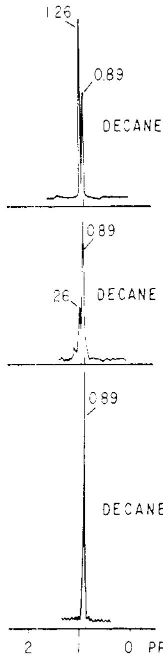


Figure 2. ^2H NMR spectra of decane-*d*: 100% ^2H (1K transients, 2.1-s repetition rate, displayed spectral width 500 Hz, 8K data points); 4.4% ^2H (670 transients, 4.4-s repetition rate, displayed spectral width 500 Hz, 4K data points); 2.0% ^2H (100 transients, 3.7-s repetition rate, displayed spectral width 500 Hz, 2K data points).

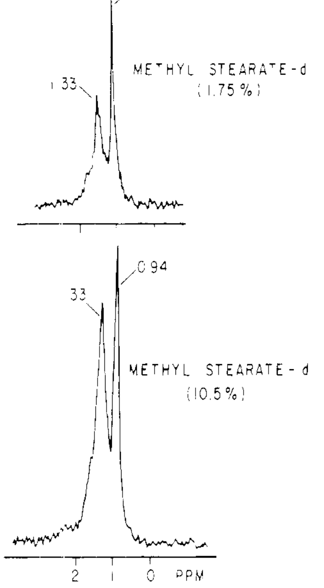


Figure 3. ^2H NMR spectra of methyl stearate-*d*: 1.75% ^2H (900 transients, 8.2-s repetition rate, displayed spectral width 1000/8 Hz, 8K data points); 10.5% ^2H (550 transients, 82-s repetition rate, displayed spectral width 1000/8 Hz, 8K data points).

porated deuterium than the terminal CH_3 group. For methyl 3-methylpentanoate-*d*, no deuterium was detected in the methylene or methine (C–H) positions. Apparently a combination of electronic and steric effects prevents the H–D exchange of these bonds.

Thus, our study shows the Pt-catalyzed activation of the C–H bonds of saturated carboxylic acids occurs, in general, in the same manner as it does in simple alkanes: it favors mainly primary C–H bonds over secondary C–H bonds. However, we have demonstrated that when this reaction is employed with functionally substituted alkanes, such as carboxylic acids, electronic effects play an important role and can influence the selectivity of the reaction.

Experimental Section

Materials. Pure D_2O (99.8%) was purchased from Aldrich.[17] K_2PtCl_4 was obtained from Ventron, K_2PtCl_6 from ICN, and pyrene from Chemical Service. Methyl 2-methyloctanoic acid was prepared according to the procedure of Pfeffer and Silbert.[18] All other organic compounds were obtained from commercial chemical supply houses. Mass spectra were obtained on a Du Pont 21-492 double-focusing instrument operating at an ionization potential of 70 eV. ^2H NMR spectra were obtained with a ^{31}P 10-mm probe of a JEOL FX-60Q NMR spectrometer.[16]

Procedure. A typical reaction medium used in this study consists of 5 mL of a 50 mol% mixture of acetic acid-*d* and D_2O containing the catalyst K_2PtCl_4 (0.4 M), $HClO_4$ (0.2 M), pyrene (0.5 M), and the carboxylic acid (0.2 or 2.0 M). The reactions were carried out in sealed ampules heated at 100 °C. The deuterated carboxylic acids were extracted from the reaction medium with hexane or ether and esterified with BF_3/MeOH reagent. Following esterification the deuterated esters were analyzed by mass spectrometry to determine the total level of deuterium incorporated (% ^2H).[19] ^2H NMR was used to ascertain the positional distribution of deuterium, in some instances with the aid of the shift reagent Eu(fod)$_3$.[16]

Acknowledgments. We acknowledge the valuable assistance received from C. J. Dooley and his staff in supplying the mass spectrometric data.

