several minutes and then irradiated under nitrogen by using a General Electric 275-W sunlamp. After 3 days, a precipitate was filtered off and the solvent removed from the filtrate in vacuo, leaving a white solid which was recrystallized twice from benzene to give a white solid: 0.46 g (22%); mp 220 °C dec; 150–160 °C remelt (lit.[8] mp 220 °C dec, 155–180 °C remelt). Anal. Calcd for $C_{29}H_{22}$: C, 94.01; H, 5.99. Found: C, 93.98; H, 5.99.

Reaction of 2 with Methyllithium. To a solution of 0.10 g (0.27 mmol) of **2** in 50 mL of dry (distilled from Na) THF was added 0.20 mL (0.30 mmol) of a 1.5 M solution of methyllithium in ether. The resulting mixture was stirred for 2 h and then treated with 10 mL of water. The solvent was removed in vacuo and the residue partitioned between 50 mL of water and 50 mL of benzene. The layers were separated, and the aqueous phase was extracted with four 150-mL portions of benzene. The combined organic extracts were dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give a creamy solid (**1c**): 0.0956 g (92%); mp 255–257 °C; ^1H NMR ($CDCl_3$) 2.15 (s, 3 H), 2.72 (s, 2 H), 4.00 (s, 1 H), 6.65–6.95 (m, 16 H); IR (KBr) 3080 (w), 3040 (w), 3020 (w), 2990 (w), 2910 (w), 1630 (m), 1450 (m), 1375 (m), 1310 (w), 1130 (w), 1005 (w), 935 (w), 810 (m), 750 (m), 685 (m), 660 (m); UV (CCl_4) 285 (2500), 275 (3500), 266 (4400), 255 (7000); mass spectrum (10 eV), *m/e* (relative intensity) 384 (4.74), 383 (34.35), 382 (100), 381 (4.60), 380 (1.23), 369 (5.65), 368 (26.51), 367 (32.09), 366 (11.09), 365 (5.22), 364 (1.66), 353 (5.76), 352 (5.48), 205 (37.00), 192 (6.05), 191 (19.30), 92 (11.87), 91 (21.95). Recrystallization from benzene–hexane gave an analytical sample. Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 93.89; H, 5.76.

Reaction of 3 with Methyllithium. To a solution of 0.15 g (0.42 mmol) of **3** in 50 mL of dry THF was added 1.0 mL (0.67 mmol) of a 1.5 M solution of methyllithium in ether. The resulting solution was stirred for 1 h and then treated with 30 mL water. A workup as described for the preceding reaction gave a white solid: 0.0763 g (49%); mp 220 °C dec (9-methyldianthracene, lit.[8] mp 220 °C dec, 155–180 °C remelt); ^1H NMR ($CDCl_3$) 2.08 (s, 3 H), 3.86 (s, 1 H), 4.45 (s, 2 H), 6.70–6.85 (m, 16 H), identical with that of the authentic sample. Anal. Calcd for $C_{29}H_{22}$: C, 94.01; H, 5.99. Found: C, 94.22; H, 5.97.

Competitive Reaction of 2 and 3 with Methyllithium. To a solution of 0.0112 g (0.0305 mmol) of **2**, 0.0114 g (0.0321 mmol) of **3** and 10 mL of dry (distilled from sodium–benzophenone) THF under nitrogen was added by syringe 0.017 mL (0.03 mmol) of a 1.8 M solution of methyllithium in ether. The resulting solution was stirred for 5 min and then treated with 10 mL of water. The THF was removed in vacuo and the residue partitioned between 30 mL of benzene and an additional 10 mL of water. The layers were separated, and the aqueous layer was extracted with 50 mL of benzene. The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give a white solid which was dried under high vacuum for several hours: ^1H NMR ($CDCl_3$, relative intensities) 2.08 (s, 9), 2.15 (s, 21), 2.72 (s, 20), 3.86 (s, 3), 4.00 (s, 7), 4.45 (s, 6), 4.55 (s, 14), 6.6–7.1 (m, 320).

