Epimerization of α- to β-*C*-Glucopyranosides under Mild Basic Conditions

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A number of β-*C*-glucopyranosides having an activated methylene or methine group bonded to the anomeric carbon are obtainable in quantitative yield from the corresponding α-isomers by simple equilibration catalysed by various bases at room temperature.

In recent years significant attention has been focussed [1] on the development of new routes to functionalized *C*-glycosides since these compounds represent a basic structural feature of many biologically active natural products [2] and are chirons for the synthesis of these or other more complex molecules.[3]

A survey of the available literature showed that β-*C*-glucopyranosides can be obtained indirectly by a variety of sound methods.[2,4] However, the only direct *C*-glucosidation leading to the preferential formation of these compounds involves the condensation of protected glucopyranosides with aromatic nucleophiles,[5a–c] or with specific nucleophiles deriving from malonic esters [6] or barbituric acids.[7] In contrast functionalized α-*C*-glucopyranosides are easily obtainable by a variety of general direct methods of *C*-glucosidation including the condensation of activated or non-activated 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose with silyl enol ethers, silyl ketenes,[5] and enamines [1a] under various mild conditions.

Since in our synthetic work we needed some functionalized β-*C*-glucopyranosides not available by direct methods, we prepared their α-isomers and treated them with bases in order to test their possible anomerization to the β-isomers. Anomerization by bases has been reported for furanoid systems [8] while in the pyranoside series only the equilibration (by potassium methoxide) of ethyl 2-(4,6-*O*-ethylidene-α-D-glucopyranosyl)-acetate has been reported.[9] After having obtained useful results we established the mildest conditions (the weakest base and lowest temperature) to accomplish the anomerization. Experimental results relative to twelve α-*C*-glucopyranosides with a methylene or a methyne group at the anomeric carbon (Table) show that anomerization occurs in many cases, in good yields and under mild conditions. When the substituent at C-1 of the pyranoside ring is a β-keto ester function [(**1a**)—(**3a**)] the epimerization occurred even after short potassium carbonate treatment. Similar treatment with potassium hydroxide or longer treatment with potassium carbonate caused the anomerization of α-*C*-glucosidic ketones (**5a**)—(**9a**). Only for the α-*C*-glucopyranosylacetates (**10a**) and (**11a**) and α-*C*-glucopyranosylmalonate (**12a**) was stronger base treatment necessary. Also, 1-(5α-cholestan-3β-yl)-2-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)ethanone (**4a**) was transformed into the β-isomer (**4b**) by treatment with potassium hydroxide. In this way we obtained two anomeric steroidal *C*-glucosides, prototypes of a new class of compounds which may be possible modulators of biological membrane fluidity.

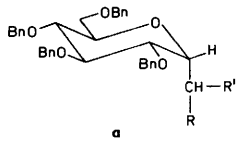
In all cases the base treatment caused an almost quantitative conversion of the α-*C*-glucopyranosides into β-*C*-glucopyranosides under the reported conditions which represent the optimized conditions with respect to obtaining the maximal ratio of thermodynamic to kinetic products (*i.e.* β to α). The most reasonable mechanism for the anomerization (Scheme 1) requires the formation of an intermediate α,β-unsaturated ester. However, all attempts to isolate or demonstrate by h.p.l.c. these intermediates were unsuccessful, probably because these compounds easily undergo intramolecular Michael-like recyclization.

In principle, during the anomerization the epimerization at the C-2 glucosidic carbon could also occur thus affording *C*-mannopyranosides. In the intermediate olefin (Scheme 1) this carbon possesses the same charge affinity of an α-carbon to a carbonyl. However, when the equilibrations were followed both by h.p.l.c. and by t.l.c. analysis no sign of new compounds corresponding to mannose isomers was found, apart from in the equilibration of α-*C*-glucopyranosylacetates (**10a**) and (**11a**) with sodium hydride. In this case when the maximal ratio of thermodynamic β-*C*-glucopyranosylacetate to kinetic α-*C*-glucopyranosylacetate was obtained the two epimeric β- and α-*C*-mannopyranosyl acetates† were detected and isolated in *ca.* 10 and 0.5% yield, respectively. In the case of the α-*C*-glucopyranosylacetylcholestane (**4a**), here synthesized for the first time starting with trimethylsiloxyvinylcholestane (**13**), it was necessary to exclude also the possible epimerization at the steroid C-3 during its transformation into the β-anomer (**4b**). However, the ^{1}H n.m.r. spectra of the anomers (**4a**) and (**4b**) showed that none of this undesired epimerization had occurred, since identical coupling constants attributable only to an axial proton at position 3 of the steroid were observed. Chemical confirmation derived from the conversion (Baeyer–Villiger oxidation followed by lithium aluminium hydride reduction) of compounds (**4a**) and (**4b**) into the cholestan-3β-ol (**15**) and the epimeric 2-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)ethanol (**14a**) and 2-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)ethanol (**14b**) respectively (Scheme 2).

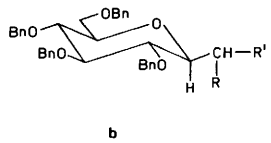
The stereochemistry of the alcohols (**14a**) and (**14b**) and that of compounds (**1b**)—(**12b**) and (**4a**) was based on the interpretation of their ^{1}H n.m.r. spectra (at 300 or 500 MHz). In particular the axial–axial relationship of the anomeric proton and that of the adjacent glucosidic proton of the β-*C*-glucosides was derived from the observed coupling constants for these protons ($J_{1,2}$ 9.1—9.5 Hz) which were in agreement with the predicted [10] values. Similarly the observed coupling constant for the same protons in the α-epimers ($J_{1,2}$ 5.5—5.6 Hz) confirmed their equatorial–axial relationship. Additional support for the spectroscopic assignment of these structures was obtained in some cases from the chemical transformations of the β-compounds into the alcohol (**14b**). The keto ester (**2b**) was decarboxylated to the methyl ketone (**5b**) which, similarly to the other β-*C*-glucopyranosidic ketones (**6b**)—(**9b**), was transformed (Baeyer–Villiger oxidation and lithium aluminium hydride reduction) into the β-*C*-glucopyranosylethanol (**14b**).

† For a simple synthesis of these compounds and their complete characterization see following paper.