Registry No. Methyl nonanoate, 1731-84-6; dimethyl azelate, 1732-10-1; methyl 2-methyloctanoate, 2177-86-8; methyl 3-methylpentanoate, 2177-78-8; methyl stearate, 112-61-8; decane, 124-18-5; K_2PtCl_4, 10025-99-7; K_2PtCl_6, 16921-30-5.

---

[17] Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

[18] P. E. Pfeffer and L. S. Silbert, *J. Org. Chem.*, **35**, 262 (1970).

[19] The total percent ^2H content was determined by mass spectroscopy after appropriate corrections for ^{13}C and ion fragmentation were made. % D was calculated according to equations found in ref. 8.

A Lactone Analogue of Germacrone

Walter Vichnewski

Nucleo de Pesquisas de Produtos Naturais do Faculdade de Farmácia e Odontologia, 14.100 Ribeirão Preto, S.P., Brasil

Werner Herz* and Narendra Kumar

Department of Chemistry, The Florida State University, Tallahassee, Florida 32306

Received January 26, 1979

Work on the structure and conformation of the sesquiterpene ketone germacrone (**1**) occupies an important place in the history of cyclodecadiene chemistry.[2-6] We now report isolation of a lactone analogue **2** from the Brazilian composite *Wunderlichia mirabilis* Riedel

---

[1] Work at The Florida State University was supported in part by a grant (CA-13121) from the U.S. Public Health Service through the National Cancer Institute. Work at Ribeirão Preto was supported in part by the Conselho Nacional de Desinvolvimento Cientifico Tecnologico.

[2] (a) F. Šorm, *Fortschr. Chem. Org. Naturst.*, **19**, 1 (1961); (b) *Pure Appl. Chem.*, **21**, 265 (1970).

[3] H. Hikino, C. Konno, T. Nakashima, T. Kohama, and T. Takemoto, *Tetrahedron Lett.*, 337 (1971).

[4] J. D. Sutherland, *Tetrahedron*, **30**, 1651 (1974).

[5] I. Horibe, H. Shigemoto, and K. Tori, *Tetrahedron Lett.*, 2849 (1975).

[6] R. K. Hill, M. G. Fracheboud, S. Sawada, R. M. Carlson, and S.-J. Yan, *Tetrahedron Lett.*, 945 (1978).

Table I. ^{1}H NMR Spectra[a]

	2	2[b]	3	4
H-1	5.06 d br (12)	4.57 d br (12)	2.75 d br (12, 1)	2.87 d br (12)
H-2a	2.38 m	1.95 m	2.05 dd br (14.6)	2.10 dd br (14, 6)
H-2b	*c*	*c*	1.37 dddd (14, 12, 12, 5)	1.55 m[c]
H-3a	*c*	*c*	2.35 ddd (13, 12, 6)	1.33 ddd (13, 12, 6)
H-3b	*c*	*c*	2.27 ddd (13, 5, 2)	2.23 ddd (13, 5, 2)
H-5	4.58 d br (9)	4.26 d br (9)	4.88 dq (9, 1.5)	2.56 d (9)
H-6	5.71 d br (9)	5.50 d br (9)	5.75 d br (9, 1.5)	1.96 d br (9, 1.5)
H-9a	3.52 d (10)	3.06 d (10)	3.11 d (14)	3.15 d (11)
H-9b	3.11 d (10)	2.73 d (10)	2.56 d	2.73 d (11)
H-13[d]	1.92 d (1.5)	1.61 d (1.5)	1.87 d (1.5)	2.06 d (1.5)
H-14	1.55 br	1.44 br	1.26	1.21
H-15[d]	1.65 br	1.13 br	1.66 d (1.5)	1.47

[a] Run in $CDCl_3$ at 270 MHz. Frequencies in ppm downfield from Me_4Si as internal standard. Coupling constants in parentheses in hertz. [b] In C_6D_6. [c] In envelope or partially obscured. [d] Intensity three protons.

