sodium borohydride in EtOH (30 μL, 0.5 M). After 30 min, 10 mL of water was added followed by 0.3 mL of HOAc. The product was extracted from the mixture with EtOAc and the extract was dried ($MgSO_4$), filtered, and evaporated to give a clear oil. Purification by HPLC (Partisil, 3% EtOH in EtOAc) afforded 6 mg of diol **9**: EIMS, m/z (relative intensity) 445 (0.5 M^+), 443 (1, M^+), 408 (35), 390 (23), 376 (20), 358 (15), 303 (22), 301 (33), 143 (55), 69 (100).

10 and 11. To a stirred solution of malyngamide C (**1**, 59 mg) in 1 mL of CH_2Cl_2 at 25 °C under nitrogen was added 0.2 mL of titanium tetraisopropoxide. The mixture was stirred overnight, then diluted with water, and extracted with CH_2Cl_2. The extract was dried ($MgSO_4$), filtered, and evaporated to yeild an oil which was purified by HPLC (Partisil, 5% EtOH in 1:1 hexane/EtOAc) to yield compounds **10** (2.2 mg) and **11** (1.7 mg).

Compound 10 had the following properties: oil, $[\alpha]_D$ +125° (c 0.16, MeOH); IR (neat 3200, 1755, 1660, 815 cm^{-1}; EIMS, m/e (relative intensity) 457 (1, M^+), 455 (4, M^+), 425 (1), 423 (3), 315 (4), 313 (9), 217 (33), 199 (18), 143 (82), 69 (100).

Compound 11 had the following properties: oil, $[\alpha]_D$ +40° (c 0.3, MeOH); IR (neat) 3360, 3110, 1735, 1650, 815 cm^{-1}; EIMS, m/z (relative intensity) 457 (8, M^+), 455 (20, M^+), 425 (2), 423 (4), 315 (15), 313 (41), 219 (30), 217 (55), 199 (43), 143 (97), 69 (100).

12 and 13. To a stirred solution of compound **8** (20 mg, 0.05 mmol) in 1.5 mL of CH_2Cl_2 cooled to 0 °C under nitrogen was added 4-(dimethylamino)pyridine (0.005 mmol) followed by triethylamine (0.12 mmol) and p-bromobenzoyl chloride (0.12 mmol). The mixture was allowed to stir at 0 °C for 6 h and at room temperature for 1 h. Water was added and the organic layer was washed with 5% HCl followed by aqueous sodium bicarbonate and saturated brine, filtered through cotton, and evaporated to give an air-sensitive oil. Purification by HPLC (Partisil, 1% EtOH in 9:1 EtOAc/hexane) gave 7.9 mg (20%) of bis(p-bromobenzoate) **12**: EIMS, m/z (relative intensity) 599 (1), 597 (1, M^+ - BrC_6H_4COOH), 397 (25), 143 (71), 69 (100); CD (MeOH) $[\Theta]_{257}$ -80 000°, $[\Theta]_{249}$ 0°, $[\Theta]_{241}$ +12 8000°.

Compound **13** was prepared by a similar procedure using p-(dimethylamino)benzoyl chloride.[16] After the reaction water was added and the organic layer was washed 2× with water followed by saturated $NaHCO_3$ and brine solutions, filtered, and evaporated to give a dark yellow residue. This material was passed through a Bond Elut silica column (Analytichem International) with EtOAc and then purified by HPLC (Partisil, 5% EtOH in EtOAc) to give a 30% yield of the bis[p-(dimethylamino)benzoate] **13**, CD (MeOH) $[\Theta]_{326}$ -177 000°, $[\Theta]_{314}$ 0°, $[\Theta]_{302}$ +114 000°.

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Registry No. **1**, 70622-52-5; **3**, 96845-19-1; **4**, 96845-20-4; **5**, 96845-21-5; **7**, 96845-23-7; **8**, 96845-22-6; **9**, 96845-24-8; **10**, 96845-25-9; **11**, 96845-26-0; **12**, 96845-27-1; **13**, 96845-28-2.

