lets of -CH_2OH), 2.83 m ($w_{1/2}$ = 10, βH-8), 2.61 (hydroxyl), 1.25 (C-10 methyl), 0.88 d and 0.84 d (J = 6, isopropyl), and 0.79 ppm (C-4 methyl). It was recovered unchanged from a refluxing solution of sodium methoxide in methanol.

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18; O, 10.44. Found: C, 78.31; H, 11.07; O, 10.6.

Oxidation of **17** with excess Jones reagent for 3 hr in the usual manner gave acid **18a** (80%) which was recrystallized from methanol-water and had mp 188–191°; $[\alpha]^{25}_{D}$ −25° ($CHCl_3$, c 0.87); ir 3600–2700 (hydroxyls), 1700 (carboxyl), and 1710 cm^{-1} (ketone); nmr at 7.36 (CO_2H), 2.83 m ($w_{1/2}$ = 10, βH-8), 1.28 (C-10 methyl), 1.21 (C-4 methyl), 0.90 d, and 0.88 d (J = 6, isopropyl).

Anal. Calcd for $C_{20}H_{32}O_3$: C, 74.96; H, 10.06; O, 14.98. Found: C, 74.85; H, 10.03; O, 15.08.

Esterification of **18a** afforded **18b** identical with the material obtained in A: ir 1720, 1250 (ester), and 1710 cm^{-1}, nmr 3.65 (methoxyl), 2.83 m ($w_{1/2}$ = 10, αH-8), 1.28 (C-10 methyl), 1.21 (C-4 methyl), 0.90 d, and 0.88 d (J = 6, isopropyl); ORD curve (c 0.046), $[\alpha]_{400}$ +23°, $[\alpha]_{308}$ 0°, $[\alpha]_{260}$ +1210°.

9β,13β-Abietan-18-oic Acid (20a). A.—A mixture of 0.25 g of **18b**, 25 ml of diethylene glycol, 2.5 g of potassium hydroxide, and 2.5 ml of anhydrous hydrazine was refluxed in a nitrogen atmosphere for 1.5 hr (140°). The condenser was removed and the temperature was allowed to rise to 210°. Refluxing was continued for 2 hr; the solution was then cooled, acidified, diluted with water, and filtered. The product was recrystallized from ethanol-water (yield 0.18 g), but the nmr spectrum indicated the presence of an impurity (15%). A second recrystallization afforded pure **20a**: mp 189–192°; $[\alpha]^{25}_{D}$ +7° ($CHCl_3$, c 0.825); ir 3600–2700 (carboxyl) and 1695 cm^{-1}; nmr signals at 1.15 (C-4 methyl), 1.07 (C-10 methyl), and 0.83 d (J = 6, isopropyl).

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18; O, 10.44. Found: C, 78.24; H, 11.09; O, 10.97.

Methylation with diazomethane gave **20b** identical with material whose preparation is described in the next paragraph.

B.—Treatment of 0.3 g of **18b** with ethanedithiol-boron trifluoride etherate in the usual manner gave, upon recrystallization of the crude product from methanol, 198 mg of the thioketal **21**. It had mp 100–101°; ir 1715 and 1220 cm^{-1} (ester); nmr 3.61 (methoxyl), 3.18 (four protons, 7-thioketal methylenes), 1.13 (C-4 methyl), 1.10 (C-10 methyl), and 0.86 d (J = 6, isopropyl). Raney nickel desulfurization of **21** produced **20b** and a small amount of another substance which appeared to be an olefin.[18] Recrystallization from methanol-water afforded pure **20b**: mp 47–49°; $[\alpha]^{25}_{D}$ +6° ($CHCl_3$, c 0.71); nmr superimposable on that of **20b** in the methyl region.

Anal. Calcd for $C_{21}H_{36}O_2$: C, 78.75; H, 11.25; O, 10.00. Found: C, 78.59; H, 11.21; O, 10.22.

Registry No.—**5**, 21577-54-8; **7**, 21577-55-9; **9**, 21537-46-2; **16a**, 21537-47-3; **16b**, 21537-48-4; **17**, 21537-49-5; **18a**, 21537-50-8; **18b**, 21537-51-9; **20a**, 21537-52-0; **20b**, 21537-53-1; **21**, 21537-54-2.

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[18] P. D. Bartlett and M. Stiles, *J. Amer. Chem. Soc.*, **77**, 2806 (1955); C. Djerassi and D. H. Williams, *J. Chem. Soc.*, 4046 (1963).

Transformations in the Resin Acid Series. Ring C

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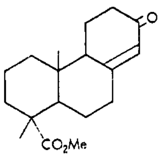
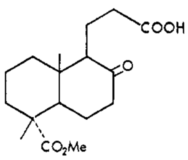
Received November 27, 1968

Transformations of the resin acid degradation products **1**, **2**, and **3** are discussed. The conversion of **1** into **8** by m-chloroperbenzoic acid has been investigated. Compound **8** undergoes a facile rearrangement to the lactone aldehyde **10**; the steric course of this arrangement is apparently different from that of the usual rearrangement of epoxy esters. Further transformations of **10** lead to a five-membered ketone **19** which also can be prepared by a route involving the benzilic acid rearrangement of the diosphenol **22**. Epoxidation of **1** afforded an epoxide **9** which was converted by boron trifluoride etherate into a mixture of **22** and **23**. The mass spectra of **22** and **23** are discussed.

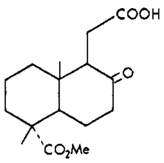
In a previous communication on the oxidative degradation of resin acids[1] we focussed attention on two objectives: (1) the selective oxidation of the isopropylidene side chain of methyl neoabietate to yield the enone ester **1**, and (2) a one-step cleavage of both the double bonds in methyl neoabietate and methyl levopimarate to afford the keto acid esters **2** and **3**, respectively. This paper reports some transformations involving the degradative products **1**, **2**, and **3**.



1

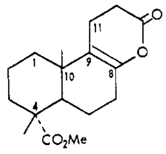


2



3

Lactonization of **2** with acetyl chloride–acetic acid gave exclusively the Δ^8-δ-lactone ester **4**, τ 8.93 (3 H singlet, C-10 Me), in 72% yield. Under similar conditions, however, lactonization of **3** afforded a mixture of the ene γ-lactones **5** and **6**, which under base (Et_3N) equilibration[2] gave predominantly the conjugated Δ^9-γ-lactone ester **6**. Treatment of **3** with acetic anhydride and sodium acetate also afforded a mixture of **5** and **6** which could be isomerized to **6** by treatment with ethanol and triethylamine. This isomerization to the Δ^9-γ-lactone provides a convenient handle for the cleavage of ring C of compound **6**.