Table. Anomerization of α-*C*-glucopyranosides to β-*C*-glucopyranosides



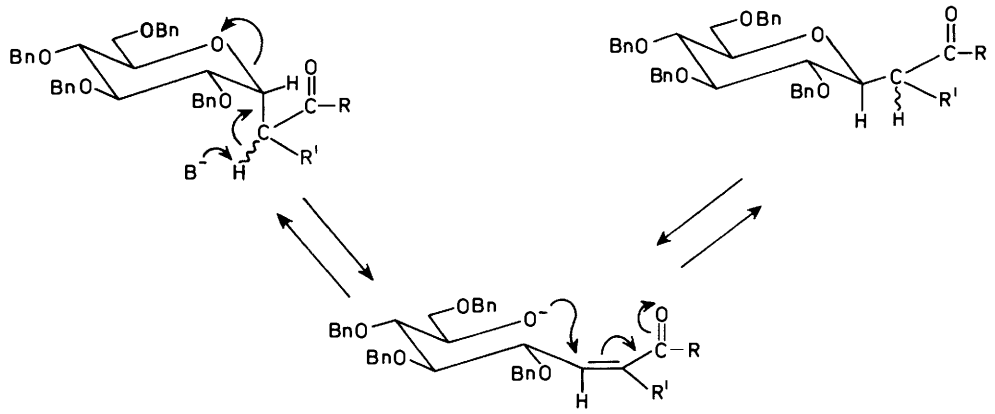
a



b

Compound	R	R′	Method, conditions[a]	β:α Anomers[b]	β-Anomer yield (%)[c]
(**1**)	CO_2Me	$COCH_2OMe$	A, 1 h	98:2	85[d]
(**2**)	CO_2Me	COMe	A, 1 h	98:2	85[d]
(**3**)	CO_2Me	COEt	A, 1 h	97:3	83[d]
(**4**)	H	$COC_{27}H_{47}$[f]	B, 4 h	98:2	85
(**5**)	H	COMe	A, 25 h	94:6[e]	81
			B, 2 h		80
(**6**)	H	COBu^t	A, 48 h	97:3[e]	80
			B, 5 h		82
(**7**)	H	COPh	A, 24 h	97:3[e]	85
			B, 1 h		87
(**8**)	H	COC_6H_4Cl-*p*	A, 20 h	95:5[e]	87
			B, 0.8 h		85
(**9**)	H	$COC_{10}H_7$[g]	A, 40 h	96:4[e]	83
			B, 2 h		85
(**10**)	H	CO_2Me	C, 7 d	96:4	85
			D, 24 h		74
(**11**)	H	CO_2Et	C, 7 d	96:4[e]	85
			D, 24 h		74
(**12**)	CO_2Et	CO_2Et	C, 0.5 h	98:2	88

[a] Base/solvent: A = K_2CO_3/MeOH; B = KOH/MeOH; C = MeONa/MeOH or EtONa/EtOH; D = NaH/THF. [b] Determined by h.p.l.c. [c] Yields refer to pure crystallized products. [d] Mixture of epimers at glucosidate carbon. [e] α- and β-Anomers were inseparable by t.l.c., and separable by h.p.l.c. [f] $C_{27}H_{47}$ = 5α-cholestan-3β-yl. [g] $C_{10}H_7$ = 2-naphthyl.



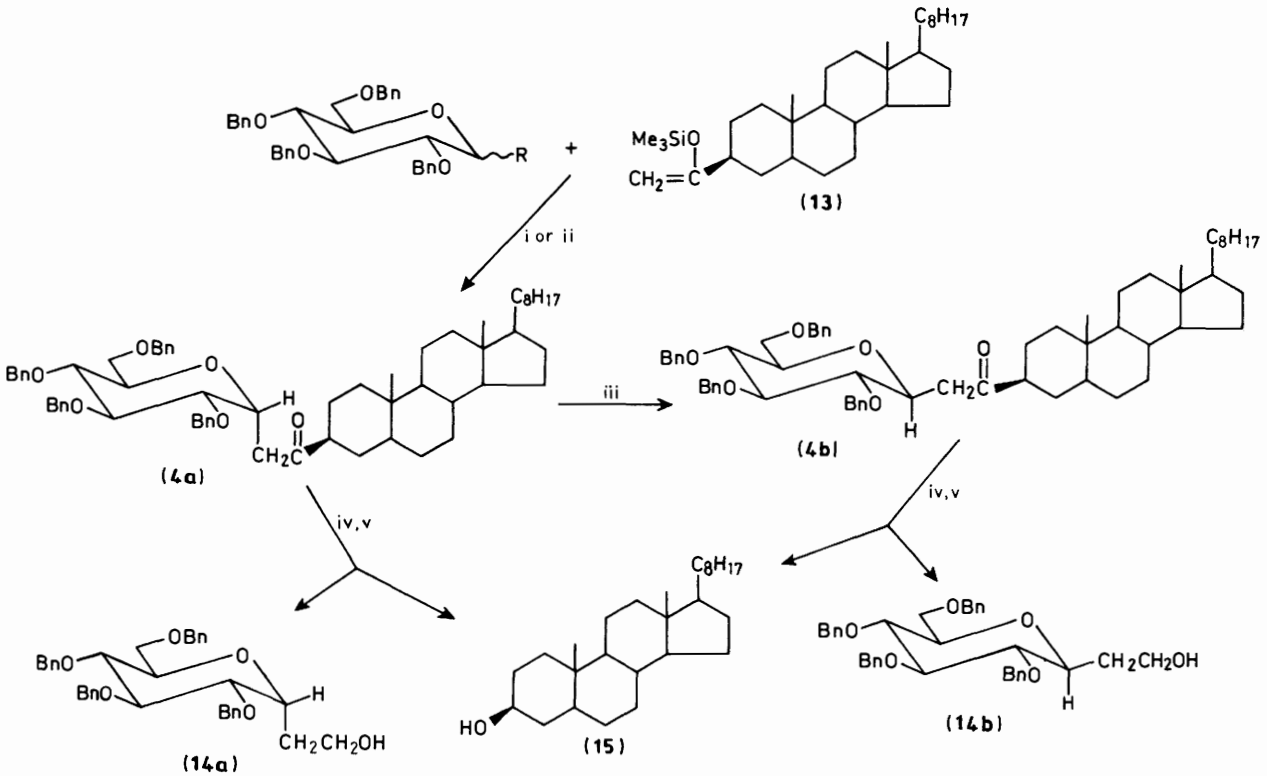
Scheme 1.

This alcohol was also obtained by reduction of the ester (**11b**) obtained by decarboxylation of the β-*C*-glucopyranosylmalonate (**12b**).

In conclusion the method reported herein represents a new route to β-*C*-glucopyranosides, having an activated methylene or methyne group bonded to the anomeric carbon, from easily available α-isomers. In addition, it is evident that undesired rearrangement of α-isomers could occur during reactions such as saponification or transesterification which require mild basic conditions.

Experimental

All m.p.s are uncorrected. I.r. spectra were recorded for solutions in $CHCl_3$ on a Perkin-Elmer 1420 spectrometer. ^1H N.m.r. spectra were recorded on a Varian EM-360L, on a Bruker CXP-300, or on a Bruker AM-500 instrument for solutions in $CDCl_3$ and are reported in δ units relative to Me_4Si. Unprimed locants refer to the acyclic ketone or ester chain, primed locants to the cholestane or aromatic moiety, and double primes to the glucopyranoside moiety. Optical rotations were measured for $CHCl_3$ solutions. The progress of all reactions and column chromatography (Silica 60, 230—400 mesh) was monitored by t.l.c. on silica gel HF_{254} microplates or on h.p. microplates. Hexane–ethyl acetate (80:20) mixture was used as developing solvent for t.l.c. and spots were detected by spraying with 70% sulphuric acid, followed by heating. H.p.l.c. analyses were performed on a Jasco twinkle pump system, a VL 614 variable-loop injector with a 20 μl sample loop, and on a Uvidec 100 II. The recorder was a Shimadzu C-R 3A Chromatopac. The analyses were carried out on a reverse-phase Lichrosorb C-18 column (3 μm; 4 × 250 mm; Merck), using as solvent system a mixture of MeOH–water (90:10); the flow rate was 1 ml min^{-1} and detection was performed at 208 nm.