(16) Decombe, J. *Bull. Soc. Chim. Fr.* **1951**, 416.

Marine Natural Products: Spongiane Derivatives from the Sponge *Igernella notabilis*

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Three new diterpene lactones, 7α,17β-dihydroxy-15,17-oxidospongian-16-one 7-butyrate (**2**), 7α,17β-dihydroxy-15,17-oxidospongian-16-one 7-acetate (**3**), and 7α,17β-dihydroxy-15,17-oxidospongian-16-one (**4**), isolated from the Caribbean sponge *Igernella notabilis* are reported. The structure of **2** was determined by X-ray analysis and those of **3** and **4** were established by comparison of their spectral data with that of **2**. Lactone **2** crystallizes in the space group $P4_1$ with cell dimensions (138 K) $a = b = 10.782$ (6) Å and $c = 18.531$ (13) Å. The crystal structure was determined from 2302 data and the final R value was 0.032.

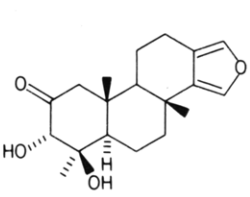
Kazlauskas et al. have reported[1] the isolation of a series of sponge diterpene metabolites designated spongianes, e.g. **1**, which are related to isoagatholactone[2], another sponge metabolite. In our continuing search for biologically active compounds, we have isolated from the Caribbean sponge *Igernella notabilis* (Duch & Mich.) three diterpene lactones **2**-**4** that have spongiane skeletons. The structure of one of these was determined by X-ray crystallographic analysis and the others by spectral comparisons.

For the major metabolite **2**, mp 197-198 °C, $[\alpha]$ -37.2°, the formula $C_{24}H_{36}O_6$ was suggested by the low-resolution FD mass spectrum, m/z 421 ($M^+ + 1$), and this was supported by ^{13}C NMR data indicating 24 carbons. The infrared spectrum contained bands at 3600, 1780, and 1730 cm^{-1}, compatible with hydroxyl, γ-lactone, and ester groups, and the latter were further evidenced by ^{13}C absorptions at δ 172.3 and 176.6. The acyl group of the ester was identified as n-butyryl by the occurrence of an ion in the FD mass spectrum corresponding to loss of $C_4H_7O_2$ (m/z 332) and by ^1H NMR data: δ 2.37 (2 H, t), 1.67 (2 H, sextet), 0.99 (3 H, t), see Table I. The ^1H NMR spectrum also showed three quaternary methyl signals (δ 0.75, 0.76, 0.93). The ^{13}C NMR spectrum revealed the presence of two acetal carbons [$-CH(O)_2$] and confirmed the absence of any double bonds. Hence, of the 7 degrees of unsaturation present in **2**, 5 were due to rings. Since the proton dispersion was inadequate to allow structure determination by NMR analysis, single-crystal X-ray diffraction was used to determine the complete structure which is shown in formula **2**.

A perspective view of **2** is shown in the ORTEP plot in Figure 1. An attempt to determine the absolute configuration of **2** by using the anomalous dispersion of Cu radiation by O atoms did not give conclusive results, but the majority of Bijvoet differences[3] (60%) out of 20 Friedel's

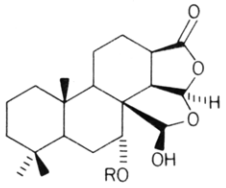
(1) Kazlauskas, R.; Murphy, P. T.; Wells, R. J.; Noack, K.; Oberhänsli, W. E.; Schonholzer, P. *Aust. J. Chem.* **1979**, *32*, 867.
(2) Kazlauskas, R.; Murphy, P. T.; Quinn, R. J.; Wells, R. J. *Tetrahedron Lett.* **1976**, 1331, 1333.