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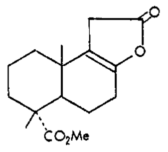

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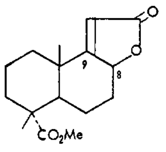
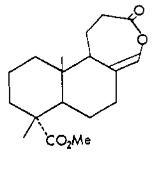
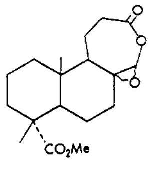


6

Oxidation of **1** with less than 2 equiv of m-chloroperbenzoic acid in methylene chloride resulted in a mixture of the Baeyer–Villiger products **7** and **8**. However, in



7



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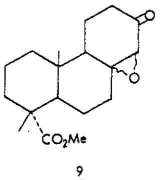

9

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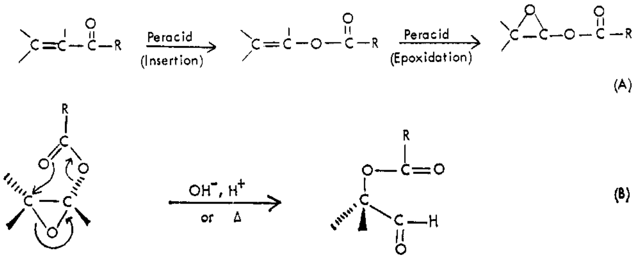
(1) S. W. Pelletier, K. N. Iyer, C. W. J. Chang, and A. Ogiso, *Tetrahedron Lett.*, 3819 (1968).

(2) M. P. Cava, W. R. Chan, R. P. Stein, and C. R. Willis, *Tetrahedron*, **21**, 2617 (1965).

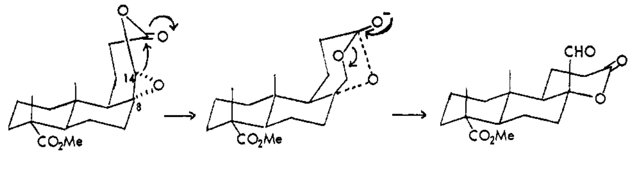
the presence of excess peroxy acid, compound **8** was the sole product. The peroxy acid oxidation of enones has been reported to yield epoxy ketone[3a] as a by-product, with the main product being formed by oxygen insertion followed by epoxidation[3b] (Scheme I, A). Generally, the yield of the epoxy ketone is minor (<5%) and in our case it was not detected. Although it is conceivable that the epoxy ketone **9**, which was prepared by alkaline hydrogen peroxide oxidation of the enone ester **1**, may lead to the epoxy ε-lactone by oxygen insertion, this was demonstrated not to be the case since treatment of the epoxy ketone **9** with peroxy acid gave little or no epoxy ε-lactone. When the isolated intermediate ene ε-lactone **7** was heated with peroxy acid, however, the crystalline epoxide **8** was obtained in 88% yield. Hence, the epoxy ε-lactone **8**, τ 5.28 (1 H singlet, $\mathrm{C}\underset{\mathrm{O}}{\bigtriangledown}\mathrm{CHOCO}$),[3c] is formed exclusively from the ene ε-lactone **7**, τ 3.85 (1 H, C=CHOCO),[3c] and not from the epoxy ketone **9**.

SCHEME I



The epoxy ε-lactone system undergoes a facile rearrangement under varying conditions.[4] Either acidic, basic, or thermal catalysis affords an aldehydo δ-lactone ester ($\nu_{\max}$ 1760, 1726, 2720 cm^{-1}) which is assigned structure **10**. Thus the rearrangement may be effected in 86% yield by treatment with aqueous methanolic sodium hydroxide at room temperature for 15 min, by treatment with ethanolic hydrochloric acid under reflux for 2 hr (78% yield), or by treatment under nitrogen for 10 min at 160° (85% yield). The disappearance of the characteristic singlet at τ 5.28 attributed to the proton on C-14 and the appearance of the sharp singlet of the aldehyde proton at 0.17 was observed in the spectrum of the reaction products.

In the usual reaction sequence, which has ample precedent in the literature,[3,5] the rearrangement follows the course as illustrated in Scheme I (B). In the cyclic epoxy ε-lactone system, however, the groups are conformationally fixed such that the lactone carbonyl is directed away from the backside of the oxiran ring and therefore cannot give an α-oriented aldehyde. It is important to note that the C-8–O bond and the C-8–C-14 bonds are not ruptured during the reaction and the thermal rearrangement may follow a pathway such as shown in **8** → **10** to give a β-oriented aldehyde.[6] Several mechanisms can be written for the acid- and base-catalyzed reactions but the evidence at hand does not allow a determination of the actual mechanistic pathway followed.



8

10

Like epoxidation of the enone **1** by hydrogen peroxide, the reaction of peroxy acid on the ene ε-lactone was assumed to yield predominantly a product with the α-epoxy configuration. At this point the assignment can only be regarded as tentative in view of the work on the dihydroabietic acids by Herz[7] and Huffman.[8] Rearrangement of the crude Baeyer–Villiger product, the epoxy ε-lactone (**8**), led exclusively to one isomer, the β-aldehydo δ-lactone ester (**10**) whose glpc behavior on two columns showed only one peak and whose tlc behavior on both alumina and silica indicated homogeneity. We are, therefore, inclined to believe that the β-aldehydo δ-lactone ester, whose configuration at C-8 is elaborated below, is derived from only one isomer, the α-epoxy ε-lactone ester (**8**).

As a preliminary step toward obtaining evidence for the configuration of the aldehyde function, **8** was selectively reduced with sodium borohydride at 0° for 5 min to afford the alcohol δ-lactone **11a** (use of excess sodium borohydride and a longer reaction time resulted in a triol–boron complex, mp 177 and 328°). When compound **11a** was heated at reflux in the presence of calcium carbonate, lead tetraacetate, and a trace of iodine in cyclohexane[9] (Scheme II), the only crystalline compound isolated after column chromatography was the furano ether **12**, mp 159–160°, τ 8.96 (3 H singlet, C-10 Me). Since the C-10-methyl absorption in **12** is shifted 0.11 ppm downfield from the position in the alcohol **11a**, the –CH$_2$OH function at C-8 is probably β oriented.

When refluxed with lead tetraacetate in benzene, compound **11a** afforded a crystalline compound having an analysis corresponding to $C_{35}H_{52}O_9$. Its infrared spectrum showed no hydroxyl absorption. The nmr spectrum indicated the dimeric nature of the compound with methyl singlets at τ 6.42 and 6.43 (2 C-4 CO$_2$Me), 8.87 and 8.88 (2 C-4 Me), and 9.28 and 9.11 (2 C-10 Me) with an AB quartet at 5.75 (–CH$_2$O–). The dimeric structure **16** was further confirmed by the mass spectrum which showed the M$^+$ peak at m/e 616. Prominent peaks appeared at m/e 323, 309, 307, and 293 with the absence of fragmentation ions between m/e 616 and 325 indicating that primary fission to the

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[3] (a) G. P. Payne and P. H. Williams, *J. Org. Chem.*, **24**, 284 (1959). (b) L. Velluz, G. Amiard, J. Martel, and J. Warrant, *Bull. Soc. Chim. Fr.*, **879**, 1485 (1957); E. Caspi and Y. Shimizu, *J. Org. Chem.*, **30**, 223 (1965). (c) J. J. Riehl, J. M. Lehn, and F. Hemmert, *Bull Soc. Chim. Fr.*, 224 (1963).

[4] C. W. J. Chang and S. W. Pelletier, *Tetrahedron Lett.*, 5483 (1966).

[5] A. L. Draper, W. J. Heilman, W. E. Schaefer, H. J. Shine, and J. N. Shoolery, *J. Org. Chem.*, **27**, 2727 (1962); R. W. Hoffman and H. J. Lethardt, *Tetrahedron Lett.*, 441 (1966).