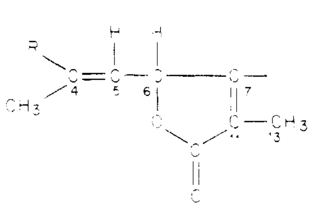
Table II. ^{13}C NMR Spectra of 1 and 2[a]

	1	2		1	2
C-1	132.54 d	133.93 d[b]	C-2	55.81 t	54.83 t[b]
C-2	24.11 t	23.77 t	C-10	126.63[c]	124.40[c,d]
C-3	38.13 t	37.48 t	C-11	134.72[c]	124.89[c,d]
C-4	137.36[c]	140.92[c]	C-12	22.25 q	172.70
C-5	125.42 d	123.37 d[b]	C-13	19.83 q	9.15 q
C-6	29.22 t	77.79 d[b]	C-14	16.69 q[d]	16.15 q[d]
C-7	129.05[c]	161.06	C-15	15.55 q[d]	15.80 q[d]
C-8	207.06	197.93			

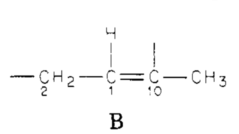
[a] Run in $CDCl_3$ at 67.90 MHz. Unmarked signals are singlets. [b] Assignment by single-frequency off-resonance decoupling. [c] For assignments see discussion in ref 7. [d] Assignments interchangeable.

(Mutisiae) and discuss its probable absolute configuration.

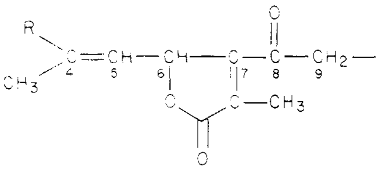
The new substance, mp 116–118 °C, $C_{15}H_{18}O_3$, had IR bands characteristic of a γ-lactone and a conjugated ketone (IR bands at 1767, 1678, 1660, and 1635 cm^{-1}). However, the short-wavelength maximum of the UV spectrum (λ_{max} 218 and 314 nm, ϵ 13 900 and 740) seemed anomalous in view of the fact that the ^{1}H NMR spectrum contained only one signal (at 5.71 ppm) conceivably within the range of a proton on an α,β-unsaturated ketone chromophone. Comparison of the ^{1}H NMR spectrum (Table I) with the ^{13}C NMR spectrum (Table II) and single-frequency off-resonance decoupling eventually established that the signal at 5.71 ppm was in fact that of H-6 (numbering as in final formula) in partial structure A which was vicinally coupled to H-5 (doublet at 4.58 ppm) and homoallylically coupled to the proton of a vinyl methyl group. In the ^{13}C NMR spectrum, C-12, C-11, and C-7 of A were represented by singlets at 172.7, 124.89, and 161.06 ppm, respectively, C-13 by a quartet at 9.15 ppm, C-6 by a doublet at 77.79 ppm, and C-5 by a doublet at 123.37 ppm.[7] C-4 of A was completely substituted and carried one of the two other vinylic methyls (somewhat broadened singlets at 1.55 and 1.65 ppm) which was trans to H-5 (no NOE). The third vinyl methyl group was included in partial structure B with H-1 (broadened doublet at 2.38 ppm) being coupled to H-2a at 2.38 ppm and H-2b in a three-proton envelope near 2.1 ppm. The corresponding carbon signals appeared at 133.93 (doublet, C-1) and 23.77 (triplet, C-2) ppm.



A



B

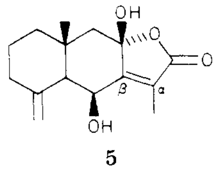


C

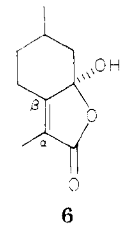
Although the UV maximum at 218 nm seemed to be satisfied by partial formula A, the ^{13}C NMR spectrum demonstrated that the third oxygen atom of the empirical formula was that of a conjugated ketone (singlet at 197.93 ppm) whose attachment to C-8 was required by the chemical shifts of the various olefinic carbons. Further expansion of A to C was then dictated by the ^{1}H NMR spectrum which exhibited an AB system centered at 3.31 ppm characteristic of a methylene group (C-9) adjacent to a carbonyl; in the ^{13}C NMR spectrum C-9 was revealed by a triplet at 54.83 ppm. Since H-9a and H-9b were not significantly split by adjacent protons, B and C which together account for 14 of the 15 carbon atoms were linked through C-9 and C-10; the fifteenth carbon atom, represented by a methylene triplet at 37.48 ppm, had to be interposed between C-2 and C-4 as in **2**. This formula nicely accounts for the high-resolution mass spectrum. The