0022-3263/85/1950-2862$01.50/0



1

(3α,19-dihydroxyspongia-13(16),14-dien-2-one)



2, R=$\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$

3, R=$\overset{O}{\overset{\|}{C}}CH_3$

4, R=H

pairs favored the configuration shown in Figure 1. Endocyclic torsion angles are given in Figure 2. The three cyclohexane rings are all in the chair conformation, although ring C deviates from the ideal chair conformation due to the cis fusion of the two five-membered rings. The tetrahydrofuran ring assumes an envelope conformation with C(17) as flap while the γ-lactone ring is in a folded envelope conformation with C(16) as flap. The tricyclo system formed by rings C, D, and E appears like a bowl, with the hydroxyl group, O(2)H, lying almost in the middle of this bowl giving short contacts, O(2)–C(16) = 2.87 Å, O(2)–C(15) = 2.87 Å, O(2)–C(11) = 2.92 Å and O(2)–C(9) = 2.94 Å.

Bond distances and angles compare well with those found in other related structures, pterokaurene L_2,[4] pteroatisene P_2,[4] forskolin,[5] and 3α,17,19-triacetoxyspongia-13(16),14-dien-2-one.[1] Bonds involving C(4), C(8), C(10), and C(14) are all 4–8σ longer than the average of other C–C single bonds. Such lengthening of bond lengths in the case of fully substituted tertiary carbon atoms is quite common.

The crystal structure of **2** is stabilized by an intermolecular hydrogen bond between the hydroxyl group, O(2), and the carbonyl oxygen, O(6), in the side chain: O(2)–H...O(6) = 2.709 Å, O(2)–H = 0.89 Å, H...O(6) = 1.90 Å, angle O(2)–H–O(6) = 151°.

Lactone **3**, mp 114–117 °C, [α] −35.0°, showed a M^+ + 1 ion at m/z 393 (field desorption) corresponding to the formula $C_{22}H_{32}O_6$ and in the high-resolution EI MS at 332.19489 corresponding to the M^+ − AcOH (calcd 332.19876). Infrared absorptions were observed at 3600, 1775, and 1730 cm^{-1} comparable to those found for **2**. The ^1H NMR spectrum of **3** was virtually identical with that of **2** except for the absence of the butyrate signals and the presence of an acetate methyl signal, see Table I. The low-resolution mass spectra of **2** and **3** were also nearly identical since molecular ions were not observed. Hence structure **3** was assigned to this lactone.

The third lactone, **4**, isolated in trace quantities, mp 199–204 °C, [α] −21.7°, exhibited hydroxyl and γ-lactone absorptions (3600, 1775 cm^{-1}) in its infrared spectrum but no other ester bands. The ^1H NMR spectrum of **4**, see Table I, was very similar to that of **2** and **3**, except that no butyrate or acetate peaks were present and the triplet (J = 2.57 Hz) associated with H-7 was observed at higher field, δ 3.55 compared to δ 4.75 in the other lactones. This is consistent with the change from an ester to a hydroxyl group at C-7. Also, the double doublet corresponding to H-14 (J = 11.0, 5.5 Hz) in **4** occurred at δ 3.55, a downfield shift of 0.68 ppm relative to that in **2** and **3**. Deshielding

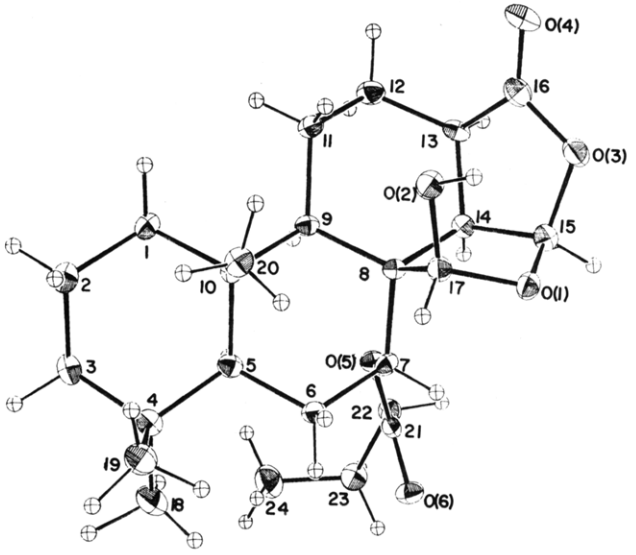


Figure 1. An ORTEP plot of **2** showing the atom numbering.