[6] M. Gorodetsky, N. Danieli, and Y. Mazur, *J. Org. Chem.*, **32**, 760 (1967). After our communication[4] appeared an identical conclusion was proposed—*i.e.*, an α epoxy ε-lactone leads to the β-aldehydo δ-lactone—by these authors in their work on the oxidation of testosterone acetate with peroxy acids. We thank Dr. Mazur for providing a copy of their manuscript prior to publication.

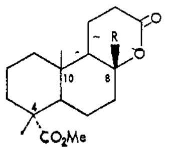
[7] W. Herz and R. N. Mirrington, *J. Org. Chem.*, **30**, 3198 (1965).

[8] Private communication, J. W. Huffman, Clemson University, Sept 26, 1967.

[9] von Ch. Meystre, K. Heusler, J. Dalvoda, P. Wieland, G. Anner, and A. Wettstein, *Helv. Chim. Acta*, **45**, 1317 (1962).

TABLE I

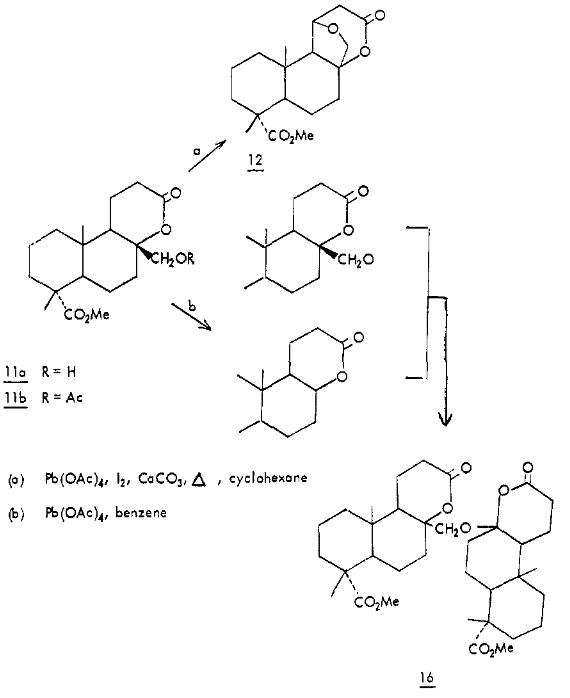
EFFECT OF VARYING THE SUBSTITUENTS AT C-8 ON THE C-10-METHYL RESONANCE



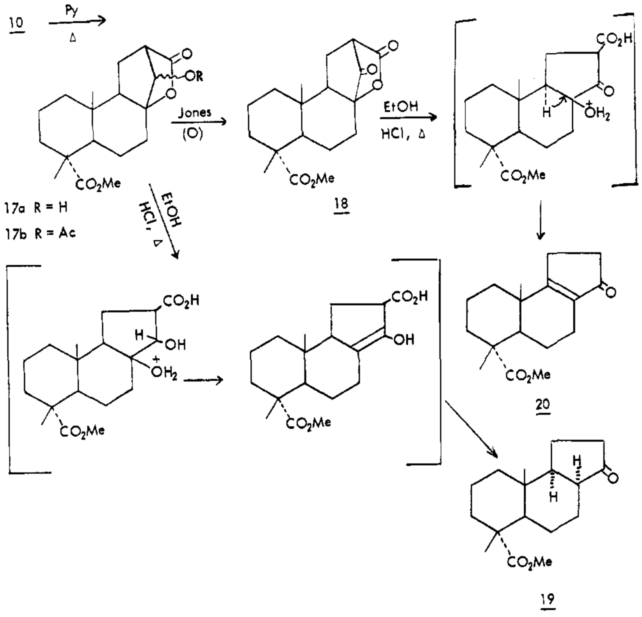
Compound	R	Mp, °C	τ			
			C-10 Me	C-4 Me	CO_2Me	(R)
10	CHO	175–177	9.17	8.80	6.30	0.17 (CHO)
13a	COOH	235–237	9.11	8.81	6.26	0.8 (COOH)
11a	CH_2OH	197–199	9.07	8.84	6.42	6.22[b] (CCH_2O)
14	$CONH_2$		8.98	8.80	6.28	3.75 ($CONH_2$)
15	CN	184–185.5	8.85	8.78	6.30	

[a] Chemical shifts measured in $CDCl_3$ with tetramethylsilane as internal standard. [b] AB quartet, J = 8 cps.

SCHEME II



SCHEME III



monomers had occurred at the ether linkage before further fragmentation ions were formed.

From an examination of Dreiding models it is clear that the α configuration of the substituents at C-8 would have little effect on the chemical shift of the C-10 methyl. Several derivatives were prepared to study the effect of different C-8 substituents on the C-10-methyl signal. The C-8-aldehydo moiety was oxidized with Jones reagent to give the acid[10] **13a** (methyl ester **13b**). Its carboxyl substituent was converted into the amide **14** *via* its acid chloride and dehydrated with phosphorus pentoxide to the nitrile **15**. The effect on the chemical shift of the C-10-methyl singlet by varying the functionality at C-8 is illustrated in Table I.

The internal Claisen-type condensation of the aldehydo function was accomplished by refluxing **10** in pyridine to afford a mixture of epimers **17a**. Oxidation of the epimeric mixture with Jones reagent yielded a compound tentatively assigned the keto γ-lactone ester structure **18** (Scheme III). The infrared spectrum in the carbonyl region suggests the presence of a strained bicyclo[2.1.1] system: ν_{max} 1818, 1779, 1724 cm^{-1}.[11]

Dehydration followed by decarboxylation of the alcohol γ-lactone ester **17a** occurred in refluxing ethanolic hydrochloric acid to yield the five-membered ketone **19**, mp 136–138°, characterized by its infrared absorption at 1750 cm^{-1}. Under the conditions employed the ketone **19** should have the thermodynamically more stable B/C *cis* junction.

When the keto γ-lactone ester **18** was allowed to react under similar conditions, the crystalline enone **20** was isolated: ν_{max} 1739, 1710, 1650 cm^{-1}. The nmr spectrum showed the normally shielded C-10 methyl now appearing at τ 8.84 due to the newly created Δ^8 system.

The epoxy ketone **9** yielded two isomeric conjugated ketones after treatment with boron trifluoride etherate in benzene (Scheme IV). The diosphenol **22** and its isomeric enone **23** were separable on preparative thick layer chromatography. The former compound can also be isolated from the acid dehydration of the keto diol **24a** which was isolated as a by-product from the partial ozonolysis of methyl neoabietate.[1] Whereas the diosphenol **22** and the ketol **23** exhibited similar but characteristic bands in the infrared spectrum, their

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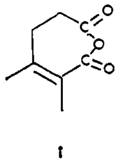
[10] *Cf.* W. Reusch and R. LeMahieu, *J. Amer. Chem. Soc.*, **85**, 1669 (1963). The acid δ-lactone system was previously obtained in the steroid series by the reaction of an epoxy ketone with hydrogen peroxide in refluxing aqueous methanolic sodium hydroxide.

