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THE OXIDATION OF POLYCYCLIC DERIVATIVES OF LEVOGLUCOSENONE

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ABSTRACT

The participation of the carbonyl oxygen atom in the acid-catalyzed hydrolysis of the epoxide group of 4,7-epoxy-1aα,2β,2aβ,4α,7α,7aβ,8β,8aα-octahydro-2,8-methaneoxireno[*h*][3]benzoxepin-3(4*H*)-one (a levoglucosenone derivative) has been investigated, and a mechanism leading to formation of the product is presented. When the carbonyl group was reduced, to eliminate the possibility of its participation in epoxide hydrolysis, rearrangement to form a septanose derivative occurred. Polycyclic-ring formation involving the carbonyl oxygen atom was also observed in the oxidation of 1,4-epoxy-1α,4α,5aβ,6β,7β,8β,9β,9aβ-octahydro-7,8-dihydroxy-6,9-methano-3-benzoxepin-5(4*H*)-one with periodic acid.

INTRODUCTION

The search for new sources of chemical compounds, coupled with the desire to utilize waste materials effectively, has stimulated interest in the pyrolysis of cellulosic waste. Pyrolysis of acid-treated newsprint yields levoglucosenone (**1**, 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose). The synthetic utility of levoglucosenone in the production of branched-chain and polycyclic carbohydrate derivatives is becoming increasingly evident[1–4]. It has also proved useful as a starting material in the synthesis of natural products[5]. Derivatives of this versatile molecule undergo intramolecular ring-formation during acid-catalyzed, epoxide hydrolysis[4,6], leading to structures having five fused rings. This phenomenon of intramolecular ring-closure in derivatives of levoglucosenone is investigated more fully herein.

RESULTS AND DISCUSSION

The major, [4 + 2] cycloaddition product of the reaction between levoglucosenone and cyclopentadiene[2] (**2**; 1,4-epoxy-1α,4α,5aβ,6β,9β,9aβ-hexahydro-

*Deceased October 1st, 1983.

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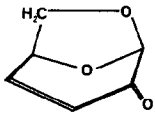
TABLE I

^{1}H-N.M.R ASSIGNMENTS[a] FOR COMPOUNDS **3** TO **13**

Proton	*Compound*										
	3	**4**	**5**	**6**	**7**[b]	**8**[c]	**9**	**10**	**11**	**12**[c]	**13**
H-1	5.04(s)	4.93(s)	5.23(s)	5.28(s)	4.92(s)	5.07(s)	5.15(d)	5.03(s)	5.34(d)	4.67(d)	5.91(d)
H-2	—	—	—	—	—	—	3.15(brs)	3.85(dd)	3.67(brd)	3.67(dd)	5.48(dd)
H-3	2.84(dd)	2.91(dd)	2.99(dd)	2.95(dd)	2.73(dd)	3.01(dd)	2.27(dd)	2.73(ddd)	2.06(m)	2.08(ddd)	2.10[d]
H-4	2.31(dd)	2.25(dd)	2.37(dd)	2.40(m)	2.29(dd)	2.54(dd)	2.21(dd)	2.08(dd)	2.06(m)	2.37(m)	2.49(ddd)
H-5	4.82(d)	4.62(d)	4.66(d)	4.70(d)	4.89(d)	4.72(d)	4.43(d)	4.30(d)	4.60(d)	4.22(m)	4.38(m)
H-6*exo*	3.86(m)	3.71(dd)	3.87(dd)	3.82(m)	3.76(dd)	3.84(dd)	3.73(dd)	3.58(dd)	3.80(dd)	3.81(dd)	4.02(d)
H-6*endo*	3.86(m)	3.76(d)	3.79(d)	3.82(m)	3.89(d)	3.89(dd)	3.77(d)	3.76(d)	3.76(d)	3.71(dd)	3.85(dd)
H-7	3.05(d)	2.19(s)	3.29(brd)	2.29(brd)	2.51(dd)	2.23(dd)	3.15(brs)	3.04(m)	2.77(brd)	2.75(m)	2.83(m)
H-8	3.08(d)	4.06(d)	4.33(d)	4.40(d)	4.39(dd)	5.57(d)	6.29(dd)	6.18(dd)	3.30(d)	3.89(brs)	4.83(brs)
H-9	3.50(d)	4.35(s)	4.55(brs)	5.37(d)	3.54(dd)	5.67(brs)	6.30(dd)	6.31(dd)	3.45(d)	3.99(d)	4.17(d)
H-10	2.78(m)	1.99(m)	2.05(d)	1.72(m)	2.37(d)	2.31(dd)	2.90(brs)	2.91(m)	2.64(brd)	2.37(m)	2.33(m)
H-11*syn*	1.51(dm)	1.86(dm)	1.86(dd)	1.89(dd)	1.90(dm)	1.97(d)	1.44(dm)	1.39(dm)	1.44(dm)	1.94(d)	1.86(d)
H-11*anti*	0.75(d)	1.29(d)	1.39(dd)	1.40(dd)	1.19(dm)	1.38(dm)	1.28(d)	1.16(dm)	0.69(d)	1.50(d)	1.56(d)
OH	—	2.84(m)	1.96(brs)	—	4.18(brs) 2.89(brs)	3.60(m)	2.10(m)	1.81(d)	2.14(m)		
CH_3	—		3.34(s)	3.32(s, OMe) 2.04(s, OAc)							2.01(s, OAc) 2.04(s, OAc) 2.07(s, OAc)

