

**(S)-13-Hydroxy-*cis*-9,*trans*-11-octadecadienoic Acid Lactone,
a 14-Membered-Ring Compound from *Monnina emarginata* Seed Oil**

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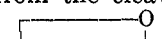
The oil extracted from *Monnina emarginata* seed contained 4% (S)-13-hydroxy-*cis*-9,*trans*-11-octadecadienoic acid lactone, coriolide, a 14-membered-ring lactone. Mass spectra of the hydrogenated lactone and the derived methyl ester established that the heterocyclic oxygen was bound to C-13 of an 18-carbon acid. Ozonolysis of the methyl dienolate from the lactone demonstrated that the conjugated diene group involved carbons 9-12. The nmr spectrum verified the *cis,trans* configuration of the diene system as well as the proximity of the carboxylate oxygen to the C-13 proton. The plain-positive optical rotatory dispersion curves of the coriolide, the corresponding saturated lactone, and the derived methyl ester indicate they each have an *S* configuration.

A large number of γ - and δ -lactones have been isolated from the bark, leaves, and roots of many varieties of plants and other natural sources. However, the authors know of only one large-ring lactone that has been isolated from seed oil and described.² In 1927, the lactone of 16-hydroxy-7-hexadecenoic acid was obtained in small amounts from the musk-scented seed oil of *Hibiscus abelmoschus* L.³ We wish to report the isolation of the lactone of a 13-hydroxyoctadecadienoic acid from the seed oil of *Monnina emarginata* (Polygalaceae), a plant native to Uruguay. Chemical and physical examinations of the 14-membered-ring lactone have demonstrated that it has the *S* configuration⁴ and that the derived methyl ester is the enantiomer of the methyl (*R*)-coriolate [methyl (*R*)-13-hydroxy-*cis*-9,*trans*-11-octadecadienoate] isolated and characterized by Tallent, *et al.*,⁵ and by Powell, *et al.*⁶

Although the lactone, (S)-coriolide (1), was only slightly separated from the nonpolar triglycerides by thin layer chromatography in petroleum ether-ethyl ether (4:1), it had a mobility approximately twice that of the least polar glycerides in benzene and was thus obtained in amounts equivalent to 4% of the oil. The infrared spectrum of the low-melting solid had two notable features: a normal ester or lactone absorption at 1745 cm^{-1} ; a conjugated *cis,trans* diene absorption in which the 982- cm^{-1} band was of reduced intensity and was broadened considerably in comparison to that of the derived methyl dienolate (Figure 1).⁷ The absorptions between 1100 and 1250 cm^{-1} show more fine structure than is normally observed for long-chain esters⁸ or glycerides.⁹ The presence of a conjugated diene chromophore was also indicated by the ultraviolet absorption maximum at 234 $\text{m}\mu$, although the molar absorptivity was somewhat reduced in comparison to

the related acyclic *cis,trans* dienolates.^{5,6} The lack of any significant proton magnetic resonance absorption between τ 4.8 and 7.2 (Figure 2) clearly indicated that the material isolated by thin layer chromatography could not be an alkyl ester or glyceride. The optical rotatory dispersion curve of the lactone was plain positive between 600 and 255 $\text{m}\mu$.

(S)-Coriolide (1) readily added 2 mol equiv of H_2 in the presence of Pd-C, Scheme I. The elution times of the hydrogenated lactone (3) were near that of methyl stearate on hydrocarbon and polyester gas-liquid chromatographic columns. A mass spectral analysis of the reduced lactone found the molecular ion peak to be m/e 282 as expected for a lactone of hydroxystearic acid. The principal high-molecular-weight fragments were m/e 264 resulting from the loss of the elements of water; m/e 211 derived from the cleavage of the C-13, C-14