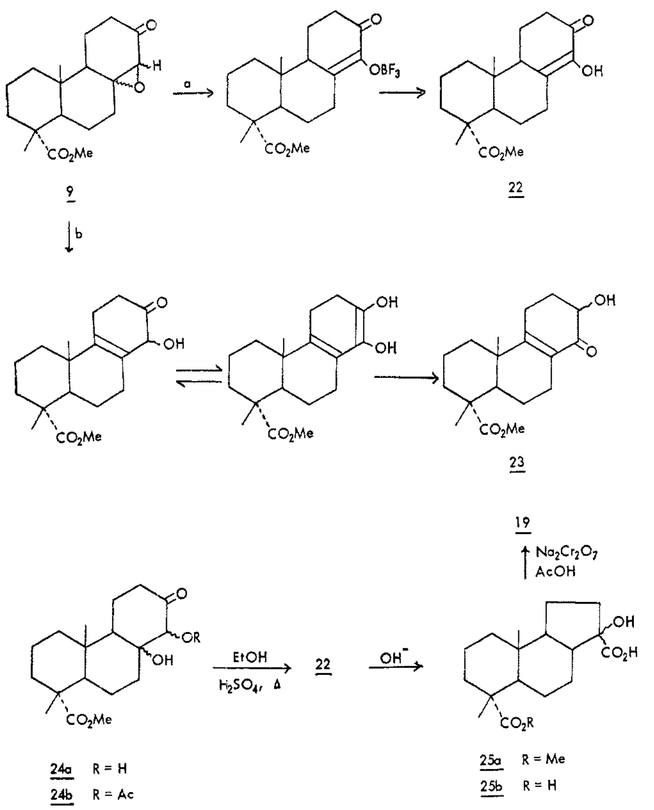
[11] A referee suggests that compound **18** does not contain a bicyclo[2.1.1] system, but rather is probably the anhydride i. However the ultraviolet spectrum of **18** shows only very low end absorption. One would expect absorption in the 217–225-mμ range[12] for an α,β-unsaturated acid derivative. The anomalous absorption at 1818 cm^{-1} may be due to the high degree of strain in the system or to dipole–dipole effects.



i

[12] A. T. Nielsen, *J. Org. Chem.*, **22**, 1539 (1957).

Scheme IV



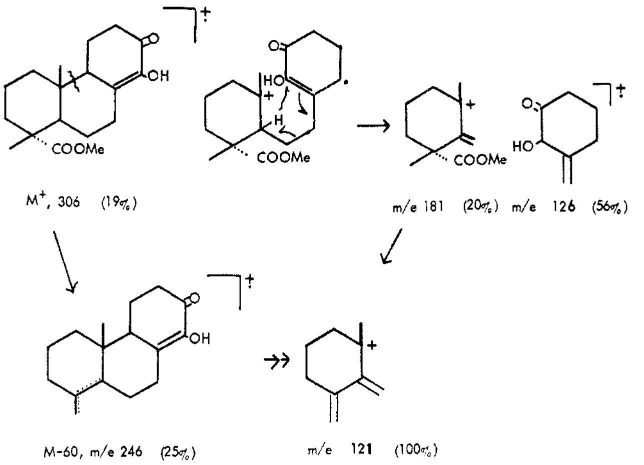
ultraviolet spectra were readily distinguishable: 22 showed a maximum at 281 mμ which shifted bathochromically 44 mμ on addition of base and 23 exhibited a maximum at 252 mμ and was not affected by base.

Of the various ring contraction methods available in the field of steroids, the benzilic acid rearrangement of diosphenols followed by oxidative decarboxylation of the resulting hydroxyacid appears to be a method of general applicability.[13–17] Following the method of Nace and Inaba[17] the diosphenol 22 was refluxed with potassium hydroxide in *n*-propyl alcohol to give the hydroxy diacid **25b** which was obtained as an amorphous solid. It seems reasonable to assume that the C-4 ester group is hydrolyzed during this treatment. The nmr spectrum of the hydroxy diacid did not exhibit any signals in the region τ 5.5–7.00 thereby confirming that the C-4 ester had in fact been hydrolyzed.

The presence of a tertiary carboxylic function at C-4 in **25b** ruled out the possibility of utilizing lead tetraacetate as the reagent of choice for oxidative decarboxylation of **25a** to the ketone **19**. This difficulty was overcome by using $Na_2Cr_2O_7$–AcOH as described by Barton, *et. al.*[14] Oxidation with $Na_2Cr_2O_7$–AcOH and subsequent methylation afforded a product which was purified by thick layer chromatography and crystallized from ether–hexane to give a compound, mp 132–134°, identical in all respects with the ketone **19**.

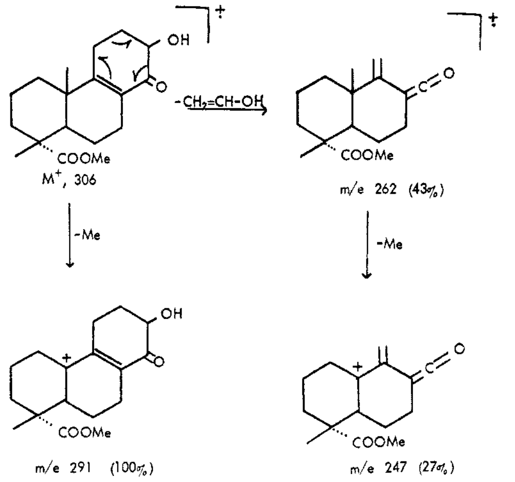
The mass spectra of the isomers 22 and 23 deserve some comment. The fragmentation pattern of the diosphenol 22 is reminiscent of the fragmentation behavior of methyl sandaracopimarate.[18] The diosphenol upon electron impact presents over-all a relatively simple pattern losing the elements of acetic acid (*m/e* 246, 25%). Loss of methyl appears insignificant (<5%). The principal fragmentation resulted in the cleavage of the 9–10 bond. One of the possible modes of fragmentation is shown in Scheme V.

Scheme V



By comparison, the isomeric conjugated ketone **23** exhibited a complex fragmentation pattern. The base peak at *m/e* 291 resulted from the loss of the C-10 methyl in the allylic position. A major fragmentation pathway is the retroaldo elimination of a vinylic alcohol unit to form the reasonably stable ion at *m/e* 262 (43%) with subsequent loss of methyl to produce the fragment at *m/e* 247 (27%). Loss of water is evidenced by a peak at *m/e* 288 which is supported by a metastable ion at *m/e* 271. This fragmentation scheme is shown in Scheme VI.

Scheme VI



Experimental Section

All melting points are corrected and were taken on a Kofler hot-stage block. Infrared spectra were determined in Nujol, unless otherwise stated, with Perkin-Elmer Model 137 Infracord and Model 237B spectrometers. Ultraviolet spectra were taken on a Perkin-Elmer Model 202 spectrophotometer. Mass spectra were taken with a Hitachi Perkin-Elmer RMU-6D2-s spectrometer operating with an ionization energy of 70 eV. The tempera-

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(13) J. F. Biellman and M. Rajić, *Bull. Soc. Chim. Fr.*, 441 (1962).

(14) E. J. Bailey, D. H. R. Barton, J. Elks, and J. F. Templeton, *J. Chem. Soc.*, 1578 (1962).

(15) G. R. Chaudhry, T. G. Halsall and E. R. H. Jones, *ibid.*, 2725 (1961).

(16) R. Hanna and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1945 (1961).

(17) H. R. Nace and M. Inaba, *J. Org. Chem.*, **27**, 4024 (1962).