[a]Assignments given in δ values; Me_4Si as internal standard; solvent $CDCl_3$; **6** and **10** recorded at 90 MHz, all others recorded at 360 MHz. [b]Solvent was acetone-d_6. [c]Solvent was methanol-d_4. [d]Obscured by acetate signals.



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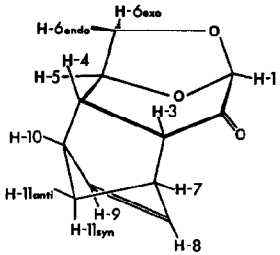

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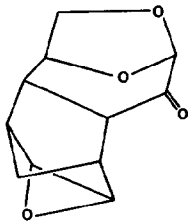

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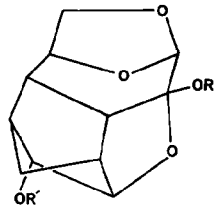
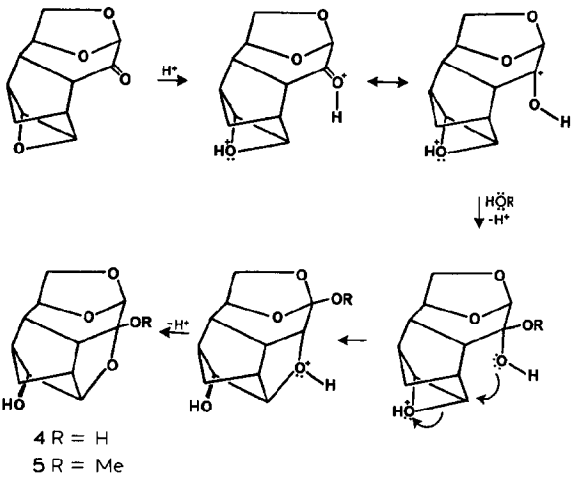


4 R = R' = H
5 R = Me, R' = H
6 R = Me, R' = Ac

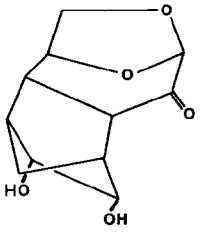


4 R = H
5 R = Me

Scheme 1

6,9-methano-3-benzoxepin-5(4*H*)-one)* was oxidized with *m*-chloroperoxybenzoic acid[4] in order to obtain the *exo* epoxide **3** (a norbornyl epoxide). The acid hydrolysis of norbornyl epoxides has led to rearranged products *via* non-classical ion-formation[7]. Upon hydrolysis of **3**, however, non-classical ion-formation did not occur;

*The numbering system employed for **2** is consistent with that used in earlier reports[2,4], and should not be confused with the IUPAC system of numbering.