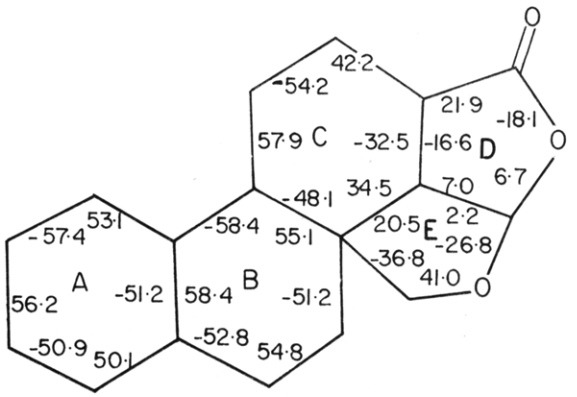


Figure 2. Endocyclic torsion angles. Estimated standard deviations range between 0.2° to 0.3°.

for the axial H-14 by a C-7 axial hydroxy group readily accounts for this shift. Since the remainder of the ^1H NMR spectrum of **4** closely parallels that of **2** and **3** structure **4** was assigned to this dihydroxy lactone.

The low-resolution mass spectrum of **4** exhibited a weak ion at m/z 332 corresponding to M^+ − 18. Only weak ions were observed at m/z 286 ad 256 whereas the MS of **2** and **3** had very strong ions at these positions. The base peak in the mass spectrum of **4** occurred at m/z 230, 1 amu higher than a much weaker ion at m/z 229 ($c_{17}H_{25}$) in the spectrum of **2** and **3**. The latter corresponds to a fragment having lost the C-7 substituent and the C-15 to C-17 moiety. In **4**, the C-7 hydroxyl group may not be lost as readily as the ester groups in **2** and **3** to give an intense m/z 286 ion and consequently a slightly different fragmentation sequence ensues to give a C_{17} oxygen-free fragment with one additional proton.

Attempts to correlate **2** with **4** by hydrolysis gave poor yields and mixtures of products.

Following the nomenclature suggested by Kazlauskas et al.,[1] the new lactones would be designated as follows: **2**, 7α,17β-dihydroxy-15,17-oxidospongian-16-one 7-butyrate; **3**, 7α,17β-dihydroxy-15,17-oxidospongian-16-one 7-acetate; **4**, 7α,17β-dihydroxy-15,17-oxidospongian-16-one.

Lactones **2**–**4** lack the oxygenation in ring A that is present in all the spongianes isolated by Kazlauskas et al.[1] and present a different oxidation pattern on carbons 15–17. The oxygens in the lactone/tetrahydrofuran rings of **2**–**4** seem conveniently arrayed to serve as a complexing moiety for cations and such complexation might play a role in the

(3) Bijvoet, J. M.; Peerdeman, A. F.; van Bommel, A. J. *Nature (London)* **1951**, *168*, 271.
(4) Murakani, T.; Tanaka, N.; Hideki, I.; Iitaka, Y. *Chem. Pharm. Bull.* **1981**, *29*, 773.
(5) Paulus, E. F. *Z. Krist.* **1980**, *153*, 43.