bond producing $[\text{CH}(\text{CH}_2)_{11}\text{C}=\text{O}]^+$; and m/e 182 arising from the loss of $\text{C}_6\text{H}_{12}\text{O}$ by cleavage between C-12 and C-13 to give $[(\text{CH}_2)_{11}\text{C}=\text{O}]^+$. The remaining ion fragments are common to long-chain esters.¹⁰ Thus the hydroxyl is bound to C-13 of an 18-carbon acid. Furthermore, the chromatographic retention times and the mass spectrum of 3 preclude the presence of appreciable amounts of dimers or other polymeric forms of 13-hydroxystearic acid and, thereby, of coriolic acid in the lactone fraction. The optical rotatory dispersion curve of 3, like that of 1, was plain positive between 600 and 250 $\text{m}\mu$.

Sodium methoxide catalyzed transmethylation of the lactone from the seed oil produced 2, which had the same thin layer chromatographic mobility as methyl 13-hydroxy-*cis*-9,*trans*-11-octadecadienoate. The infrared, ultraviolet, and nmr spectra of the ester were comparable to those of methyl coriolate.^{5,6} The hydroxy ester 2 was ozonized, and the products were identified as described by Kleiman, *et al.*^{11,12} A six-carbon aldehyde (36%), a seven-carbon hydroxyaldehyde (22%), a nine-carbon aldehyde ester (24%), and a nine-carbon diester (18%) were the major products. Thus the conjugated dienol group must comprise C-9 through C-13 of a C_{18} acid. The formation of a six-carbon aldehyde and a seven-carbon hydroxyaldehyde

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(2) For an extensive review of unusual fatty acids found in plants, see C. R. Smith, Jr., "The Chemistry of Fats and Other Lipids," R. T. Holman, Ed., Pergamon Press, Oxford, in press; I. A. Wolff, *Science*, **154**, 1140 (1966).

(3) M. Kerschbaum, *Ber.*, **60**, 902 (1927), and references cited therein.

(4) R. S. Cahn, *J. Chem. Educ.*, **41**, 116 (1964), and references cited therein.

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(10) R. Ryhage and E. Stenhagen, *Ark. Kemi*, **15**, 545 (1960); R. Ryhage and E. Stenhagen, in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 9.

(11) R. Kleiman, G. F. Spencer, F. R. Earle, and I. A. Wolff, *Lipids*, **4**, 135 (1969).

(12) G. F. Spencer, R. Kleiman, F. R. Earle, and I. A. Wolff, *Anal. Chem.*, **41**, 1874 (1969).

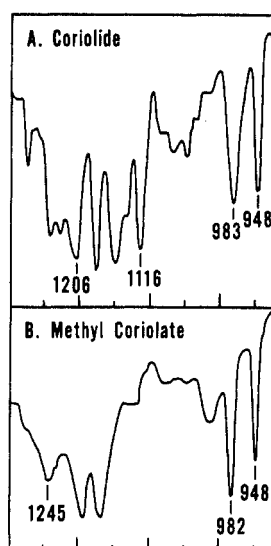
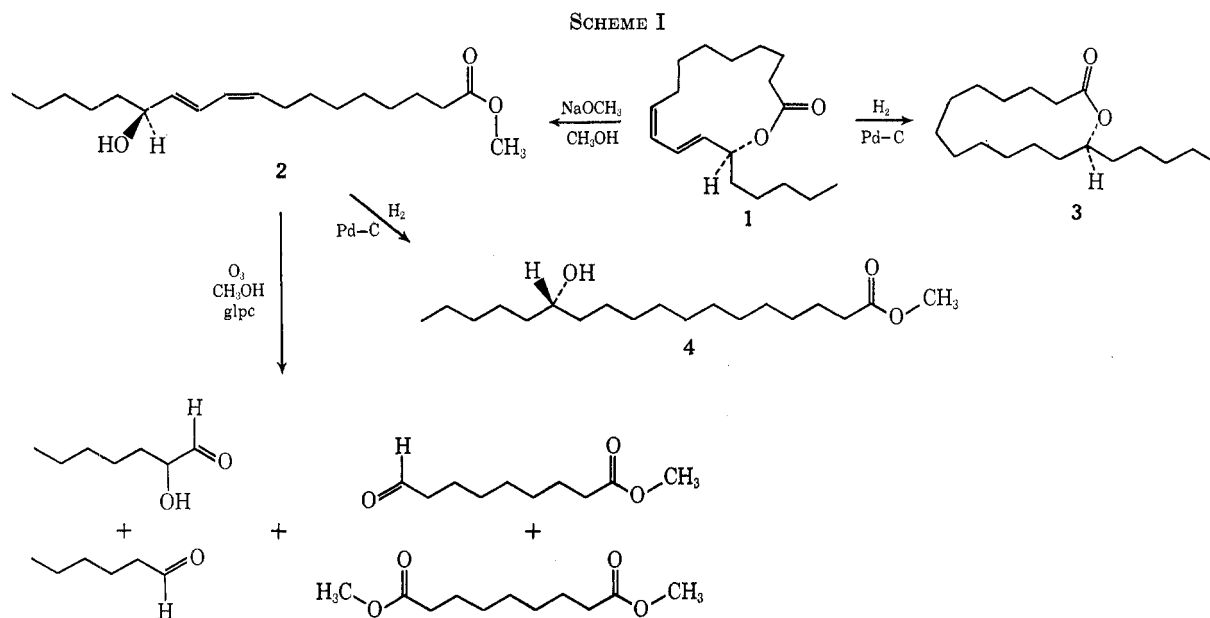


