The Action of Ozone on the Trimethyl Ester of Maleopimaric Acid. Terpenes. VI[1,2]

L. H. ZALKOW AND N. N. GIROTRA

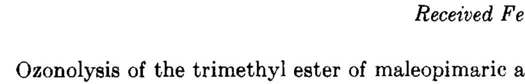
Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma

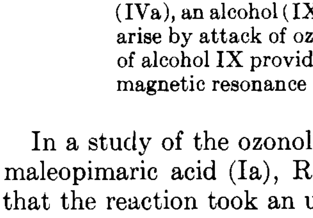
Received February 21, 1963

Ozonolysis of the trimethyl ester of maleopimaric acid (Ia) has been shown to yield, in addition to the previously reported α,β-unsaturated ketone II and diene III, the following crystalline products: a saturated ketone (IVa), an alcohol (IX), a γ-lactone (VIII), a δ-lactone (X), and two acids (XII and XIII). All of these compounds arise by attack of ozone on the isopropyl group, rather than the expected reaction at the double bond. Isolation of alcohol IX provides evidence for the oxidation scheme suggested earlier by Ruzicka and Kaufmann.[3] Nuclear magnetic resonance was employed in the structure and stereochemical elucidation of the various products.

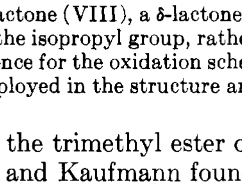
In a study of the ozonolysis of the trimethyl ester of maleopimaric acid (Ia), Ruzicka and Kaufmann found that the reaction took an unusual course.[3,4] Oxidation of the isopropyl group occurred rather than cleavage of the double bond, as evidenced by the isolation of the α,β-unsaturated ketone II and the diene III.

The stereochemistry of the Diels–Alder adduct of levopimaric acid and dimethyl maleate is now well established; the adduct possesses the absolute configuration as depicted in Ia.[5–9] An examination of a molecular model of Ia clearly indicates that both faces of the double bond are blocked, thus suggesting an explanation for the abnormal ozonolysis observed by Ruzicka and Kaufmann.[3] They suggested the following scheme to explain the reaction.



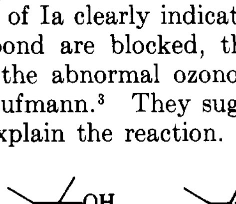


Ia, C-15 carbomethoxy group β
b, C-15 carbomethoxy group α



IIa, C-15 carbomethoxy group β
b, C-15 carbomethoxy group α

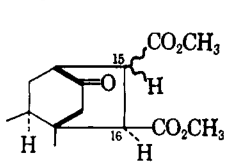
(The α-configuration signifies that the group lies behind the general plane of the ring system, where in the β-configuration the group lies in front of the plane.[10])



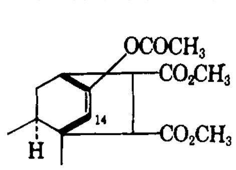
III

We have had occasion to repeat the ozonolysis of Ia and have found that IIa is indeed the major product of the reaction, but, in addition, six other crystalline compounds, previously unreported, have been isolated. All of these products arise by oxidation of the isopropyl group and offer strong support for the oxidation scheme proposed by the earlier workers.[3]

Following the previous procedure a solution of Ia in acetic acid was exposed to a steady stream of oxygen containing ozone for forty-eight hours. The crude product was separated into acidic (~20%) and neutral (~80%) fractions. The neutral fraction was further separated into nonketonic (~25%) and ketonic (~75%) fractions using Girard's T reagent. Hydrolysis of the Girard derivative gave the previously reported ketone IIa, together with a second ketone, IVa ($C_{24}H_{34}O_7$). Nuclear magnetic resonance spectroscopy proved to be particularly useful in arriving at the structure of IVa. Ayer, McDonald, and Stothers[6] have made a detailed study of the n.m.r. spectra of derivatives of maleopimaric acid. These workers observed that, in compounds such as I and II, the double bond at C-13–C-14 has a long range shielding effect on protons of the methyl group at C-10. These protons appear at ~δ 0.50 in compounds such as I and II, whereas the protons of the methyl group at C-4 appear at approximately δ 1.10. Removal of C-13–C-14 double bond results in a shift of the C-10 methyl protons to ~δ 1.0.