Scheme 2. *Reagents:* i, (R = α-Cl) CF_3SO_3Ag; ii, (R = β-$OCOCF_3$) BF_3·Et_2O; iii, KOH–MeOH; iv, CF_3CO_3H–CH_2Cl_2; v, $LiAlH_4$

Mass spectra were recorded on a Varian 112 S mass spectrometer (direct inlet). Work-up refers to evaporation of the reaction solvent under reduced pressure, dissolution of the residue in dichloromethane, washing with water to neutrality, drying (Na_2SO_4), and removal of the solvent under reduced pressure.

Compounds (**1a**)—(**3a**) were prepared according to ref. 1*a*, compounds (**5a**), (**6a**), and (**12a**) according to ref. 5*b*, compounds (**7a**)—(**9a**) according to ref. 5*a*, and compounds (**10a**) and (**11a**) by Wittig–Horner reaction.* Light petroleum refers to the fraction boiling in the range 65—95 °C.

Synthesis of 1-(5α-*Cholestan*-3β-*yl*)-2-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*glucopyranosyl*)*ethanone* (**4a**).—(i) To a solution of 3β-acetylcholestane[11] (2.0 g), in a mixture of triethylamine (0.86 ml) and trimethylchlorosilane (0.78 ml) in acetonitrile, a solution of sodium iodide (930 mg) in acetonitrile (6.2 ml) was added dropwise and the mixture was stirred at room temperature for 3 h. After extraction with pentane and work-up, 3β-(1-trimethylsiloxyvinyl)-5α-cholestane (**13**) (1.8 g) was obtained as solid residue, which showed correct mass and ^1H n.m.r. spectra: δ_H(60 MHz) 3.0 (1 H, m, 3-H_a) and 3.8 (2 H, br d, *J* 4.0 Hz, CH_2=).

The silyl enol ether (**13**) (1.8 g) without additional purification was treated with 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl chloride (688 mg) and silver(I) triflate (380 mg) in dry dichloromethane (40 ml). The solution was stirred at room temperature in the dark for 15 min and treated with saturated aqueous sodium chloride (10 ml). Filtration over a pad of Celite and work-up afforded 1-(5α-*cholestan*-3β-*yl*)-2-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*glucopyranosyl*)*ethanone* (**4a**) (865 mg, 75%), m.p. 90—92 °C (from di-isopropyl ether–methanol) (Found: C, 80.8; H, 9.0. $C_{63}H_{84}O_6$ requires C, 80.7; H, 9.0%); $[\alpha]_D^{20}$ +30.0° (*c* 1); $\nu_{max.}$ 1 705 cm^{-1}; δ_H(500 MHz) 0.63 (3 H, s, 18′-H_3), 0.71 (3 H, s, 19′-H_3), 2.34 (1 H, dddd, *J* 3.5, 3.5, 12.6, and 12.6 Hz, 3′-H_a), 2.68 (1 H, dd, $J_{2a,2b}$ 16.1 and $J_{2a,1''}$ 7.7 Hz, 2-H_a), 2.85 (1 H, dd, $J_{2b,2a}$ 16.1 and $J_{2b,1''}$ 5.6 Hz, 2-H_b), 3.57—3.72 (5 H, overlapping, 3″-, 4″-, and 5″-H, and 6″-H_2), 3.75 (1 H, dd, $J_{2'',3''}$ 9.1 and $J_{2'',1''}$ 5.6 Hz, 2″-H), 4.46, 4.47, 4.55, 4.57, 4.60, 4.78, 4.79, and 4.91 (8 H, 8 × d, *J* 11.2—11.9 Hz, benzylic), 4.77 (1 H, ddd, $J_{1'',2a}$ 7.7, $J_{1'',2b}$ 5.6, and $J_{1'',2''}$ 5.6 Hz, 1″-H), and 7.16—7.37 (20 H, m, ArH).

(ii) In an alternative method, 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (400 mg) was treated with a solution of trifluoroacetic anhydride (TFAA) (0.12 ml) in dichloromethane (20 ml) at room temperature for 30 min. The solvent, the excess of anhydride, and the formed trifluoroacetic acid were evaporated off under reduced pressure and the residual oil was dissolved in dichloromethane (20 ml) and treated with the silyl enol ether (**13**) (1.8 g). Boron trifluoride–diethyl ether complex (0.28 ml) was added and the solution was stirred for 30 min. Neutralization with aqueous sodium hydrogen carbonate and work-up afforded, after chromatography, 1-(5α-cholestan-3β-yl)-2-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)ethanone (**4a**) (312 mg, 45%). This compound showed identical physicochemical properties with those reported above.

Anomerization.—With potassium carbonate (method A), potassium hydroxide (method B), sodium alkoxides (method C), or sodium hydride (method D). A solution of the α-*C*-glucopyranoside (1 mmol) in the smallest possible amount of methanol or tetrahydrofuran (THF) was added to a saturated solution of potassium carbonate or of the alkoxide (0.94 mmol) in methanol or THF (15 ml). The solution was kept at room temperature for the indicated time (Table) and worked up. The reaction product was purified by direct crystallization if not differently indicated.

Methyl 4-*Methoxy*-3-*oxo*-2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*butanoate* (**1b**).—Anomerization of the α- isomer

* See footnote on p. 1275.

(**1a**) (method A) afforded *methyl* 4-*methoxy*-3-*oxo*-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*butanoate* (**1b**) (7:3 mixture of epimers at C-2, not separable by t.l.c. but separable by h.p.l.c.), m.p. 80—82 °C (from di-isopropyl ether) (Found: C, 71.8; H, 6.5. $C_{40}H_{44}O_9$ requires C, 71.8; H, 6.6%); $[\alpha]_D^{20}$ +0.3° (*c* 1); $\nu_{max.}$ 1 730 and 1 710 cm^{-1}; δ_H(300 MHz) (major epimer) 3.30 (3 H, s, 4-OMe), 3.50 (3 H, s, CO_2Me), 3.88 (1 H, d, $J_{2,1''}$ 6.5 Hz, 2-H), 4.07 (1 H, dd, $J_{1'',2''}$ 9.5 and $J_{1'',2}$ 6.5 Hz, 1″-H), and 4.17 (2 H, s, CH_2OMe); (minor epimer) 3.28 (3 H, s, 4-OMe), 3.62 (3 H, s, CO_2Me), 3.96 (1 H, dd, $J_{1'',2''}$ 9.5 and $J_{1'',2}$ 3.8 Hz, 1″-H), 4.01 (1 H, d, $J_{2,1''}$ 3.8 Hz, 2-H), and 4.06 (2 H, s, CH_2OMe); *m*/*z* 668 (M^+), 576 ($M^+ - 92$), 470 ($M^+ - 198$), and 362 ($M^+ - 306$).

