ANNULATED SUGARS: FORMATION AND REACTIONS OF SOME CYCLO-BUTANOHEXOPYRANOSIDES

DAVID ROY HICKS*, JOHN LAURENT PRIMEAU**, AND BERT FRASER-REID[†]

Guelph–Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, University of Waterloo, Waterloo, Ontario N2L 3G1 (Canada)

ABSTRACT

The preparation of cyclobutanopyranosides by [2 + 2] photoadditions to methyl 2,3-dideoxy-2-*C*-methyl-α-D-*glycero*-hex-2-enopyranosid-4-ulose has been explored. Vinyl acetate adds readily, giving a mixture of diastereomers in good yield. Attempts to deacetylate the photoadduct causes gross decomposition. However, the addition of excess of methyl-lithium converts the carbonyl group into a tertiary alcohol and cleaves the acetate. Attempts to deoxygenate selectively the secondary hydroxyl of the resulting diol were unsuccessful. With ethylene, the photoaddition requires several days and the risk of photodecomposition is high. Some transformations of the photoadducts are described.

INTRODUCTION

The interest in the use of carbohydrate derivatives in synthetic organic chemistry can be gauged by the fact that, beginning with Vol. 9, there is a chapter in the Specialist Periodical Reports on Carbohydrate Chemistry entitled "The Synthesis of Optically Active Non-Carbohydrate Compounds". Prior to 1975, there were few reports[1] on the use of sugars as starting materials for organic synthesis, but three review articles have been subsequently published[2-4], none of which was able to keep abreast of developing trends. Although many targets have been selected, there has been a marked emphasis on the polyoxomacrolides[5]. By contrast, there have been few reports on the development of sugars as synthons for carbocyclic systems[6] and, because of their central role in organic chemistry and their abundance and variety amongst natural products, we have initiated a program in this area.

Theoretically, there are several procedures that could be explored for cyclisation of an aldose to give a cycloalkane derivative[6a,6b]. However, such an approach could not utilise the major stereocontrolling force associated with the anomeric effect.

Accordingly, we have sought to use alkyl α-D-hexopyranosides as templates. The basic strategy[7] has been to fuse a carbocyclic ring to the α-D-hexopyranoside, to give an "annulated sugar", and then cleave the sugar ring to leave behind the carbocycle. This strategy has been applied to obtain the (+)- and (−)-forms of chrysanthemum dicarboxylic acid from a hexopyranoside precursor[8]. In that study, the annulated sugar was a cyclopropanohexopyranoside, and the successful transformation into each antipode of the target rested on an epimerisation at C-2 or C-3. However, such epimerisations might not always be possible, and, as a case in point, we have considered an approach to the boll-weevil pheromone grandisol (cis-2-isopropenyl-1-methyl-cyclobutane-ethanol)[9] the antipodes of which, (+)-1 and (−)-1, are shown in Scheme 1. Since C-1 of 1 is tetra-substituted, the "key epimerisation" technique used in the chrysanthemic acid project cannot be employed. Hexopyranoside substrates for cyclobutane annulation would need a C-methyl substituent at C-2, C-3, or C-4, and although these possibilities exist[10,11], we consider here only the enones 2 and 7.

Scheme 1
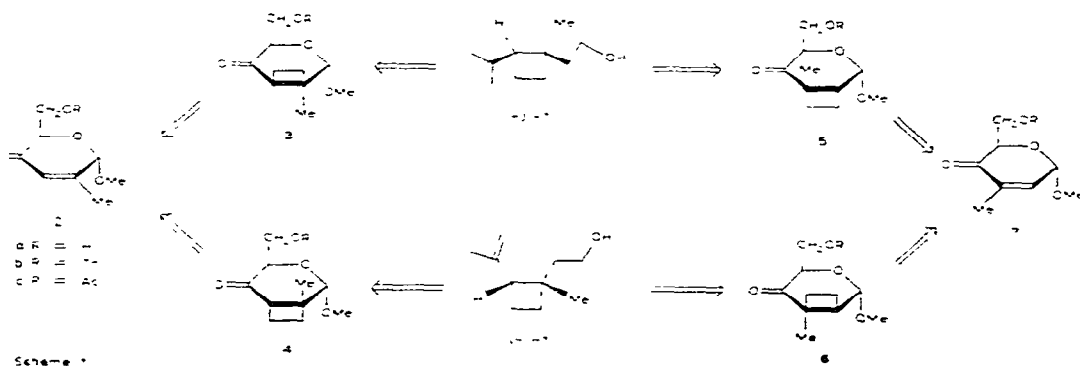
Annulation of 2 and 7 would lead to two sets of diastereomers 3/4, and 5/6; 3 and 5 are correlated with (+)-1, whereas 4 and 6 are correlated with (−)-1. Two approaches are therefore possible, depending on the stereoselectivity in the cyclo-butanation process: A, if cyclobutanation occurred selectively from one face of the hexopyranoside substrate, then both 2 and 7 would have to be used in order to obtain both (+)-1 and (−)-1; B, if cyclobutanation occurred non-stereoselectively, then both enantiomers could be prepared from either 2 or 7. This approach also requires the isolation of 3–6; if annulation is α-specific, 4 and 5 would be needed and, if β-specific, 3 and 6.

