{18}O_5$ (326.348): C, 69.93; H, 5.56. Found: C, 69.71; H, 5.60.

1,6-Anhydro-2,3-*O*-fluoren-9-ylidene-β-D-talopyranose (53). To a solution of **49** (0.32 g, 1.0 mmol) in dry dichloromethane (1 mL) was added $AlCl_3$ (0.13 g, 1 equiv) The solution was a stirred for 1 min at room temperature, then diluted with dichloromethane, washed with aqueous 5% $NaHCO_3$ and water until neutral. The organic layer was dried (Na_2SO_4) and concentrated. The resulting crude syrup was purified by column chromatography (eluant G) to give **53** (0.30 g, 94%); $[\alpha]_D$ -46.8° (*c* 0.12); R_f 0.67 (solvent H).

Anal. Calcd for $C_{19}H_{16}O_5$ (324.332): C, 70.36; H, 4.97. Found: C, 70.61; H, 4.90.

1,6-Anhydro-4-*O*-fluoren-9-yl-β-D-talopyranose (54), 1,6-Anhydro-3-*O*-fluoren-9-yl-β-D-talopyranose (55), and 1,6-Anhydro-2-*O*-fluoren-9-yl-β-D-talopyranose (56). Compound **49** was hydrogenolysed as described above (**47**→**52**). Column chromatography of the crude product (eluant G) gave the following compounds.

Compound **53**: 25%

Compound **55**: 40%; $[\alpha]_D$ -51.3° (*c* 0.05); R_f 0.44 (solvent H).

Anal. Calcd for $C_{19}H_{18}O_5$ (326.348): C, 69.93; H, 5.56. Found: C, 69.69; H, 5.60.

Compounds **54** and **56**: 24% (~1:1 inseparable mixture); $[\alpha]_D$ -30.8° (*c* 0.20); R_f 0.23 (solvent H).

Anal. Calcd for $C_{19}H_{18}O_5$ (326.348): C, 69.93; H, 5.56. Found: C, 70.20; H, 5.50.

2-*O*-Acetyl-1,6-anhydro-3,4-*O*-fluoren-9-ylidene-β-D-talopyranose (57). To a solution of **49** (0.15 g, 0.46 mmol) in pyridine (2 mL) was added acetic anhydride (2 mL).

The mixture was stirred for 2 h, then concentrated. The residue was purified by column chromatography (eluant F) to give **57** (0.16 g, 96%); the product crystallized upon standing, mp 172-174 °C; $[\alpha]_D$ -45.0° (*c* 0.10); R_f 0.40 (solvent F). ^1H NMR: δ 5.53 (d, 1H, H-1), 5.31 (t, 1H, H-3), 5.09-4.88 (m, 3H, H-2,4,6), 4.78 (t, 1H, H-5), 3.89 (dd, 1H, H-6'), and 2.05 (s, 3H, CH_3CO); ^{13}C NMR: δ 170.15 ($CH_3\underline{C}O$), 114.10 (C-9'), 97.77 (C-1), 73.42, 72.34, 70.77, 70.34 (C-2,3,4,5), 64.62 (C-6), and 20.66 ($\underline{C}H_3CO$).

Anal. Calcd for $C_{21}H_{18}O_6$ (366.370): C, 68.85; H, 4.95. Found: C, 68.99; H, 4.90.

4-*O*-Acetyl-1,6-anhydro-2,3-*O*-fluoren-9-ylidene-β-D-talopyranose (58). Compound **53** (0.10 g, 0.31 mmol) was acetylated as described above. Column chromatography of the mixture (eluant F) gave **58** (0.10 g, 91%); the product crystallized upon standing, mp 213-215 °C; $[\alpha]_D$ -83.7° (*c* 0.15); R_f 0.45 (solvent F). ^1H NMR: δ 5.60 (d, 1H, H-1), 5.34-5.20 (m, 2H, H-3,4), 4.61-4.49 (m, 3H, H-2,5,6), 3.90 (dd, 1H, H-6'), and 2.03 (s, 3H, CH_3CO); ^{13}C NMR: δ 170.01 ($CH_3\underline{C}O$), 114.66 (C-9'), 99.52 (C-1), 75.51, 72.01, 70.93, 67.87 (C-2,3,4,5), 64.44 (C-6), and 20.75 ($\underline{C}H_3CO$).

Anal. Calcd for $C_{21}H_{18}O_6$ (366.370): C, 68.85; H, 4.95. Found: C, 68.94; H, 4.93.

1,6-Anhydro-2-*O*-benzyl-3-*O*-fluoren-9-yl-β-D-galactopyranose (59). Compound **50** (0.10 g, 0.24 mmol) was converted to **59** as described in the synthesis of **52**. Column chromatography of the crude product (eluant G) gave **59** (0.09 g, 92%); $[\alpha]_D$ -48.2° (*c* 0.39); R_f 0.36 (solvent G).

Anal. Calcd for $C_{26}H_{24}O_5$ (416.473): C, 74.98; H, 5.81. Found: C, 75.21; H, 5.85.

1,6-Anhydro-2-*O*-benzyl-3-*O*-fluoren-9-yl-β-D-talopyranose (60). Compound **51** (0.12 g, 0.29 mmol) was hydrogenolysed as described in the synthesis of **52**. Column chromatography of the crude product (eluant F) gave **60** (0.10 g, 80%); $[\alpha]_D$ -28.9° (*c* 0.34); R_f 0.48 (solvent G).

Anal. Calcd for $C_{26}H_{24}O_5$ (416.473): C, 74.98; H, 5.81. Found: C, 74.73; H, 5.77.

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