Figure 1.—Infrared spectra of (*S*)-13-hydroxy-*cis*-9,*trans*-11-octadecadienoic acid lactone [(*S*)-coriolide] and the derived methyl ester in carbon tetrachloride (10%) between 1350 and 920 cm^{-1} .

requires that the hydroxyl be bound to C-13. Ozonolysis of the coriolate isolated by Tallent, *et al.*,^{12,13} yielded a similar group of compounds. The observed nmr coupling constants (Table I) indicate that the *trans*

	Coriolide (lactone)	Methyl coriolate (hydroxy ester)
$J_{8,9}$	~4	8
$J_{9,10}$	11	10.5
$J_{10,11}$	10.5	10.5
$J_{11,12}$	14.5	14.5
$J_{12,13}$	4	6

double bond must be situated between the hydroxyl group and the *cis* double bond.⁵

(13) W. H. Tallent, J. Harris, G. F. Spencer, and I. A. Wolf, *Lipids*, **3**, 425 (1968).

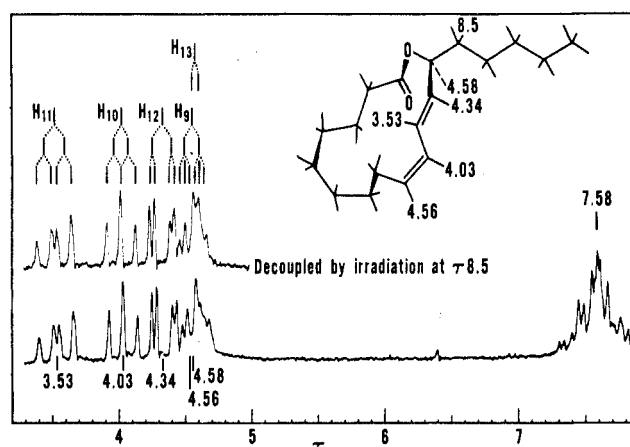


Figure 2.—Proton resonance spectrum of (*S*)-coriolide in deuteriochloroform between τ 3.2 and 7.8.