Table I. Partial ^{1}H NMR Data for 2, 3, and 4

H at C	2, δ (mult, J in Hz)	3, δ (mult, J in Hz)	4, δ (mult, J in Hz)
5α	1.28 (dd, 14.9, 2.4)	1.28 (dd, 14.9, 2.4)	
6α	1.85 (dt, 14.9, 2.4, 2.4)	1.85 (dt, 14.9, 2.4, 2.4)	
6β	1.64 (dt, 14.9, 14.9, 2.4)[a]		
7	4.76 (t, 2.85)	4.75 (t, 2.52)	3.55 (t, 2.57)
11β	1.99 (dq, 12.6, 12.6, 12.6, 4.1)	1.95 (dq, 12.6, 12.6, 12.6, 4.1)	1.97 (dq, 12.6, 12.6, 12.6, 4.1)
11α	~1.5	~1.5	
12β	2.38 (dm, 14.4)	2.37 (dm, 14.4, ~2.8)	2.36 (dm, 13.8)
12α	~1.6	~1.6	
13	2.74 (br, dd, 11.6, 7.4)	2.74 (dd, 11.3, 7.7)	2.79 (dd, 11.4, 7.6)
14	2.85 (dd, 11.6, 5.9)	2.87 (dd, 11.5, 5.9)	3.55 (dd, 11.0, 5.5)
15	6.04 (d, 5.9)	6.03 (d, 5.9)	6.09 (d, 5.6)
17	5.48 (s)	5.48 (s)	5.39
18	0.75	0.77	0.87
19	0.78	0.81	0.90
20	0.93	0.93	0.97
$C(O)(CH_2)_2CH_3$	2.37 (t), 1.67 (sextet),[a] 0.99 (t)	2.14 (3 H, s, OAc)	

[a] Seen only by difference double resonance.

biological activity of these compounds. Lactone **2** has been found to be mildly cytotoxic, ED_{50} in PS, 6.5 mcg/mL.[6]

After completion of this work we became aware of a preliminary report[7] of a compound having the same structure as **2** but with the functional groups at C-16 and -17 interchanged and undefined stereochemistry.

Experimental Section

General experimental and instrumental descriptions are as recorded previously[8] except that NMR spectra were taken on a Varian XL-300 spectrometer at 300 MHz for proton and 75 MHz for carbon, and applied Science 5μ, 10 × 25 cm, C-18 reversed-phase columns were used for HPLC separations.

Isolation of 2, 3, and 4. Specimens of the sponge *Igernella notabilis* were collected at −10 to −15 M near St.John, U.S. Virgin Islands, and transported frozen to Oklahoma. Freshly thawed material (wet weight, 400 g) was extracted with chloroform–methanol (1:1) on a shaker for 3 days and then again with fresh solvent for 1 week. The combined concentrated extracts were partitioned between methylene chloride and water in a continuous liquid–liquid extractor[9] for 24 h. Evaporation of the methylene chloride yielded 3.18 g of dark green residue, which was resolved by using vacuum liquid chromatography (VLC)[10] (5% MeOH/$CHCl_3$); 10 fractions were collected. Rechromatography of fractions 7 and 8 using HPLC [H_2O/MeOH (1/9); 5 μm, C-18], yielded three pure compounds, **2**, **3**, and **4**.

Crystallization of the major HPLC fraction from benzene yield white crystals of **2**: mp 197–198 °C; [α] −37.2° ($CHCl_3$); IR (neat) 3600, 3200–3500 (br d), 1780 (vs), 1730 (vs), 1370, 1260, 1175, 1075, 980 cm^{-1}; ^{1}H NMR, see Table I; also complex absorptions δ 0.8–1.0; 1.10–1.90; ^{13}C NMR ($CDCl_3$), 75 MHz, assignment by analogy to model compounds) δ 13.82 (q, C-4′), 15.28 (q, C-20), 16.21 (t, C-11 or 12), 18.72 (2C, t, C-2, C-11 or 12), 21.20 (q, C-19), 23.32 (t, C-3′), 24.62 (t, C-6), 32.76 (s, C-4), 33.03 (q, C-19), 36.69 (t, C-2′), 37.73 (d, C-13), 39.26 (s, C-10), 38.88 (t, C-1), 41.90 (t, C-3), 42.24 (d, C-14), 48.50 (d, C-5 or -9), 49.64 (d, C-5 or -9), 50.84 (s, C-8), 72.67 (d, C-7), 103.57, 104.38 (ea d, C-15, -17), 172.98 (s, C-1), 177.28 (s, C-16); C_6D_6, 75 MHz) 13.84, 15.36, 16.51, 18.99, 19.04, 21.29, 23.74, 24.92, 32.85, 33.29, 36.63, 37.50, 38.09, 39.17, 42.42, 42.64, 48.89, 50.02, 50.98, 72.86, 103.66, 104.34, 172.35, 176.59; mass spectrum (field desorption, low resolution), *m/z* 421 ($MH^+ - C_4H_8O_2$), 286; 70-eV, low-resolution EI mass spectrum, *m/z* (relative intensity), 286 (100), 271 (12.1), 259 (18.5), 258 (81.4), 229 (20.3), 162 (22.2), 145 (21.5), 137 (21), 124 (15.2), 123 (22.7), 109 (39.8), 105 (28.8), 93 (21), 91 (44.9), 89 (40.7); high-resolution mass spectrum, obsd *m/e* (composition, calcd millimass) 332.19632 ($C_{20}H_{28}O_4$, 332.19876), 314.18895 ($C_{20}H_{26}O_3$, 314.18820), 286.19443 ($C_{19}H_{26}O_2$, 286.19328), 258.19538 ($C_{18}H_{26}O$, 258.19837), 229.19677 ($C_{17}H_{25}$, 229.19536), 134.10389 ($C_9H_{10}O$, 134.07317), 124.12478 (C_9H_{16}, 124.12520), 109.10306 (C_8H_{13}, 109.10173).

