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DESULFONYLOXYLATIONS OF SOME SECONDARY *p*-TOLUENESULFONATES OF GLYCOSIDES BY LITHIUM TRIETHYLBOROHYDRIDE; A HIGH-YIELDING ROUTE TO 2- AND 3-DEOXY SUGARS

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ABSTRACT

Lithium triethylborohydride (LTBH) reacts readily with *p*-toluenesulfonates of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**4**) to give deoxyglycosides in >90% yield. Thus, the 2,3-ditosylate (**1**) and the 3-monotosylate (**2**) thereof afford methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexopyranoside (**7**) in highly regio- and stereo-selective reactions that proceed *via* methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (**6**), and the 2-monotosylate (**8**) of **4** gives the 3-deoxy-α-D-*arabino* isomer (**12**) of **7** *via* the corresponding 2,3-anhydro-α-D-mannopyranoside **11**. In the series of the corresponding β anomers, the 3-monotosylate **14** and the 2-monotosylate **16** are similarly desulfonyloxylated, with equal ease, but furnish mixtures of regioisomeric deoxyglycosides, namely, the 3- and 2-deoxy-β-D-*ribo* derivatives **20** and **21**, and the 2- and 3-deoxy-β-D-*arabino* derivatives **22** and **23**, respectively. It could be shown that this difference is due to the failure of the intermediary, β-glycosidic epoxides **18** and **19** (the anomers of **6** and **11**) to obey the Fürst–Plattner rule in their reductive ring-opening with LTBH. The β-glycosidic 2,3-ditosylate **15** reacts less readily, and gives **20–23**, with **20** preponderating. The 2-*O*-methyl-3-*O*-tosyl-β-D-glucopyranoside **24** is partly desulfonylated and partly desulfonyloxylated, whereas its 3-*O*-methyl-2-*O*-tosyl isomer **27** undergoes desulfonylation exclusively. The reductions of **1**, **2**, and **8** by LTBH are compared with those previously effected by lithium aluminum hydride, which are slower, involve considerable desulfonylation, and afford lower yields of deoxyglycosides, with the main products differing from those obtained by the action of LTBH. Mechanistic differences associated with the two reductants are discussed.

INTRODUCTION

In a synthesis recently performed in this laboratory[1], lithium triethylborohydride[2] (Super Hydride ®, LTBH) proved to be a very efficient reagent for the reductive debromination of a bromodeoxy sugar. In concurrent work, we have examined the possible use of this reagent for the reduction of carbohydrate *p*-toluenesulfonates. The aim of the study was to discover whether it offered any advantages

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over lithium aluminum hydride (LAH), the more-familiar reductant whose action on sugar sulfonic esters has been widely utilized and extensively reviewed[3-5]. It is well known that LAH may cause either C–O fission (desulfonyloxylation) or S–O fission (desulfonylation), depending on the structure of the sulfonate. For primary sulfonates, the former type of cleavage normally prevails, whereas for secondary ones, the latter type is usually observed, although exceptions[6-14] have been noted. We have now determined that, for a number of secondary tosylates derived from methyl 4,6-*O*-benzylidene-α- and -β-D-glucopyranoside, the action of LTBH does not in every respect parallel that of LAH. Firstly, with LTBH, desulfonyloxylations were found to proceed at much higher rates than with LAH, leading in the majority of cases studied to deoxyglycosides in excellent yields, and accompanied by negligible proportions of undesirable side-products; and secondly, mechanistic differences cause the two reductants to give different patterns concerning the regio- and stereo-chemistry of the deoxyglycosides produced. Following their description, the results with LTBH will in subsequent paragraphs be compared with those previously obtained with LAH, and a few additional observations regarding the action of the latter reagent will be reported.

RESULTS AND DISCUSSION

Reactions with lithium triethylborohydride

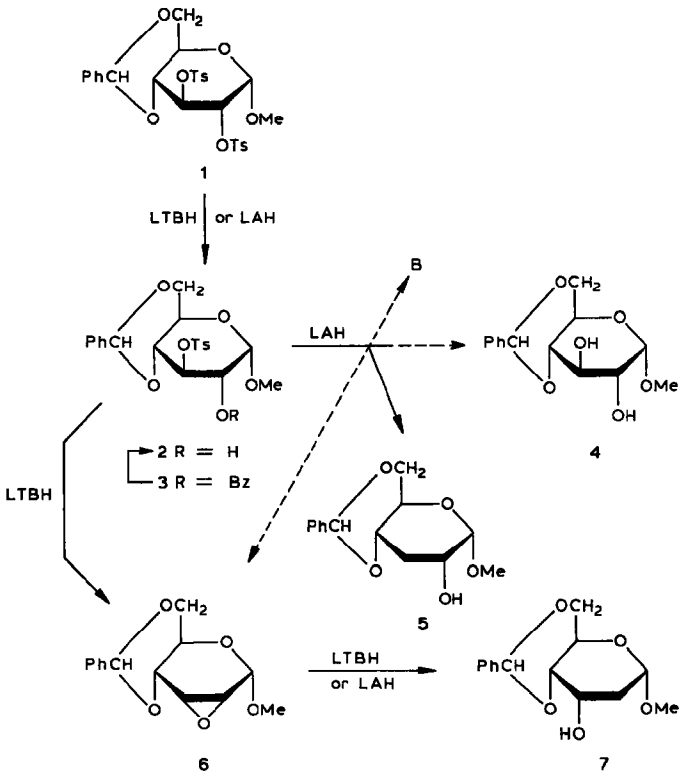
Methyl 4,6-*O*-benzylidene-2,3-di-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside (**1**) was treated with LTBH (6 mol. equiv.) in boiling oxolane for 30 min, to give a 96% yield of methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexopyranoside (**7**), together with mere traces of the parent diol **4**. The reaction was presumed to proceed *via* the 3-monotosylate **2** and the α-D-*allo* 2,3-epoxide **6**, and the use of either of these intermediates as the starting compound for the process was, therefore, expected to give **7** in similar yields. When **2** was treated at *room temperature* with only 3 mol. equiv. of LTBH, traces of **6** and **7** were revealed by t.l.c. to have arisen after 45 min, but most of compound **2** remained unaffected. When the mixture was then boiled under reflux for 30 min, all of the **2** was converted into **6**, but little, if any, additional **7** was formed, and the chromatographic picture remained unchanged during a further 30 min of heating. Evidently, the proportion of reductant provided in this instance had been insufficient for complete reduction; and indeed, the introduction of an additional 1.5 mol. equiv. of LTBH at this point caused complete conversion of **6** into **7** within 15 min. The product was obtained crystalline in 92.5% yield. An experiment starting with crystalline **6** also gave **7**, in 96% yield.

The 2-monotosylate **8** reacted with LTBH (4.3 mol. equiv.) in boiling oxolane to furnish, after 20 min, the 3-deoxy-α-D-*arabino* glycoside **12**, accompanied by a small proportion of the diol **4**, isolated in yields of 90 and 4.6%. An experiment performed at room temperature, and with only 3.3 mol. equiv. of hydride present, demonstrated that the reaction took its course *via* the α-D-*manno* epoxide **11**, which was obtained crystalline (yield, 12%) after a reaction time of 24 h, along with **12**

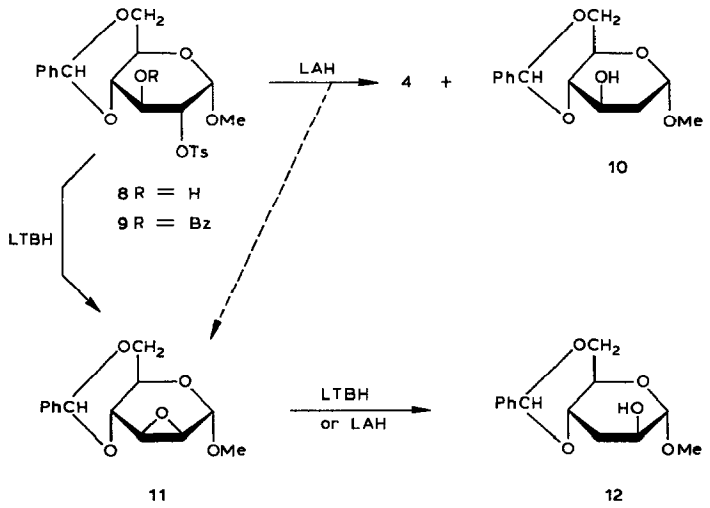
(82%) and **4** (3.8%). A reduction experiment that started with **11** likewise afforded a high yield of **12**.

For analogous studies in the β-glycosidic series, the tosylates **14**, **15**, and **16** were prepared from methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**13**). An improvement was introduced in the somewhat laborious method for obtaining the monotosylates **14** and **16** by the rather non-selective, partial tosylation[15,16] of **13**. It consisted of converting the 2-monotosylate **16** into its 3-acetate **17**, which is more readily separable from the ditosylate **15** that is unavoidably present and difficult to remove by chromatography alone. For the regeneration of **16** from its acetate, it was considered desirable (although, perhaps, not absolutely necessary) to avoid basic conditions; a high-yielding (94%) alternative was therefore adopted, involving acid-catalyzed methanolysis of the acetic ester group (and the benzylidene acetal), followed by re-acetalation of the glycoside with α,α-dimethoxytoluene.