We now report the preparation of some cyclobutanopyranosides that are plausible synthons of 1.

RESULTS AND DISCUSSION

For approach A, our attempts to achieve specific cyclobutanation were based on the two-step formation of 2,3-cyclopropanohexopyranosid-4-uloses by photo-alkylation of 2b with methanol followed by cyclisation of the derived sulfonate[12,13].
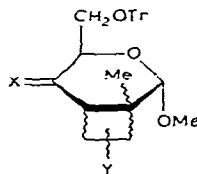
CH$_2$OTr

CH$_2$OTr

CH$_2$OTr
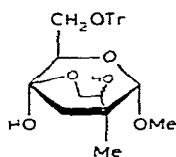
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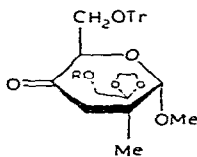
9a R = H
9b R = Ts

10

	X	Y
a	O	OAc
b	Me, OH	OH
c	Me, OH	OTs
d	Me, OH	I
e	Me, OH	OAc
f	Me, OH	O
g	Me, OH	H

The extreme ease of this cyclisation was in marked contrast to some examples in the literature[14], and it was hoped therefore that it might also be possible to form a four-membered ring in spite of the generally discouraging prospects for such reactions[15]. Although ethylene glycol photo-added to 2b in excellent yield, the product existed as the hemiacetal[12] 8 and attempts to force it open failed. The ethylene acetal of glycol-aldehyde also gave a photoadduct[12] (9a), but cyclisation of the derived sulfonate 9b could not be effected under a variety of experimental conditions.

We next considered photochemical [2 + 2] cycloaddition reactions, which are highly favoured routes to cyclobutane annulation[16,17] and have been explored in the sugar series[18]. Ethylene has low solubility in organic solvents, and such derivatives as 1,1-dimethoxyethylene[19], 1,2-dichloroethylene[20], vinyl acetate[21], and allene[22] have been used with subsequent removal of the unwanted substituent(s) from the cyclobutane ring.

Photoaddition of vinyl acetate to 2b was not expected to be regio- or stereo-selective[21], and the product (10a) showed several acetyl signals in the [1]H-n.m.r. spectrum. Scheme 1 shows that C-4 of 3 and 4 becomes part of the isopropenyl function of 1, and a methyl group is needed at this position. Excess of methyl-lithium was allowed to react with 10a, so that carbonyl addition and acetate cleavage occurred simultaneously to give the diol mixture 10b. Attempts to remove the secondary hydroxyl group from 10b via the sulfonate (10c), iodide (10d), acetate (10e) (by photolysis[23]), or ketone (10f) (by the Cagliotto reaction[24,25]) failed to yield 10g.