Table II. Atomic Parameters

atom	x	y	z	U(eq)
O1	0.7811 (1)	−0.1673 (1)	0.54990	0.0179 (4)
O2	0.6612 (1)	−0.2978 (1)	0.6212 (1)	0.0194 (4)
O3	0.8573 (1)	−0.1290 (1)	0.6654 (1)	0.0218 (5)
O4	0.7938 (2)	−0.1911 (2)	0.7742 (1)	0.0258 (5)
O5	0.5132 (1)	0.0878 (1)	0.5239 (1)	0.0148 (4)
O6	0.5547 (1)	0.1470 (1)	0.4104 (1)	0.0185 (5)
C1	0.2300 (2)	−0.1942 (2)	0.6190 (1)	0.0195 (6)
C2	0.1198 (2)	−0.2391 (2)	0.5743 (2)	0.0238 (7)
C3	0.1030 (2)	−0.1611 (2)	0.5070 (2)	0.0249 (7)
C4	0.2186 (2)	−0.1555 (2)	0.4584 (1)	0.0211 (7)
C5	0.3323 (2)	−0.1190 (2)	0.5057 (1)	0.0155 (6)
C6	0.4530 (2)	−0.1045 (2)	0.4631 (1)	0.0160 (6)
C7	0.5531 (2)	−0.0389 (2)	0.5066 (1)	0.0142 (6)
C8	0.5790 (2)	−0.1022 (2)	0.5800 (1)	0.0134 (6)
C9	0.4534 (2)	−0.1207 (2)	0.6204 (1)	0.0133 (6)
C10	0.3534 (2)	−0.1938 (2)	0.5764 (1)	0.0144 (6)
C11	0.4701 (2)	−0.1615 (2)	0.6995 (1)	0.0172 (6)
C12	0.5477 (2)	−0.0669 (2)	0.7411 (1)	0.0203 (6)
C13	0.6722 (2)	−0.0384 (2)	0.7062 (1)	0.0163 (6)
C14	0.6743 (2)	−0.0223 (2)	0.6238 (1)	0.0145 (6)
C15	0.8018 (2)	−0.0741 (2)	0.6017 (1)	0.0185 (6)
C16	0.6601 (2)	−0.2170 (2)	0.5627 (1)	0.0155 (6)
C17	0.7755 (2)	−0.1298 (2)	0.7211 (1)	0.0199 (7)
C18	0.2353 (2)	−0.2786 (2)	0.4173 (1)	0.0281 (7)
C19	0.1956 (2)	−0.0541 (3)	0.4018 (2)	0.0321 (8)
C20	0.3923 (2)	−0.3302 (2)	0.5651 (1)	0.0187 (6)
C21	0.5266 (2)	0.1727 (2)	0.4721 (1)	0.0148 (6)
C22	0.5058 (2)	0.3025 (2)	0.4996 (1)	0.0174 (6)
C23	0.4308 (2)	0.3827 (2)	0.4471 (1)	0.0213 (6)
C24	0.2951 (2)	0.3470 (3)	0.4452 (2)	0.0326 (8)