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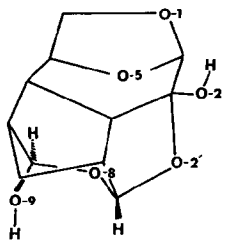

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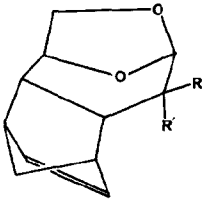
TABLE II

SELECTED COUPLING CONSTANTS (Hz) FOR COMPOUNDS **3** TO **13**

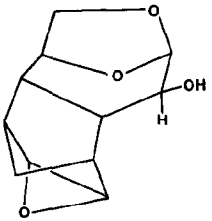
Coupling constant	*Compound*										
	3	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
$J_{1,2}$	—[a]	—	—	—	—	—	4.3	~0	3.6	7.6	8.3
$J_{2,3}$	—	—	—	—	—	—	sm	~10	~0	~9	~9
$J_{3,4}$	10.1	5.4	5	4.4	11.1	~10	9.8	10.0	—	~9	11.9
$J_{5,6exo}$	3.9	5.0	5.1	4.2	5.0	5.3	4.6	3.8	4.5	4.8	~0
$J_{3,7}$	4.5	~0	sm	~0	5.3	~5	3.3	4.0	sm	3.7	sm
$J_{3,8}$	—	4.9	5.1	~5	—	~6	—	—	—	0	0
$J_{4,10}$	3.7	10.4	10	~7	4.6	~8	3.7	4.4	sm	3.3	2.4
$J_{7,8}$	~0	~0	~0	sm	0.9	~0	~2	2.0	~0	~0	~0
$J_{7,11syn}$	2	~0	~3	2.7	~0	~0	~3	~1	~2	~0	~0
$J_{7,11anti}$	—	—	~2	1.5	—	~5	sm	0.5	—	sm	sm
$J_{8,9}$	3.6	—	~0	sm	5.9	—	5.5	5.6	3.1	~0	sm
$J_{9,10}$	~0	~0	~0	~0	~0	~2	~3	2.8	sm	5.7	4.2
$J_{10,11anti}$	~0	—	~0	~0	~0	~5	sm	~0.5	1.5	sm	sm
$J_{6exo,6endo}$	—	6.4	6.5	6.0	7.4	6.6	6.9	6.8	6.9	13.8	9.2
$J_{11syn,11anti}$	10.1	10.2	9.6	9.6	10.2	12.1	~17	8.1	9.8	11.5	10.5

[a]Could not be measured.

instead, an intramolecular cyclization took place, producing the pentacyclic product[4] **4**. To determine the nature of the participation of the carbonyl group at C-2 (for numbering, see **2**), the acid-catalyzed solvolysis of **3** was performed by using methanol as the solvent instead of water. The product isolated, **5**, contained no carbonyl absorbance in its i.r. spectrum. The ^{1}H-n.m.r. spectrum contained a methoxyl singlet and a single, alcohol proton (exchangeable with deuterium, see Table I). To determine the position of the hydroxyl group, **5** was acetylated with acetic anhydride in pyridine, to produce acetate **6**. The position of the alcohol group was determined by intercomparison of the ^{1}H-n.m.r. spectra of **5** and **6**. The *endo* proton of an *exo* norbornyl alcohol has been found to shift by between 1.04 and 1.16 p.p.m. downfield when the alcohol is acetylated[8,9]. Upon acetylation of **5**, a single acetoxyl resonance was observed at 2.04 p.p.m. in the ^{1}H-n.m.r. spectrum of **6**, and the signal associated with H-9 shifted downfield 0.82 p.p.m. (from 4.55 to 5.37 p.p.m.), indicating that the hydroxyl group was on C-9 of **5** (with the methoxyl group on C-2).