The 3- and 2-monotosylates **14** and **16** were reduced by LTBH as readily as their anomers, both furnishing crystalline deoxyglycosides in ~95% yield. However, in contrast to the α series, each of the tosylates gave two, positionally isomeric, products in substantial proportions. Thus, **14** yielded 59% of the 3-deoxy-β-D-*ribo*-

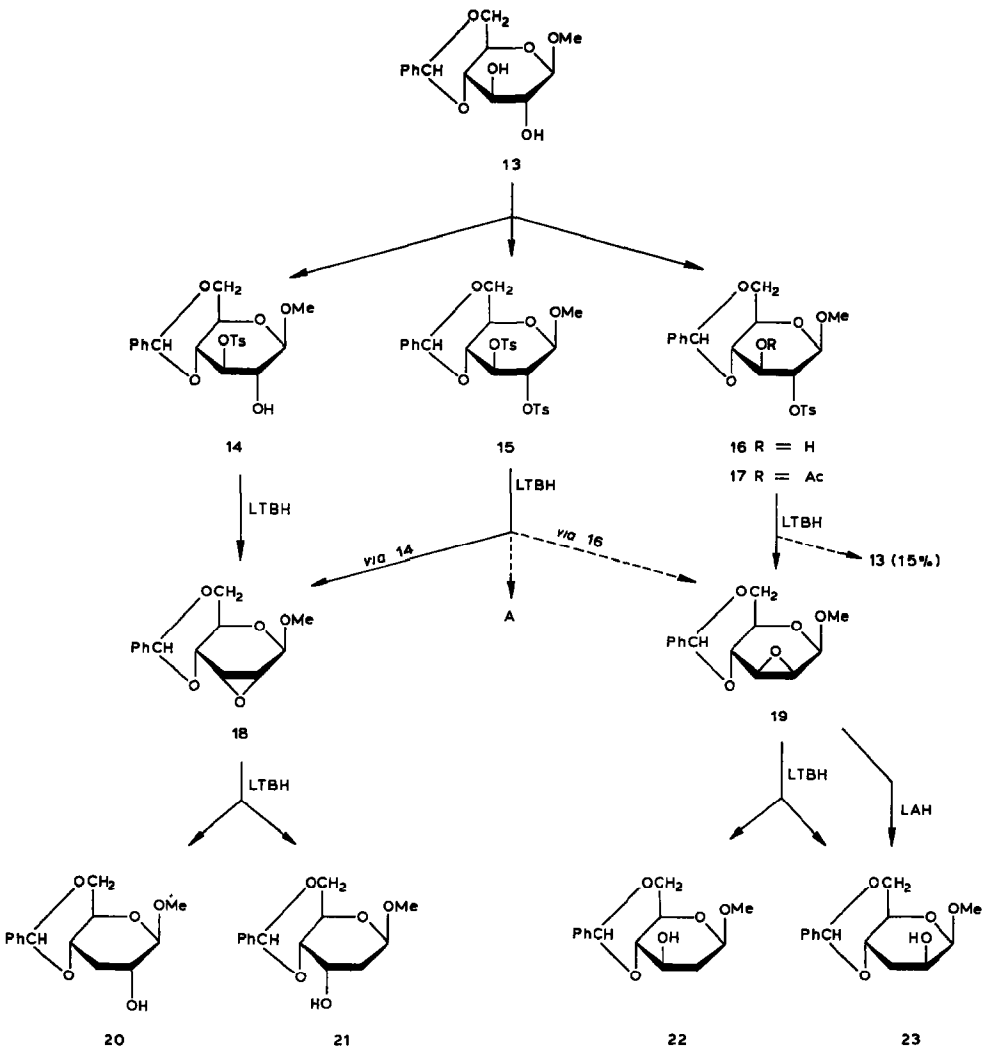


Bz = PhCO
Ph = C_6H_5
Ts = $SO_2C_6H_4Me$-*p*



hexopyranoside **20** and 36% of the 2-deoxy-β-D-*ribo* isomer **21**; and **16** produced nearly equal proportions of the 2-deoxy-β-D-*arabino* (**22**) and 3-deoxy-β-D-*arabino* (**23**) isomers. It appeared reasonable to assume that these reactions would involve the epoxides **18** and **19**, respectively, as intermediates, in analogy to the α series, and the concomitant expectation was that the resulting products of reduction should be **21** and **23**, *i.e.*, the products of diaxial ring-opening according to the Fürst–Plattner rule[17]. For an explanation of the origin of the unexpected isomers **20** and **22**, a direct displacement of the tosyloxy group by hydride ion was, at first sight, perceived as a possibility. (For at least one different tosylate, LTBH was, in fact, found capable of such a substitution; see later.) Nevertheless, diequatorial opening of the oxirane rings in violation of the rule had to be considered as an alternative. Although we are not aware of precedents for abnormal *hydride* reductions of the conformationally quite rigid molecules **6**, **11**, **18**, and **19**, Lemieux and co-workers[18] had found that **18** does behave abnormally in ring opening with sodium iodide, giving at least 20% of the unexpected (diequatorial) iodohydrin, whereas **6**, **11**, and their α-D-*gulo* and β-D-*talo* isomers obey the rule strictly, affording almost quantitative yields of the diaxial iodohydrins. Consequently, we performed an LTBH reduction of **18**, and found its exceptional behavior confirmed. The deviation from the rule was even more striking, for the glycosides **20** and **21** were isolated in yields of 68 and 30%, respectively. Comparison of these yields with the very similar ones (59 and 36%) obtained from the reaction of **14** suggested that desulfonyloxylation of the latter proceeds mainly through **18**.

We then convinced ourselves that the epoxide **19** is reduced by LTBH in a similar, abnormal way. It reacted at room temperature to give, within 10 min, a mixture of approximately equal parts of **22** and **23**. Although this result satisfactorily explained the course of reduction of the 2-tosylate **16**, there remained an element of surprise, because **19** had previously been reported[15] to furnish **23** on reduction with LAH, in what appeared to be a straightforward way; the product was isolated in



good yield, and no mention was made of a possible, simultaneous formation of then-unknown **22**. In order to determine whether **22**, whose physical constants and mobility in t.l.c. are now known to differ little from those of **23**, had escaped detection in the earlier work[15], we examined the product of LAH reduction of **19** by ^{1}H-n.m.r. and i.r. spectroscopy, but found no trace of it; pure **23** was isolated in 75% yield. The differing regioselectivities of the two hydride reagents will receive further comment later.

In contrast to the facile transformation that occurred with the α-glycoside **1**, reduction of the β-glycosidic 2,3-ditosylate **15** proceeded relatively sluggishly, requiring overnight heating for completion, and it gave several products. The principal products isolated were the deoxyglycosides **20** (57%) and **21** (11%), which, in view

TABLE I

^{1}H-CHEMICAL SHIFTS (δ) OF CHARACTERISTIC SIGNALS FOR TOSYLATES AND DEOXY DERIVATIVES OF METHYL 4,6-*O*-BENZYLIDENE-α- AND -β-D-GLUCOPYRANOSIDE IN $CDCl_3$ SOLUTION[a]

Compound	Ph-*CH*	*OMe*	*TsO-2*		*TsO-3*		*Ph*[b]
			Aryl[c]	C-*Me*	*Aryl*[c]	C-*Me*	
1	5.22	3.32	7.79, 7.71; 7.30, 7.22	2.38	7.59, 7.51; 6.90, 6.82	2.20	7.26s
2	5.34	3.47			7.73, 7.65; 7.01, 6.93	2.30	7.28m
3	5.40	3.40			7.65, 7.57; 6.85, 6.77	2.19	7.35m
8	5.47	3.33	7.87, 7.79; 7.36, 7.28	2.43			7.36m
9	5.46	3.47	7.63, 7.55; 6.99, 6.91	2.22			7.30m
14	5.34	3.57			7.75, 7.67; 7.02, 6.94	2.30	7.32m
15	5.26	3.06	7.83, 7.75; (7.28)[d], 7.20	2.38	7.71, 7.63; 6.94, 6.86	2.22	7.29s
16	5.50	3.29	7.86, 7.78; (7.34)[d], 7.26	2.45			7.36m
17	5.46	3.29	7.78, 7.70; (7.32)[d], 7.24	2.44			7.33m
24	5.36	3.53, 3.39			7.75, 7.67; 7.05, 6.97	2.29	7.35s
27	5.51	3.35, 3.35	7.86, 7.78; (7.33)[d], 7.25	2.43			7.36m
A[e]	5.43	3.26	7.83, 7.69; (7.36)[d], 7.22	2.40			7.36m
B[f]	5.62, 5.52, 5.42	3.38, 3.33, 3.27	7.82, 7.74				7.3m
5	5.465[g]	3.435[g]					7.35m
7	5.59[h]	3.39[h]					7.36m
10	5.52[i]	3.31[i]					7.39m
12	5.54[i]	3.38					7.36m
20	5.51[i]	3.56					7.36m
21	5.555[h]	3.48[h]					7.38m
22	5.51[j]	3.48[j]					7.38m
23	5.52[h]	3.53[h]					7.36m

[a]For further, distinctive signals, see the Experimental section and the literature cited therein. [b]In the case of a multiplet, the value refers to the strongest line. [c]Line positions for the AB system of the *p*-tolyl group are given. [d]Calculated value for line obscured by Ph signal. [e]From 60-MHz spectrum. [f]Mixture of by-products; resonances indicated are additional to those for admixed **1**. [g]Average from 10 spectra; $\pm$0.015. [h]Average from 6 spectra; $\pm$0.01. [i]Average from 4 spectra; $\pm$0.02. [j]Average from 10 spectra; $\pm$0.01.