(18) H. E. Audier, S. Bory, M. Fétizon, and N. T. Anh, *Bull. Soc. Chim. Fr.*, 4002 (1966).

ture of the ion source was about 200°. Nmr spectra were taken in deuteriochloroform, unless otherwise stated, with a Varian A-60 or HA-100 spectrometer. Rotations were recorded in ethanol or chloroform using a Perkin-Elmer Model 141 polarimeter. Ozonolysis was carried out using a Welsbach T-408 ozonator. Vapor phase chromatography was carried out using 4% QF-1 and 5% SE-30 $^1/_8$ in. × 10 ft columns in a Varian Aerograph 1520B instrument.

Lactonization of the Keto Acid Ester 2.—To 300 mg of the vacuum-dried keto acid ester **2**, was added 1.5 ml of glacial acetic acid and 7 ml of acetyl chloride. The resulting yellow solution was refluxed for 20 hr in an oil bath. A syrupy gum was obtained after stripping the solution to dryness and flashing it several times with benzene to remove residual acetyl chloride and acetic acid. The syrupy residue in methylene chloride was spread on a preparative tlc plate (SiO_2–HF, 2 mm thick on a 200 × 400 mm plate) and eluted with chloroform. The largest band visible on exposure to uv light was collected and washed with ethyl acetate into a column. Continuous washings gave 217 mg of the Δ^8-lactone ester **4**: mp 117–120° (hexane–ether) (recrystallization from the same solvent gave material melting at 128–130°); $\nu_{\max}$ (CCl_4) 1779, 1730, 1686, 1250, 1235 cm^{-1}; τ 8.93 (C-10–Me), 8.79 (C-4 Me), 6.30 (CO_2Me); $[\alpha]_D$ 46.5° ($CHCl_3$).

Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27. Found: C, 69.66; H, 8.33.

Lactonization of the Keto Acid Ester 3. Method A.—A solution of 120 mg of keto acid ester **3** in 5 ml of acetic anhydride was refluxed for 1.5 hr under an atmosphere of nitrogen. Freshly fused sodium acetate (40 mg) was added and the mixture was refluxed for 2.5 hr in an atmosphere of nitrogen. The solvent was removed and the product was taken up in 50 ml of ether. The ether layer was washed with five 10-ml portions of water, dried over sodium sulfate, and evaporated to dryness. The residue (107 mg) showed two spots on tlc (silica gel G, $CHCl_3$); absorption at $\nu_{\max}$ 1800, 1760, 1730, 1645 cm^{-1} indicated the presence of lactones **5** and **6**.

The mixture of ene lactones (102 mg) in 10 ml of ethanol was treated with 10 drops of triethylamine and the mixture was refluxed for 15 hr. Evaporation of solvent afforded a residue (97 mg) which showed mainly one spot on tlc. The main product was isolated by preparative tlc on silica gel and crystallized from ether–hexane as fine needles (59 mg), mp 154–155°. Compound **6** showed $\nu_{\max}$ 1760, 1735, 1645 cm^{-1}; $\lambda_{\max}$ (EtOH) 215 mμ (ϵ 15,250); τ 8.79 (C-4 Me), 8.74 (C-10 Me), 6.32 (CO_2Me).

Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 68.80; H, 8.03.

Method B.—A solution of 115 mg of keto acid ester **3** in 10 ml of acetyl chloride and 0.5 ml of acetic acid was refluxed overnight. Evaporation of solvent afforded a residue (96 mg) which proved to be a mixture of **5** and **6**. The mixture was refluxed for 2 hr with 10 ml of ethanol and 10 drops of triethylamine. The usual work-up followed by preparative tlc afforded the ene lactone **6**, 62 mg, mp 153–154°.

Reaction of the Enone Ester (1) with *m*-Chloroperbenzoic Acid.—To the enone ester **1** (1.16 g) dissolved in methylene chloride (10 ml) was added a methylene chloride (10 ml) solution of *m*-chloroperbenzoic acid (F & M, 88% assay, 1.24 g). The resulting clear solution was stirred under nitrogen. After 1–2 hr at room temperature the reaction solution turned turbid, an additional 10 ml of methylene chloride was added and the reaction mixture was refluxed for 5 hr. The solution was then treated with 10% sodium sulfite solution until no iodine was liberated from a 1% KI solution (5 ml added initially).

The organic layer was separated, washed with three 25-ml portions of saturated sodium bicarbonate solution and then with three 100-ml portions of distilled water, and dried over sodium sulfate. Evaporation to dryness yielded a white crystalline solid, mp 118–126°.

The epoxy ϵ-lactone ester (**8**) crystallized preferentially from ethanol as long silky needles, mp 140.5–141.5°, 0.395 g.

A second crop was obtained by reducing the volume of ethanol to give 0.386 g of needles which proved to be a mixture. The needles, recombined with the mother liquor, were taken to dryness *in vacuo*, spotted over preparative plates (silica gel HF), and developed with chloroform. The first fraction was collected filtered, and washed with ethyl acetate to give an oil which crystallized from hexane to give the enol ϵ-lactone ester (**7**), mp 129–131°, as long colorless needles: $\nu_{\max}$ ($CHCl_3$) 1170, 1739, 1667 cm^{-1}; τ (CCl_4) 9.11 (C-10 Me), 8.86 (C-4 Me), 6.36 (CO_2Me), 3.85 (C=CHOCO); $[\alpha]_D$ −23.5° ($CHCl_3$).

Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.69; H, 8.54.

The second fraction afforded 0.172 g of long needles (EtOH): mp 142–144°; total yield of **8**, 43%. The analytical sample was recrystallized from MeOH: mp 148.5–150.5°; $\nu_{\max}$ 1754, 1709 cm^{-1}; τ (CCl_4) 9.01 (C-10 Me), 8.83 (C-4 Me), 6.38 (CO_2Me), 5.28 ($\mathrm{CC}\underset{\mathrm{O}}{\triangledown}\mathrm{CHCOO}$); $[\alpha]_D$ 106° ($CHCl_3$).

Anal. Calcd for $C_{18}H_{20}O_5 \cdot {}^1/_4MeOH$ (dried for 72 hr at 50° under high vacuum): C, 66.36; H, 8.19. Found: C, 66.45; H, 8.56.

Epoxidation of the Enol Lactone Ester (7).—The enol ϵ-lactone ester (31 mg) and *m*-chloroperbenzoic acid (43 mg) were dissolved in 10 ml of methylene chloride and refluxed under nitrogen for 5 hr. The reaction mixture was diluted with 10 ml of methylene chloride and washed with 20 ml of 10% sodium sulfite solution, followed by washes with saturated sodium bicarbonate and brine. The organic layer was separated, dried (Na_2SO_4), and evaporated to a crystalline residue. The residue crystallized readily from ethanol as silky fine needles, 28.6 mg (88%), mp 147–149°.

Rearrangement of the Epoxy ϵ-Lactone Ester (8).—To a well-stirred suspension of 0.918 g of epoxy ϵ-lactone ester **8** in 25 ml of methanol (ice bath) was added on aqueous solution of 5 ml of 2 *N* sodium hydroxide. After 15 min at room temperature the volume was reduced to *ca.* 10 ml *in vacuo* and acidified with dilute HCl. The precipitate was collected, washed with cold water, and dried to give 0.652 g of small prisms, mp 175–176° (softened at 170°).