The aromatic absorptions for **1c**, **2**, **3**, and **7** all occurred in the same region (6.6–7.1 ppm). Peak assignments for the remainder of the spectrum are as follows: 2.08 (CH_3, **7**), 3.86 (bridgehead proton at C-10′, **7**), 4.45 (bridgehead protons at C-9′ and C-10, **7**), 2.15 (CH_3, **1c**), 2.72 (cyclopropyl protons, **1c**), 4.00 (bridgehead proton, **1c**), 2.72 [cyclopropyl protons, **2** (could not be separated from cyclopropyl protons of **1c**)], 4.55 (bridgehead protons, **3**).

Acknowledgment. This research was supported in part by a University of Illinois Biomedical Research Grant and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society. J.Z.S. thanks Proctor and Gamble Corp. and the University of Illinois Foundation for fellowships.

Registry No. **1a**, 55043-43-1; **1c**, 87568-72-7; **2**, 19770-71-9; **3**, 17938-63-5; **4**, 87568-73-8; **5**, 87568-74-9; **6**, 72423-84-8; **7**, 87568-75-0; **8**, 87568-76-1; **9**, 87568-77-2; *O*-(mesitylsulfonyl)hydroxylamine, 36016-40-7.

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Structure of Teucroxide. Application of Natural-Abundance ^{13}C–^{13}C Coupling Constants Observed via Double-Quantum Coherence

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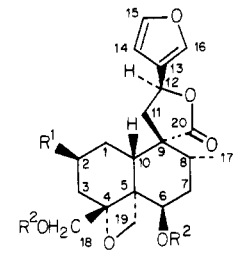
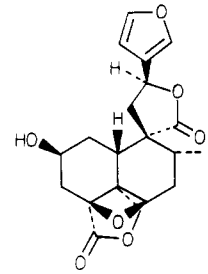
The neoclerodane diterpenoids of *Teucrium chamaedrys L.* (Labiatae) have been the subject of a number of investigations.[2] Now we have isolated from this plant a new neoclerodane diterpenoid, teucroxide, the structure of which (**1**) was established mainly by ^1H and ^{13}C NMR spectroscopic studies.

Combustion analysis and mass spectrometry indicated the molecular formula $C_{20}H_{26}O_7$ for teucroxide (**1**). Its IR spectrum was consistent with the presence of a furan ring (3150, 3130, 3120, 1600, 1508, 880 cm^{-1}), a γ-lactone group (1760 cm^{-1}), and hydroxyl groups (3460, 3360, 3290 cm^{-1}). The presence of three hydroxyl groups was established by the formation, on treatment with Ac_2O–pyridine, of a triacetate, $C_{26}H_{32}O_{10}$ (**2**), the IR spectrum of which showed no OH absorption.





3

1, R^1 = OH; R^2 = H
2, R^1 = OAc; R^2 = Ac
4, R^1 = R^2 = H
5, R^1 = H; R^2 = Ac

The most important information for the structural elucidation of the new clerodane type diterpene **1** was provided by its ^1H NMR spectrum and by that of its triacetyl derivative **2**. Effectively, these spectra (Table I) showed typical signals of a secondary methyl group, a β-substituted furan ring, and a C(20)–C(12*S*) lactone grouping identical with those previously found in several neoclerodane diterpenoids.[2] An AB system at δ 4.57 and 3.76 (J = 12 Hz) in the ^1H NMR spectrum of teucroxide (**1**) (solvent, pyridine-d_5) was attributed to the C(18) hydroxymethylene grouping, which on acetylation appeared at δ 4.14 and 4.07 (solvent, $CDCl_3$) or at δ 4.51 and 4.44 (solvent, C_6D_6) in

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0022-3263/83/1948-5123$01.50/0

Table I. ^{1}H NMR Spectral Parameters of Compounds 1 and 2[a]