Methyl 3-*Oxo*-2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)-*butanoate* (**2b**).—Anomerization of the α-isomer (**2a**) (method A) afforded *methyl* 3-*oxo*-2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*gluco-pyranosyl*)*butanoate* (**2b**) (6:4 mixture of epimer at C-2, not separable by t.l.c. or h.p.l.c., ratio determined by ^1H n.m.r.), m.p. 68—70 °C (from di-isopropyl ether) (Found: C, 73.2; H, 6.3. $C_{39}H_{42}O_8$ requires C, 73.3; H, 6.6%); $[\alpha]_D^{20}$ +4.9° (*c* 1); $\nu_{max.}$ 1 730 and 1 710 cm^{-1}; δ_H(300 MHz) (major epimer) 2.27 (3 H, s, COMe), 3.47 (3 H, s, CO_2Me), 3.51 (1 H, dd, $J_{2'',1''}$ 9.5 and $J_{2'',3''}$ 9.5 Hz, 2″-H), 3.71 (1 H, d, $J_{2,1''}$ 7.0 Hz, 2-H), and 4.06 (1 H, dd, $J_{1'',2''}$ 9.5 and $J_{1'',2}$ 7.0 Hz, 1″-H); (minor epimer) 2.17 (3 H, s, COMe), 3.62 (1 H, dd, $J_{2'',1''}$ 9.5 and $J_{2'',3''}$ 9.5 Hz, 2″-H), 3.66 (3 H, s, CO_2Me), 3.74 (1 H, d, $J_{2,1''}$ 5.5 Hz, 2-H), and 3.96 (1 H, dd, $J_{1'',2''}$ 9.5 and $J_{1'',2}$ 5.5 Hz, 1″-H); *m*/*z* 638 (M^+), 546 ($M^+ - 92$), 440 ($M^+ - 198$), and 332 ($M^+ - 306$).

Methyl 3-*Oxo*-2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)-*pentanoate* (**3b**).—Anomerization of the α-isomer (**3a**) (method A) afforded *methyl* 3-*oxo*-2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*gluco-pyranosyl*)*pentanoate* (**3b**) (6:4 mixture of epimers at C-2, not separable by t.l.c. but separable by h.p.l.c.), m.p. 63—64 °C (from methanol) (Found: C, 73.7; H, 6.8. $C_{40}H_{44}O_8$ requires C, 73.6; H, 6.8%); $[\alpha]_D^{20}$ 0.0° (*c* 1); $\nu_{max.}$ 1 730 and 1 710 cm^{-1}; δ_H(300 MHz) (major epimer) 0.99 (3 H, t, *J* 7.0 Hz, CH_2Me), 2.40—2.70 (2 H, overlapping CH_2Me), 3.46 (3 H, s, CO_2Me), 3.52 (1 H, dd, $J_{2'',1''}$ 9.5 and $J_{2'',3''}$ 9.5 Hz, 2″-H), 3.76 (1 H, d, $J_{2,1''}$ 7.0 Hz, 2-H), and 4.08 (1 H, dd, $J_{1'',2''}$ 9.5 and $J_{1'',2}$ 7.0 Hz, 1″-H); (minor epimer) 0.90 (3 H, t, *J* 7.0 Hz, CH_2Me), 2.40—2.70 (2 H, overlapping, CH_2Me), 3.64 (3 H, s, CO_2Me), 3.66 (1 H, dd, $J_{2'',1''}$ 9.5 and $J_{2'',3''}$ 9.5 Hz, 2″-H), 3.78 (1 H, d, $J_{2,1''}$ 5.5 Hz, 2-H), and 3.99 (1 H, dd, $J_{1'',2''}$ 9.5 and $J_{1'',2}$ 5.5 Hz, 1″-H); *m*/*z* 652 (M^+), 560 ($M^+ - 92$), 454 ($M^+ - 198$), and 346 ($M^+ - 306$).

1-(5α-*Cholestan*-3β-*yl*)-2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*gluco-pyranosyl*)*ethanone* (**4b**).—Anomerization of the α-isomer (**4a**) (method B) afforded 1-(5α-*cholestan*-3β-*yl*)-2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*ethanone* (**4b**), m.p. 96—97 °C (from diethyl ether–methanol) (Found: C, 80.8; H, 9.0. $C_{63}H_{84}O_6$ requires C, 80.7; H, 9.0%); $[\alpha]_D^{20}$ +7.6° (*c* 1); $\nu_{max.}$ 1 705 cm^{-1}; δ_H(500 MHz) 0.63 (3 H, s, 18′-H_3), 0.73 (3 H, s, 19′-H_3), 2.32 (1 H, dddd, *J* 3.5, 3.5, 12.6, and 12.6 Hz, 3′-H_a), 2.54 (1 H, dd, $J_{2a,2b}$ 15.4 and $J_{2a,1''}$ 8.5 Hz, 2-H_a), 2.63 (1 H, dd, $J_{2b,2a}$ 15.4 and $J_{2b,1''}$ 2.61 Hz, 2-H_b), 3.31 (1 H, dd, $J_{2'',3''}$ 9.1 and $J_{2'',1''}$ 9.1 Hz, 2″-H), 3.40 (1 H, ddd, $J_{5'',4''}$ 9.1, $J_{5'',6''b}$ 4.2, and $J_{5'',6''a}$ 2.1 Hz, 5″-H), 3.59—3.74 (4 H, overlapping, 3″- and 4″-H, and 6″-H_2), 3.77 (1 H, ddd, $J_{1'',2''}$ 9.1, $J_{1'',2a}$ 8.5 and $J_{1'',2b}$ 2.6 Hz, 1″-H), 4.47, 4.56, 4.57, 4.61, 4.80, 4.86, 4.88, and 4.90 (8 H, 8 × d, *J* 10.5—12.6 Hz, benzylic), and 7.16—7.37 (20 H, m, ArH).