IVa, C-15 β-carbomethoxy
b, C-15 α-carbomethoxy



V

The signal at highest field in the n.m.r. spectrum of IVa appeared at δ 0.83, and the vinylic proton present in the spectra of Ia (δ 5.31) and IIa (δ 6.90) was absent. Both Ia and IIa gave a positive test for a double bond with tetranitromethane, but IVa did not. The n.m.r. spectrum of IVa also indicated the absence of an isopropyl group, and of a methyl group attached to a carbonyl group (as present in IIa at δ 2.36). On the basis of these facts together with the elemental analysis and infrared spectrum, it appeared likely that this ketone possessed structure IVa. Since the double bond in Ia was so hindered as to be unaffected by ozone, it seemed possible that the Baeyer–Villiger reaction on IIa would likewise proceed without attack on the double

---

(1) Generous support of this investigation by grant NSF-GP-233 of the National Science Foundation is gratefully acknowledged.

(2) "The Conversion of 2-Acetoxypulegone to Menthofuran. Terpenes. V," L. H. Zalkow, J. W. Ellis, and Sister M. Roger Brennan, *J. Org. Chem.*, **28**, 1705 (1963).

(3) L. Ruzicka and St. Kaufmann, *Helv. Chim. Acta*, **23**, 1346 (1940).

(4) Sir John Simonsen, "The Terpenes," Vol. 3, Cambridge University Press, Cambridge, England, 1952, p. 434.

(5) L. H. Zalkow, R. A. Ford, and J. P. Kutney, *J. Org. Chem.*, **27**, 3535 (1962).

(6) W. A. Ayer, C. E. McDonald, and J. B. Stothers, *Can. J. Chem.*, **41**, 1113 (1963).

(7) W. L. Meyer and R. W. Hoffman, *Tetrahedron Letters*, No. **16**, 691 (1962).

(8) W. H. Schuller and R. V. Lawrence, *J. Am. Chem. Soc.*, **83**, 2563 (1961).

(9) A. W. Burgstahler, H. Ziffer, and U. Weiss, *ibid.*, **83**, 4660 (1961).

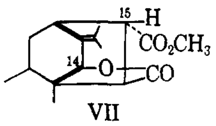
(10) Definitive rule for nomenclature of steroids, *ibid.*, **82**, 5577 (1960).

bond and would lead, therefore, to ester V. Hydrolysis of ester V should give IVa. This was found to be the case. Treatment of IIa with peroxytrifluoroacetic acid gave V in good yield. The n.m.r. spectrum of V showed the C-14 vinyl proton at δ 5.34, upfield from the C-14 proton in IIa, since in the latter compound the double bond is conjugated. The methyl protons of the acetoxy group in V appeared at δ 2.18 and the C-10 methyl protons at δ 0.75.

Acid-catalyzed hydrolysis of V at room temperature gave IVa identical in all respects with that isolated from the ozonolysis reaction. The optical rotatory dispersion curve of IVa showed a strong negative Cotton effect in methanol which was unchanged upon the addition of hydrochloric acid. This is characteristic of ketones which are unable to form ketals.[11] Thus, structure IVa is firmly established.

A second compound, VI, was isolated in low yield from the Baeyer-Villiger reaction. This substance was found not to be the tetramethyl ester resulting from the insertion of an oxygen atom on the methyl side of ketone IIa; the latter ester, XIIIa (following), was available for comparison. The infrared and n.m.r. spectra of VI showed it to be an alcohol and to contain three carbomethoxy groups. Since the C-10 methyl protons appeared at δ 0.67 in the n.m.r., the C-13–C-14 double bond was apparently still present. However, no vinylic protons were evident and an unexplained 3-proton signal was present at δ 3.05. No satisfactory structure for VI can be offered at this time.