	1[b]	2[c]	2[d]
H-2α	4.90[e]	5.76 (m, $W_{1/2}$ = 23)	5.41 (m, $W_{1/2}$ = 22)
H-3β	*f*	*f*	1.80 (dd, $J_{3\beta,2\alpha}$ = 14.5; $J_{3\beta,2\alpha}$ = 9.5)
H-3α	*f*	*f*	2.20 (dd, $J_{3\alpha,3\beta}$ = 14.5; $J_{3\alpha,2\alpha}$ = 5.7)
H-6α	4.90[e]	6.03 (dd, $J_{6\alpha,7\alpha} \simeq J_{6\alpha,7\beta}$ = 3)	5.64 (dd, $J_{6\alpha,7\beta} \simeq J_{6\alpha,7\alpha}$ = 3)
H-7β	*f*	*f*	1.86 (ddd, $J_{7\beta,7\alpha}$ 14.5; $J_{7\beta,6\alpha} \simeq J_{7\beta,8\beta}$ = 3)
H-11$_A$	*f*	*f*	2.50 (dd, $J_{11A,11B}$ = 14; $J_{11A,12}$ = 8.5)
H-11$_B$	*f*	*f*	2.39 (dd, $J_{11B,11A}$ = 14; $J_{11B,12}$ = 8.5)
H-12	5.57 (t, $J_{12,11A} = J_{12,11B}$ = 8.5)	5.12 (t, $J_{12,11A} = J_{12,11B}$ = 8.5)	5.38 (t, $J_{12,11A} = J_{12,11B}$ = 8.5)
H-14	6.53 (br t, J = 1.5)	6.26 (br t, J = 1.7)	6.35 (br t, J = 1.7)
H-15	7.65 (dd, $J_{15,14} = J_{15,16}$ = 1.5)	7.19 (dd, $J_{15,14} = J_{15,16}$ = 1.7)	7.40 (dd, $J_{15,14} = J_{15,16}$ = 1.7)
H-16	7.70 (m, $W_{1/2}$ = 3)	7.15 (m, $W_{1/2}$ = 3)	7.42 (m, $W_{1/2}$ = 3)
Me-17	1.00 (d, $J_{17,8}$ = 6.5)	0.92 (d, $J_{17,8}$ = 6.5)	0.94 (d, $J_{17,18}$ = 6.5)
H-18$_A$	4.57 (d, $J_{18A,18B}$ = 12)	4.51 (d, $J_{18A,18B}$ = 12)	4.14 (d, $J_{18A,18B}$ = 12)
H-18$_B$	3.76 (d, $J_{18B,18A}$ = 12)	4.44 (d, $J_{18B,18A}$ = 12)	4.07 (d, $J_{18B,18A}$ = 12)
H-19$_A$	4.97 (d, $J_{19A,19B}$ = 8)	5.03 (d, $J_{19A,19B}$ = 8)	4.68 (d, $J_{19A,19B}$ = 8)
H-19$_B$	4.33 (d, $J_{19B,19A}$ = 8)	4.43 (d, $J_{19B,19A}$ = 8)	4.20 (d, $J_{19B,19A}$ = 8)
AcO		2.00 (s)	2.08 (s)
		2.01 (s)	2.09 (s)
		2.02 (s)	2.11 (s)

[a] In ppm from Me_4Si; J values in hertz. [b] At 90 MHz, pyridine-d_5. [c] At 400 MHz, C_6D_6. [d] At 400 MHz, $CDCl_3$. [e] Overlapped signals. [f] Could not be identified.

the ^{1}H NMR spectrum of the triacetyl derivative **2**. An unresolved signal integrating for two hydrogens at δ 4.90 was assigned to the geminal protons of the two secondary hydroxyl groups of teucroxide (solvent, pyridine-d_5), because they were deshielded upon acetylation (Table I, compound **2**). Finally, an AB system at δ 4.97 and 4.33 in **1** (solvent, pyridine-d_5) and δ 4.68 and 4.20 ($CDCl_3$ solution) or δ 5.03 and 4.43 (C_6D_6 solution) in the triacetyl derivative **2** was assigned to the 4α,19-oxetane grouping because its J_{gem} value of 8 Hz was in agrement with this structural feature,[3] it was not downfield shifted on acetylation, and the presence of a cyclic ether function in teucroxide was clearly established by molecular formula requirements.

One of the secondary hydroxyl groups of teucroxide must be placed between two methylene groups, because its geminal proton appeared as a broad multiplet ($W_{1/2}$ = 22 Hz) in compound **2**. Thus in a clerodane skeleton, only the C(2) position is likely for this hydroxyl group.[2h] Moreover, as can be seen in the Drieding model of teucroxide (**1**), ring A shows a twist conformation close to that found by X-ray diffraction analysis in chamaedroxide (**3**), a neoclerodane diterpenoid also isolated from *Teucrium chamaedrys*.[2h] In this conformation the C-3β proton is pseudoaxial, and consequently, the C-3α proton and the C-2β substituent are pseudoequatorial, while the C-2α substituent is pseudoaxial. Since the C(3) methylene protons appeared at δ 2.20 (H-3α) and 1.80 (H-3β) in the ^{1}H NMR spectrum of **2** (solvent, $CDCl_3$) as the AB part of an ABX system with $J_{3\alpha,3\beta}$ = 14.5 Hz, $J_{3\alpha,2}$ = 5.7 Hz, and $J_{3\beta,2}$ = 9.5 Hz, it is clear that the C(2) hydroxyl group of teucroxide is β and pseudoequatorial, because in the alternative C-2α OH configuration, the $J_{3\alpha,2\beta}$ and $J_{3\beta,2\beta}$ values must be almost identical.