1-(2,3,4,6-*Tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*propan*-2-*one* (**5b**).—Anomerization of the α-isomer (**5a**) (method A or B) afforded 1-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*propan*-2-*one* (**5b**), m.p. 70—71 °C (from methanol) (Found: C, 76.6; H, 6.8. $C_{37}H_{40}O_6$ requires C, 76.5; H, 6.9%); $[\alpha]_D^{20}$ −6.0° (*c* 1); $\nu_{max.}$ 1 715 cm^{-1}; δ_H(500 MHz) 2.12 (3 H, s, COMe), 2.55 (1 H, dd, $J_{1a,1b}$ 15.4 and $J_{1a,1''}$ 8.4 Hz, 1-H_a), 2.69 (1 H, dd, $J_{1b,1a}$ 15.4 and $J_{1b,1''}$ 3.5 Hz, 1-H_b), 3.30 (1 H, dd, $J_{2'',1''}$ 9.1 and $J_{2'',3''}$ 9.1 Hz, 2″-H), 3.43 (1 H, ddd, $J_{5'',4''}$ 9.8, $J_{5'',6''b}$ 6.3, and $J_{5'',6''a}$ 2.8 Hz, 5″-H), 3.61—3.68 (3 H, overlapping, 4″-H and 6″-H_2), 3.70 (1 H, dd, $J_{3'',2''}$ 9.1 and $J_{3'',4''}$ 9.1 Hz, 3″-H), 3.75 (1 H, ddd, $J_{1'',2''}$ 9.1, $J_{1'',1a}$ 8.4 and $J_{1'',1b}$ 3.5 Hz, 1″-H), 4.48, 4.56, 4.58, 4.61, 4.80, 4.86, 4.89, and 4.91 (8 H, 8 × d, *J* 10.5—12.6 Hz, benzylic), and 7.14—7.34 (20 H, m, ArH); *m*/*z* 580 (M^+), 488 ($M^+ - 92$), 382 ($M^+ - 198$), and 274 ($M^+ - 306$).

3,3-*Dimethyl*-1-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)-*butan*-2-*one* (**6b**).—Anomerization of the α-isomer (**6a**) (method A or B) afforded 3,3-*dimethyl*-1-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*butan*-2-*one* (**6b**), m.p. 49—50 °C (from methanol) (Found: C, 77.1; H, 7.5. $C_{40}H_{46}O_6$ requires C, 77.1; H, 7.45%); $[\alpha]_D^{20}$ −32.5° (*c* 1); $\nu_{max.}$ 1 715 cm^{-1}; δ_H(500 MHz) 1.05 (9 H, s, CMe_3), 2.51 (1 H, dd, $J_{1a,1b}$ 16.8 and $J_{1a,1''}$ 2.8 Hz, 1-H_a), 2.63 (1 H, ddd, $J_{1b,1a}$ 16.8 and $J_{1b,1''}$ 9.1 Hz, 1-H_b), 3.34 (1 H, dd, $J_{2'',1''}$ 9.1 and $J_{2''3''}$ 8.4 Hz, 2″-H), 3.40 (1 H, ddd, $J_{5'',4''}$ 9.1, $J_{5,6''b}$ 3.5 and $J_{5'',6''a}$ 2.1 Hz, 5″-H), 3.62 (1 H, dd, $J_{6''a,6''b}$ 11.2 and $J_{6''a,5''}$ 2.1 Hz, 6″-H_a), 3.66 (1 H, dd, $J_{6''b,6''a}$ 11.2 and $J_{6''b,5''}$ 3.5 Hz, 6″-H_b), 3.67 (1 H, dd, $J_{4'',3''}$ 9.1 and $J_{4'',5''}$ 9.1 Hz, 4″-H), 3.72 (1 H, dd, $J_{3'',4''}$ 9.1 and $J_{3'',2''}$ 8.4 Hz, 3″-H), 3.82 (1 H, ddd, $J_{1'',2''}$ 9.1, $J_{1'',1b}$ 9.1 and $J_{1'',1a}$ 2.8 Hz, 1″-H), 4.47, 4.54, 4.59, 4.63, 4.82, 4.89, 4.91, and 4.92 (8 H, 8 × d, *J* 10.5—11.9 Hz, benzylic), and 7.16—7.35 (20 H, m, ArH); *m*/*z* 622 (M^+), 530 ($M^+ - 92$), 424 ($M^+ - 198$), and 316 ($M^+ - 306$).

2-(2,3,4,6-*Tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*acetophenone* (**7b**).—Anomerization of the α-isomer (**7a**) (method A or B) afforded 2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*aceto-phenone* (**7b**), m.p. 81—82 °C (from methanol) (Found: C, 78.6; H, 6.6. $C_{42}H_{42}O_6$ requires C, 78.5; H, 6.6%); $[\alpha]_D^{20}$ −30.6° (*c* 1); $\nu_{max.}$ 1 690 cm^{-1}; δ_H(500 MHz) 3.07 (1 H, dd, $J_{2a,2b}$ 16.1 and $J_{2a,1''}$ 8.4 Hz, 2-H_a), 3.11 (1 H, dd, $J_{2b,2a}$ 16.1 and $J_{1b,1''}$ 3.5 Hz, 2-H_b), 3.43 (1 H, dd, $J_{2'',1''}$ 9.1 and $J_{2'',3''}$ 9.1 Hz, 2″-H), 3.45 (1 H, ddd, $J_{5'',4''}$ 9.1, $J_{5'',6''b}$ 3.5, and $J_{5'',6''a}$ 2.1 Hz, 5″-H), 3.63 (1 H, dd, $J_{6''a,6''b}$ 11.2 and $J_{6''a,5''}$ 2.1 Hz, 6″-H_a) 3.65 (1 H, dd, $J_{6''b,6''a}$ 11.2 and $J_{6''b,5''}$ 3.5 Hz, 6″-H_b), 3.69 (1 H, dd, $J_{4'',3''}$ 9.1 and $J_{4'',5''}$ 9.1 Hz, 4″-H), 3.76 (1 H, dd, $J_{3'',2''}$ 9.1 and $J_{3'',4''}$ 9.1 Hz, 3″-H), 3.97 (1 H, ddd, $J_{1'',2''}$ 9.1, $J_{1'',2a}$ 8.4, and $J_{1'',2b}$ 3.5 Hz, 1″-H), 4.41, 4.52, 4.58, 4.68, 4.81, 4.89, 4.94, and 4.94 (8 H, 8 × d, *J* 10.5—12.6 Hz, benzylic), 7.14—7.36 (20 H, m, ArH), 7.41 (2 H, dd, *J* 7.2 and 7.2 Hz, 3′- and 5′-H), 7.53 (1 H, ddd, *J* 7.2, 7.2, and 1.4 Hz, 4′-H), and 7.85 (2 H, dd, *J* 7.2 and 1.4 Hz, 2′- and 6′-H); *m*/*z* 642 (M^+), 550 ($M^+ - 92$), 444 ($M^+ - 198$), and 336 ($M^+ - 306$).