An additional 140 mg of the aldehyde δ-lactone ester was obtained after ether extraction of the aqueous solution and was crystallized from carbon tetrachloride. The analytical sample was recrystallized from CCl_4–CH_2Cl_2: $\nu_{\max}$ 1760, 1726 cm^{-1}; for nmr, see Table I; $[\alpha]_D$ −109° ($CHCl_3$).

Anal. Calcd for $C_{18}H_{26}O_5$: C, 67.06; H, 8.17. Found: C, 67.12; H, 8.09.

Acid Isomerization of the Epoxy ϵ-Lactone Ester (8).—To 100 mg of the epoxy ϵ-lactone ester suspended in 5 ml of ethanol, 1 ml of 6 *N* hydrochloric acid was added and the mixture was refluxed for 2 hr. The mixture was taken to dryness (102 mg) and recrystallized to give needles, mp 148–159°. Tlc on silica gel showed the presence of two spots, one of which appeared to be starting material. The mixture was chromatographed over Florisil to give 78 mg (78%) of the aldehyde δ-lactone ester which on recrystallization from carbon tetrachloride–methylene chloride melted at 173–174°. This product was shown to be identical (ir and tlc) with the product isolated from the action of base on **8**.

Thermal Isomerization of the Epoxy ϵ-Lactone Ester (8).—The epoxy ϵ-lactone ester (22 mg) was heated in an open test tube at 165° for 10 min (under nitrogen). The melt was crystallized to give needles: first crop, 16.7 mg, mp 162–170°; second crop, 3.1 mg, mp 152–156°. The combined crystals and mother liquors were chromatographed over 2 g of Florisil and eluted with chloroform. The resulting crystals, 17 mg, melted at 172–173°, and were identical (ir and tlc) with the samples isolated from the base and acid rearrangement of **8**.

Epoxidation of the Enone Ester (1).—To the cooled (15–20°) solution of 146 mg of enone ester **1** dissolved in 2 ml of methanol was added a cooled solution of 0.25 ml of 30% hydrogen peroxide in one portion. The clear solution was allowed to stand for 3 hr after which time 1 ml of water was added. After some time crystalline needles of the epoxy ketone (**9**), 118 mg (75%), mp 98–101° separated. The analytical sample was crystallized from petroleum ether (40–50°): mp 110–111°; $\nu_{\max}$ 1735 (ester), 1712 (ketone), 887, 860 cm^{-1}; τ (CCl_4) 9.17 (C-10 Me), 8.85 (C-4 Me), 6.62 (CO_2Me), 7.02 [$\mathrm{C}\underset{\mathrm{O}}{\triangledown}\mathrm{C}\mathbf{H}\text{-}\mathrm{CO}$] $[\alpha]_D$ 21° ($CHCl_3$).

Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.55; H, 8.56.

Boron Trifluoride Treatment of the Epoxy Ketone (9).—To a stirred solution of 200 mg of the epoxy ketone **9** dissolved in 10 ml of benzene was added 5 drops of boron trifluoride etherate. Stirring was allowed to continue for 1 hr, water was added, and the aqueous solution was extracted with three 25-ml portions of ether. The dried (Na_2SO_4) ethereal solution was reduced to dryness *in vacuo* to give an oil, 187 mg. Preparative chromatography on silica gel HF yielded as the more mobile band, the diosphenol **22**, and as the less mobile band, its isomer **23**.

The bands were collected and washed with EtOAc. The diosphenol **22**, 91 mg, was not obtained crystalline but was shown to be identical (tlc, ir, and uv) with the diosphenol obtained from the dehydration of the keto diol **24a**. The infrared spectrum exhibited peaks at 3425 (OH), 1735 (CO_2Me), 1675, and 1650 (enone) cm^{-1} and its uv spectrum showed λ_{max} (EtOH) at 280 mμ, shifting bathochromically to 321 mμ on addition of 1 drop of 2% methanolic KOH. Mass spectrum showed mol wt 306 and *m/e* 306 (19%), 246 (25%), 181 (20%), 126 (56%), 121 (100%).

The less mobile band yielded an oil, 40 mg, which crystallized from hexane–ether: mp 143–143.5°; ν_{max} 3475 (OH), 1735 (CO_2Me), 1675, 1625 (enone); λ_{max} (EtOH) at 252 mμ (no base shift); τ 8.90 (C-10 Me), 8.83 (C-4 Me), 6.63 (CO_2Me); mass spectrum, mol wt 306 and *m/e* 306 (11.5%), 291 (100%), 262 (43%), 247 (27%).

Jones Oxidation of the Aldehydo Lactone Ester (10).—To 100 mg of the aldehydo δ-lactone ester **10** dissolved in 35 ml of acetone (ice bath) was added dropwise 0.35 ml of Jones solution. The cooled flask was allowed to attain room temperature over a period of 3 hr. The greenish solution was reduced *in vacuo* to a volume of *ca.* 10 ml and 50 ml of cold water was added. Extraction with three 25-ml portions of ether, drying the organic layer over sodium sulfate, and evaporating to dryness *in vacuo* yielded the crystalline acid **13a**, 97 mg (93%), mp 235–237° (from ether–hexane). The analytical sample crystallized from ethyl acetate as long prisms: mp 235–237°; ν_{max} ($CHCl_3$), 3226–2632 (broad), 1761 (sh), 1736 cm^{-1}; for nmr, see Table I: $[\alpha]_D$ −51.8° ($CHCl_3$).

Anal. Calcd for $C_{18}H_{26}O_6$: C, 63.88; H, 7.74. Found: C, 63.91; H, 7.77.

The dimethyl ester **13b** was prepared with ethereal diazomethane and crystallized from petroleum ether (50–55°)–ether to give heavy prisms: mp 128–129.5°; ν_{max} (CCl_4) 1752, 1739 cm^{-1}; τ 8.81 (C-4 Me), 9.22 (C-10 Me), 6.26 (C-4 CO_2Me), 6.16 (C-8 CO_2Me).

Anal. Calcd for $C_{19}H_{28}O_6$: C, 64.75; H, 8.01. Found: C, 64.85; H, 8.26.

Preparation of the Cyano Lactone Ester (15).—To 140 mg of the acid lactone ester **13a** in 2 ml of chloroform was added 2 ml of distilled thionyl chloride. The mixture was refluxed for 5 hr on a steam bath and left overnight at room temperature (14 hr). The excess thionyl chloride was removed *in vacuo* and the residue was flashed to dryness with several portions of benzene to give the acid chloride as a yellow oil, 148 mg, having ν_{max} (film) 1802, 1767, and 1730 cm^{-1}.

The above crude acid chloride in 25 ml of dry benzene was treated with dry ammonia at 5–10°. After saturation it was allowed to stand for 15 min and then reduced to dryness. The residue, dissolved in methylene chloride, was washed with water, dried ($MgSO_4$), and evaporated to dryness to afford an oil, 114 mg. The crude amide was chromatographed over 5 g of silica gel (80–200 mesh) and the amide lactone ester **14** was collected as an oil: 59 mg; ν_{max} (film) 3559, 3448, 3279, 1724, 1681 cm^{-1}; for nmr, see Table I.