On the other hand, the other secondary hydroxy group of teucroxide (**1**) must be at the C-6β axial position, because its geminal proton showed a triplet ($J_{6\alpha,7\alpha} = J_{6\alpha,7\beta}$ = 3 Hz) in the ^{1}H NMR spectrum of compound **2**, in complete agreement with the previously reported data[2g,h,3] for this structural feature in clerodane diterpenoids. This conclusion was also supported by the fact that neither of the two protons at C(19) in compound **1** and **2** showed any long-range coupling in their ^{1}H NMR spectra.[4]

Table II. ^{13}C Chemical Shifts of Compounds 1, 2, 4, and 5[a]

	compounds				
C no.	1[b]	2[c]	2[d]	4[c,e]	5[c,e]
1	32.4 t	28.8 t	29.2	21.3 t	21.4 t
2	63.3 d	67.1 d	67.6	16.9 t	16.6 t
3	40.4 t	34.1 t	34.6	30.0 t	29.1 t
4	88.7 s	85.8 s	86.6	88.6 s	86.4 s
5	47.8 s	46.2 s	46.7	47.5 s	46.5 s
6	69.1 d	72.3 d	72.6	69.6 d	73.0 d
7	33.6 t	30.1 t	30.7	33.1 t	29.9 t
8	32.4 d	33.0 d	33.3	32.2 d	32.9 d
9	51.9 s	51.1 s	51.8	52.3 s	52.0 s
10	36.6 d	37.6 d	38.1	37.9 d	38.9 d
11	41.7 t	41.4 t	41.4	41.7 t	41.5 t
12	72.1 d	72.1 d	72.6	72.4 d	72.2 d
13	126.1 s	124.8 s	126.0	125.2 s	125.1 s
14	108.7 d	108.0 d	109.0	108.2 d	108.1 d
15	144.3 d	144.0 d	144.8	144.1 d	144.2 d
16	140.1 d	139.5 d	140.6	139.6 d	139.6 d
17	16.7 q	16.4 q	16.8	16.6 q	16.5 q
18	66.1 t	66.5 t	67.0	66.2 t	66.9 t
19	71.6 t	71.3 t	71.5	71.8 t	71.7 t
20	177.9 s	176.7 s	177.6	178.1 s	177.5 s
$OCOCH_3$		170.4 s	170.6		170.9 s
		169.8 s	170.2		170.0 s
		169.4 s	170.0		
$OCOCH_3$		21.3 q	21.2		21.3 q
		21.3 q	21.2		20.9 q
		20.8 q	20.8		

[a] In ppm relative to Me_4Si. [b] In pyridine-d_5. [c] In $CDCl_3$. [d] In pyridine-d_5 at 60 °C by taking the low-field triplet of the solvent for 149.9 ppm; multiplicities determined from APT-type spectra.[5] [e] Taken from ref 5.

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(4) See ref 2h and references therein.

All the above conclusions on the structure of teucroxide (1) were in complete agreement with the ^{13}C NMR spectral data of compounds 1 (solvent, pyridine-d_5) and 2 (solvent, $CDCl_3$). Effectively, comparison of ^{13}C chemical shifts (Table II) of these compounds with those reported[5] for montanin D (4) and its diacetate (5) showed that the C-(5)–C(9), and C(11)–C(20) carbon atom resonances were identical in 1 and 4 and in 2 and 5, whereas the differences in their C(1)–C(4) and C(10) carbon atom shifts were only explained by the presence in teucroxide (1) and in its derivative 2 of a C-2β pseudoequatorial OH or OAc function, respectively. In particular, the small γ-effects observed on C(4) and C(10) carbon atoms of compounds 1 ($\Delta\delta_{C(4)} = +0.1$, $\Delta\delta_{C(10)} = -1.3$) and 2 ($\Delta\delta_{C(4)} = -0.6$, $\Delta\delta_{C(10)} = -1.3$) clearly confirmed the C-2β pseudoequatorial configuration of their oxygenated functions.