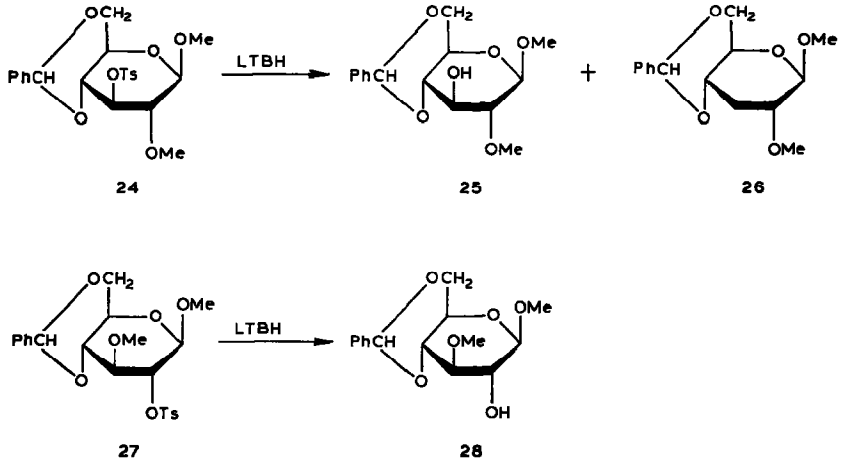
of the foregoing discussion, may be assumed to have arisen* largely *via* **14** and, thence, **18**. A fraction of mixed deoxyglycosides (~13%, free from tosyl derivatives) was judged by its n.m.r. spectrum to consist of about equal parts of the 2- and 3-deoxy-β-D-*arabino* isomers **22** and **23**. In addition, several fast-moving, minor by-products were formed. One of these (designated A) was isolated, although impure, in an amount sufficient for a preliminary examination by ^{1}H-n.m.r. spectroscopy,

*There is an analogy for the somewhat lower reactivity[17] of **15**, as compared to **1**. The former had been found[9] to be unreactive under conditions of alkaline hydrolysis that cause the conversion[19–21] of **1** into the oxirane **6**. However, a high-yielding conversion of **15** into **18** was later achieved[18] by use of slightly modified conditions.

which revealed it to be a benzylidenated methyl glycoside bearing a tosyloxy group at C-2, yet differing from **16**. (See Table I for characteristic signals useful for the differentiation of deoxyglycosides and tosylates dealt with in this article. Chemical-shift differences in the resonances both for the aromatic and the methyl protons of tosyl groups, and shielding effects noticed and discussed[16] for benzylidenic methine and anomeric methoxyl signals, may serve to identify the location of tosyl groups.) The byproduct A showed resonances in the region (δ 1–2) associated with endocyclic methylene groups; conceivably, it was the 3-deoxy analog of **16** (*i.e.*, the tosylate of **20**)*.

These results indicated that LTBH reacts with **15** along at least two, and possibly three, different pathways. Detosylation at O-2 initiates what appears to be the main course of reaction, which leads to **20** and **21** through an intermediary *allo* epoxide (**18**), and thus parallels the exclusive path followed for **1**, the non-specific, epoxide-opening aside. Unlike with **1**, however, detosylation at O-3 evidently competes to a noticeable, if small, extent, as must be concluded from the formation of **22** and **23**, which requires the intermediacy of the 2-tosylate **16** and the *manno* epoxide **19**. Furthermore, if the by-product A does indeed possess the structure of a 3-deoxy-glycoside 2-tosylate, as tentatively suggested, a third mode of reaction would be indicated for **15**, namely, direct desulfonyloxylation at C-3 without the intervention of an epoxide; most of the resultant product (A) would subsequently suffer detosylation to give **20**, which would account for a ratio of **20**:**21** greater than that produced in the reduction of **18**.

The ability of LTBH to cause such direct desulfonyloxylation was demonstrated with methyl 4,6-*O*-benzylidene-2-*O*-methyl-3-*O*-*p*-tolylsulfonyl-β-D-glucopyranoside



*Hedgley *et al.*[9] obtained a 38% yield of **20** on treatment of **15** with LAH in boiling oxolane, and reported no other products. In boiling 1,4-dioxane, the yield was 22%, and methyl 4,6-*O*-benzylidene-2,3-dideoxy-β-D-*erythro*-hexopyranoside was formed as a second product.

TABLE II

PRODUCTS OBTAINED FROM SOME GLYCOSIDE TOSYLATES BY REACTION WITH LITHIUM ALUMINUM HYDRIDE

Starting compound	*LAH (mol. equiv.)*	*Reaction time (h)*	*Isolated products (%)*									*References*[a]
			1	**2**	**8**	**4**	**5**	**7**	**10**	*Others*	*~Total*	
1	2.5	18	1.9[b]	7.1		19.5	44				91	11
	4	18	3.2[c]	6.8		29.1	43.6				90	11
	5.6	40	6.4[d]			15	[~46	~7.5	~7.5][e]		82.5	12
	5.6	3.5	[f]	[f]	3.7		[f]					12
	3.8	26	13.3	16.9		12.8	[~36	~9][g]		~12[h]	100	*
2	2.3	18		10.9[i]		30.1	30.3				71	11
	4.3	20				15		71[j]			86	12
	7.7	8		tr.		25		35[j]			60	*
3	4.9	20		3.7		6.3	[~68	~5][k]			83	12
	7.9	9		27.5		12	[~39	~12][k]			90.5	*
8	3.2	18			tr.	50			9		59	11
	2.3	18			6	54			1.6[l]	1.6[m]	75	11
	7.7	19				76.5			19	tr.[n]	95.5	*
9	4.7	20				54			29		83	12

[a]An asterisk refers to this paper. [b]Plus a fraction (18.3%) of **1** containing small proportions of four other products (t.l.c.). [c]Plus a fraction (7.3%) consisting of **1**, **2**, **8**, and traces (tr.) of **5** and **10** (t.l.c.). [d]Mixed with an unidentified substance (B?; see text). [e]Mixture (61%), with component ratio determined by n.m.r.; only part of the **5** was isolated. [f]Detected by t.l.c., but not isolated. [g]Mixture (45.1%), with component ratio determined by n.m.r. [h]A mixture (~2:1, by n.m.r.) of by-products B and **1**. [i]Mixture of **2**, **5**, and **6**. [j]Mixture of **5** (major) and **7** (minor). [k]Ratio in mixture determined by n.m.r. [l]Plus a mixture (11.5%) of **8** and **10**. [m]Compound **11**. [n]Compound **12**.

(**24**). It gave the products of O–S fission (**25**) and C–O fission (**26**) in yields of 58 and 35%, respectively. Nevertheless, O–S fission was the favored event, and it could be expected to predominate even more strongly in the case of the isomeric, 3-methyl ether 2-tosylate **27**. This was borne out when **27** was found to give solely the alcohol **28**, isolated in 95% yield. The reactions of the methyl ethers **24** and **27** were both rather slow, requiring 1 day at 67° for completion. On account of this slowness, it may be concluded that a direct desulfonyloxylation, such as occurs with **24**, makes no significant contribution to the yield of **20** produced in the fast reduction of the monotosylate **14** (that seems wholly epoxide-mediated), although it may play an appreciable role in the relatively slow transformations of **15**. The non-occurrence of desulfonyloxylation for **27** reinforces the conclusion that **16** yielded **22** by way of abnormal cleavage of the intermediary **19**, and not by direct substitution.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-α-D-glucofuranose reacted with LTBH exclusively by O–S fission, as it did[9] with LAH.

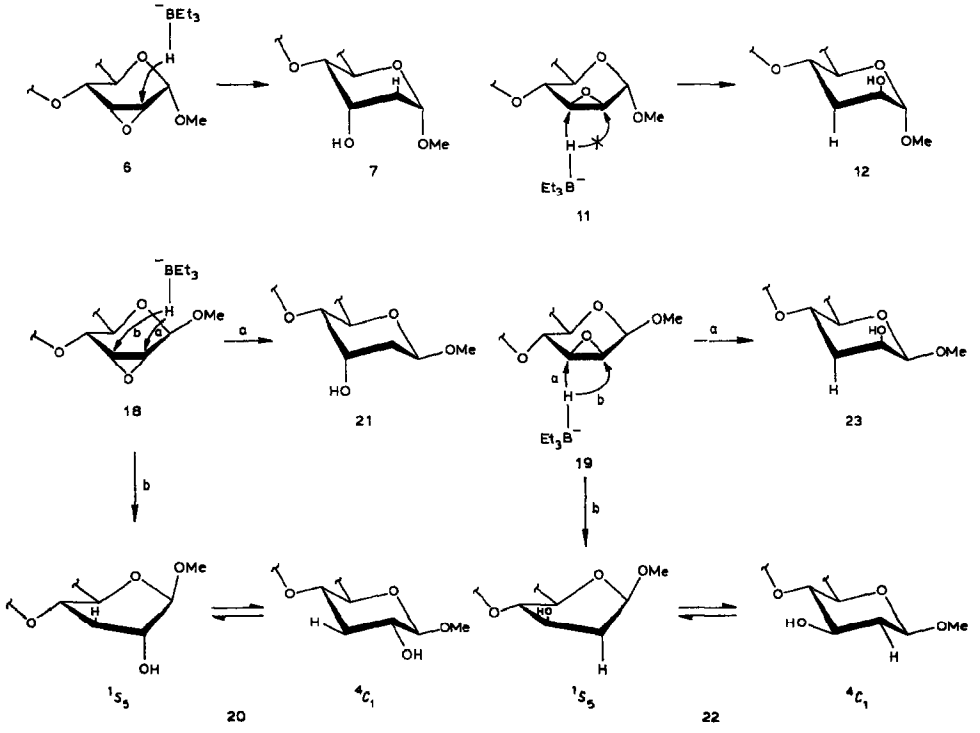
Reactions with lithium aluminum hydride

In sharp contrast to the aforedescribed, facile reduction of the ditosylate **1** with LTBH, to give almost quantitatively the 2-deoxyglycoside **7**, reaction of **1** with LAH in boiling oxolane for 16 h, first performed by Vis and Karrer[6], was claimed to afford a 66% yield of the 3-deoxyglycoside **5**; no other products, except for a small amount of the diol **4**, were detected at the time. The formation of **5** was difficult to explain by a mechanism involving a 2,3-anhydroglycoside intermediate, as both the α-D-*allo* (**6**) and the α-D-*manno* (**11**) epoxide had been shown[22] to give, on reduction with LAH, not **5** but the deoxyglycosides **7** and **12**, respectively. The matter was reinvestigated in detail by Jarý[11] and Umezawa[12] and their co-workers, who employed chromatography[11,12] and ^{1}H-n.m.r. spectroscopy[12] for the isolation and identification of products, and who also included in their studies the monotosylates **2** and **8**, and some related compounds. The chemistry proved rather more complicated than had previously been presumed. Table II shows the pertinent results of the Czechoslovak and Japanese workers, together with those of our own experiments that were performed for confirmation. Considering the variations in such parameters as reaction times, molar excesses of reductant used, and total percentages of products accounted for after chromatographic processing, the results obtained by the three groups are, in the main, in good harmony.