Attention was then turned to the addition of ethylene to 2, since, for these types of addition, high yields of photoproducts may be obtained at low temperatures[26] chosen to enhance the solubility of ethylene. However, between $-40°$ and $-60°$ in various solvents and with photolysis from 15–48 h, the maximum yield of photo-adduct(s) was 10%. At higher temperatures using water-cooled vessels, the optimum conditions involved a 2% solution of the acetate 2c in benzene. Complete reaction of 2c required 10–12 days, but the optimum balance between photoaddition and photodecomposition was achieved in 5–6 days. Column chromatography then gave
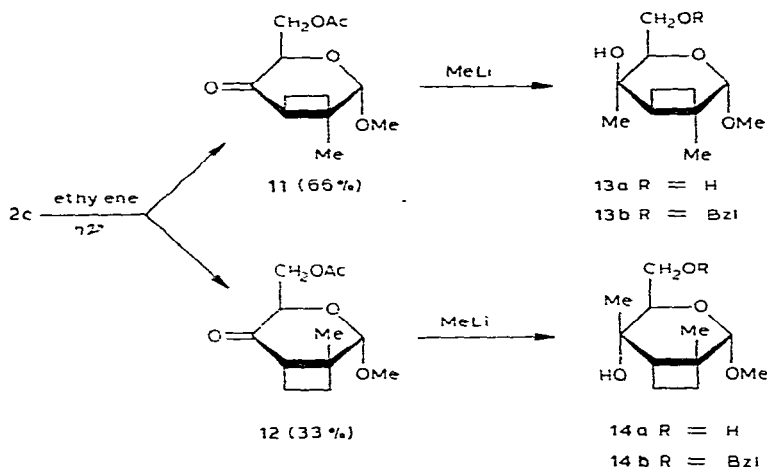
2c and a mixture of photoadducts comprising two of the four possible diastereomeric products, judged from the ^{1}H-n.m.r. spectrum which showed two OMe signals at 3.42 and 3.50 p.p.m., and two CMe signals at 1.22 and 1.38 p.p.m., both in the ratio 2:1.

Although *trans*-fused cyclobutanes are known[27], they usually isomerise to *cis* on chromatography[19] and it was therefore assumed that the foregoing photoadducts were 11 and 12. The mixture, which could not be resolved by t.l.c., was used in the next reaction.

Models of 11 and 12 show that each has a convex surface (α in 11, and β in 12) and some stereoselection was predicted for reagent-approach. Addition of methyl-lithium to the mixture of 11 and 12 gave only two (of the possible four)

TABLE I

ASSIGNMENT OF ^{13}C-N.M.R. SPECTRA (INTERNAL Me$_4$Si) OF 13b AND 14b

Carbon atom	Chemical shifts (δ)		$\Delta\delta$
	13b′	14b′	
C-3′	17.0	18.9	1.9
Me-4	23.1	23.4	0.3
Me-2	26.2	28.1	1.9
C-2′	30.7	27.4	−3.3
C-2	47.8	42.0	−5.8
C-3	48.4	51.1	2.7
MeO-1	55.3	55.1	−0.2
C-4	69.6	67.8	−1.8
C-6 or CH_2Ph	69.9	70.0	0.1
C-5	72.0	66.9	−5.1
C-6 or CH_2Ph	73.8	73.8	0.0
C-1	103.5	104.6	1.1

products, which were isolated by chromatography in yields of 52 and 23 %, respectively. The mass spectra of **11** and **12** (see Experimental) were similar, confirming that they were structural isomers. The less polar (R_F 0.46) product, which crystallised readily from ether, was **13a**. The more polar product **14a** (R_F 0.36) could not be crystallised. The corresponding monobenzyl ethers **13b** and **14b** were obtained by benzylation at room temperature of each isomer separately, or of the mixture of diols and then subsequent separation.

^{1}H-N.m.r. data were of limited value for the assignment of structure to **13** and **14**, since there are no vicinal protons on the sugar ring. However, assignment of the majority of the signals (Table I) in the ^{13}C-n.m.r. spectra was straightforward. The assignments for C-2^1 and C-3^1 were not clear-cut, and the γ-effect rule (Stothers[28]) was invoked which states that a carbon in *gauche* orientation to another carbon or hetero atom is shielded relative to its *anti* counterpart. It is clear that, in the conformation **13b'** (based on Dreiding models), C-3^1 should be strongly shielded by HO-4. Hence, the signals at 17.0 and 30.7 p.p.m. ($\Delta\delta$ 13.7 p.p.m.) are assigned to C-3^1 and C-2^1, respectively. For **14b'**, the $\Delta\delta$ value (8.5 p.p.m.) should be less, since C-2^1 and C-3^1 are *gauche* to O-4 and O-1, respectively.


13 b'   14 b'
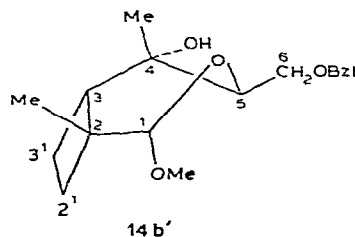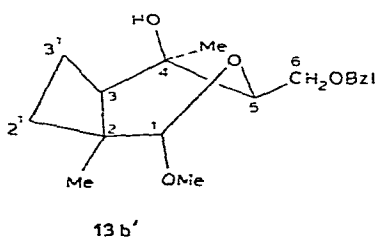
Also, for the conformations **13b'** and **14b'**, there should be a marked difference in the resonances for C-5, which is *gauche* to C-3^1 in **14b**, but *anti* in **13b**. Accordingly, the C-5 resonance for **14b** was assigned at 66.9 p.p.m., and for **13b** at 72.0 p.p.m. The signal for Me-2 occurs at higher field in **13b** because of the γ-effect of MeO-1.