---

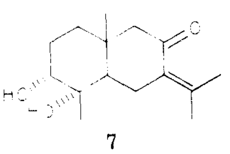
(7) We were somewhat dubious about how three of the vinylic carbon singlets (those at 161 and 141 ppm and one of the two near 124 ppm) should be allocated among C-4, C-7, and C-11. Comparison with the recently reported[8] ^{13}C NMR spectra of **5** ($\delta(C_\alpha) = 122.8$, $\delta(C_\beta) = 156.9$) and **6** ($\delta(C_\alpha) = 122.8$, $\delta(C_\beta) = 161.1$) showed that the signal at lowest field was that of C-7, but while we expected that in comparison with **5** and **6** C-11, now in the β position of an α,β-unsaturated ketone system, would be shifted to lower field (cf. 145.5 ppm for C-11 of cuauhtemone **7**[9]), the 141-ppm signal seemed preempted by C-4 which in costunolide and other simple *trans,trans*-germacradienolides is found near 141 ppm. To help with the assignments the ^{13}C NMR spectrum of germacrone (kindly supplied by Professor M. A. Schwartz) was recorded and is also listed in Table II. C-8 of **1** was considerably more deshielded than expected (cf. 202 ppm for cuauhtemone); consequently assignment of the second lowest singlet at 137.36 ppm to C-11 rather than to C-4 was not clear-cut. A tentative proposal for the vinylic singlets of 1 which is in reasonable accord with the ^{13}C NMR spectra of costunolide, on the one hand, and cuauhtemone and similar substances, on the other, is given in Table I; analogy then would require allocation of the 141-ppm singlet of **2** to C-4 and one of the 124-ppm singlets to C-11.



5



6



7

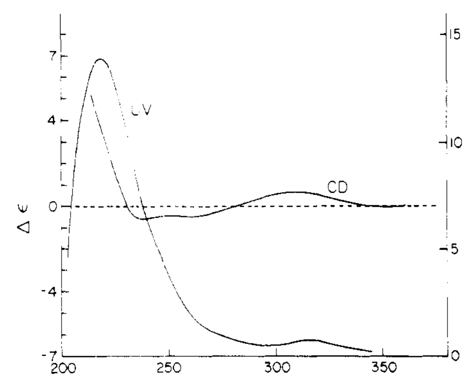
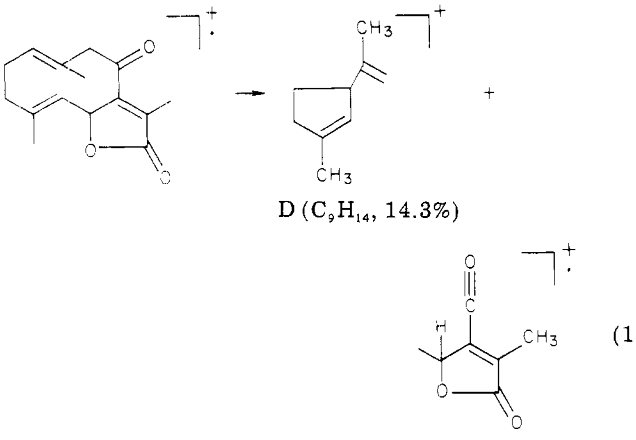


Figure 1. UV spectrum and CD curve of 2.

base peak is represented by the right-hand fragment E from the cleavage illustrated (1), with an appreciable amount of the charge residing on the left-hand fragment, probably D. The only other intense ion representing the entire left half of the molecule is $C_9H_{13}^+$ (58%, D–H) which must result from hydrogen transfer from the left half, probably the C-4 methyl group, to the right half of the molecule prior to cleavage.