In **1**, LAH first causes detosylation at O-2 to give **2**, thus behaving qualitatively like LTBH, or like sodium methoxide, whose strong tendency to cause hydrolytic cleavage of the 2-*O*-tosyl group in **1** is well established[19–21]. However, from this point onward, the principal actions of the two reductants differ. The formation, by LAH, of the main product (**5**) from **2** (or from **3**, following debenzoylation) has been explained[11,12] in terms of desulfonyloxylation at C-3 by an intramolecular transfer of hydride ion from an alkoxyaluminum hydride complex ($R\text{-}O\text{-}AlH_3^-$) that incorporates O-2. (Such complexation evidently lessens the propensity of the oxygen atom to engage in an epoxide-forming displacement.) Similarly, the moderate

proportion of the 2-tosylate **8**, which escapes initial detosylation to **4**, reacts through a C-3-alkoxyaluminum hydride complex, to give the 2-deoxyglycoside **10**. This mechanism, proposed earlier[10] for a similar desulfonyloxylation, was supported by studies[11,12] on secondary tosylates lacking a free, or potentially-free, adjacent *trans*-hydroxyl group, and analogies can be cited for some other LAH reductions in the carbohydrate field[23a-d] and elsewhere[23e,f]. However, complexation at O-2 does not completely forestall formation of the epoxide **6**, as is seen from the fact that **7** (which requires **6** as a precursor) is a minor, although by no means negligible, product in the reactions of **1**, **2**, and **3** (see Table II).

Contrary to the situation with LAH, an internal-transfer mechanism cannot operate for the monovalent hydride, LTBH, so that in its presence, **2** and **8** are freely transformed into the corresponding oxiranes, wherefrom the deoxyglycosides **7** and **12** arise as single products. There are, in these cases, no impediments to the approach of the reductant that is required for the favored, diaxial ring-opening (see Scheme 1, **6**→**7** and **11**→**12**). In the *β*-glycoside **18**, on the other hand, axial approach to C-2 involves a transition state that seems sufficiently disfavored, for polar reasons, to allow for predominance of the alternative attack leading to **20**. For **19**, the "normal" approach (to C-3) is *cis* to O-4, which may imply a certain degree of hindrance, so that the "abnormal", but unhindered, approach to C-2 becomes competitive. This



Scheme 1

alternative venue is unavailable for **11**, as it is effectively blocked by the adjacent, quasiaxial methoxyl group (see Scheme 1). The very factor that may be responsible for the lack of regioselectivity in the reaction of **19** with LTBH, namely, the orientation of O-4, might well contribute to the regiospecificity apparently prevailing in its reaction with LAH. Thus, prior coordination[23d] of aluminum hydride with O-4 could be of significance in this case.

One point in which our findings differ from those of Umezawa *et al.*[12] concerns the formation of a small proportion (~7.5%) of **10** in the reaction of **1**, presumed to have arisen following a partial detosylation to **8**, with the latter being isolable after a short reaction-time (see Table II, 3rd and 4th entries). We did not detect any **10** among the products from **1** (see Table II, 5th entry), although this deoxyglycoside is readily distinguishable from **5** and **7** in n.m.r. spectra (see Table I)*. Given the aforementioned, superior reactivity exhibited by the α-glycoside **1** at O-2, in fission by alkali or LTBH, we consider that, for this compound, a noticeable, competing detosylation at O-3 would be unlikely, although a somewhat lesser selectivity exists for its β anomer.

Furthermore, the reaction mixture produced from **1** showed in t.l.c. a spot, slightly less mobile than that of unconsumed **1**, that had been ascribed to an unidentified substance[12]. Noticing this spot, too, we found it conspicuous by an olive color (fading with time to brownish) that was seen after application of a sulfuric acid spray. The material giving this spot (designated B) was obtained by column chromatography as an inhomogeneous syrup that contained, in addition to some **1**, three spectroscopically discernible components in roughly comparable proportions. They appeared to be benzylidenated glycoside monotosylates, as judged by the presence, in the ^{1}H-n.m.r. spectrum, of the appropriate aromatic signals, 3 benzylidenic methine singlets, 3 methoxyl singlets, and 3 *C*-Me (tosyl) singlets, in addition to the signals attributable to admixed **1** (see Table I). Compounds **2** and **8** could be excluded on both spectroscopic and chromatographic grounds, and, as there were no resonances for methylene groups in the high-field region, saturated deoxyglycoside tosylates could also be ruled out. There were, however, three small (presumably one-proton) singlets at δ 6.98, 7.02, and 7.11. which were possibly due to alkenic protons. It is conceivable that these by-products were unsaturated species originating from dehydrotosyloxylations akin to those effected[24] by soda-lime in 4,6-*O*-benzylidene-2(or 3)-deoxy-3(or 2)-*O*-tosylhexopyranosides.

It has been stated that LAH reduction of **8** or **9** gives **10** as the sole deoxy glycoside[11,12], and we, too, could isolate only **10**. However, t.l.c. of the crude product clearly indicated the presence of a very small proportion of a substance which, we assume, was the isomer **12**, and for one fraction of processed mother liquors, n.m.r.

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*We did observe **10** among the products obtained from a sample of **1** that was contaminated by **8**. Originating from incomplete tosylation of **4**, the contaminant was still present in recrystallized **1**. The two compounds are difficult to distinguish by melting points or t.l.c., and, in our experience, purity can only be ensured through examination of their n.m.r. spectra.

signals tentatively assignable to it were noticed. Its occurrence would be in harmony with the isolation[11], in 1.6% yield, of its epoxide precursor[22] **11**, under conditions of incomplete reduction of **8**. Although these observations imply that LAH does not reduce **8** exclusively by the internal-transfer mechanism, it doubtless exhibits a high tendency so to operate.

EXPERIMENTAL

General methods. — Oxolane refers to a reagent-grade product that was dried, immediately before use, by refluxing it, under nitrogen, over potassium metal in the presence of benzophenone. Lithium triethylborohydride (LTBH) was purchased from Aldrich Chemical Co. as an M solution in oxolane. Melting points were determined in capillaries in an electrically heated, aluminum-block apparatus (Gallenkamp). Optical rotations were measured at ~25° with a Perkin–Elmer 141 polarimeter, and refer to chloroform solutions, unless otherwise specified. Column chromatography was performed on Silica Gel 60 (E. Merck AG, Germany), and, for t.l.c., precoated plates of silica gel SIL-25 UV_{254} (Macherey-Nagel & Co., Germany) were used. Spots were made visible by spraying the plates with 5% sulfuric acid in ethanol, and heating them briefly on a hot plate. Unless otherwise indicated, the following solvent combinations (v/v) were used for chromatography: (*A*) 2:1 ethyl acetate–hexane, (*B*) the same solvents, but 1:1, (*C*) the same, but 1:2, (*D*) the same, but 1:3, (*E*) the same, but 1:4, (*F*) 1:2 ethyl acetate–petroleum ether (b.p. 30–60°), (*G*) the same, but 1:3, and (*H*) the same, but 1:4. Infrared spectra were recorded with a Unicam SP 1100 spectrometer and used routinely for confirmation of product identity. Standard, ^{1}H-n.m.r. spectra (100 MHz) were recorded for all of the starting glycosides, to ensure their purity, and for authentic samples of reaction products, where available, to facilitate identification. For the routine evaluation of chromatographic fractions, 60-MHz spectra obtained with a Varian EM 360A instrument were found entirely adequate.

Preparation of the starting sulfonic esters. — *A. Methyl 4,6-O-benzylidene-2,3-di-O-p-tolylsulfonyl-α-D-glucopyranoside* (**1**). Compound **1** was prepared[25] from methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**4**). The stout prisms, $[\alpha]_D$ +13.0° (*c* 3), melted at 154–155°, as reported[25], but a chromatographically purified sample had m.p. 159–160° and showed small differences in the fingerprint region of the i.r. spectrum (Nujol mull). The dimorphous form[25] (needles of m.p. 147–148°) was not encountered. The ^{1}H-n.m.r. data agreed with those reported[16] for the 6,6′-*d* compound; additional data ($CDCl_3$): δ 4.18 (dd, $J_{5,6e}$ 3.6, $J_{6a,6e}$ 9 Hz, H-6*e*), 3.58 (t, H-6*a*, $J_{5,6a}$ 9 Hz), and data in Table I.

B. Methyl 4,6-O-benzylidene-3-O-p-tolylsulfonyl-α-D-glucopyranoside (**2**) *and its benzoate* (**3**). The diol **4** was selectively benzoylated[26,27], to give its 2-monobenzoate, m.p. 169–170°. If the product was judged by its n.m.r. spectrum[12] to be not entirely pure, it was purified by l.c., using solvent *D*. The benzoate was *p*-toluenesulfonylated[28], to give **3**, m.p. 187.5°, $[\alpha]_D$ +89.8° (*c* 1); lit.[28] m.p. 188–189°, $[\alpha]_D$ +88.5°; ^{1}H-

n.m.r. data in $CDCl_3$: δ 8.09 and 7.45 (m, OBz), 5.40 (s, for *Ph*CH superposed on t for H-3), 5.2–5.1 (m, 2 H, H-1,2), 4.32 (dd, $J_{5,6e}$ 3.8, $J_{6a,6e}$ 9 Hz, H-6*e*), 3.97 (dt, H-5), 3.75 (t, $J_{5,6a} = J_{6a,6e} = 9$ Hz, H-6*a*), 3.71 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H-4), and data in Table I.

To generate **2**, a partial suspension of LAH (50 mg) in a small amount of ether was introduced, with swirling, into an ice-cold solution of **3** (600 mg) in oxolane (10 mL) and ether (20 mL). Inspection by t.l.c. (solvent *B*) showed that, although most of **3** (R_F 0.75) had reacted within 5 min, some of it still remained after 15 min. An additional 10 mg of LAH was added, and the mixture was processed after a further 5 min by pouring it into ice–water containing some sulfuric acid. The aqueous phase was extracted twice with ether and twice with ethyl acetate, and the combined organic phases were dried (K_2CO_3), and evaporated, to give crude **2** (R_F 0.40) as a dry, crystalline mass. Chromatography on silica gel (15 mL in a 15-cm column), using solvent *B* as eluant, removed traces of contaminants (**3** and **6**, R_F 0.75 and 0.5), and gave pure **2** (431 mg, 89%); m.p. 167°, $[\alpha]_D$ +33° (*c* 1); lit.[12] m.p. 165°, $[\alpha]_D$ +33° (for **2** prepared similarly, but in boiling oxolane) and [21] m.p. 164°, $[\alpha]_D$ +32.5° (for **2** obtained from **1**, in 17% yield, by partial, alkaline hydrolysis).