To 60 mg of amide **14** in 5 ml of benzene was added 100 mg of P_2O_5. The mixture was refluxed for 26 hr. Water was added and the mixture was extracted with chloroform which was dried over Na_2SO_4. The solvent was removed *in vacuo* to give an oil which crystallized from CCl_4, 47 mg, mp 181–182°. A second recrystallization from CCl_4 increased the melting point to 184–184.5°. The cyano lactone ester **15** had ν_{max} ($CHCl_3$) 1765, and 1720 cm^{-1} but no absorption for C≡N; M$^+$ 319 (8.8%), *m/e* (% intensity) 260 (100), 244 (11), 233 (93); for nmr, see Table I.

Alcohol δ-Lactone Ester (11a).—To a stirred soln of 210 mg of the aldehyde δ-lactone **10** in 10 ml of methanol cooled in an ice bath was added 30 mg of sodium borohydride. The reaction was allowed to proceed for 5 min when the reaction was quenched with dilute hydrochloric acid. Extraction with chloroform and drying with sodium sulfate, followed by evaporation *in vacuo*, gave 178 mg of the alcohol **11a**. It readily crystallized from ether and was recrystallized from ethyl acetate: mp 197–199° (softened at 155°); ν_{max} 3534 (OH), 1733 (CO_2Me), 1712 (lactone) cm^{-1}; for nmr, see Table I; $[\alpha]_D$ 8.0° ($CHCl_3$).

Anal. Calcd for $C_{18}H_{28}O_5$: C, 66.64; H, 8.70. Found: C, 66.61; H, 8.66.

When excess $NaBH_4$ was used a second crystalline compound, separable by column chromatography and having double mp 177–180 and 325° (from ether) was obtained: ν_{max} 3636, 1735 cm^{-1}; τ 9.30 (C-10 Me), 8.96 (C-4 Me), 6.26 (CO_2Me), 6.03 ($-CH_2O-$).

Acetate δ-Lactone Ester (11b).—To the cooled flask containing 31 mg of the title compound and 0.5 ml of acetic anhydride was added 3 drops of pyridine. After standing for 5 min the flask was removed from the ice bath and left at room temp for 18 hr. The reaction solution was diluted with cold water, poured onto ice, and extracted with ether. The combined, dried ether extracts (over Na_2SO_4) were evaporated *in vacuo*. Adding several portions of benzene to the residue and repeated flash evaporation yielded a gum, 32 mg. Tlc showed one spot on silica gel using chloroform as the eluent. No hydroxyl absorption in the ir spectrum was observed. The oil was crystallized from petroleum ether (50–55°)–ether at −70° to give crystals: mp 92–94°; τ 9.11 (C-10 Me), 8.89 (C-4 Me), 8.00 (OCOMe), 6.47 (CO_2Me), 5.8 (AB quartet, J = 12 cps, $-CH_2O-$).

Anal. Calcd for $C_{20}H_{30}O_6$: C, 65.55; H, 8.25. Found: C, 65.44; H, 8.35.

Dehydration of the Keto Diol Ester (24a).—To 37 mg of the keto diol ester (**24a**) suspended in 8 ml of ethanol was added 0.2 ml of concentrated H_2SO_4. The flask was heated at 105° (oil bath) when the compound dissolved to give a clear solution. After refluxing for 5 hr the ethanol was removed *in vacuo*, water was added, and the aqueous solution was extracted with chloroform. Evaporation to dryness gave 37 mg of an oil; tlc on silica gel G showed essentially one spot.

Purification of the compound was done preparatively on a 5 × 20 cm plate (0.75 mm thick) eluting with 2% MeOH in $CHCl_3$. The product (**22**) was collected as the first fraction (24 mg) and starting material as the second fraction (4 mg).

The diosphenol (**22**) was recrystallized from hexane: mp 124–125°; ν_{max} (CH_2Cl_2 film) 3425 (OH), 1730 (ester), 1675, 1649 (C=CCO), 1250 cm^{-1}; ν_{max} (EtOH) 280 mμ (ϵ 11,000); $[\alpha]_D$ −16.7° (EtOH).

Anal. Calcd for $C_{18}H_{26}O_5$: C, 70.56; H, 8.55. Found: C, 70.25; H, 8.55.

Internal Condensation of the Aldehydo δ-Lactone Ester (10).—The aldehydo δ-lactone ester (60 mg) in 3 ml of pyridine was refluxed for 6 hr. The reaction mixture was poured into 20 ml of 6 *N* HCl solution and extracted with chloroform. The combined, dried (Na_2SO_4) extracts showed essentially one spot on tlc (silica gel G, 5% MeOH in $CHCl_3$). The solvent was removed *in vacuo* to give a crystalline residue (**17a**), 52 mg (87%). Recrystallization from ethyl acetate yielded rectangular plates (sparingly soluble in $CHCl_3$). A second recrystallization from acetone–petroleum ether (50–55°) gave small rectangular plates, mp 184.5–210°. Further recrystallization from hot ethyl acetate gave thick rectangular prisms, whose mp was not improved: ν_{max} ($CHCl_3$) 3450 broad (OH), 1786 (γ-lactone), 1725 (CO_2Me) cm^{-1}; τ 9.07 (C-10 Me), 8.82 (C-4 Me), 6.34 (CO_2Me), 5.88 (d, J = 1, cps $\mathrm{H}\underset{|}{\overset{|}{\mathrm{C}}}\mathrm{OH}$), 7.17 (m, C-12 H).

Anal. Calcd for $C_{18}H_{26}O_5$: C, 67.06; H, 8.13. Found: C, 66.98; H, 8.13.

Acetate 17b. To 25 mg of **17a** in 1 ml of acetic anhydride was added 0.1 ml of pyridine. The reaction flask was heated at 50° for 15 hr. The solution was poured into a cold saturated brine solution. Extraction with chloroform, removal of solvent *in vacuo*, and flashing the residue with benzene several times gave an additional 5 mg totaling 21 mg of **17b**. Recrystallization from hexane–ether gave **17b** as rosettes: mp 166–167°; ν_{max} ($CHCl_3$) 1785 (γ-lactone), 1740 (acetate), 1725 (ester) 1243 cm^{-1}; τ 9.00 (C-10 Me), 8.82 (C-4 Me), 7.93 ($OCOCH_3$), 7.16 (m, C-12 H), 5.10 (d, J = 2 cps, −CHOH).

Anal. Calcd for $C_{20}H_{28}O_6$: C, 65.91; H, 7.74. Found: C, 66.09; H, 7.73.

Reaction of the Alcohol δ-Lactone Ester (11a) with Lead Tetraacetate and Iodine.—A mixture of 930 mg of vacuum-dried lead tetraacetate, 345 mg of powered calcium carbonate, and 40 ml of Spectrograde cyclohexane was refluxed for 15 min. To this mixture was added 225 mg of **11a** and 108 mg of iodine crystals. Heating the stirred mixture with a 250-W infrared lamp was continued for 1 hr. The mixture was filtered and the insoluble salts were washed with ether. The organic fractions were combined and washed with saturated aqueous sodium thiosulfate and water. The dried (Na_2SO_4) extracts yield a gum, 221 mg. Tlc on silica gel G showed at least four spots. The crude gum was chromatographed over 6.5 g of Florisil and eluted with chloroform.