9 R = OH, R' = H
10 R = H, R' = OH



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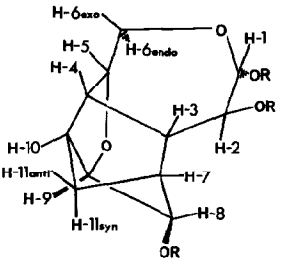
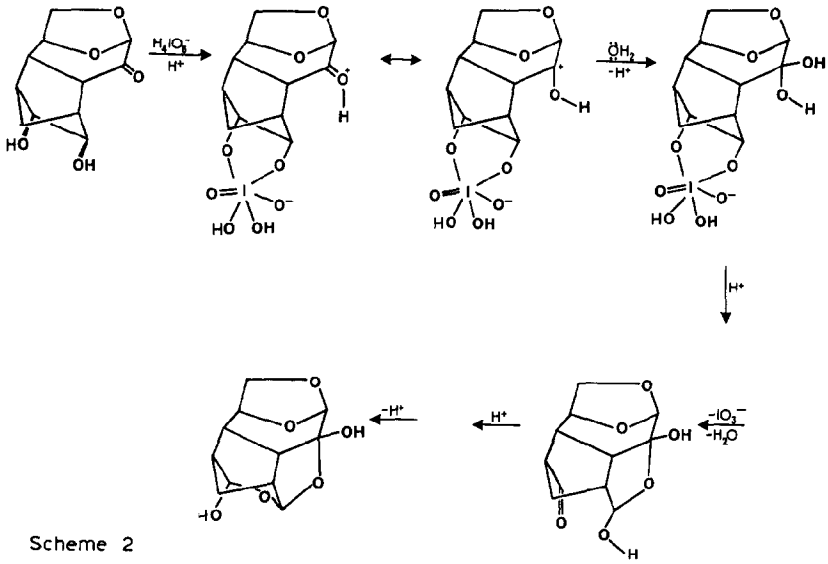


12 R = H
13 R = Ac

A mechanism for the formation of these products may be postulated as shown in Scheme 1. The first step is protonation of the epoxide, together with the carbonyl group of **3**, to form a *gem*-diol (water)–hemiacetal (methanol), with the nonbonded electrons on the alcoholic oxygen atom acting as a nucleophile towards C-8, initiating bonding, and opening of the epoxide ring. The loss of a proton completes the reaction, and yields the product.

Acetal formation between C-2 and C-8 was also observed in a similar system. The *cis, exo* diol[4] **7** was oxidized with periodic acid, to yield a single, crystalline product (**8**). The i.r. spectrum of **8** did not show a carbonyl-stretching band, but did contain two bands in the alcohol region. The structure was assigned, based on the i.r. and ^{1}H-n.m.r. evidence, as containing a hemiacetal at C-2, an acetal at C-8, and a hemiacetal at C-9. Inspection of Dreiding models indicated that the pyranose ring defined by C-7, C-8, O-8, and C-9–C-11 may adopt either a boat or a chair conformation. In either case, the large coupling observed between H-3 and H-8 ($J_{3,8}$ ~6 Hz, see Table II) is consistent with the "W" configuration, which favors long-range coupling[10]. However, a dihedral angle of ~55° between H-7 and H-8 (measured from a Dreiding model) in a chair form is consistent with the observation of little or no coupling ($J_{9,8}$ ~0 Hz) between these two protons. In a boat form, the dihedral angle between H-7 and H-8 is ~25°, for which a larger coupling-constant could be expected, according to the trend predicted by the Karplus equation[11]. A chair conformation also minimizes the nonbonded interaction of H-9 with the oxygen atom in the original pyranose ring, and was chosen as the correct conformation for the new pyranose ring, as shown for **8**.