Alternatively, sodium methoxide (10 drops of a freshly-prepared, saturated solution in methanol) was added during 1 h to a chilled (−15°) solution of **3** (100 mg) in 1:1 methanol–chloroform (5 mL). The mixture was kept for 5 h at 0–2°; conversion into **2** was then complete, and only a trace of **6** was seen (t.l.c. with solvent *B*). De-ionization, and evaporation, of the solution gave **2** (79 mg, 98%; dried in high vacuum); m.p. 163–165°, unchanged after recrystallization from dichloromethane–petroleum ether. Similar methanolyses had given[12] 83 and[29] 52% yields. The i.r. spectrum was identical with that of **2** from the preceding procedure; ^{1}H-n.m.r. data in $CDCl_3$: δ 4.85 (t, $J_{2,3} = J_{3,4} = 9$ Hz, H-3), 4.84 (d, $J_{1,2}$ 3.5 Hz, H-1), 4.26 (dd, $J_{5,6e}$ 3.5, $J_{6a,6e}$ 9 Hz, H-6*e*), 4.0–3.5 (m, 4 H, H-2,4,5,6*a*), 2.66 (d, *J* 9.8 Hz, OH), and data in Table I.

*C. Methyl 4,6-*O*-benzylidene-2-*O*-p-tolylsulfonyl-α-*D*-glucopyranoside* (**8**) *and its benzoate* (**9**). Compound **8** was prepared from **4** by selective *p*-toluenesulfonylation[19,21,30]. Recrystallized first from 99% ethanol and then from ethyl acetate, it had m.p. 154–155° and $[\alpha]_D$ +62° (*c* 1.5); lit.[21] m.p. 155°, $[\alpha]_D$ +63.5°. (A modification melting[16] at 136–138° was not observed.) Crude **8** tends to contain some ditosylate **1**, which is not revealed by t.l.c. as it migrates at almost the same rate as **8**. However, it can be readily detected in the ^{1}H-n.m.r. spectrum. For effective retention of the contaminant in the mother liquor during recrystallization of **8**, it is important to allow the hot solution to cool slowly to room temperature, and to avoid refrigeration. For **8**, ^{1}H-n.m.r. data in $CDCl_3$: δ 4.82 (d, $J_{1,2}$ 3.5 Hz, H-1), 4.36 (dd, $J_{2,3}$ 9.3 Hz, H-2), 4.30–3.30 (m, 5 H, H-3,4,5,6,6′), 2.57 (d, *J* 2.5 Hz, OH), and data in Table I.

A sample of the benzoate **9** was desired for purposes of spectral comparison. It was obtained in 87% yield by customary *p*-toluenesulfonylation[28,30] of methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside, and showed m.p. 221–222°,

$[\alpha]_D$ +52.6° (*c* 1.1) after recrystallization from ethyl acetate–hexane; lit.[19] m.p. 212–213°, $[\alpha]_D$ +51.6°. The ^{1}H-n.m.r. data for a solution in $CDCl_3$ were in full agreement with those reported[31]; see Table I for selected signals. Additional data: δ 4.33 (dd, $J_{5,6e}$ 3.6, $J_{6a,6e}$ 9 Hz, H-6*e*), 4.01 (dt, H-5), 3.76 (t, $J_{5,6a}$ 9.5 Hz, H-6*a*), and 3.72 (t, $J_{3,4}$ 9.5, $J_{4,5}$ 9 Hz, H-4).

*D. Methyl 4,6-*O*-benzylidene-3-*O*-p-tolylsulfonyl-β-*D*-glucopyranoside* (**14**), *and methyl 4,6-*O*-benzylidene-2-*O*-p-tolylsulfonyl-β-*D*-glucopyranoside* (**16**) *and its 3-acetate* (**17**). Partial *p*-toluenesulfonylation of methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**13**) proceeds with less selectivity than for the α-anomeric diol **4**; invariably, substantial proportions of the ditosylate **15** are produced, together with small to moderate proportions of the monotosylates **14** and **16**, but the latter can nevertheless be isolated, although somewhat laboriously. The following modification of published procedures[15,16] proved fairly satisfactory. A solution of **13** (5.0 g) in dichloromethane (30 mL) and pyridine (20 mL) was stored in a refrigerator, and *p*-toluenesulfonyl chloride (7.0 g, 2 mol. equiv.) was added in several, small portions during the course of 7 days. Monitoring by t.l.c. (solvent *B*) indicated that, after 10 days, only a small amount of starting **13** (R_F <0.1) remained besides the tosylated products (R_F 0.3 and 0.5). Treatment of the mixture with crushed ice and water precipitated a solid product which, after thorough washing with water, followed by drying, was chromatographed on a column of silica gel (200 g) by use of solvent *E*, to give a mixture of **15** and **16** (R_F 0.48 in t.l.c. with solvent *B*; ratio 5.6:1, by n.m.r.), followed by chromatographically pure **14** (R_F 0.30; 1.64 g, 21.4%), and unchanged **13** (R_F < 0.1; 0.36 g, 7.2%).

Recrystallized from ethanol, the 3-tosylate **14** had m.p. 159.5–160°, $[\alpha]_D$ −78.5° and $[\alpha]_{546}$ −94.3° (*c* 2); lit.[16] m.p. 155–156°, $[\alpha]_D$ −81.4° and[15] m.p. 162–163°, $[\alpha]_{546}$ −86.5 ±5°. The ^{1}H-n.m.r. data ($CDCl_3$) agreed in essence with those reported[16], except that all resonances were found at slightly lower field (by 0.06–0.09 p.p.m.). The H-3 signal was at δ 4.75 (t, $J_{2,3} = J_{3,4} = 8.7$ Hz), and the H-6*e* signal, at 4.33 (dd, $J_{5,6e}$ 4.5, $J_{6a,6e}$ 10 Hz); see also, Table I.

Chromatographic separation of **15** and **16**, although reportedly possible[15,16], is rather difficult, and inconvenient on a large scale. It was much facilitated by first converting **16** into its acetate **17**. To this end, a mixture of the two esters (9.0 g, obtained from several experiments as just described, but not necessarily with exactly the same component ratio) was treated overnight at room temperature with acetic anhydride (5 mL) and pyridine (20 mL). Customary processing gave a material (10 g) which was chromatographed on a column of silica gel (275 g). Elution was started with 1:99 ethyl acetate–hexane, and the proportion of the former was gradually increased to 10%, at which point the acetate **17** began to emerge. After recrystallization from ethanol, the long needles of **17** (3.6 g) had m.p. 160–161°, $[\alpha]_D$ −39.3° and $[\alpha]_{546}$ −46.6° (*c* 0.65); lit.[15] m.p. 158–160°, $[\alpha]_{546}$ −41 ±2°; ^{1}H-n.m.r. data in $CDCl_3$: δ 5.39 (t, *J* 9 Hz, H-3), 4.59 (dd, $J_{1,2}$ 7.7, $J_{2,3}$ 9 Hz, H-2), 4.38 (d, *J* 7 Hz, H-1), 4.34 (dd, $J_{5,6e}$ 4.5, $J_{6a,6e}$ 10 Hz, H-6*e*), 3.9–3.4 (m, H-4,5,6*a*), 2.06 (s, 3 H, OAc), and data in Table I.

For regeneration of **16**, the acetate **17** (1.80 g) was stirred overnight in absolute methanol (40 mL) to which acetyl chloride (2 mL) had been added. T.l.c. with ethyl acetate indicated the eventual replacement of all of **17** (R_F ~0.5) by a slow-moving product (R_F ~0.3) that resulted from deacetylation and debenzylidenation. The mixture was stirred for 5 min with added α,α-dimethoxytoluene (2 mL) and then evaporated at 35°, to give a dark syrup. This was passed through a short column of silica gel by means of hexane to which were added increasing proportions (1–10%) of ethyl acetate. Compound **16** (1.55 g, 94%) crystallized from the chromatographic solvent as long needles, m.p. 122–122.5°, $[\alpha]_D$ −44.8° and $[\alpha]_{546}$ −54.4° (*c* 0.55); lit.[16] m.p. 122–123°, $[\alpha]_D$ −54.1°, and[15] m.p. 123–124°, $[\alpha]_{546}$ −51.5 ±2°. The ^{1}H-n.m.r. data for a solution in $CDCl_3$ were in accord with those given[16], except that all signals were found at somewhat lower field (by 0.08–0.1 p.p.m.); see also, Table I.

*E. Methyl 4,6-*O*-benzylidene-2,3-di-*O*-p-tolylsulfonyl-β-*D*-glucopyranoside* (**15**). Compound **15** was prepared by treatment of the diol **13** with *p*-toluenesulfonyl chloride (3 mol. equiv.) in pyridine[32,33]. For an improved yield (80%) and a shortened reaction-time (3–4 days at room temperature), we found it useful to add to the reaction mixture a small amount (15 mg per g of **13**) of 4-(dimethylamino)pyridine as a catalyst[34]. Recrystallized from 99% ethanol and then from ethyl acetate (without refrigerating the solution), **15** had m.p. 187–188°, $[\alpha]_D$ −60.0° (*c* 1.2); lit.[33] m.p. 182–183°, $[\alpha]_D$ −62.8° and[16] −60.7°. The lower-melting, unstable crystal modification[16,32,33] was not encountered. The ^{1}H-n.m.r. spectrum was essentially in accord with the reported[16] data; H-6*e* resonated at δ 4.25 (dd, $J_{5,6e}$ 4, $J_{6a,6e}$ 9.5 Hz), and H-4, 5, and 6*a* resonated at δ 3.75–3.25 (m, 3 H); see also, Table I.