After *ca.* 35 ml of eluate was collected (first fraction containing the first two spots), further chloroform eluates gave a second fraction of 47 mg of oil which crystallized on drying under high vacuum. Crystallization from hexane–ether gave the furano ether **12**, mp 156–159°. Recrystallization from hexane–ether gave small crystals: mp 160–163°; ν_{max} ($CHCl_3$) 1754, 1737 cm^{-1}; τ 8.93 (C-10 Me), 8.82 (C-4 Me), 7.13 (2 H, complex multiplet, C-12 CH_2), 6.32 (CO_2Me), 6.12 (2 H, AB quartet, C-8 CH_2O), 5.63 (1 H triplet, C-11 H); mass spectrum, M^+ 322.

Anal. Calcd for $C_{18}H_{26}O_5$ (322): C, 67.06; H, 8.13. Found: C, 67.23; H, 8.29.

Action of Lead Tetraacetate on the Alcohol δ-Lactone Ester (11a) in Benzene.—Compound **11a** (114 mg), 240 mg of lead tetraacetate (dried over KOH), and 10 ml of benzene (dried over sodium) were refluxed for 16 hr after which time the reaction mixture was poured into 100 ml of water and diluted with 30 ml of ether. The organic layer was separated and washed with three 25-ml portions of water, dried over Na_2SO_4, and flashed to dryness to give 113 mg of a gum, which was chromatographed in chloroform over 6.4 g of silica gel (B and A, 80–200 mesh).

The major compound (**16**) was preceded by a minor component (not isolated) and followed by the starting material, 25 mg. Monitoring of the combined eluates was accomplished by tlc using silica gel G/5% MeOH in $CHCl_3$. The dimer **16** was crystallized from pentane–trace ether: mp 172–173°; ν_{max} 1730, 1242 cm^{-1}; τ 9.27 and 9.10 (C-10 Me), 8.85 and 8.87 (C-4 Me), 6.42 and 6.43 (C-4 CO_2Me), 5.77 (AB quartet, J = 12.5 cps, $-CH_2O-$).

Anal. Calcd for $C_{35}H_{52}O_9$: C, 68.15; H, 8.50. Found: C, 68.11; H, 8.28.

Jones Oxidation of the Bicyclic Alcohol γ-Lactone Ester (17a).—To an ice-cooled solution of 58 mg of **17a** in 10 ml of acetone was added 0.5 ml of Jones reagent. The reaction mixture was left in the ice box for 19 hr and worked up by being poured into brine and extracted with chloroform. The combined chloroform extracts were washed with water and dried over Na_2SO_4. Evaporation of the solvent *in vacuo* left 56 mg of a gum, which on addition of ether precipitated 10 mg of starting material. The mother liquor was chromatographed in chloroform on Florisil and crystallized from petroleum ether (50–55°) to give 44 mg of small crystals of **18**: mp 130.5–132°; ν_{max} (CCl_4) 1818, 1776, 1724 cm^{-1}; τ 9.22 (C-10 Me), 8.85 (C-4 Me), 7.12 (C-12 H), 6.38 (CO_2Me).

Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.61; H, 7.53.

Action of Acid and Heat on the Keto Lactone Ester (18).—To 170 mg of **18** in 10 ml of EtOH was added 2 ml of 6 *N* HCl solution. The mixture was heated under nitrogen for 25 hr, followed by dilution with water and extraction with chloroform. The dried (Na_2SO_4) organic extract was flashed to dryness to give 127 mg of an oil. Tlc on silica gel G, 2% MeOH in $CHCl_3$, showed the presence of some starting material. The product (**20**) crystallized from pentane as thick needles: mp 100–111°; 99 mg; ν_{max} (CCl_4) 1730, 1701, 1642 cm^{-1}; τ 8.84 (C-10 Me), 7.74 (C-4 Me), 6.28 (CO_2Me).

Anal. Calcd for $C_{17}H_{24}O_2$: C, 73.88; H, 8.75. Found: C, 73.71; H, 9.03.

Dehydration of the Alcohol γ-Lactone Ester (17a).—The alcohol γ-lactone ester (30 mg), suspended in a mixture of 1 ml of EtOH, 2 ml of water, and 0.5 ml of HCl, was refluxed under nitrogen for 18 hr. The reaction mixture was poured into 20 ml of brine and extracted with chloroform. The dried (Na_2SO_4) extract yielded an oil, 22 mg, upon evaporation *in vacuo*, and showed essentially one spot on tlc.

The sample on sublimation [bath temperature 103°/(170 μ)] afforded a white crystalline material (**19**), mp 125–128°. Recrystallization from pentane gave long rectangular plates: mp 136–138°; ν_{max} (CCl_4) 1750 (C=O), 1735 (CO_2Me) cm^{-1}; 9.07 (C-10 Me), 8.82 (C-4 Me), 6.41 (C-4 CO_2Me); mass spectrum, *m/e* (% intensity) 278 (58.5), 260 (52), 244 (metastable), 219 (89), 201 (base peak, 100), 185 (metastable), 149 (30), 137 (61), 123 (63).

Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 73.51; H, 9.53.

Benzilic Acid Rearrangement of the Diosphenol (22).—A solution of 40 mg of the diosphenol **22** in 1 ml of aqueous potassium hydroxide (5.6 g in 10 ml of water) and 16 ml of *n*-propyl alcohol was refluxed for 20 hr, poured into 50 ml of water, and acidified with concentrated hydrochloric acid. The resulting mixture was extracted with three 30-ml portions of ether. The ether extract was washed four times with water and dried over anhydrous sodium sulfate, and the ether removed to give 31 mg of a semisolid residue (**25a**): ν_{max} ($CHCl_3$) 3500, 3200, and 1700 cm^{-1}, indicating the presence of hydroxyl and carboxyl functions. This product resisted crystallization.

Oxidative Decarboxylation of the Hydroxy Diacid (25a).—Sodium dichromate dihydrate (250 mg) was added to a solution of 28 mg of **25a** in 10 ml of acetic acid, and the mixture was allowed to stand at room temperature for 24 hr, after which it was poured into ice-cold water.

The aqueous mixture was extracted with four 20-ml portions of ether. The ether extract was washed thrice with water and dried over anhydrous magnesium sulfate, and the ether was removed to afford 19 mg of a residue which was methylated with ethereal diazomethane. The methylated product, on chromatography over silica gel and elution with chloroform, afforded 14 mg of a semicrystalline solid, which, on sublimation and crystallization from pentane, gave a crystalline product identical with **19** (melting point, mixture melting point, and vpc).

Registry No.—**4**, 21347-61-5; **6**, 21347-42-2; **7**, 14022-52-7; **8**, 21347-44-4; **9**, 21347-45-5; **10**, 21371-71-1; **11a**, 21347-46-6; **11b**, 21347-47-7; **12**, 21347-48-8; **13a**, 14021-11-5; **13b**, 21347-50-2; **14**, 21371-72-2; **15**, 21347-51-3; **16**, 21347-52-4; **17a**, 21347-53-5; **17b**, 21347-54-6; **18**, 21347-55-7; **19**, 21347-56-8; **20**, 21347-57-9; **22**, 21347-58-0; **23**, 21347-59-1; **25a**, 21347-60-4.

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