4′-*Chloro*-2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)-*acetophenone* (**8b**).—Anomerization of the α-isomer (**8a**) (method A or B) afforded the 4′-*chloro*-2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*acetophenone* (**8b**), m.p. 44—45 °C (from methanol) (Found: C, 74.5; H, 6.1. $C_{42}H_{41}ClO_6$ requires C, 74.5; H, 6.1%); $[\alpha]_D^{20}$ −28.0° (*c* 1); $\nu_{max.}$ 1 695 cm^{-1}; δ_H(500 MHz) 3.00 (1 H, dd, $J_{2a,2b}$ 16.1 and $J_{2a,1''}$ 7.7 Hz, 2-H_a), 3.06 (1 H, dd, $J_{2b,2a}$ 16.1 and $J_{2b,1''}$ 3.5 Hz, 2-H_b), 3.41 (1 H, dd, $J_{2'',1''}$ 9.1 and $J_{2'',3''}$ 9.1 Hz, 2″-H), 3.42 (1 H, ddd, $J_{5'',4''}$ 9.8, $J_{5'',6''b}$ 3.5, and $J_{5'',6''a}$ 2.1 Hz, 5″-H), 3.61 (1 H, dd, $J_{6''a,6''b}$ 11.2 and $J_{6''a,5''}$ 2.1 Hz, 6″-H_a), 3.65 (1 H, dd, $J_{6''b,6''a}$ 11.2 and $J_{6''b,5''}$ 3.5 Hz, 6″-H_b), 3.68 (1 H, dd, $J_{4'',5''}$ 9.8 and $J_{4'',3''}$ 9.1 Hz, 4″-H), 3.75 (1 H, dd, $J_{3'',2''}$ 9.1 and $J_{3'',4''}$ 9.1 Hz, 3″-H), 3.92 (1 H, ddd, $J_{1'',2''}$ 9.1, $J_{1'',2a}$ 7.7, and $J_{1'',2b}$ 3.5 Hz, 1″-H), 4.41, 4.51, 4.58, 4.68, 4.81, 4.89, 4.94, and 4.94 (8 H, 8 × d, *J* 10.5—12.6 Hz, benzylic), 7.15—7.35 (20 H, m, ArH), 7.36 (2 H, d, *J* 7.8 Hz, 3′- and 5′-H), and 7.75 (2 H, d, *J* 7.8 Hz, 2′- and 6′-H); *m*/*z* 676 (M^+), 584 ($M^+ - 92$), 478 ($M^+ - 198$), and 370 ($M^+ - 306$).

2-(2,3,4,6-*Tetra*-O-*benzyl*-β-D-*glucopyranosyl*)-2′-*acetonaphthone* (**9b**).—Anomerization of the α-isomer (**9a**) (method A or B) afforded 2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)-2′-*acetonaphthone* (**9b**), m.p. 100—101 °C (from di-isopropyl ether) (Found: C, 79.8; H, 6.3. $C_{46}H_{44}O_6$ requires C, 79.7; H, 6.4%); $[\alpha]_D^{20}$ −33.2° (*c* 1); $\nu_{max.}$ 1 685 cm^{-1}; δ_H(500 MHz) 3.20 (1 H, dd, $J_{2a,2b}$ 16.1 and $J_{2a,1''}$ 7.7 Hz, 2-H_a), 3.24 (1 H, dd, $J_{2b,2a}$ 16.1 and $J_{2b,1''}$ 3.5 Hz, 2-H_b), 3.47 (1 H, ddd, $J_{5'',4''}$ 9.1, $J_{5'',6''b}$ 3.5, and $J_{5'',6''a}$ 2.1 Hz, 5″-H), 3.48 (1 H, dd, $J_{2'',1''}$ 9.1 and $J_{2'',3''}$ 9.1 Hz, 2″-H), 3.62 (1 H, dd, $J_{6''a,6''b}$ 11.2 and $J_{6''a,5''}$ 2.1 Hz, 6″-H_a), 3.66 (1 H, dd, $J_{6''b,6''a}$ 11.2 and $J_{6''b,5''}$ 3.5 Hz, 6″-H_b), 3.71 (1 H, dd, $J_{4'',3''}$ 9.1 and $J_{4'',5''}$ 9.1 Hz, 4″-H), 3.78 (1 H, dd, $J_{3'',2''}$ 9.1 and $J_{3'',4''}$ 9.1 Hz, 3″-H), 4.03 (1 H, ddd, $J_{1'',2''}$ 9.1, $J_{1'',2a}$ 7.7, and $J_{1'',2b}$ 3.5 Hz, 1″-H), 4.48, 4.49, 4.58, 4.73, 4.83, 4.91, 4.95, and 4.96 (8 H, 8 × d, *J* 10.5—11.9 Hz, benzylic), 7.15—7.39 (20 H, m, ArH), 7.54 (1 H, ddd, *J* 7.8, 7.8, and 1.2 Hz, 6′- or 7′-H), 7.59 (1 H, ddd, *J* 7.8, 7.8, and 1.2 Hz, 7′- or 6′-H), 7.84 (1 H, d, *J* 7.8 Hz, 4′-H), 7.86 (1 H, d, *J* 7.8 Hz, 5′- or 8′-H), 7.90 (1 H, d, *J* 7.8 Hz, 8′- or 5′-H), 7.95 (1 H, dd, *J* 7.8 and 1.2 Hz, 3′-H), and 8.32 (1 H, br s, 1′-H); *m/z* 692 (M^+), 600 (M^+ − 92), 494 (M^+ − 198), and 386 (M^+ − 306).

Methyl 2-(2,3,4,6-*Tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*acetate* (**10b**).—(i) Anomerization of the α-isomer (**10a**) (method C) afforded the *methyl* 2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*acetate* (**10b**), m.p. 65—66 °C (from light petroleum) (Found: C, 74.4; H, 6.7. $C_{37}H_{40}O_7$ requires C, 74.5; H, 6.7%); $[\alpha]_D^{20}$ −3.0° (*c* 1); $\nu_{max.}$ 1 732 cm^{-1}; δ_H(300 MHz) 2.48 (1 H, dd, $J_{2a,2b}$ 15.0 and $J_{2a,1''}$ 8.0 Hz, 2-H_a), 2.73 (1 H, dd, $J_{2b,2a}$ 15.0 and $J_{2b,1''}$ 4.0 Hz, 2-H_b), 3.36 (1 H, dd, $J_{2'',1''}$ 9.5 and $J_{2'',3''}$ 9.5 Hz, 2″-H), 3.45 (1 H, ddd, $J_{5'',4''}$ 9.5, $J_{5'',6''a}$ 3.0, and $J_{5'',6''b}$ 3.0 Hz, 5″-H), 3.60 (3 H, s, CO_2Me), 3.65 (1 H, dd, $J_{4'',5''}$ 9.5 and $J_{4'',3''}$ 9.5 Hz, 4″-H), 3.69 (2 H, d, *J* 3.0 Hz, A_2 part of A_2X system, 6″-H_2), 3.72 (1 H, d, $J_{3'',4''}$ 9.5 and $J_{3'',2''}$ 9.5 Hz, 3″-H), 3.75 (1 H, ddd, $J_{1'',2''}$ 9.5, $J_{1'',2a}$ 8.0, and $J_{1'',2b}$ 4.0 Hz, 1″-H), 4.50, 4.56, 4.60, 4.62, 4.81, 4.87, 4.91, and 4.92 (8 H, 8 × d, *J* 10.5—12.0 Hz, benzylic), and 7.10—7.65 (20 H, m, ArH); *m/z* 596 (M^+), 504 (M^+ − 92), 398 (M^+ − 198), and 290 (M^+ − 306).