From the point of view of ^{13}C–^{13}C coupling constants, teucroxide (1) appeared a highly interesting structure since it contains a four-membered and two five- and six-membered rings. Therefore, an investigation aimed at obtaining natural-abundance ^{13}C–^{13}C coupling constants on the triacetyl derivative 2 was undertaken with the recently developed one-dimensional INADEQUATE technique.[6] This study afforded further evidence for the proposed structure and confirmed the carbon signal assignments.

The one-dimensional INADEQUATE experiment was first attempted at 50.31 MHz with a Bruker WM-200 spectrometer. The double-quantum pulse sequence was used.[6] A solution of 2 was prepared in xylene-d_{10} (800 mg of 2 in 2 mL of solvent) and then the pulse sequence was optimized for $^1J_{CC} = 60$ Hz ($J\tau = 1/4$) with the intention of measuring all the one-bond coupling constants in one experiment. Data were accumulated at 110 °C, overnight, using a relaxation delay of 3.0 s. The number of data points was 16K with a frequency range of 8500 Hz. However, this experiment allowed only the determination of one-bond ^{13}C–^{13}C coupling constants for linkages involving sp^2 carbon atoms. The intensity of the satellite lines representing carbon bonds between sp^3-hybridized atoms was low, precluding a precise evaluation of the corresponding coupling constants.

In order to improve the signal to noise ratio and the digital resolution, the spectral study was attempted again with a Bruker WM-400 spectrometer operating at 100.62 MHz. A solution of 2 was prepared in pyridine-d_5 (800 mg of 2 in 2 mL of solvent) and then the pulse sequence was optimized for $^1J_{CC}$ 45 ($J\tau = 1/4$), and data were accumulated, with a relaxation delay of 3.0, overnight at 60 °C in order to shorten spin–lattice relaxation times relative to the previous experiment. The number of data points was 64K with a frequency range of 13 889 Hz (only the high-field part of the spectrum), giving a digital resolution of 0.42 Hz/point. Resolution enhancement was applied.[7]

Analysis of the results of the two experiments permitted the assignment of the satellite pairs and the determination of all the one-bond ^{13}C–^{13}C coupling constants for the triacetyl derivative 2 of the naturally occurring diterpenoid 1 (Table II, Figures 1 and 2). The intensity of the satellite lines for the C(9)/C(20) linkage was low because of the quaternary nature of these carbon atoms. As shown in Figure 1, the data were in excellent agreement with the proposed molecular framework of 2. The small one-bond

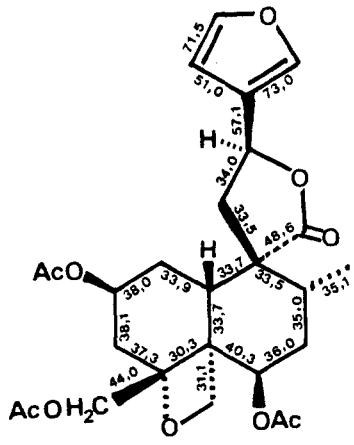

Figure 1. Natural-abundance one-bond ^{13}C–^{13}C coupling constants (hertz) in compound 2. The methyl carbon of the three acetates showed $^1J_{CC} = 60 \pm 0.5$ Hz.