The specific rotation, $[\alpha]_{26.5}^{300} +103^\circ$ (*c* 0.14, hexane), of 2 was comparable in magnitude, but opposite in sign, to that observed for methyl (*R*)-13-hydroxy-*cis*-9,*trans*-11-octadecadienoate.^{5,14,15} Therefore, the hydroxy ester derived from the lactone and the lactone itself have the *S* or *L* configuration.¹⁴ Methyl (*S*)-9-hydroxy-*trans*-10,*trans*-12-octadecadienoate (methyl dimorphecolate), although a member of the *D* family of hydroxy acids, likewise has a plain-positive optical rotatory dispersion curve between 275 and 589 $\mu\mu$.¹⁶ This similarity is as expected since the hydroxyls of methyl dimorphecolate and of the ester from the lactone have the same effective stereochemical arrangement near the active chromophore.¹⁷

The dienolate derived from the lactone also absorbed 2 mol equiv of hydrogen. The R_f of the hy-

(14) C. R. Smith, Jr., in "Topics in Lipid Chemistry," Vol. I, F. D. Gunstone, Ed., Logos Press, London, in press.

(15) Unpublished results of this laboratory have demonstrated that methyl coriolate has nearly the same ORD curve in either hexane or methanol between 285 and 600 $\mu\mu$.

(16) T. H. Applewhite, R. G. Binder, and W. Gaffield, *J. Org. Chem.*, **32**, 1173 (1967).

(17) (a) C. Djerassi, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," G. Sneath, Ed., Heyden and Son, London, 1967, Chapter 2; (2) A. Moscovitz, ref 17a., Chapter 3; (c) E. U. Condon, W. Setar, and H. Eyring, *J. Chem. Phys.*, **5**, 753 (1937).

droxystearate **4** was comparable to that of methyl 13-hydroxyoctadecanoate and appreciably greater than that of the 9-hydroxy isomer.¹⁸ The mass spectrum of the hydrogenated ester was as expected for methyl 13-hydroxystearate.¹⁰ Cleavage on each side of the hydroxy-bound carbon produced the prominent high-molecular-weight fragments, m/e 243, $[\text{CH}(\text{OH})(\text{CH}_2)_{11}\text{CO}_2\text{CH}_3]^+$, and m/e 214, $[(\text{CH}_2)_{11}\text{CO}_2\text{CH}_3]^+$. The other major, high-molecular-weight ion, m/e 211, was derived from the m/e 243 ion fragment by the loss of the elements of methanol.¹⁰

In view of these results, the lactone obtained from the oil of *M. emarginata* seed must be derived from 13L-hydroxy-*cis*-9,*trans*-11-octadecadienoic acid. The nmr spectrum of the lactone (Figure 2) is in agreement with the assigned structure. The C-13 and C-9 protons were shown to resonate at τ 4.58 and 4.56, respectively, by irradiation at τ 8.5 (C-14 protons). The C-13 proton (H-C-O-) absorbed about 20 cps further downfield than the γ protons of 2-pentenoic acid γ -lactone (β -angelic acid) and the bisbutenolide of *Pterogorgia anceps*.¹⁹ The larger shift observed for the coriolidide could be caused by the close proximity of the carboxyl oxygen and the accompanying sp^2 -electron cloud of the carboxylate to the C-13 proton. Both the resonance frequency and spin-spin coupling constants of the C-12 and C-13 protons differed significantly from those of the open-chain ester (Table I and Figure 2). While models of the lactone can be made to take a variety of conformations, including several with the sp^2 oxygen of the carboxyl group directed toward the center of the ring, there is only one general type of conformation without eclipsed C-H bonds and with the carbonyl oxygen directed outside the ring. Models of the lactone (Stuart-Briegleb and Dreiding type) in this conformation require that the carboxyl sp^2 oxygen bond be essentially parallel to the C-13 C-H bond and *exo* to the ring with the oxygen between 2.5 and 2.0 Å from the C-13 proton. In addition, both of the C-H bonds at C-8 are found on the *exo* side of the plane of the C-9 double bond. This conformation is consistent with the observed infrared and nmr spectra.