*F. Methyl 4,6-*O*-benzylidene-2-*O*-methyl-3-*O*-p-tolylsulfonyl-β-*D*-glucopyranoside* (**24**). Compound **24** was prepared from **14** by Kuhn methylation[35], with the procedure following a recent example[36]. A single methylation for 3 h afforded crystalline **24** in 95% yield, without the need for chromatographic purification. The long prisms obtained from 99% ethanol had m.p. 139–139.5°, $[\alpha]_D$ −84.3° (*c* 2); lit.[37] m.p. 135–136°; ^{1}H-n.m.r. data ($CDCl_3$): δ 4.80 (t, $J_{2,3} = J_{3,4}$ = 9 Hz, H-3), 4.40–4.25 (m, 2 H), 3.80–3.05 (m, 4 H, overlapping two 3-proton singlets for 2 OMe groups), and data in Table I.

*G. Methyl 4,6-*O*-benzylidene-3-*O*-methyl-2-*O*-p-tolylsulfonyl-β-*D*-glucopyranoside* (**27**). A mixture of **15** and **16** (see section D) was methylated (compare section F), and the fast-moving **27** thereby formed was separated from **15** by column chromatography on silica gel (solvent *H*). It crystallized from ethanol as beautiful prisms, m.p. 137.5–138°, $[\alpha]_D$ −32.7° (*c* 3.3); lit.[38a] m.p. 125–126°, $[\alpha]_D$ −34.1 ±3° (solvent not given); ^{1}H-n.m.r. data ($CDCl_3$): δ 4.60–4.45 (m, 3 H) and 3.9–3.4 (m, 4 H), and data in Table I.

Reductions with lithium triethylborohydride (LTBH). — A. General procedure, exemplified by the reaction of **1**. To a solution of **1** (3.0 g, 5.08 mmol) in oxolane (30 mL) was added LTBH (30 mL, M solution in oxolane), and the mixture was boiled under reflux in a nitrogen atmosphere. After 30 min, when t.l.c. (solvent *B*)

indicated the complete replacement of **1** (R_F 0.75) by a product (R_F 0.4). the excess of hydride was decomposed by careful addition of water (200 mL) to the cooled mixture, and most of the oxolane was removed by evaporation. The remaining, largely aqueous phase and semisolid residue were extracted three times with dichloromethane, and the extract was washed with a small amount of water (with the addition of sodium or ammonium chloride, if necessary, to destabilize persistent emulsions), dried ($MgSO_4$), and evaporated, to give a white, solid product. As t.l.c. revealed a minor contamination by **4** (R_F 0.1), the material was passed through a short column of silica gel by means of solvent *F*, whereby **4** was completely retained, and pure **7** (1.30 g, 96%) was obtained. Recrystallized from ethyl acetate–petroleum ether, it was isomerically pure according to its n.m.r. spectrum, and had m.p. 130–131°, $[\alpha]_D$ +141.0° (*c* 2.2), in good agreement with **7** prepared from **2** and **6** (see the following sections); lit.[12] m.p. 129–131°, $[\alpha]_D$ +140°, and[39] m.p. 125–126°, $[\alpha]_D$ +140.3°; ^{1}H-n.m.r. data ($CDCl_3$): δ 7.6–7.2 (m, 5 H, Ph), 5.60 (s, *Ph*CH), 4.77 (dd, J ~1.3 and 3.7 Hz, H-1), 4.40–4.05 and 3.90–3.50 (m, 3 and 2 H, for H-3,4,5,6, and 6′), 3.39 (s, 3 H, OMe), 3.02 (d, J 6.5 Hz, exchangeable, OH), 2.19 (ddd, $J_{1,2e}$ 1.3, $J_{2e,3}$ 3.2, $J_{2e,2a}$ 15.0 Hz, H-2*e*), and 1.95 (dt, $J_{1,2a} = J_{2a,3}$ = 3.6, $J_{2a,2e}$ 15.0 Hz, H-2*a*). The J values agreed well with those measured[39] for **7** in C_6D_6.

A sample of **7** was acetylated with acetic anhydride in pyridine. The ^{1}H-n.m.r. data for the *acetate* in $CDCl_3$ were: δ 7.55–7.25 (m, 5 H, Ph), 5.58 (s, *Ph*CH), 4.27 (q, $J_{2a,3} = J_{2e,3} = J_{3,4}$ = 3 Hz, H-3), 4.71 (dd, J ~1 and 4 Hz, H-1), 4.45–4.0 (m, 2 H, H-5,6*e*), 3.71 (t, $J_{5,6a} = J_{6a,6e}$ = 12 Hz, H-6*a*), 3.67 (dd, $J_{3,4}$ 3, $J_{4,5}$ 9.2 Hz, H-4), 3.37 (s, 3 H, OMe), 2.30 (ddd, $J_{1,2e}$ 1, $J_{2e,3}$ 3, $J_{2a,2e}$ 15 Hz, H-2*e*), 2.12 (s, 3 H, OAc), and 1.97 (center of m for H-2*a*, partly obscured by OAc signal).

A sample of **7** was converted into its *tosylate*[40]; ^{1}H-n.m.r. data ($CDCl_3$): δ 7.78, 7.70, 7.08, and 7.00 (lines of AB quartet, 4 H, Ts), 7.34 (s, 5 H, Ph), 5.45 (s, *Ph*CH), 4.85 (q, $J_{2a,3} = J_{2e,3} = J_{3,4}$ = 3 Hz, H-3), 4.73 (dd, J ~0.8 and 4.5 Hz, H-1), 4.4–4.15 (m, 2 H, H-5,6*e*), 3.63 (t, $J_{5,6a} = J_{6a,6e}$ = 12 Hz, H-6*a*), 3.56 (dd, $J_{3,4}$ 3, $J_{4,5}$ 9 Hz, H-4), 3.37 (s, 3 H, OMe), 2.45 (ddd, $J_{1,2e}$ 0.8, $J_{2e,3}$ 3, $J_{2a,2e}$ 15 Hz, H-2*e*), 2.32 (s, 3 H, *C*-Me), and 2.02 (ddd, J 3, 4.5, and 15 Hz, H-2*a*).

B. Reaction of **2**. The reaction of **2** (140 mg, 0.32 mmol) with LTBH solution (1.0 mL) in oxolane (5 mL) was initially monitored at room temperature (t.l.c. with solvent *A*). Only traces of **6** (R_F 0.66) and **7** (R_F 0.55) were seen, besides unchanged **2** (R_F 0.61), after 45 min. When the mixture was then boiled under reflux, all of **2** disappeared within 30 min, and **6** appeared to be the main product, with little additional **7** to be seen. There was no change in t.l.c. after continued refluxing for 30 min, but, upon addition of further LTBH (0.5 mL), all of the **6** was converted into **7** within 15 min. Processing gave a colorless oil, homogeneous in t.l.c. Crystallization occurred spontaneously, and **7** (79 mg, 92.5%) was isolated after trituration with a small amount of ether; m.p. 128–129°, $[\alpha]_D$ +139.8° (*c* 2.1).

C. Reaction of **6**. The epoxide[25] **6** (300 mg) in oxolane (3 mL) was allowed to react with LTBH (3 mL) for 30 min at room temperature, affording **7** (290 mg, 96%),

m.p. 130°, $[\alpha]_D$ +141.7° (*c* 1.2). With LAH, the same conversion required prolonged heating at the reflux temperature[22,41].

D. Reaction of **8**. Compound **8** (400 mg, 0.92 mmol) and LTBH (4 mL, 4.3 mol. equiv.) in oxolane (3 mL) were boiled under reflux for 30 min. T.l.c. with solvent *B* showed that all of **8** was consumed after 20 min. The crude product obtained after processing contained a small amount of diol **4**, and was, therefore, purified by passage through a short column of silica gel. Elution was started with 1:10 ethyl acetate–petroleum ether, and continued with increasing proportions of ethyl acetate added to the eluant. There were isolated the deoxyglycoside **12** (220 mg, 90%) and the diol **4**, m.p. 166–167° (12 mg, 4.6%). Recrystallized from ethyl acetate–petroleum ether, **12** had m.p. 112–113°, $[\alpha]_D$ +94° (*c* 1.5); lit.[38b] m.p. 110–111°, $[\alpha]_D$ +95 ±1°, and[42] m.p. 111.5–113°, $[\alpha]_D$ +95.5°; ^{1}H-n.m.r. data ($CDCl_3$): δ 7.5–7.2 (m, 5 H, Ph), 5.54 (s, *Ph*CH), 4.49 (d, $J_{1,2}$ 1.1 Hz, H-1), 4.23 (dd, $J_{5,6a}$ 10, $J_{6a,6e}$ 16 Hz, H-6*a*), 4.0–3.7 (m, 4 H, H-2,4,5,6*e*), 3.38 (s, 3 H, OMe), 2.75 (s, broad, exchangeable, OH), and 2.10–1.95 (m, 2 H, H-3,3′).

Reduction of **8** as just described, but with only 3 mL (3.3 mol. equiv.) of LTBH solution, and for 24 h at room temperature, furnished a product in which was present an additional component, identified as the epoxide **11**. Separation by p.t.l.c. (solvent *B*) gave **11** (29 mg), **12** (200 mg), and **4** (11 mg). Compound **11** had m.p. 149–150°, $[\alpha]_D$ +101° (*c* 0.5); lit.[28] m.p. 145–146°, $[\alpha]_D$ +103.2°. The identity of the compound was confirmed by its ^{1}H-n.m.r. spectrum.

E. Reaction of **11**. Independently prepared[30] **11** (1.00 g) in oxolane (10 mL) and LTBH (8 mL, 0.95M solution in oxolane) were allowed to react for 30 min at the reflux temperature. The reaction was then not quite complete (t.l.c. with solvent *B*), but was complete on continued heating (30 min) with additional LTBH (1 mL). Addition of a little water to the cooled mixture, and evaporation of the solvent (with several added portions of dichloromethane) gave a residue which was extracted with fresh dichloromethane (50 mL). The extract was washed with water (4 × 20 mL), dried (K_2CO_3), and concentrated. On addition, to the concentrate, of petroleum ether to incipient opalescence, and storage overnight at −20°, **12** crystallized as stout prisms (708 mg), m.p. 113°, $[\alpha]_D$ +94.6° (*c* 2.3); further crops (m.p. 110–111°) from the mother liquor raised the yield to 882 mg (87.5%). Similar yields had been obtained[22,43] by reduction of **11** with LAH.