D (C_9H_{14}, 14.3%)

(1)

E ($C_6H_4O_3$, 100%)

The new substance is a lactone analogue of germacrone (1). Its IR and UV spectra compare with those of 1 which has IR bands at 1681 and 1660 cm^{-1} and UV maxima at 213 (shoulder at 240) and 315 nm (log ε 4.10, 3.47, 2.55)[4] if allowance is made for the additional presence of the α,β-unsaturated lactone function. The π,π^* absorption of the latter combines with the 213-nm band resulting from transannular interaction of the two endocyclic double bonds[4] to mask the π,π^* transition of the α,β-unsaturated ketone (Figure 1). Partial overlap of the latter with the n,π^* transition of the lactone may be responsible for the shape of the CD curve (Figure 1) in the 250-nm region. The CD curve also exhibits a shoulder at 328 nm (n,π^* transition of the α,β-unsaturated ketone) on the long-wavelength side of a somewhat stronger band centered at 310 nm which is due to the inherently dissymmetric chromophore of the β,γ-unsaturated ketone system. The presence of this system is also evidenced by the typical enhancement of the UV band near 310 nm.

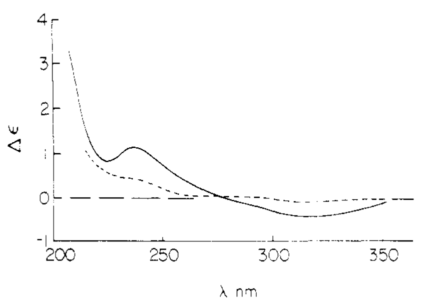
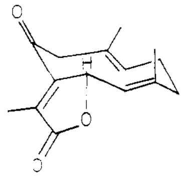
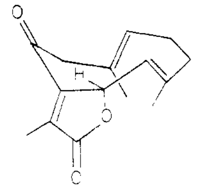


Figure 2. CD curves of 3 (- - -) and 4 (—).

That 2 assumes the C,C or crown conformation previously deduced for germacrone[5] and most other *trans,trans*-1,5-cyclohexadienes[6] was indicated by the properties of two transformation products.[10] Exposure of 2 to excess *m*-chloroperbenzoic acid furnished a monoepoxide 3 and a diepoxide 4. Epoxidation of the 1,10 double bond and retention of the 4,5 double bond in the monoepoxide was evident from the ^{1}H NMR spectrum (Table I), H-1 having experienced a large diamagnetic shift and the H-9a,b AB system a smaller diamagnetic shift. The H-5 signal appeared at somewhat lower field due to the difference in anisotropic shielding by the 1,10 double bond and the new epoxide. Observation of a NOE between H-1 and H-5 (11.5% enhancement of H-5 signal upon irradiation of H-1) showed that these hydrogens were syn. The situation is thus similar to that prevailing in germacrone and its epoxides;[5] however, because of the dissymmetry at C-6 of 2, expoxidation of the C,C-conformation F and the C′,C′-conformation G (with the absolute configuration arbitrarily shown as 6*S*) would give rise to diastereomeric rather than enantiomeric mono- and diepoxides. An examination of models suggests that the large value of $J_{5,6}$ (9 Hz) is more consonant with the C,C than the C′,C′ conformation; in that case 3 and 4 would be 1*S*,6*S*,10*S* and 1*S*,4*S*,5*S*,6*R*,10*S*,[11] respectively, as shown in the formulas, or their mirror images.