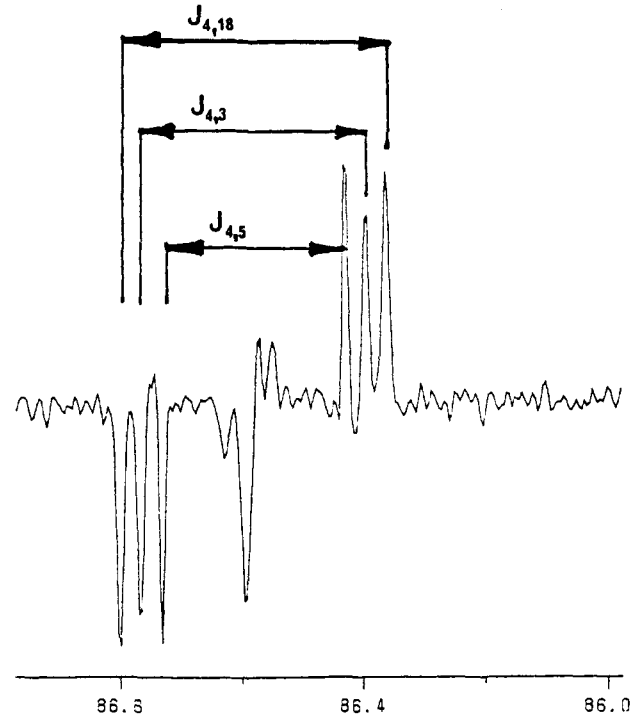

Figure 2. The C-4 signal from the 100.62-MHz INADEQUATE ^{13}C NMR spectrum of 2 recorded in pyridine-d_5 at 60 °C. Satellites of strongly reduced intensity can be detected for a two-bond coupling (8 Hz) probably within the oxetane system.

^{13}C–^{13}C coupling constants within the oxetane ring are consistent with previously published data on related heterocyclic systems.[9]

The absolute configuration of teucroxide was not ascertained. However, we suppose that this substance belongs to the neoclerodane series, like all the other diterpenoids cooccurring in the same plant.[2] The oxetane ring moiety is a very rare feature in natural products, and only a few compounds possessing this function have been described.[4]

Experimental Section

Melting points were determined in a Kofler apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 141 polarimeter with a 1-dm cell. Elemental analyses were carried out in Madrid[1a] with the use of a Perkin-Elmer 240 analyzer. IR

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spectra were determined on a Perkin-Elmer 257 spectrometer. ^1H and ^{13}C NMR spectra were measured at 90 and 400 MHz and 20.15, 50.31, and 100.62 MHz, respectively, in pyridine-d_5, $CDCl_3$, or C_6D_6 solution with Me_4Si as an internal standard. Assignments of ^{13}C chemical shifts were made with the aid of off-resonance, APT-type, and noise-decoupled ^{13}C NMR spectra.

Mass spectra were obtained by electron impact on a Hitachi Perkin-Elmer RMU-6MG instrument.

Isolation of Teucroxide (1). Dried and finely powdered *T. chamaedrys* L. (aerials parts, 2.2. kg), collected near Cimelos del Pinor (Guadalajara, Spain), were extracted with acetone as previously described.[2g] The most polar chromatographic diterpenoid, eluted from a silica gel column with $CHCl_2$–MeOH (6:1), was teucroxide (1): 1062 mg, mp 183–184 °C (from AcOEt); $[\alpha]^{22}_D$ −29.2° (*c* 0.545, pyridine); IR (KBr) 3460, 3360, 3290, 3150, 3130, 3120, 2960, 2910, 2890, 1760, 1600, 1508, 1470, 1360, 1325, 1315, 1190, 1165, 1065, 1025, 975, 960, 880, 835, 820, 740, 720, 620, 600 cm^{-1}; UV (EtOH) λ_{max} 210 nm (log ϵ 3.60), furan ring; ^1H NMR (pyridine-d_5), see Table I; ^{13}C NMR (pyridine-d_5), see Table II; mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) 378 (M^+, 3) 360 (36), 347 (48), 342 (3), 329 (6), 311 (5), 301 (4), 286 (7), 283 (13), 266 (14), 179 (38), 178 (21), 161 (26), 145 (21), 133 (26), 108 (37), 105 (38), 95 (100, base peak), 94 (62), 91 (50), 81 (90), 79 (40), 77 (43), 69 (32), 67 (31), 65 (32), 55 (53), 53 (52), 43 (98). Anal. Calcd for $C_{20}H_{26}O_7$: C, 63.48; H, 6.93. Found: C, 63.21; H, 6.96.