This analysis shows that addition of ethylene to **2** occurred mainly from the β-face to give **11**, and therefore the crystalline diol is **13a**.

Since further processing of the cyclobutanopyranosides might require both
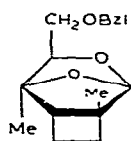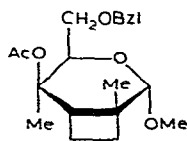
15   16

hydroxyl groups to be protected, some relevant reactions of the diol **13a** were studied. Selective benzylation of the primary hydroxyl group in **13a** to give **13b** was effected at room temperature (see above). However, the use of benzyl chloride–sodium hydride–methyl sulfoxide[29] at 40° or benzyl bromide–sodium hydroxide–tetrahydro-

furan[30] failed to benzylate the tertiary hydroxyl group. More-forcing conditions[31] (sodium hydride–methyl sulfoxide–benzyl chloride at 65°) gave a product which showed no i.r. absorption for hydroxyl. However, the [1]H-n.m.r. spectrum revealed only one benzyl group and the loss of MeO-1. The presence of two CMe signals at 1.25 and 1.35 p.p.m., and the fact that the signal for H-1 (although shifted to much lower field) was still a singlet, suggested that no skeletal rearrangement had occurred. Since the M$^{\pm}$ ion had m/z 274, the 1,4-anhydro structure **15** was assigned. Dreiding models indicated that the axial HO-4 in **13** is well placed to interact with C-1; when a solution of **13b** in aqueous 1,4-dioxane containing a trace ($<0.05\%$) of sulfuric acid was stored at room temperature for 3 h, **15** was obtained in near quantitative yield.

Not unexpectedly, treatment of **13b** with acetic anhydride and pyridine did not acetylate HO-4. Inclusion of 4-dimethylaminopyridine[32] did not help and use of acetic anhydride and a trace of toluene-p-sulfonic acid gave **15**. Treatment of **13b** with boiling acetic anhydride for 24 h gave the acetate **16** and **15** in the ratio 2:1.

Further work on these projects is in progress.

EXPERIMENTAL

Melting points were determined in capillary tubes in a Mel-Temp block and are uncorrected. Elemental analyses were performed by Micro-analyses Laboratory (Toronto). N.m.r. spectra (CDCl$_3$, internal Me$_4$Si) were recorded with Varian T-60, HA-100, or HR-220 spectrometers; J values reported are spacings measured directly from the spectra. I.r. spectra were recorded for solutions in CHCl$_3$ with a Beckman model IR-10 spectrometer and a 0.1-mm sodium chloride cell. Optical rotations were determined on a Carl Zeiss model LEP nür 370740 Lichtelektrisches Präzision polarimeter at 23°.

T.l.c. was performed on silica gel HF-254 (Merck) with ethyl acetate–light petroleum (b.p. 30–60°) mixtures A, 1:4; B, 1:2; and C, 1:10.

Photoaddition of vinyl acetate to **2b**. — A solution of enone **2b** (1.2 g, 2.9 mmol) and vinyl acetate (18.0 g, 0.2 mmol) in acetonitrile (80 mL) in a Pyrex photolysis tube was cooled by a cold finger extending into the solution. Nitrogen was continuously bubbled through the solution *via* a glass capillary tube, and irradiation was carried out at 350 nm by using a Rayonet Photochemical Reactor (model RPR-100). After 12 h, t.l.c. indicated that **2b** had been consumed and that a new compound, which gave an elongated spot (R_F 0.47–0.60; solvent B), had been formed. The product (1.08 g, 75%) obtained upon evaporation of the solvent was dissolved in ether and stirred with neutral alumina (activity 1) for 3 h, to convert any *trans*-addition products into the *cis* isomers[16]. The [1]H-n.m.r. spectrum of the crude product indicated a complex mixture with several OMe, CMe, and OAc signals present, but there were no resonances for vinyl protons. The mass spectrum showed peaks at m/z 423 (M$^+$ — Ph) and 257 (M$^+$ — Tr) consistent with structure **10a**.