F



G

The following very tenuous argument can be advanced for the absolute configuration of 2. Comparison of the CD curves of 2–4 (Figures 1 and 2) demonstrates that the β,γ-unsaturated ketone function produces a positive contribution to the long-wave Cotton effect. On the basis of the generalized octant rule,[12,13] this points to the absolute configuration shown in the formulas, i.e., 6*S* for 2 and 3 and 6*R* for 4. The relatively small rotational strength of 2 in the 320-nm region may be due to the geometry of the β,γ-unsaturated ketone system[12] with the plane of the 1,10 double bond at approximately 90° to the ketone carbonyl. It has been pointed out,[15] however, that in such a case the generalized octant rule must be applied with caution as the contribution derived from the chirality of the chro-

---

[8] N. F. Roque, Z. S. Ferreira, O. R. Gottlieb, R. L. Stephens, and E. Wenkert, *Rev. Latinoam. Quim.*, **9**, 25 (1978).

[9] K. Nakanishi, R. Crouch, O. Miura, X. A. Dominguez, A. Zaumudia, and R. Villareal, *J. Am. Chem. Soc.*, **96**, 609 (1974).

[10] The aromatic solvent induced shift method[5] was not useful for distinguishing between C and T conformations of 2 since all protons exhibited quite large positive Δ(δ)'s (Table I).

[11] The descriptor of C-6 changes from *S* to *R* on expoxidation of the 4,5 double bond.

[12] A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962).

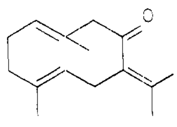
[13] G. Snatzke, *Tetrahedron*, **21**, 413 (1965).

[14] This is so even if 2 were in the C′,C′ conformation. Regardless of the conformation adopted by the 10-membered ring, the 1,10 double bond falls in the rear upper left octant.

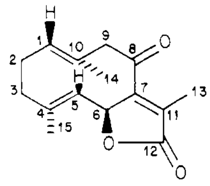
[15] D. A. Lightner, D. E. Jackson, and G. D. Christiansen, *Tetrahedron Lett.*, 4467 (1978).

mophore may be overshadowed by contributions from the dissymmetric environment. In the present case the latter contributions seem to be weakly negative.

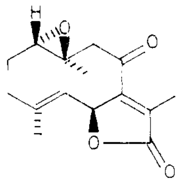
The absolute configurations shown in the formulas harmonize (model) with the positive Cotton effect in the 240-nm region if, as is generally assumed, the chirality of an α,β-unsaturated ketone chromophore is related to the sign of the π,π^* Cotton effect. However, since the sign and shape of the CD curves of 2–4 in the 240-nm region result from superposition of two Cotton effects—n,π^* of lactone and π,π^* of ketone—the observed agreement may be entirely fortuitous.



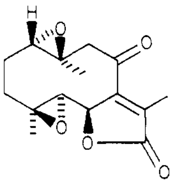
1



2



3



4

Experimental Section

Aerial parts (5.5 kg) (except for the wood) of *Wunderlichia mirabilis* Riedel, collected by Dr. Hermogenes de Freitas Leitão Filho in Serra da Canastra, Minas Gerais, Brasil, in December 1977, were extracted with $CHCl_3$ giving 140 g of crude extract which was worked up in the usual manner.[16] The resulting 15 g of crude gum was chromatographed over 420 g of silica gel, 450-mL fractions being eluted in the following order: 1–3 (hexane–EtOAc, 6.6:1), 4–13 (hexane–EtOAc, 4:1), 14–21 (hexane–EtOAc, 2.8:1), 22–31 (hexane–EtOAc, 2.2:1), 32–46 (EtOAc), 47–54 (EtOAc–MeOH, 2:1), 55 (MeOH). The solids of fractions 4 and 5 were combined and purified by recrystallization from hexane to give 220 mg of **2**: mp 116–118 °C; IR (KBr) 1767, 1678, 1660, 1635, 990, 980, 898, 850 cm^{-1}; UV λ_{max} 218, 314 nm (ϵ 13 900, 740): CD curve (MeOH) $[\Theta]_{308}$ 22 900, $[\Theta]_{257}$ −15 300 (minimum), $[\Theta]_{254}$ −15 200 (inflecton), $[\Theta]_{238}$ −19 000 (minimum), $[\Theta]_{214}$ 17 000 (last reading).