Scheme 2

A mechanism for the formation of **8** is presented in Scheme 2. The first step is formation of the cyclic ester involving the glycol, along with protonation of the carbonyl group, forming a *gem*-diol at C-2. Protonation of an oxygen atom in the ester allows the nonbonded electrons on O-2 to attack the C-8 center, completing the first ring and cleaving the ester. Hemiacetal formation at C-9 completes the second, pyranose ring, and results in the product.

To hydrolyze the epoxide ring of molecules of this type without assistance from the hydrated carbonyl (or hemiacetal) group, the ketone of **2** was reduced with sodium borohydride in water to yield two isomeric alcohols, **9** and **10**, in 69 and 30% yield, respectively. The two isomers were readily distinguished on the basis of their ^{1}H-n.m.r. spectra, H-1 of the *threo* isomer **9** appearing as a doublet ($J_{1,2}$ 4.3 Hz; dihedral angle measured from Dreiding model, 30°), and H-1 of the *erythro* isomer **10** appearing as a singlet (dihedral angle between H-1 and H-2, 85°)*. Because O-2 of the *threo* isomer **9** cannot participate in epoxide ring-opening, **9** was chosen for epoxidation and subsequent hydrolysis. The epoxidation of **9** resulted in an 86% yield of the *exo* epoxide **11**, whose ^{1}H-n.m.r. spectrum was similar to that of **3** (see Table I).

A solution of the epoxide **11** in dilute sulfuric acid was kept for 15 h, to hydrolyze the epoxide, and a single, crystalline product, **12**, was isolated in quantitative yield. The ^{1}H-n.m.r. spectrum of **12** indicated that a rearrangement had occurred. To aid in the interpretation of the ^{1}H-n.m.r. spectrum of **12**, its tri-*O*-acetyl derivative (**13**) was prepared. By the downfield shifts of H-1, H-2, and H-8, the structure of **12** was determined to be as shown, namely, a septanose derivative hav-

*Compounds **9** and **10** have also been reported by Bhaté and Horton[6], in yields of 39 and 53%, respectively.

ing an oxygen bridge between C-5 and C-9, and this structure was confirmed by single-crystal X-ray crystallography[12]. Septanoid forms of free sugars are uncommon, owing to their instability relative to the furanoid and pyranoid forms; however, some derivatives of septanoses are known to be stable[13].

The *trans* disposition of H-1 and H-2 is indicated by the large spin–spin coupling-constant of 7.6 Hz for **12** (dihedral angle of 179° measured in the solid state) and 8.3 Hz for **13**. A value of ~9 Hz for $J_{2,3}$ of **12** and **13** is of the same order as $J_{1,2}$, indicating that H-2 and H-3 are also *trans* to one another (dihedral angle also 179° for **12** in the solid state). The H-8*endo*, H-9*exo* configuration should result in a small value for $J_{8,9}$ (*exo-endo* norbornyl coupling has been found to be ~2 Hz)[14]. However, there was no observable coupling between H-8 and H-9 in the ^{1}H-n.m.r. spectrum of **12**, which could be due to the strain exerted by the oxygen bridge between C-9 and C-5. The rigid, polycyclic structure of **12** favors long-range "W" coupling, which is observed between H-7 and H-9, and H-7 and H-10 (seen as a sharpening of one signal in the ^{1}H-n.m.r. spectrum upon spin–spin decoupling of the other).

The mechanism of formation of **12** is of interest, as the original pyranoid ring of **11** can be opened by attack on either C-1 or C-5. An understanding of the mechanism will lead to new methods of synthesizing unusual, polycyclic, carbohydrate derivatives.