Methyl 6-O-acetyl-2,3-dideoxy-2,3-C-ethylene-2-C-methyl-α-D-lyxo- and -α-D-ribo-hexopyranosid-4-ulose (**11** *and* **12**). — A solution of the acetylated enone **2c** (2.0 g, 9.3 mmol) in dry benzene (100 mL) was cooled by a cold finger extending into the solution. Ethylene was bubbled into the solution through a capillary, and irradiation was as described above. After 4–5 days, t.l.c. indicated that a new compound had been formed which ran as an elongated spot, R_F 0.43–0.46 (solvent *B*). The mixture was then concentrated and the residue was subjected to column chromatography (solvent *B*), to give **2c** (1.233 g, 62%) and the mixture **11** + **12** (0.427 g, 19%). Mass spectrum (**11** + **12**): m/z 241 (M^+ − 1), 224 (M^+ − H_2O), and 182 (M^- − HCOOMe). ^{1}H-N.m.r. data: δ 1.1 (s, C-Me), 1.36 (s, C-Me), 1.7–2.8 (m, cyclobutyl), 2.1 (s, OAc), 3.4 (s, OMe), 3.5 (s, OMe), and 4.1–4.6 (m, H-1,5,6,6′).

Methyl 2,3-dideoxy-2,3-C-ethylene-2,4-di-C-methyl-α-D-talo- and -α-D-allo-pyranoside (**13a** *and* **14a**). — A solution of the mixture **11** + **12** (0.344 g, 1.42 mmol) in dry ether (10 mL) under dry nitrogen was cooled in an ice bath and treated with ethereal ∼2M methyl-lithium (3.5 mL). The mixture was stirred at 0° for 2.5 h, and t.l.c. (ether) then indicated the absence of **11** + **12** and the presence of two products, R_F 0.46 and 0.36. The mixture was diluted with ether (10 mL), washed with saturated, aqueous ammonium chloride (20 mL), saturated, aqueous sodium hydrogencarbonate (20 mL), and water (20 mL), dried (Na_2SO_4), and concentrated. The residue was subjected to column chromatography (ether), to give **13a** (0.158 g, 51.5%) and **14a** (0.070 g, 22.8%).

Compound **13a** had m.p. 77.5–79.5° (from ether), $[\alpha]_D^{23}$ +77° (*c* 1, chloroform). ^{1}H-N.m.r. data: δ 1.15 (s, 6 H, 2 CMe), 1.8–2.2 (m, 5 H, cyclobutane), 2.85 (bs, 2 H, 2 OH), 3.4 (s, 3 H, OMe), 3.5–4.1 (m, 3 H, H-5,6,6′), and 4.5 (s, 1 H, H-1). Mass spectrum: m/z 216 (M^+), 215 (M^+ − 1), 167, (10.3), 165 (13.7), 155 (57.0), 149 (6.8), 141 (6.0), 139 (6.0), 137 (7.7), 125 (10.2), 123 (19.7), 113 (7.7), 111 (18.8), 109 (22.3), 107 (22.0), 97 (42.8), 95 (43.0), 91 (15.7), 85 (35.7), 81 (100), 71 (7.0), 69 (6.8), and 67 (9.6).

Anal. Calc. for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 61.06; H, 9.23.

Compound **14a** was an oil, $[\alpha]_D^{23}$ +43° (*c* 0.9, chloroform). ^{1}H-N.m.r. data: δ 1.08 (s, 3 H, CMe), 1.09 (s, 3 H, CMe), 1.40–2.40 (m, 7 H, cyclobutyl and OH), 3.4 (s, 3 H, OMe), 3.8–4.0 (m, 3 H, H-5,6,6′), and 4.4 (s, 1 H, H-1). Mass spectrum: m/z 167 (1.8%), 165 (0.9), 155 (100), 149 (5.4), 141 (5.4), 139 (3.6), 137 (3.6), 125 (18.0), 123 (27.0), 113 (23.6), 111 (36.0), 109 (20.0), 107 (10.9), 97 (27.2), 85 (36.0), 91 (9.0), 85 (85.4), 81 (90.0), 71 (54.0), 69 (18.0), and 67 (18.0).