(ii) Anomerization of the α-isomer (**10a**) (method D) and chromatography afforded sequencially methyl 2-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)acetate (**10b**) (74.3%), m.p. 65—66 °C (from light petroleum), identical in all respects with that reported above; methyl 2-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)acetate (**10a**) (3.1%); methyl 2-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)acetate (0.43%), m.p. 39—40 °C (from light petroleum); and methyl 2-(2,3,4,6-tetra-*O*-benzyl-β-D-mannopyranosyl)acetate (9.1%); both mannopyranosylacetates showed physicochemical properties identical with those of authentic samples obtained as reported in the accompanying paper.[10]

Ethyl 2-(2,3,4,6-*Tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*acetate* (**11b**).—(i) Anomerization of the α-isomer (**11a**) (method C) afforded *ethyl* 2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*acetate* (**11b**), m.p. 43.5—45 °C (from light petroleum) (Found: C, 74.7; H, 6.9. $C_{38}H_{42}O_7$ requires C, 74.7; H, 6.9%); $[\alpha]_D^{20}$ −2.2° (*c* 1); $\nu_{max.}$ 1 732 cm^{-1}; δ_H(300 MHz) 1.19 (3 H, t, *J* 7.0 Hz, CO_2CH_2Me), 2.46 (1 H, dd, $J_{2a,2b}$ 15.5 and $J_{2a,1''}$ 8.3 Hz, 2-H_a), 2.73 (1 H, dd, $J_{2b,2a}$ 15.5 and $J_{2b,1''}$ 3.5 Hz, 2-H_b), 3.36 (1 H, dd, $J_{2'',1''}$ 9.5, and $J_{2'',3''}$ 9.5 Hz, 2″-H), 3.45 (1 H, ddd, $J_{5'',4''}$ 9.5, $J_{5'',6''a}$ 3.0, and $J_{5'',6''b}$ 3.0 Hz, 5″-H), 3.66 (1 H, dd, $J_{4'',3''}$ 9.5 and $J_{4'',5''}$ 9.5 Hz, 4″-H), 3.69 (2 H, d, *J* 3.0 Hz, A_2 part of A_2X system, 6″-H_2), 3.72 (1 H, dd, $J_{3'',2''}$ 9.5 and $J_{3'',4''}$ 9.5 Hz, 3″-H), 3.75 (1 H, ddd, $J_{1'',2''}$ 9.5, $J_{1'',2a}$ 8.3, and $J_{1'',2b}$ 3.5 Hz, 1″-H), 4.08 (2 H, q, *J* 7.0 Hz, OCH_2Me), 4.51, 4.57, 4.61, 4.63, 4.81, 4.87, 4.91, and 4.92 (8 H, 8 × d, *J* 10.5—11.0 Hz, benzylic), and 7.10—7.65 (20 H, m, ArH); *m/z* 610 (M^+), 518 (M^+ − 92), 412 (M^+ − 198), and 304 (M^+ − 306).

(ii) Anomerization of ethyl 2-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)acetate (**11a**) (method D) and chromatography afforded first a mixture of anomers (**11a**) and ethyl 2-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl) acetate (**11b**) (77.5% yield) in the ratio 4:96 (h.p.l.c.). The mixture afforded by crystallization the pure β-anomer (**11b**), m.p. 44—45 °C (from light petroleum), identical with that reported above. The second eluted compound (9.5% yield) was a mixture of two components (h.p.l.c.), separable by preparative h.p.t.l.c. (Silica gel 60 F_{254} precoated, Merck, developing three times with hexane–ethyl acetate 80:20) into ethyl 2-(2,3,4,6-tetra-*O*-benzyl)-α-D-mannopyranosyl acetate and ethyl 2-(2,3,4,6-tetra-*O*-benzyl)-β-D-mannopyranosyl acetate. Both isomers were identical with authentic samples obtained as reported in the accompanying paper.

Diethyl 2-(2,3,4,6-*Tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*malonate* (**12b**).—Anomerization of the α-isomer (**12a**) (method C) afforded *diethyl* 2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)-*malonate* (**12b**), m.p. 49—50 °C (from di-isopropyl ether-light petroleum) (Found: C, 72.2; H, 6.8. $C_{41}H_{46}O_9$ requires C, 72.1; H, 6.8%); $[\alpha]_D^{20}$ +3.2° (*c* 1); $\nu_{max.}$ 1 728 cm^{-1}; δ_H(300 MHz) 1.19 (3 H, t, *J* 7.0 Hz, CH_2Me), 1.22 (3 H, t, *J* 7.0 Hz, CH_2Me), 3.52 (1 H, ddd, $J_{5'',4''}$ 9.0, $J_{5'',6''a}$ 2.5 and $J_{5'',6''b}$ 2.5 Hz, 5″-H), 3.67—3.79 (5 H, overlapping, 2″-, 3″-, 4″-H, and 6″-H_2), 3.78 (1 H, d, $J_{2,1''}$ 5.0 Hz, 2-H), 4.00 (1 H, dd, $J_{1'',2''}$ 9.5, $J_{1'',2}$ 5.0 Hz, 1″-H), 4.03 (1 H, dq, *J* 10.5 and 7.0 Hz, C*H*HMe), 4.08 (1 H, dq, *J* 10.5 and 7.0 Hz, C*H*HMe), 4.12 (2 H, q, *J* 7.0 Hz, CH_2Me), 4.53, 4.61, 4.65, 4.70, 4.84, 4.87, 4.94, and 4.99 (8 H, 8 × d, *J* 10.5—11.5 Hz, benzylic), and 7.10—7.65 (20 H, m, ArH); *m/z* 682 (M^+), 590 (M^+ − 92), 484 (M^+ − 198), and 376 (M^+ − 306).

Baeyer–Villiger (*B.–V.*) *Oxidation and Lithium Aluminium Hydride Reduction. General Procedure.*—A solution of the *C*-glucopyranoside (1 mmol) in dichloromethane (5 ml) was added, at 0 °C, to a solution of trifluoroperacetic acid in dichloromethane [prepared by adding TFAA (21.3 ml) to hydrogen peroxide (3.8 ml; 30%) in dichloromethane (23.4 ml) at 0 °C]. The mixture was stirred at room temperature for 30 min and then was poured into 2% aqueous potassium carbonate and extracted with dichloromethane. The extract was washed with water, dried, and evaporated under reduced pressure. The residue was dissolved in dry diethyl ether (100 ml) and lithium aluminium hydride (100 mg, 2.5 mmol) was added. The mixture, after being stirred at room temperature for 2 h and worked up, afforded a crude product which was chromatographed.