EXPERIMENTAL

General. — All melting points were determined with a Fisher–Johns melting-point apparatus and are uncorrected. Infrared spectra were recorded with a Nicolet MX-1 spectrometer. All thin-layer chromatography (t.l.c.) assays were conducted on Baker-flex silica gel IB2-F (J. T. Baker Chemical Co.), and detection was achieved by ultraviolet (u.v.) absorbance or by spraying with 1:2:37 anisaldehyde–sulfuric acid–ethanol and heating. Silica used for column separations was supplied by E. Merck (silica gel 60, 70–230 mesh). 90-MHz, ^{1}H-n.m.r. spectra were recorded with a Jeol FX-90Q instrument, and ^{1}H-n.m.r. (360 MHz) and ^{13}C-n.m.r. (90.6 MHz) spectra were recorded at Colorado State University.

Solvolysis of **3** *in methanol–sulfuric acid (to give* **5**). — The epoxide **3** (0.376 g, 1.8 mmol) was dissolved in a solution of sulfuric acid (0.5 mL) in methanol (50 mL). T.l.c. (5:4:1 acetone–ethyl acetate–water) immediately after dissolution showed the loss of starting material and the presence of one product, at R_F 0.66. Water (35 mL) was added to the solution, and then barium carbonate to neutralize the acid, the suspension was filtered, and the filtrate evaporated. The crude solid remaining, which was contaminated with inorganic salts, was extracted with absolute ethanol. Crystals of **5** (0.253 g, 58%) were obtained from the extract; m.p. 120.5–121.5°; ν_{max}^{KBr} 3320 (O–H stretch), 2984, 2950 (C–H), and 1130, 1115, 1100 cm^{-1} (acetal).

Anal. Calc. for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 59.92; H, 6.82.

Acetylation of **5** *(to give* **6***).* — To a solution of acetal **5** (0.13 g, 0.5 mmol) in dry pyridine (1.5 mL) was added acetic anhydride (1.5 mL); the solution was stirred for 16 h at room temperature, and then methanol was added, to decompose the excess of acetic anhydride. The solution was evaporated, and the clear oil remaining was eluted through a column (20 × 85 mm) of silica with 1:1 hexane–ethyl acetate, to yield acetate **6** (R_F 0.24, 1:1 hexane–ethyl acetate) as colorless crystals (0.072 g, 51%); m.p. 101–102°; ν_{max}^{KBr} 3600, 3536 (O–H stretch), 2967, 2900 (C–H), 1745, 1734 (C=O), and 1115, 1105 cm^{-1} (acetal).

Anal. Calc for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.93; H, 6.50.

Oxidation of the diol **7** *with periodic acid (to give* **8***).* — A solution of diol **7** (0.279 g, 1.2 mmol) in aqueous 0.1M periodic acid (15 mL) was kept in the dark for 18 h at ambient temperature. The acid was then neutralized with barium carbonate, the suspension filtered, and the solid successively washed with absolute ethanol and ethyl acetate. T.l.c. (ethyl acetate) indicated one product (R_F 0.15). The filtrate and washings were combined, and evaporated, to yield product **8** (0.283 g, 97%); m.p. 161–163°; ν_{max}^{KBr} 3436, 3341 (O–H stretch), 2941, 2892 (C–H), and 1105, 1100, 1095 cm^{-1} (hemiacetal–acetal).

Anal. Calc. for $C_{11}H_{14}O_6$: C, 54.54; H, 5.83. Found: C, 54.07; H, 5.85.

Reduction of **2** *with sodium borohydride in water (to give* **9** *and* **10***).* — To a suspension of compound **2** (0.898 g, 4.7 mmol) in water (10 mL) was added a solution of sodium borohydride (0.344 g; 1.9 mol. equiv.) in water (10 mL). Reaction was complete within 1.5 h at room temperature. Acetone was added to decompose any remaining sodium borohydride, and the solution was extracted with chloroform (3 × 30 mL). The extracts were combined, washed once with water, dried (anhydrous sodium sulfate), and filtered. T.l.c. (1:1 hexane–ethyl acetate) then showed two major products, **9** (R_F 0.20) and **10** (R_F 0.44). The filtrate was evaporated, to yield a clear oil which was eluted through a column (30 ×210 mm) of silica with 1:1 hexane–ethyl acetate, resulting in separation of the two isomers: the *threo* isomer **9** (0.632 g, 59%), m.p. 71–72°, and the *erythro* isomer **10** (0.273 g, 30%), m.p. 86–87°; for **9**: ν_{max}^{KBr} 3280 (O–H stretch), 2966 (C–H), and 1066 cm^{-1} (C–O); for **10**: ν_{max}^{KBr} 3485, 3398 (O–H stretch), 2969, 2936 (C–H), and 1040 cm^{-1} (C–O).