Methyl 6-O-benzyl-2,3-dideoxy-2,3-C-ethylene-2,4-di-C-methyl-α-D-talo- and -α-D-allo-pyranosides (**13b** *and* **14b**). — (*a*) To a solution of **13a** + **14a** (0.370 g, 1.72 mmol) in dry *N,N*-dimethylformamide (10 mL) was added sodium hydride (0.368 g, 15.0 mmol). The mixture was stirred at room temperature for 45 min and then benzyl chloride (1.2 mL) was added. The reaction was complete in 3 h and two new compounds had been formed, R_F 0.45 and 0.35 (solvent *A*). Methanol (5 mL) was added, the mixture was stirred for 15 min and then concentrated, and the residue was

subjected to chromatography, to give **13b** (0.258 g, 49.2%) and **14b** (0.106 g, 20.5%) as syrups.

Compound **13b** had $[\alpha]_D^{23}$ +86° (c 1.3, chloroform). Mass spectrum: m/z 291.1589 (calc. for M⁻ − Me, 291.1596) and 246 (M⁺ − HCOOMe).

Compound **14b** had $[\alpha]_D^{23}$ + 52° (c 1.1, chloroform). Mass spectrum: m/z 291 (M⁺ − Me) and 245 (M⁺ − 1 − HCOOMe).

See Table I for ¹³C-n.m.r. data.

(*b*) Treatment of **13a** and **14a** separately with benzyl chloride as in (*a*) gave **13b** and **14b**, respectively.

1,4 - Anhydro - 6 - O -benzyl-2,3-dideoxy-2,3-C-ethylene-2,4-di-C-methyl-β-D-talo-pyranoside (**15**). — To a solution of **13b** (0.21 g, 0.68 mmol) in 1,4-dioxane (5 mL) was added 10% sulfuric acid (5 drops). The mixture was stirred at room temperature for 3 h. and t.l.c. then indicated that all of **13b** had reacted and that a new compound, R_F 0.70 (solvent *A*), had been formed. The mixture was neutralised with solid sodium hydrogencarbonate, filtered through Celite, and concentrated. The residue was extracted with ethyl acetate, and the extract was filtered and concentrated, to give **15** (0.168 g, 92%) as a syrup, which had no i.r. absorption for hydroxyl or carbonyl. $[\alpha]_D^{23}$ +11° (c 0.7, chloroform). ¹H-N.m.r. data: δ 1.25 (s, 3 H, CMe), 1.35 (s, 3 H, CMe), 1.55–2.1 (m, 5 H, cyclobutyl), 3.37 (ABM, 2 H, J_{AB} 10.0, J_{AM} 7.0, J_{BM} 5.0 Hz, H-6,6'), 3.58 (dd, 1 H, $J_{5,6}$ 7.0, $J_{5,6}$ 5.0 Hz, H-5), 4.52 (AB quartet, 2 H, J_{AB} 110 Hz, PhCH₂), 5.02 (s, 1 H, H-1), and 7.35 (s, 5 H, Ph). Mass spectrum: m/z 274.1694 (calc. for M⁺ 274.1703).

Methyl 4-O-acetyl-6-O-benzyl-2,3-dideoxy-2,3-C-ethylene-2,4-di-C-methyl-α-D-talopyranoside (**16**). — A solution of **13b** (0.153 g, 0.5 mmol) in acetic anhydride (10 mL) was boiled under reflux for 12 h. T.l.c. then indicated that no **13b** remained and that two products had been produced, R_F 0.35 and 0.44 (solvent *C*). The cooled mixture was poured into ice-cold, saturated, aqueous sodium hydrogencarbonate (20 mL), stirred for 15 min, and extracted with ether (20 mL). The extract was washed with saturated, aqueous hydrogencarbonate (10 mL) and water (10 mL), dried (Na₂SO₄), and concentrated. The residue was subjected to column chromatography (solvent *C*), to give **16** (0.083 g, 48%) and **15** (0.048 g).

Compound **16** was a syrup, $[\alpha]_D^{23}$ +24° (c 0.8, chloroform), ν_{max} 1730 cm⁻¹ (acetate). Mass spectrum: m/z 317.1746 (calc. for M⁺ − OMe 317.1753) and 227 (M⁺ − CH₂O − PhCH₂). ¹H-N.m.r. data: δ 1.05 (s, 3 H, CMe), 1.55 (s, 3 H, CMe), 1.4–2.0 (m, 5 H, cyclobutyl), 1.92 (s, 3 H, OAc), 3.4 (s, 3 H, OMe), 3.8 (bs, 3 H, H-5,5,6'), 4.65 (bs, 3 H, PhCH₂, H-1), and 7.35 (s, 5 H, Ph).

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