F. Reaction of **14**. A mixture of **14** (500 mg), oxolane (5 mL), and LTBH solution (4 mL) was examined by t.l.c. (solvent *C*) after it had been kept for 5 min at 25°. It showed a spot attributable to the epoxide **18** (R_F 0.5), besides that of **14** (R_F 0.2). The mixture was then boiled under reflux, whereupon a third spot (R_F 0.3) soon began to appear. After 30 min, the spot at R_F 0.5 had vanished, and only those at R_F 0.2 and 0.3 remained. Of these, the former showed a somewhat different shade of color than was produced by the starting **14**, and it consisted, in fact, of a reduction product (**20**) that had the same mobility, whereas the faster spot was that of the isomer **21**. Heating was stopped, the mixture was processed, and the products were

separated by p.t.l.c. (solvent *C*), to give **20** (181 mg, 59%) and **21** (110 mg, 36%), both as long needles crystallizing from ethyl acetate–hexane.

The 3-deoxy isomer **20** had m.p. 176–176.5°, $[\alpha]_D$ −58.7° (*c* 1.2); lit.[9,44–46] m.p. 165, 168–169, 174, and 173–174.5°, and $[\alpha]_D$ +59.5 (inadvertent reversal of sign?), −60.5, −61, and −61.5°. The ^{1}H-n.m.r. data for a solution in $CDCl_3$ were in complete agreement with those published[46]; additional data: δ 4.33 (dd, $J_{5,6e}$ 4.5, $J_{6a,6e}$ 10.3 Hz, H-6*e*), 3.56 (s, 3 H, OMe), and 2.56 (broad s, exchangeable, OH).

The 2-deoxy isomer **21** had m.p. 103–104°, $[\alpha]_D$ −32.3° (*c* 0.85); lit.[39] m.p. 96–97°, $[\alpha]_D$ −34°; ^{1}H-n.m.r. data ($CDCl_3$): δ 7.5–7.2 (m, 5 H, Ph), 5.56 (s, *Ph*CH), 4.82 (dd, $J_{1,2e}$ 2.4, $J_{1,2a}$ 9.5 Hz, H-1), 4.34 (dd, $J_{5,6e}$ 4, $J_{6a,6e}$ 9.5 Hz, H-6*e*), 4.17 (narrow m, H-3), 3.97 (sx, $J_{4,5}$ ~9 Hz, H-5), 3.73 (t, $J_{5,6a}$ 9.5 Hz, H-6*a*), 3.53 (dd, partially overlapped by OMe signal, $J_{3,4}$ 2.7 Hz, H-4), 3.49 (s, 3 H, OMe), 2.57 (broad s, exchangeable, OH), 2.15 (dt with broadened lines, $J_{1,2e}$ 2.4, $J_{2e,3}$ 3.6, $J_{2a,2e}$ 14.5 Hz, H-2*e*), and 1.70 (ddd, $J_{1,2a}$ 9.5, $J_{2a,3}$ 3.0, $J_{2a,2e}$ 14.5 Hz, H-2*a*). The *J* values agree well with those given[39] for **21** in C_6D_6.

G. Preparation and reduction of **18**. For the preparation[18,47] of **18**, a sample of pure **14** was at hand, and was used instead of its benzoate[47] or[18] **15**. The sample (1.05 g) in chloroform(5 mL) was treated with M sodium methoxide in methanol (7 mL) for 2 h at room temperature. The solvent was evaporated, and the residue dissolved in dichloromethane (100 mL), which was then washed several times with water, dried ($MgSO_4$), and evaporated, to give a white solid (0.63 g). Recrystallization from methanol afforded **18** (588 mg, 97%); m.p. 140–141°, $[\alpha]_D$ −14° (*c* 0.9); lit.[18] m.p. 133–135°, $[\alpha]_D$ −15°, and[47] m.p. 138°, $[\alpha]_D$ −15.6°. The identity of the product was confirmed by its ^{1}H-n.m.r. spectrum.

To a solution of **18** (200 mg) in oxolane (3 mL) were added, at room temperature, three 1-mL portions of LTBH solution during 90 min. All of the **18** had disappeared after 2 h, and only two slow-moving spots, migrating like authentic **20** and **21**, were seen in t.l.c. (solvent *C*). Processing of the reaction mixture, and separation of the products by p.t.l.c. (solvent *C*), gave **20** (137 mg, 68%) and **21** (61 mg, 30%), identified by their i.r. and n.m.r. spectra with the products described under F.

H. Reaction of **16**. A mixture of **16** (800 mg), oxolane (8 mL), and LTBH solution (7 mL) was boiled under reflux for 25 min. Processing, followed by passage of the crude product through a short column of silica gel by means of solvent *B*, gave a fraction of deoxyglycosides (470 mg, 96%) that appeared homogeneous in t.l.c., but contained two components (**22** and **23**) as judged by the presence of two methoxyl signals (δ 3.48 and 3.53) in the n.m.r. spectrum. Further elution gave the diol **13** (8 mg, 1.5%), m.p. 206°, identified by its i.r. spectrum. Crystallization of the mixture of deoxyglycosides from ethyl acetate–hexane furnished **22**, m.p. 155–156°, raised to 158–159° by recrystallization, and undepressed in admixture with an authentic sample; $[\alpha]_D$ −73.8° and $[\alpha]_{546}$ −89.4° (*c* 1.7); lit.[48] m.p. 155–156 to 159–160° and $[\alpha]_D$ −66.2 to −69° for samples of various origins. The i.r. spectra of **22** and a previous sample were superposable, and the ^{1}H-n.m.r. data were as reported[48].

The mother liquor from the crystallization gave **23** (slightly contaminated by **22**), m.p. 161–162°, raised to 167–167.5° by one recrystallization from chloroform–hexane, and 169–170° in admixture with an authentic sample having m.p. 173°; $[\alpha]_D$ −65.6° and $[\alpha]_{546}$ −78.2° (*c* 3.65); lit.[15] m.p. 172–174°, $[\alpha]_{546}$ −75 ±2°, and[45] m.p. 171–172°, $[\alpha]_D$ −66.3°. The i.r. spectrum was identical with that of authentic **23** (section I), as was also the ^{1}H-n.m.r. spectrum, except for the presence of weak signals due to traces of admixed **22**.

I. Reactions of **19**. The epoxide **19** was prepared from **16** as described[15], in 87% yield; m.p. 192–193°, $[\alpha]_D$ −29.3° and $[\alpha]_{546}$ −35.5° (*c* 2.6); lit.[15] m.p. 185–187°, $[\alpha]_{546}$ −28.5 ±3° and[16] m.p. 188°, $[\alpha]_D$ −29°. A sample of **19** (80 mg) in oxolane (1 mL) was allowed to react with LTBH solution (0.5 mL) for 10 min at room temperature. Processing gave a syrup (80 mg) from which crystals (55 mg, m.p. ~137°) were subsequently obtained. The ^{1}H-n.m.r. spectra of the syrup and of the crystals were essentially identical with each other and with the spectrum of the mixture of **22** and **23** obtained from **16** (section H), indicating the presence of approximately equal proportions of the isomers.

A sample of **19** (75 mg) was reduced with LAH in boiling ether during 1 h, exactly as described[15], to give pure **23** (56 mg after recrystallization; 74%); m.p. 173°; ^{1}H-n.m.r. data ($CDCl_3$): δ 7.4 (m, 5 H, Ph), 5.52 (s, *Ph*CH), 4.43 (d, $J_{1,2}$ 1.5 Hz, H-1), 4.30 (dd, $J_{5,6e}$ 4.3, $J_{6a,6e}$ 10 Hz, H-6*e*), 4.1–3.2 (m, unresolved, H-2,4,5,6*a*), 3.53 (s, 3 H, OMe), 2.50 (s, OH), 2.40 (dt, $J_{2,3e} \approx J_{3e,4} \approx 4$ Hz, $J_{3a,3e}$ 14 Hz, H-3*e*), and 1.77 (m, $J_{3a,4}$ 12 Hz, H-3*a*).

J. Reaction of **15**. A mixture of ditosylate **15** (1.0 g), oxolane (5 mL), and LTBH solution (10 mL) was boiled overnight under reflux. (In a pilot experiment, 3 strong spots for reaction products were already indicated by t.l.c. after 45 min, but processing had shown that much unreacted **15** was still present at that point.) From the processed, crude mixture was then obtained pure **20** (205 mg) by crystallization from hot carbon tetrachloride. The mother liquor was subjected to p.t.l.c. (solvent *G*), and there were obtained, in order of decreasing mobility: (*a*) unidentified material (~15 mg), (*b*) by-product A (25 mg; see the discussion), (*c*) compound **21** (50 mg, 11%), and (*d*) a mixture (140 mg) of **20** and other deoxy glycosides. The last-mentioned mixture was rechromatographed, to give pure **20** (51 mg; thus raising its yield to 256 mg, 56.8%) and a mixture (60 mg, 13%) of deoxyglycosides whose n.m.r. spectrum showed the same characteristic features as those of the mixtures of **22** and **23** obtained from **16** and **19** (sections H and I).

K. Reaction of **24**. A mixture of **24** (200 mg), oxolane (3 mL), and LTBH solution (4 mL) was allowed to react at reflux temperature for 24 h. Monitoring by t.l.c. (solvent *G*) indicated conversion of **24** (R_F 0.2) into **25** (R_F 0.1) and **26** (R_F 0.3) which, after the usual processing, were separated by p.t.l.c. (solvent *F*). This yielded **25** (76.5 mg, 58%) and **26** (44 mg, 35%) in crystalline form.