Anal. Calc. for $C_{11}H_{14}O_{13}$: C, 68.02; H, 7.27. Found (for **9**): C, 67.71; H, 7.38; (for **10**): C, 68.08; H, 7.40.

Epoxidation of **9** *with* m-*chloroperoxybenzoic acid (to give* **11***).* — To a solution of alkene **9** (0.543 g, 2.8 mmol) in chloroform (10 mL) was added a solution of *m*-chloroperoxybenzoic acid (1.7 g, 3 mol equiv.) in chloroform (10 mL). Reaction was complete in 0.5 h, t.l.c. in 1:1 hexane–ethyl acetate then showing one product (R_F 0.13). The suspension was filtered, the filtrate evaporated, and a solution of the white residue (containing both product and *m*-chloroperoxybenzoic acid) in the minimal volume of ethyl acetate eluted through a column (30 × 140 mm) of silica with 1:1 hexane–ethyl acetate, yielding crystalline **11** (0.502 g, 86%); this was recrystallized from hexane–ethyl acetate; m.p. 128–129°; ν_{max}^{KBr} 3395 (O–H stretch), 2961 (C–H), 1069, 1055 (C–O), and 841 cm^{-1} (epoxide C–C).

Anal. Calc. for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.75; H, 6.84.

Hydrolysis of the epoxide ring of **11** *in acid (to give* **12**). — To a solution of epoxide **11** (0.371 g, 1.8 mmol) in oxolane (THF, 20 mL) was added a solution of conc. sulfuric acid (1.0 mL) in water (30 mL). After 15 h at room temperature, barium carbonate was added to neutralize the acid, the suspension was filtered, and the filtrate was evaporated, to yield a colorless, oily solid. T.l.c. (2:1 ethyl acetate–ethanol) showed one spot (R_F 0.47), and a trace of inorganic matter at the origin. Therefore, the solid was taken up in acetone–methanol, the suspension filtered, and the filtrate evaporated, to yield a colorless oil (0.416 g, 100%) which crystallized from acetone by slow evaporation, to yield **12**; m.p. 158–160°; ν_{max}^{KBr} 3415, 3290 (O–H stretch), 2965, 2887 (C–H), and 1098, 1066, 1055, 1044, 1026, and 1006 cm^{-1} (C–O).

Anal. Calc. for $C_{11}H_{16}O_5$: C, 57.89; H, 7.07. Found: C, 58.00; H, 6.91.

Acetylation of **12** *(to give* **13**). — Triol **12** (0.387 g, 1.7 mmol) was dissolved in a solution of pyridine (4 mL) in acetic anhydride (4 mL). After 16 h at room temperature, methanol was added to decompose any remaining acetic anhydride, and the solution was evaporated (using toluene), to yield a colorless oil. T.l.c. (1:1 hexane–ethyl acetate) showed the major product (R_F 0.36) and two trivial products (R_F 0.27 and 0.45). The oil was eluted through a column (30 × 120 mm) of silica with 1:1 hexane–ethyl acetate, to yield **13** (0.212 g, 35%) as a colorless, frothy oil; ν_{max}^{KBr} 2977, 2897 (C–H stretch), 1748 (C=O), and 1242 cm^{-1} (C–O).

Anal. Calc. for $C_{17}H_{22}O_8$: C, 57.62; H, 6.26. Found: C, 57.78; H, 6.30.

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