If the C-9 proton signal is indeed in the form of a doublet of triplets as shown in Figure 2, the dihedral angles between the two C-8 protons and the C-9 proton would be expected to be either equal (*ca.* 55 or 125°) or approximately 35 and 145°. A model of the lactone can be constructed most easily with the latter conformation. Irradiation at τ 4.62 (C-9 and C-13 protons) simplified the triplet centered at τ 4.03 (C-10 proton) and the quartet at τ 4.34 (C-12 proton). Thus the protons of the lactone have resonance frequencies similar to those of methyl coriolate.⁶ The coupling constants of the vinyl protons (Table I) further substantiate the geometric configuration assigned to the lactone.

The absorptivity of the diene chromophore of the lactone is *ca.* 90% of that of the related acyclic ester. A similar difference between the absorptivity of the cyclotetradecadiene (22.8×10^3) and that of the cyclo-

octadecadiene (24.7×10^3) has been observed.²¹ Such diminutions in absorptivity have frequently been ascribed to the nonplanarity of the ground-state form of the conjugated systems.²²⁻²⁵ In a study of two series of methylated aromatic carbonyls, Braude, *et al.*,²³ correlated the dipole moments of these compounds with losses of coplanarity of the carbonyl and phenyl groups. Corresponding with the changes in dipole moments were decreased molar absorptivities. Although Hubert and Dale²¹ say the diene group of the cyclotetradecadiene is planar, the Braude relationship ($\cos^2\theta = \epsilon_{\text{obsd}}/\epsilon_0$)²⁴ suggests that the two double bonds of coriolidide and those of the cyclic diene are slightly twisted, 19 and 16°, respectively, from coplanarity. The models of the lactone with the least nonbonding interaction between neighboring hydrogens also required that the conjugated diene be distorted from planarity. However, the diene group of the coriolidide models could easily be made coplanar by a slight rotation of several of the carbon-carbon bonds in the ring. Hubert and Dale²¹ noted that the cyclotetradecadiene is the "smallest one (cyclic diene) for which a practically strain-free molecular model can be constructed having all single bonds staggered and the correct stereochemistry²⁵ about the planar *cis-trans* diene grouping."

A correlation between Cotton effects in optical rotatory dispersion curves or circular dichroism measurements and the stereochemistry of a large number of γ - and δ -lactones has been made by Jennings, *et al.*²⁷ Beecham²⁸ has likewise posited a relationship based on the "chirality of the lactone ring" rather than the lactone sector rule. While extrapolation from a six-membered ring to a 14-membered one is fraught with difficulties, it is noteworthy that most of the best model of (*S*)-coriolidide and the reduced lactone (**3**) fall in or near one of the positive lactone sectors²⁷ and has a ring chirality, as defined by Beecham,²⁸ that predicts a positive Cotton effect. Further, if the observation of Klyne, *et al.*,²⁹ that a plain positive curve precedes a positive Cotton effect holds for large-ring lactones as well as those with smaller rings, then (*S*)-coriolidide appears to effect the same type of optical rotatory dispersion as has been observed for the small-ring lactones.

The magnitude of rotation of **3** is 60-70% of that of (*S*)-coriolidide and is of the same sign in that portion of the spectrum which is accessible to us. In **1**, the ring with its twisted diene grouping may constitute an inherently dissymmetric chromophore, but apparently the $n \rightarrow \pi^*$ transition of the lactone grouping makes a greater contribution to the observed optical activity of **1** than do transitions associated with the diene chromophore.