Compound **25** had m.p. 175–176°, $[\alpha]_D$ −68.7° (*c* 0.5); lit.[37] m.p. 170–171°, $[\alpha]_D$ −69.2°; ^{1}H-n.m.r. data ($CDCl_3$): δ 7.6–7.2 (m, 5 H, Ph), 5.52 (s, *Ph*CH), 4.35 (dd, $J_{5,6e}$ 4.3, $J_{6a,6e}$ 10.5 Hz, H-6*e*), 4.33 (d, $J_{1,2}$ 7.6 Hz, H-1), 3.8–3.2 (m, 10 H,

H-3,4,5,6*a*, and 2 OMe signals at δ 3.63 and 3.57), 3.06 (dd, $J_{2,3}$ 8.6 Hz, H-2), and 2.74 (d, J 2 Hz, exchangeable, OH).

Compound **26** had m.p. 150–152°, $[\alpha]_D$ −73.6° (*c* 0.6), and no literature reference was found; ^{1}H-n.m.r. data ($CDCl_3$): δ 7.6–7.2 (m, 5 H, Ph), 5.50 (s, *Ph*CH), 4.34 (dd, $J_{5,6e}$ ~4, $J_{6a,6e}$ 10 Hz, H-6*e*), 4.32 (d, $J_{1,2}$ 7.5 Hz, H-1), 3.75 (t, $J_{5,6a}$ 10 Hz, H-6*a*), 3.56 and 3.47 (s, 3 H each, 2 OMe, superposed on unresolved m for H-4 and -5), 3.21 (ddd, $J_{2,3e}$ 5.2, $J_{1,2}$ 7.5, $J_{2,3a}$ 11.2 Hz, H-2), 2.51 (m, $J_{3e,4}$ 3.8, $J_{3a,3e}$ ~12 Hz, H-3*e*), and 1.63 (q, $J_{3a,4}$ ~11.7 Hz, H-3*a*). Minor signals were attributable to contamination by starting **24**, amounting to ~6% (estimated from the intensity of the *C*-Me signal at δ 2.30).

L. Reaction of **27**. A mixture of **27** (300 mg), oxolane (6 mL), and LTBH solution (6 mL) was boiled under reflux for 22 h, after which time all of **27** (R_F 0.4) had been replaced by a single spot (R_F 0.1) for **28** (t.l.c. with solvent *F*). Processing required no chromatography; the crude product (187 mg, 94.7%) was recrystallized from ethyl acetate–hexane, to afford pure **28**, m.p. 171.5–172°, $[\alpha]_D$ −47.0° (*c* 1.1); lit.[38a] m.p. 174°, $[\alpha]_D$ −50 ±2°; ^{1}H-n.m.r. data (60 MHz) ($CDCl_3$): δ 7.4 (m, 5 H, Ph), 5.52 (s, *Ph*CH), 3.67 and 3.58 (s, 2 OMe, superposed on ring-proton signals that were all unresolved in the regions δ 4.5–4.1 and 3.9–3.6), and 2.85 (d, J ~2 Hz, OH).

Reduction with lithium aluminum hydride. — A. Reaction of **1**. To a partial suspension of LAH (0.50 g, 13.2 mmol) in dry oxolane (8 mL) was added dropwise a solution of **1** (3.10 g, 5.25 mmol) in oxolane (12 mL). The mixture was boiled under reflux for 22 h, and for a further 4 h following the addition of 0.25 g (6.60 mmol) of LAH. The mixture was cooled, carefully poured into chilled ethyl acetate (50 mL), agitated with ice–water (150 mL) that contained sulfuric acid (3 g) [or, in similar experiments, sodium hydrogensulfate (8 g)], successively extracted with ethyl acetate (4 × 75 mL) and ether (50 mL), and the combined extracts washed with a small volume of sodium hydrogencarbonate solution, passed through dry filter-paper, and evaporated without prior application of a drying agent. The partially crystalline residue showed, in t.l.c. with solvent *B*, a brown spot of **4** (R_F 0.1), a strong double spot having a black front and a dark-brown rear-part and comprising **2**, **5**, and **7** (R_F 0.37–0.45), an olive-green spot due to the by-products designated B (R_F 0.68), a dark-brown spot of residual **1** (R_F 0.75), and faster-moving trace-spots. Separation was performed on a column of silica gel (25 mL) by use of solvent *B*, 10-mL fractions being collected. Compound **1** began to emerge after a forerun (20 mL) that contained malodorous, non-carbohydrate material and other impurities. Mixed fractions were appropriately pooled, and rechromatographed. Early fractions (containing mainly **1** and B) deposited, on standing of the solutions, pure **1** as large prisms that were collected; the mother liquor was evaporated for rechromatography, and all fractions, except those containing appreciable proportions of B, gave dry, crystalline materials on evaporation. The following materials were obtained: (*a*) unchanged **1** (13.3%) in crystalline crops (177 mg, m.p. 159–160°, $[\alpha]_D$ +13.7° [*c* 2]; and 125 mg, m.p. 153–154°) and as a partly crystalline mixture (330 mg) composed of **1** (~110 mg) and B (~220 mg) as indicated by the 100-MHz, ^{1}H-n.m.r. spectrum (see Table I

and the Discussion); (*b*) a 4:3 mixture (98 mg, ratio estimated by n.m.r.) of B and **2**, corresponding to ~56 and 42 mg, respectively; (*c*) several mixture fractions amounting to 975 mg, and containing **2**, **5**, and **7**; and (*d*) the diol **4** (190 mg, 12.8%), whose elution was completed by use of solvent *A*; m.p. 163–164°, raised to 167–168° by recrystallization from ethyl acetate–cyclohexane (lit.[25] m.p. 163–164° and[11] 168–169°).

In the combined, mixture fractions *c*, the molar ratio **2**:(**5** + **7**) was determined, by n.m.r. spectroscopy, to be 1:3, corresponding to calculated amounts of 345 mg (15.1%) of **2**, and 630 mg (45.1%) of **5** + **7**. The deoxyglycosides were present in the ratio of ~4:1. Repeated chromatography of the mixture furnished **2**, m.p. 160–162°, R_F 0.63 or 0.45 (t.l.c. with solvents *A* or *B*), free from **5** and **7**. The latter two glycosides virtually coincided in t.l.c. (R_F 0.5 with solvent *A*, and 0.4 with *B*), as was verified with authentic samples, and they were not satisfactorily separable on columns. On one occasion, a small amount (25 mg) of **7** crystallized fortuitously in fairly pure form (m.p. 122–124°); its ^{1}H-n.m.r. and i.r. spectra agreed with those of pure **7** obtained by LTBH reduction. Fractions of fairly pure **5** melting as high as 180–182° were isolated, but they still contained some **7**, whose signals were visible in their spectra. A vacuum-sublimed[6] sample of **5** appeared to be free from **7**, and had m.p. 187°, $[\alpha]_D$ +119.5° (*c* 1.4); lit.[6] m.p. 186.5–187.5°, $[\alpha]_D$ +126.9°, and[11] m.p. 186–187 to 190–191°, $[\alpha]_D$ +123 and +124.1°, and[22,49] m.p. 190–191°, $[\alpha]_D$ +115.8 ±3°. Elevated $[\alpha]_D$ values may signify a contamination by **7**, which is more highly dextrorotatory (+140°) than **5**. The ^{1}H-n.m.r. data agreed with those reported[12] for **5**.

B. Reactions of **3** *and* **2**. Compound **3** (590 mg, 1.1 mmol) and LAH (330 mg, 7.9 mol. equiv.) were allowed to react in boiling oxolane (30 mL) as described for **1**, but for only 9 h. The crude product obtained on processing as described showed spots at R_F 0.15 (**4**), 0.5 (**5** + **7**), and 0.63 (**2**), as well as faster-moving trace-spots in t.l.c. with solvent *A*. Column chromatography on silica gel (16 mL) with solvent *A* gave pure **2** (69 mg), m.p. 163°; a mixture fraction (176 mg) containing **2** and the deoxyglycosides (**5** and **7**) in the molar ratio of 1:3 (by n.m.r. spectroscopy), which corresponded to 62 mg of **2** and 114 mg of (**5** + **7**); a mixture (35 mg) of **5** and **7**; and finally **4** (37 mg), m.p. 167–168°. The ratio of **5**:**7** was ~3.25:1 (by n.m.r. spectroscopy). The percentage yields are listed in Table II.

An analogous experiment using compound **2** (200 mg) gave the results shown in Table II.

C. Reaction of **8**. Reduction of **8** (1.00 g, 2.29 mmol) with LAH (670 mg, 7.7 mol. equiv.) in boiling oxolane during 19 h, followed by processing as described in section A, gave a crude, crystalline product that showed spots attributable to **4** (R_F 0.1) and deoxyglycosides (R_F 0.42, almost black, due to **10**, with a faint brown, satellite spot at R_F 0.37, presumably due to **12**), and fast-moving traces of impurities (solvent *B*). Chromatography on silica gel (12 mL) with solvent *B* gave fractions showing only the aforementioned, black spot, together with its weak, companion spot. (These were more clearly separated in t.l.c. with solvent *A*: R_F 0.57 and 0.47.) Therefrom was obtained **10** (114 mg, 19%) as long needles having m.p. 144–147°,

m.p. 146–147° after recrystallization from ethyl acetate–cyclohexane or 95% ethanol, and m.p. 148–149° from ethyl acetate; $[\alpha]_D$ +97.5° (*c* 1.3, acetone); lit.[50] m.p. 151–152°, $[\alpha]_D$ +90° (acetone). The i.r. spectrum was distinctly different from those of **5**, **7**, and **12**; ^{1}H-n.m.r. data (60 MHz) ($CDCl_3$): δ 7.4 (m, 5 H, Ph), 5.52 (s, *Ph*CH), 4.73 (dd, $J \sim 1$ and 4 Hz, H-1), 4.3–3.3 (unresolved m, 5 H), 3.30 (s, 3 H, OMe), 2.83 (broad s, OH), 2.18 (ddd, $J_{1,2e} \sim 1$, $J_{2e,3}$ 5, $J_{2a,2e}$ 13 Hz, H-2*e*), and 1.68 (o, $J_{1,2a} \sim 4$, $J_{2a,3}$ 11, $J_{2a,2e}$ 13 Hz, H-2*e*).

The bulk of the slow-moving product was eluted with solvent *B*, and additional amounts were eluted with solvent *A*, followed by ethyl acetate. A total of 495 mg (76.5%) of crystalline **4** was thus obtained.

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