B.-V. Oxidation and $LiAlH_4$ *Reduction of* 1-(5α-*Cholestan*-3β-*yl*)-2-(2,3,4,6-*tetra*-O-*benzyl*-α-D-*glucopyranosyl*)*ethanone* (**4a**).—The α-*C*-glucopyranoside (**4a**) gave, after reduction and chromatography, (i) cholestan-3β-ol (**15**) (74%), m.p. 138—140 °C (from methanol); $[\alpha]_D^{20}$ +24° (*c* 1), identical with an authentic sample (^1H n.m.r. and mixed m.p.); and (ii) 2-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)ethanol (**14a**) (72%), m.p. 65—66 °C (from hexane) (Found: C, 76.0; H, 7.1. Calc. for $C_{36}H_{40}O_6$: C, 76.0; H, 7.1%); $[\alpha]_D^{20}$ +28.0° (*c* 1) {lit.,[5d] oil; $[\alpha]_D^{20}$ +29.7° (*c* 0.6 in CH_2Cl_2)}; δ_H(300 MHz) 1.91 (1 H, ddt, $J_{2a,2b}$ 15.0, $J_{2a,1}$ 5.0, and $J_{2a,1''}$ 4.0 Hz, 2-H_a), 2.05 (1 H, ddt, $J_{2b,2a}$ 15.0, $J_{2b,1''}$ 9.5, and $J_{2b,1}$ 5.0 Hz, 2-H_b), 2.46 (1 H, m, OH), 3.49 (1 H, dd, $J_{6''a,6''b}$ 10.0 and $J_{6''a,5''}$ 8.5 Hz, 6″-H_a), 3.56 (1 H, dd, $J_{2'',1''}$ 5.5 and $J_{2'',3''}$ 9.0 Hz, 2″-H), 3.63 (1 H, dd, $J_{6''b,6''a}$ 10.0 and $J_{6''b,5''}$ 2.0 Hz, 6″-H_b), 3.71 (1 H, dd, $J_{3'',2''}$ 9.0 and $J_{3'',4''}$ 9.0 Hz, 3″-H), 3.73 (1 H, dd, $J_{4'',3''}$ 9.0 and $J_{4'',5''}$ 9.0 Hz, 4″-H), 3.74—3.82 (3 H, m, 5″-H and 1-H_2), 4.21 (1 H, ddd, $J_{1'',2''}$ 5.5, $J_{1'',2b}$ 9.5, and $J_{1'',2a}$ 4.0 Hz, 1″-H), 4.46, 4.48, 4.56, 4.61, 4.71, 4.79, 4.81, and

4.91 (8 H, 8 × d, *J* 10.5—12.0 Hz, benzylic), and 7.10—7.65 (20 H, m, ArH).

B.–V. Oxidation and $LiAlH_4$ *Reduction of* 1-(5α-*Cholestan*-3β-*yl*)-2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*ethanone* (**4b**).—The β-*C*-glucopyranoside (**4b**) gave, after reduction and chromatography, (i) cholestan-3β-ol (**15**) (75%), m.p. 138—140 °C (from methanol), identical with that reported above; and (ii) 2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*ethanol* (**14b**) (74%), m.p. 76—77 °C (from di-isopropyl ether) (Found: C, 76.1; H, 7.1. $C_{36}H_{40}O_6$ requires C, 76.0; H, 7.1%); $[\alpha]_D^{20}$ +2.4° (*c* 1); δ_H(300 MHz) 1.75 (1 H, ddt, $J_{2a,2b}$ 14.5, $J_{2a,1'}$ 8.5, and $J_{2a,1}$ 5.0 Hz, 2-H_a), 2.05 (1 H, ddt, $J_{2b,2a}$ 14.5, $J_{2b,1'}$ 2.5, and $J_{2b,1}$ 4.0 Hz, 2-H_b), 2.66 (1 H, m, OH), 3.34 (1 H, dd, *J* 9.0 and 9.0 Hz), 3.46 (1 H, ddd, $J_{5'',4''}$ 9.0, $J_{5'',6''a}$ 5.0, and $J_{5'',6''b}$ 2.0 Hz, 5″-H), 3.50 (1 H, ddd, $J_{1'',2''}$ 9.0, $J_{1'',2a}$ 8.5, and $J_{1'',2b}$ 2.5 Hz, 1″-H), 3.57 (1 H, dd, *J* 9.0 and 9.0 Hz), 3.58 (1 H, dd, $J_{6''a,6''b}$ 10.0 and $J_{6''a,5''}$ 5.0 Hz, 6″-H_a), 3.66 (1 H, dd, $J_{6''b,6''a}$ 10.0 and $J_{6''b,5''}$ 2.0 Hz, 6″-H), 3.69 (1 H, dd, *J* 9.0 and 9.0 Hz), 3.74—3.82 (2 H, m), 4.50, 4.54, 4.55, 4.63, 4.82, 4.88, 4.89, and 4.92 (8 H, 8 × d, *J* 10.5—12.0 Hz, benzylic), and 7.10—7.65 (20 H, m, ArH).

B.–V. oxidation and $LiAlH_4$ reduction was also performed on 1-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)propan-2-one (**5b**), 3,3-dimethyl-1-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)butan-2-one (**6b**), 2-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)acetophenone (**7b**), 4′-chloro-2-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)acetophenone (**8b**), and 2-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-2′-acetonaphthone (**9b**). In all cases 2-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)ethanol (**14b**) was obtained (in yields better than 70%), showing m.p. 76—77 °C, $[\alpha]_D^{20}$ +2.4 ± 0.3° (*c* 1), and other physicochemical properties identical with those reported above.

Decarboxylation of Methyl 3-*Oxo*-2-(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*butanoate* (**2b**).—A mixture of the β-*C*-glucopyranoside (**2b**) (100 mg) and potassium carbonate (27 mg) was refluxed in dimethylformamide (3 ml) containing thiophenol (36 μl) for 2 h. Usual work-up and rapid chromatography afforded 1-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)propan-2-one (**5b**) (60 mg), m.p. 70—71 °C (from methanol); $[\alpha]_D^{20}$ −6.2° (*c* 1), identical with that reported above.

Decarboxylation of Diethyl 2-(2,3,4,6-*Tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*malonate* (**12b**).—The β-*C*-glucopyranoside (**12b**) (200 mg) was heated at 180 °C in a mixture of dimethyl sulphoxide [5 ml, containing water (100 μl)] and sodium chloride (200 mg) for 3 h. Work-up and rapid chromatography afforded ethyl 2-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-acetate (**11b**) (150 mg), m.p. 44—45 °C (from light petroleum), identical with that reported above. The product was indistinguishable from the starting malonate (**12b**) by t.l.c. but was separable by h.p.l.c.

Lithium Aluminium Hydride Reduction of Methyl 2-(2,3,4,6-*Tetra*-O-*benzyl*-β-D-*glucopyranosyl*)*acetate* (**10b**).—The β-*C*-glucopyranoside (**10b**) (596 mg) was dissolved in dry diethyl ether (100 ml) and lithium aluminium hydride (100 mg) was added. The mixture, after being stirred at room temperature for 2 h and worked up, afforded 2-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)ethanol (**14b**) (85%), m.p. 76—77 °C (from di-isopropyl ether), identical with that reported above. The same compound (**14b**) was obtained by similar reduction of ethyl 2-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)acetate (**11b**).

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