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Experimental Section

Thin layer chromatographic analyses and separations utilized 0.25- or 1.0-mm layers of silica gel G³⁰ in benzene (solvent A) or petroleum ether (bp 40–60°)—ethyl ether (2:1) (solvent B). Preparative tlc plates were sprayed with 0.2% (w/v) solutions of 2',7'-dichlorofluorescein in 95% ethanol, and the products were located by viewing under a uv lamp. Analytical tlc plates were sprayed with CrO₃-H₂SO₄-H₂O (2:49:49, w/v/v) and heated to 120–140° for 30 min or placed in an I₂ chamber to locate the spots. Ir spectra were determined with a Perkin-Elmer Infracord Model 337. Uv spectra were obtained in hexane with a Beckman DK-2A spectrometer. Nmr spectra were measured in deuteriochloroform solutions with a Varian HA-100 spectrometer and tetramethylsilane as an internal standard. The ORD curve and specific rotation were obtained with a Cary Model 60 recording spectropolarimeter. A Nuclide 12-90 G mass spectrometer was used to obtain the mass spectra. Glpc analyses were made on a Packard 7401 gas chromatograph equipped with dual glass columns and flame ionization detectors. One column (356 × 0.6 cm) was packed with 5% LAC-2-R-446 on Chromosorb W, acid washed, DMCS treated, and the other column (122 × 0.6 cm) was packed with 5% Apiezon L on Chromosorb W, acid washed, DMCS treated. Retention times are expressed as equivalent chain lengths (ecl).³¹

Isolation and Chromatographic Properties of Lactone 1.—Ground *M. emarginata* seed and pericarp were extracted with petroleum ether (bp 40–60°) in a Soxhlet extractor. Evaporation of the solvent left a light yellow oil in amounts equivalent to 20% of dry seed. Portions of the oil were chromatographed on 1.0-mm plates in solvent B. The triglyceride-lactone band (*R_f* 0.6) was scraped from the plates and eluted from the silica gel with hexane-ether (1:1) to give a mixture of glycerides and lactone in amounts equivalent to 63.4% of the seed oil recovered from the tlc plates. Rechromatography of the nonpolar glyceride-lactone mixture in benzene (1-mm plates) separated the lactone (*R_f* 0.5) from the glycerides (*R_f* 0.2–0.3). The lactone constituted 6.5% of the glyceride-lactone mixture or 4% of the recovered, fractionated seed oil. The lactone had the following properties: mp 39.5–42°; ir (CCl₄, 10%, and neat) 3010 (sh), 2935 (s), 2855 (s), 1740 (s), 1465 (m), 1445 (m), 1370 (m), 1345 (sh), 1275 (w), 1245 (m), 1229 (m), 1206 (m), 1178 (m), 1135 (sh), 1116 (m), 983 (m), 948 (m) cm⁻¹ (The ratio of the intensities of the 983–948-cm⁻¹ bands was 1.03; Chipault and Hawkins⁷ gave a ratio of 1.20 for acyclic *cis,trans* dienes); uv max (hexane) 234 mμ (ε 23.3 × 10³); [α]₂₅^D +32° (c 2.56, hexane); ORD, [α]_{26.5}^D +27° (c 1.06, methanol), [α]₅₅₀ +32, [α]₅₀₀ +40, [α]₄₅₀ +53, [α]₄₀₀ +73, [α]₃₅₀ +104, [α]₃₀₀ +184, [α]₂₆₀ +323°. Pertinent part of the nmr spectrum is displayed in Figure 2; glpc on LAC-2-R-446; ecl (relative amounts), 21.1 (36–48%), 21.4 (56–46%). The cause of the apparent isomerization during glpc analyses is unknown.

Hydrogenation of Lactone.—A 21.0-mg sample of coriolid (7.5 × 10⁻⁵ mol) absorbed 3.66 ml of H₂ (15.1 × 10⁻⁵ mol) over 10% Pd-C in hexane at 24° and atmospheric pressure. The bulk of the catalyst was removed by centrifugation. The supernatant liquid was chromatographed on a 0.25-mm layer of silica gel with benzene, and the band due to the lactone 3 was removed. The uv spectra of the recovered lactone (15 mg) did not show any maximum at 233 mμ or at longer wavelengths. The ir spectrum

(CCl₄, 1%) was qualitatively the same as that of the unsaturated lactone, except for the absorptions normally associated with the olefinic groups (3010, 983, and 948 cm⁻¹). The reduced lactone, which had an ecl of 17.6 on the Apiezon L column and of 18.6 on the R-446 column, was more than 99% pure by glpc. The mass spectrum (70 eV) of the saturated lactone was *m/e* (relative intensity) 282 (3), 264 (24), 211 (28), 182 (23), 125 (13), 111 (19), 98 (39), 83 (43), 71 (19), 55 (100); ORD, [α]_{26.5}^D +20° (c 0.36, methanol), [α]₅₅₀ +25, [α]₅₀₀ +29, [α]₄₅₀ +38, [α]₄₀₀ +50, [α]₃₅₀ +71, [α]₃₀₀ +112, [α]₂₅₀ +267°.