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37; mol wt 246.1255. Found: C, 73.24; H, 7.48; mol wt (mass spectrometry) 246.1278.

Other significant peaks in the high-resolution mass spectrum appeared at *m/e* (composition, %) 231 ($C_{14}H_{15}O_3$, $M^+ - CH_3$, 5.6), 228 ($C_{15}H_{16}O_2$, $M^+ - H_2O$, 4.6), 218 ($C_{14}H_{18}O_2$, $M^+ - CO$, 8.0), 217 ($C_{14}H_{17}O_2$, 11.4), 213 ($C_{14}H_{13}O_2$, 5.2), 204 ($C_{13}H_{16}O_2$, 5.2), 203 ($C_{13}H_{15}O_2$, 12.1), 200 ($C_{14}H_{16}O$, 5.5), 190 ($C_{11}H_{10}O_3$, 6.2), 185 ($C_{13}H_{13}O$, 5.6), 163 ($C_9H_7O_3$, 17.3), 149 ($C_9H_9O_2$, 19.0), 135 ($C_8H_7O_2$, 19.8), 124 ($C_6H_4O_3$, 100), 122 (C_9H_{14}, 14.3), 121 (C_9H_{13}, 58).

Epoxidation of 2. To an ice-cold solution of 50 mg of **2** in 3 mL of $CHCl_3$ was added 100 mg of *m*-chloroperbenzoic acid in 5 mL of $CHCl_3$. The solution was stirred for 1 h at 0 °C, washed with $NaHCO_3$ solution and water, and dried and evaporated. The residue was purified by TLC (silica gel, MeOH–$CHCl_3$, 2:1). The upper band containing the monoepoxide **3** was recrystallized from $CHCl_3$–hexane: yield 20 mg, mp 171–172 °C. The NMR spectrum is given in Table I.

Anal. Calcd for $C_{15}H_{18}O_4$: mol wt 262.1204. Found: mol wt (mass spectrometry) 262.1195 (3.3%).

Other significant peaks in the high-resolution mass spectrum appeared at *m/e* (composition, %) 247 ($M^+ - CH_3$, 1.0), 244 ($M^+ - H_2O$, 2.2), 234 ($M^+ - CO$, 0.6), 234 ($C_{14}H_{14}O_4$, 0.9), 219 ($C_{13}H_{15}O_3$, 3.4), 204 ($C_{12}H_{12}O_3$, 12.8), 202 ($C_{13}H_{14}O_2$, 2.4), 201 ($C_{13}H_{13}O_2$, 2.5), 194 ($C_{10}H_{10}O_4$, 1.8), 192 ($C_{11}H_{12}O_3$, 2.2), 191 ($C_{12}H_{15}O_2$, 1.6), 189 ($C_{11}H_9O_3$, 1.7), 187 ($C_{12}H_{11}O_2$, 1.4), 179 ($C_{10}H_{11}O_3$, 3.2), 178 ($C_{11}H_{14}O_2$, 5.4), 178 ($C_{10}H_{10}O_3$, 3.1), 177 ($C_{11}H_{13}O_2$, 7.6), 176 ($C_{11}H_{12}O_2$, 4.8), 175 ($C_{11}H_{11}O_2$, 3.9), 161 ($C_{10}H_9O_2$, 3.7), 150 ($C_9H_{10}O_2$, 6.5), 149 ($C_9H_9O_2$, 7.4), 140 ($C_7H_8O_3$, 88), 137 ($C_9H_{13}O$, 4.0), 135 ($C_9H_{11}O$, 4.1), 133 (C_9H_9O, 4.0), 131 (C_9H_{11}, 4.9), 124 ($C_6H_4O_3$, 55.9), 124 ($C_8H_{12}O$, 12.7), 81 (C_6H_9, 100).