For 3: mp 114–117 °C; [α] −35.0° ($CHCl_3$); IR (neat) 3600, 3200–3500 (br d), 1775 (vs), 1730 (vs), 1365, 1375, 1250, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz), see Table I, also complex absorption from 0.8–1.0, 1.10–1.80; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.26, 16.21, 18.76, 21.17, 21.47, 23.35, 24.64, 29.78, 32.73, 33.05, 37.60, 38.28, 38.95, 41.77, 42.31, 48.59, 49.49, 73.03, 103.61, 104.35 (carbonyl region not scanned); mass spectrum (field desorption, low resolution), *m/z* 393 (MH^+, 70 eV; low-resolution EI mass spectrum, *m/z* (relative intensity) 332 (1.4), 314 (5.5), 286 (100), 258 (68.4), 229 (17.5), 162 (35.3), 149 (21.5), 145 (23.9), 137 (37.3), 124 (37.3), 123 (38.1), 109 (70.7), 105 (31.3), 95 (25.8), 91 (35.3); high-resolution

(6) Gueran, R. I.; Greenberg, N. H.; Macdonald, M. M.; Schumacher, A. M.; Abbott, B. J. *Cancer Chemother. Rep., Part* 3, *Sept. 1972*, No. 2. Effective doses (ED_{50}) in the tissue culture tests are expressed as concentrations in μg/mL of test material in the growth medium that causes 50% inhibition of cell growth. "Active" materials display an ED_{50} <20 μg/mL. KB refers to a cell culture of a human carcinoma of the nasopharynx. PS refers to in vitro lymphocytic leukemia.

(7) Karuso, P.; Poiner, A.; Taylor, W. C. Abstracts, Royal Australian Chemical Institute, 8th National Conference, Perth, Australia, May 13–18, 1984.

(8) Gunasekera, S. P.; Schmitz, F. J. *J. Org. Chem.* **1983**, *48*, 885.

(9) Ciereszko, L. S. *J. Chem. Educ.* **1966**, *43*, 252.

(10) Green, B.; Kilcoyme, J. P.; Targett, N. M. *J. Org. Chem.* **1979**, *44*, 4962.

mass spectrum, obsd m/e (composition, calcd millimass) 332.19489 ($C_{20}H_{28}O_4$, 332.19876), 314.18755 ($C_{20}H_{26}O_3$, 314.18820), 304.20156 ($C_{19}H_{28}O_3$, 304.20385), 288.20633 ($C_{19}H_{28}O_2$, 288.20893), 286.19460 ($C_{19}H_{26}O_2$, 286.19328), 258.19644 ($C_{18}H_{26}O$, 258.19837), 229.19613 ($C_{17}H_{25}$, 229.12286), 124.12273 (C_9H_{16}, 124.12520), 109.10213 (C_8H_{13}, 109.10173).

For 4: mp 199–204 °C; [α] −21.7° (MeOH); IR (neat) 3108–3615 (br d), 1755 (vs), 1459, 1252, 1123, 1063, 1039, 970 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) see Table I, also complex absorption from δ 0.8–1.0, 1.10–1.80); 70 eV low-resolution EI mass spectrum, m/z (relative intensity) 332 (2.4), 288 (2.9), 286 (3.0), 260 (3.8), 258 (3.8), 231 (21.7), 230 (100), 215 (9.7), 181 (23), 124 (66.2), 123 (38.9), 109 (94.7).