Transmethylation of Lactone.—(*S*)-Coriolid (18 mg) was mixed with 1.0 ml of 0.5 M NaOCH₃ in CH₃OH at 24° and allowed to stand with occasional shaking for 45 min. After dilution with 4 ml of salt water, the base was neutralized with dilute sulfuric acid. The products were extracted from the aqueous methanol with ether, and the extract was dried with anhydrous Na₂SO₄. Evaporation of the solvent yielded 19.2 mg of oil. Tlc of the oil in solvent B indicated two products: unreacted lactone (*R_f* 0.65) and a hydroxy ester (*R_f* 0.35) with a mobility identical with that of methyl 13-hydroxy-*cis*-9, *trans*-11-octadecadienoate. Preparative tlc (0.25-mm plate) in solvent B separated the hydroxy ester (13 mg) from the lactone (3.4 mg). The ester 2 had spectral properties essentially identical with those of known methyl coriolate:^{5,6} ir (CCl₄, 10%) 3615 (sharp), 3500 (broad), 3005 (sh), 2920 (s), 2850 (s), 1735 (s), 1450 (m), 1430 (m), 1410 (w), 1370 (sh), 1360 (m), 1245 (m, broad), 1195 (m), 1170 (m), 1015 (w, broad), 982 (m), 948 (m) cm⁻¹ (the ratio of the 982–948-cm⁻¹ absorptivities was 1.22 in agreement with the value reported by Chipault and Hawkins⁷); uv max (hexane) 234 mμ (ε 26.3 × 10³); nmr spectrum comparable to that reported by Tallent, *et al.*,⁵ [α]_{26.5}^D +103° (c 0.14, hexane).

Hydrogenation of Dienoloate.—The transmethylation product, 8.8 mg (2.9 × 10⁻⁵ mol), absorbed 1.3 ml of H₂ (5.3 × 10⁻⁵ mol) at 24° under the conditions used to reduce the lactone. The resulting white solid (4), mp 49–50°, was found by glpc on the R-446 column to be a mixture of methyl hydroxystearate, ecl 24.8 (85%), and methyl ketostearate, ecl 24.0 (13%).¹³ The mobilities of the hydrogenation products in solvent B, *R_f* 0.33 and 0.56, were identical with those of methyl 13-hydroxystearate and methyl 13-ketostearate, respectively. Methyl 9-hydroxystearate had an *R_f* of 0.22. The prominent ion fragments in the mass spectrum (70 eV) of the reduced hydroxy ester were *m/e* (relative intensity) 264 (8), 241 (41), 214 (49), 211 (84), 175 (10), 171 (18), 143 (27), 87 (67), 55 (83), 18 (100). Fragments associated with methyl 13-oxooctadecanoate¹⁰ were observed also.

Ozonolysis of Methyl Dienoloate.—The methyl dienoloate (1 mg) was ozonized for 2 min (>11 × 10⁻⁶ mol of ozone/min) at room temperature in 5 ml of CH₃OH. The methanol solution (15 μl) was then injected directly on the glpc columns, and the products were identified as described by Kleiman, *et al.*^{11,12} The averaged mole percentages of the four principal products (90% of peak areas) were C₆ aldehyde (36%), C₇ α-hydroxyaldehyde (22%), C₉ aldehyde ester (24%), and C₉ diester (18%).

Registry No.—1, 24058-12-6; 2, 24058-13-7.

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(30) The mention of firm names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

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