Compound 2. A solution of 750 mg of teucroxide (1) in 20 mL of pyridine and 5 mL of acetic anhydride was allowed to stand overnight at room temperature. The reaction mixture was poured into ice–water and extracted with $CHCl_3$. A workup in the usual manner yielded, after purification by column chromatography, 990 mg of 2: mp 115–118 °C (from MeOH); $[\alpha]^{19}_D$ −20.4° (*c* 0.90, $CHCl_3$); IR (KBr) 3170, 3140, 3020, 2970, 2940, 2890, 1760, 1740, 1720, 1600, 1505, 1440, 1370, 1240, 1190, 1160, 1035, 1025, 985, 930, 910, 880, 860, 810, 740, 730 cm^{-1}; UV (EtOH) λ_{max} 215 nm (log ϵ 3.49), furan ring; ^1H NMR ($CDCl_3$ and C_6D_6), see Table I; ^{13}C NMR ($CDCl_3$), see Table II; mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) 504 (M^+, 3) 444 (12), 431 (46), 402 (16), 384 (28), 371 (4), 342 (10), 329 (28), 324 (12), 308 (15), 290 (60), 283 (33), 275 (12), 268 (21), 248 (41), 174 (73), 145 (40), 143 (36), 119 (38), 95 (94), 91 (52), 81 (85), 43 (100, base peak). Anal. Calcd for $C_{26}H_{33}O_{10}$: C, 61.89; H, 6.39. Found: C, 61.76; H, 6.47.

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Synthesis of 2-Methyl-3-hydroxy-4*H*-pyran-4-one and 4-Hydroxy-5-methyl-2*H*-furan-3-one from Carbohydrates

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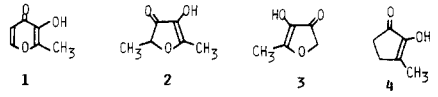
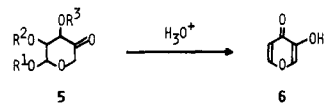
Cyclic α-diketones, such as 2-methyl-3-hydroxy-4*H*-pyran-4-one (**1**, maltol),[1] 2,5-dimethyl-4-hydroxy-2*H*-furan-3-one (**2**, furaneol),[2,3] 4-hydroxy-5-methyl-2*H*-furan-one (**3**), and 2-hydroxy-3-methylcyclopent-2-en-1-one (**4**, cyclotene)[4] have been known to be important key flavors in a variety of foods, and much effort has been devoted to their synthesis.



Although some routes of the synthesis of **1**–**3** have been developed so far by utilizing carbohydrates as starting compounds,[5] the yields or availability of the starting carbohydrates are not always satisfactory. Thus, it seems worthwhile to develop new methods of synthesizing α-diketones from the most easily available carbohydrates. This paper describes the synthesis of **1** from D-glucose and the synthesis of **3** from D-xylose and from D-xylitol.

Synthesis of 1 from D-Glucose. The structure of **1** is characterized by a methyl group on C-2 and a hydroxyl group on C-3 of the 4*H*-pyran-4-one skeleton. The construction of the 3-hydroxy-4*H*-pyran-4-one skeleton from glucose is expected to be accomplished by the oxidation of only one hydroxyl group of glucose at the C-4 position, since it has already been found by us[1] and other groups[1,5] that the 1,2,3-trihydroxy-4-ketotetrahydropyran skeleton **5** can be transformed to the 3-hydroxy-4*H*-pyran-4-one skeleton **6** by treatment of **5** with aqueous acid (eq 1).



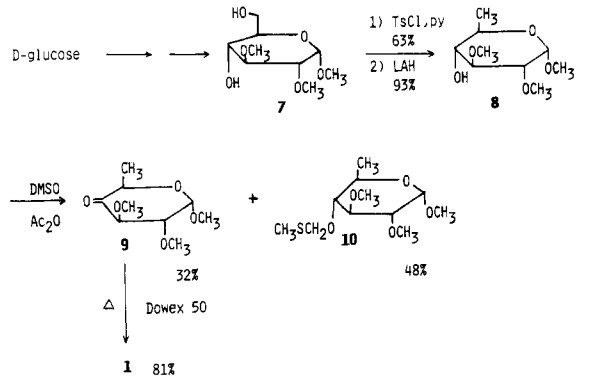
(1)

5 **6**

R^1, R^2, R^3 = alkyl, hydrogen, benzoyl, or acyl group

The methyl group on C-2 of **1** may be easily formed by the reductive removal of a hydroxyl group on C-6 of glucose. In fact, the synthesis of **1** from glucose was achieved by the procedures shown in Scheme I.

Scheme I



Methyl 2,3-di-*O*-methyl-α-D-glucopyranoside (**7**), easily prepared from D-glucose by the reported method,[6] was tosylated to give methyl 2,3-di-*O*-methyl-6-*O*-tosyl-α-D-glucopyranoside, and the tosylate was subsequently re-

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