X-ray Analysis of 2. Crystal data: $C_{24}H_{36}O_6$, M_r = 420.6, tetragonal, $P4_1$; $a = b$ = 10.782 (6) Å, c = 18.531 (13) Å, v = 2154.3 Å^3 at 138 K, Z = 4, D_x = 1.296 gm cm^{-3}, $F000$ = 912, μ(Mo Kα) = 0.5 cm^{-1}. The intensities of all 2302 unique reflections with $2\theta \leq 53°$ were collected at 138 ± 2 K using graphite-monochromated Mo Kα radiation on an Enraf-Monius CAD-4 diffractometer using techniques described before;[11] 2152 reflections were considered observed on the basis, $I \geq 2\sigma(I)$. The structure was solved by direct methods using the program MULTAN[12] and refined using anisotropic temperature factors with full-matrix least-squares methods.[13] Hydrogen atoms located from a difference Fourier map were refined isotropically. Refinement converted to a final R = 0.032, R_w = 0.036, $s = [\sum w\Delta F^2/(m-n)]^{1/2}$ = 1.4, Δ/σ (average) = 0.1. The final atomic parameters are listed in Table II.

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Supplementary Material Available: Bond distances, bond angles, and anisotropic thermal parameters for non-hydrogen atoms and hydrogen atom parameters (4 pages). Ordering information is given on any current masthead page.

(11) Eng-Wilmot, D. L.; Rahman, A.; Mendenhall, J. V.; Grayson, S. L.; van der Helm, D. *J. Am. Chem. Soc.* **1984**, *106*, 1285.
(12) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. "MULTAN78", Program for the Automatic Solution of Crystal Structures, University of York, England.
(13) Sheldrick, G. M. "SHELX76". Program for Crystal Structure Determination, University of Cambridge, England.

Stereochemistry of the Photoinduced Addition of Nucleophiles to the Enone of Decompostin†

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Irradiation of decompostin (1) in methanol gave 6-*epi*-methoxydesacetyldecompostin (**2b**). Irradiation of a benzene solution of decompostin in the presence of a nucleophile [ROH; R = H, Me, or $CH(CH_3)_2$] gave the products **3a–c** in a regio- and stereospecific manner. The structure and stereochemistry of **3b** were proven by X-ray diffraction analysis of a single crystal.

The photochemical addition of alcohols to cycloalkenes has been studied extensively.[1] A highly strained "twisted" double bond has been postulated as the intermediate responsible for the products observed.[2] Spectroscopic evidence for the formation of a "twisted" double bond on laser photolysis of 1-phenylcyclohexene has been described by Salem et al.[3] The photoadditions of alcohols and other nucleophiles to cyclohexenone, cycloheptenones, and cyclooctenones have been also investigated and found to proceed in a regio- and stereospecific manner.[4] In all the examples described in the literature, the double bond is located in the same ring as the ketonic group.[2-4]

Decompostin is a natural product isolated from *Cacalia decomposita* A. Gray. Its structure[5] and absolute configuration[6] were shown to be 1. The ketone group at C-9 is cross-conjugated with the furan group and the 1,10 double bond. We decided to study the photoaddition of alcohols and other nucleophiles to the 1,10 double bond of decompostin.

Results and Discussion

Irradiation of 1 in methanol gave as the main isolated product the 6-*epi*-methoxy derivative **2a**, obtained previously[6] by saponification of decompostin in methanolic solution. Formation of **2a** could be explained by the loss of the acetate in a vinylogous β-cleavage photoreaction and

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(1) Kropp, P. J. "Organic Photochemistry", Padwa, A., Ed.; Marcel Dekker Inc.: New York, 1979; Vol. 4, Chapter 1, p 1.
(2) Schuster, D. I. In "Rearrangements in Ground and Excited States", de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 167.
(3) Bonneaw, R.; Joussot-Dubier, J.; Salem, L.; Yarwood, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 4329.
(4) Hart, H.; Chen, B.; Jeffares, M. *J. Org. Chem.* **1979**, *44*, 2722 and references there cited.
(5) Rodríguez-Hahn, L.; Guzmán, A.; Romo, J. *Tetrahedron* **1968**, *24*, 477.
(6) Samek, Z.; Harmatha, J.; Novotny, L.; Sorm, F.; *Collect. Czech. Chem. Commun.* **1969**, *34*, 2792.

0022-3263/85/1950-2865$01.50/0