The lower band from the TLC purification furnished the diepoxide 4 which was recrystallized from $CHCl_3$: yield 15 mg, mp 185–186 °C. The NMR spectrum is given in Table I.

Anal. Calcd for $C_{15}H_{18}O_5$: mol wt 278.1153. Found: mol wt (mass spectrometry) 278.1158 (1.0%).

Other significant peaks in the high-resolution mass spectrum appeared at *m/e* (composition, %) 260 ($C_{15}H_{16}O_4$, 2.9), 249 ($C_{14}H_{17}O_4$, 9.8), 235 ($C_{13}H_{15}O_4$, 19.1), 231 ($C_{14}H_{15}O_3$, 4.1), 222 ($C_{12}H_{14}O_4$, 2.8), 221 ($C_{13}H_{17}O_3$, 10.5), 220 ($C_{12}H_{12}O_4$, 9.1), 218 ($C_{13}H_{14}O_3$, 8.5), 217 ($C_{13}H_{13}O_3$, 18.3), 207 ($C_{12}H_{15}O_3$, 12.3), 193 ($C_{11}H_{13}O_3$, 23.0), 192 ($C_{11}H_{12}O_3$, 20.4), 191 ($C_{11}H_{11}O_3$, 17.6), 178 ($C_{10}H_{10}O_3$, 21.5), 176 ($C_{11}H_{12}O_2$, 30.3), 175 ($C_4H_{11}O_2$, 19.2), 161 ($C_{10}H_9O_2$, 14.0), 150 ($C_9H_{10}O_2$, 13.9), 149 ($C_9H_9O_2$, 15.3), 138 ($C_7H_6O_3$, 15.5), 131 ($C_{10}H_{11}$, 15.0), 125 ($C_6H_5O_3$, 40.3), 124 ($C_6H_4O_3$, 100).

Registry No. 1, 6902-91-6; **2**, 70224-78-1; **3**, 70224-79-2; **4**, 70224-80-5.

---

[16] W. Herz and G. Högenauer, *J. Org. Chem.*, **27**, 905 (1962).

Rotenoid Interconversion. Synthesis of Deguelin from Rotenone

Peter B. Anzeveno

Pharmaceutical Research and Development—Medicinal Chemistry Group, The Dow Chemical Company, Indianapolis, Indiana 46268

Received January 29, 1979

During an investigation of the inhibitory effects of various naturally occurring rotenoids on slow reacting substance of anaphylaxis (SRS-A), an important chemical mediator in the allergic response mechanism, we were met by the need to provide greater and more readily accessible amounts of deguelin (**1**) than we could obtain from natural sources. Consequently, we sought a convenient preparation of **1**.

The reported deguelin syntheses[1] are lengthy and low-yielding processes. Moreover, none afford optically pure product. Since we considered that a new deguelin total synthesis was unjustified, we thought a logistically better solution to our problem would be the development of a scheme for the conversion of the readily available (−)-rotenone (**2**) to **1**. An important benefit of this strategy was that it allowed the preparation of natural **1**. We have recently succeeded in achieving this conversion to natural (−)-**1** and, in this note, describe our results.

Unai and Yamamoto have reported the selective cleavage of the E ring of rotenone by reaction with boron tribromide (1 equiv) in dichloromethane at −10 °C.[2] The 1′,5′-seco bromide **3** so obtained possesses natural rotenoid stereochemistry at the B/C ring juncture. Our initial strategy (Scheme I) was to convert **3**, by syn elimination of phenylsulfinic or -seleninic acid from the sulfoxide (selenoxide) **4**, to diene **5** and thence to **1** by acid-catalyzed cyclization of **5**.

---

[1] (a) H. Fukami, J. Oda, S. Sakata, and M. Nakajima, *Agric. Biol. Chem.*, **25**, 252 (1961); (b) H. Omokawa and K. Yamashita, *ibid.*, **38**, 1731 (1974).

[2] T. Unai and I. Yamamoto, *Agric. Biol. Chem.*, **37**, 897 (1973).