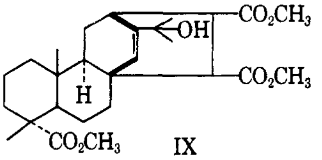
When Ia, IIa, and IVa were refluxed in alkaline solution, the resulting acids re-esterified with diazomethane, the respective, isomeric compounds Ib, IIb, and IVb were obtained. The trimethyl ester Ib was identical with that obtained from the Diels-Alder reaction between methyl abietate and fumaric acid followed by esterification with diazomethane. The more stable *trans* isomers have been assigned structures in which the C-15 carboxyl group is down (α), since Ayer, *et al.*,[6] reported the conversion of Ib to a γ-lactone, VII, with the oxygen atom attached at C-14. The corresponding isomer of VII with the C-15 carboxyl group up (β) has been reported from this laboratory previously.[5]



VII

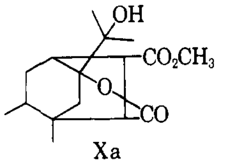
After chromatography on alumina, the nonketonic portion of the neutral fraction obtained from the ozonolysis of Ia yielded three previously unreported compounds, VIII (m.p. 220–221°), IX (m.p. 194–196°), and X (m.p. 264–265°). In addition, the ultraviolet spectrum of the *noncrystalline part of this fraction* indicated the presence of approximately 15% of the previously reported diene III.

Compound IX, when treated with phosphorus oxychloride in pyridine, gave a substance which had the same ultraviolet spectrum as III. The infrared and n.m.r. spectra of IX and its conversion to a diene with the ultraviolet chromophore of III support the structure shown later. The presence of a hydroxyl group was shown by the band at 3472 cm.$^{-1}$ in the infrared, and by n.m.r. (δ 5.0, which disappears on the addition of deuterium oxide). Three carbomethoxy groups were established by three sharp signals (three protons each) at δ 3.58, 3.60, 3.67 in the n.m.r., and by a band at 1727 cm.$^{-1}$ in the infrared. The double bond at C-13–C-14 was apparent from the position of the C-10 methyl protons at δ 0.62 and by the C-14 vinyl proton at δ 5.70. The double bond also gave a weak peak at 1638 cm.$^{-1}$ in the infrared. The two methyl groups flanking the carbon atom containing the hydroxyl group have n.m.r. signals at δ 1.22 and δ 1.28, downfield from where the isopropyl methyl protons appeared in I (δ 1.08). The isolation of IX provides strong support for Ruzicka's proposed oxidation scheme.

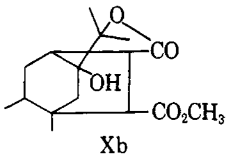


IX

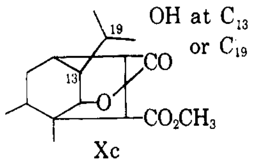
Compound X ($C_{26}H_{38}O_7$), obtained in very low yield, exhibited a hydroxyl group (3401 cm.$^{-1}$) and three carbonyl bands (1739, 1718, and 1691 cm.$^{-1}$) in its infrared spectrum. The band at highest wave length has been assigned to a δ-lactone and the other two are assigned to the A- and D-ring ester groups. Since X had no signals in its n.m.r. spectrum at field higher than δ 1.0, and gave a negative test with tetranitromethane, the absence of a double bond was concluded. On the basis of this evidence structures Xa and Xb are



Xa



Xb



Xc

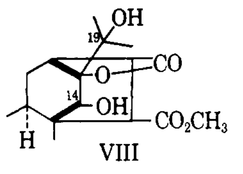
suggested for this compound. Another structure containing a δ-lactone (Xc) was not considered a likely possibility because of the absence of a signal in the n.m.r. corresponding to the C-14 proton.

The third crystalline compound isolated from the nonketonic fraction has been assigned structure VIII. Compound VIII exhibited a hydroxyl band (3448 cm.$^{-1}$) and a band due to a γ-lactone (1786 cm.$^{-1}$) in the infrared. The n.m.r. spectrum showed that it contained only two carbomethoxy groups and no C-13–C-14 double bond (tetranitromethane test was negative). Methyl protons of the isopropyl group were moved downfield (δ 1.35 and 1.47) showing that an oxygen atom was attached at C-19. The C-14 proton appeared at δ 4.35. If the lactone had been attached at C-14, then this latter proton would have been expected to give a signal at $\sim\delta$ 5.00; however, the attachment of a hydroxyl group at C-14 is completely consistent with the observed data.[5]

The acids XII and XIII were isolated from the acidic fraction of the ozonolysis product; after esterification

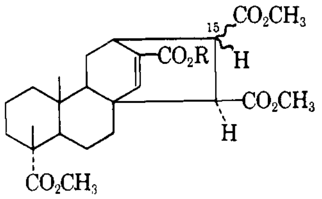
---

[11] C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 143.



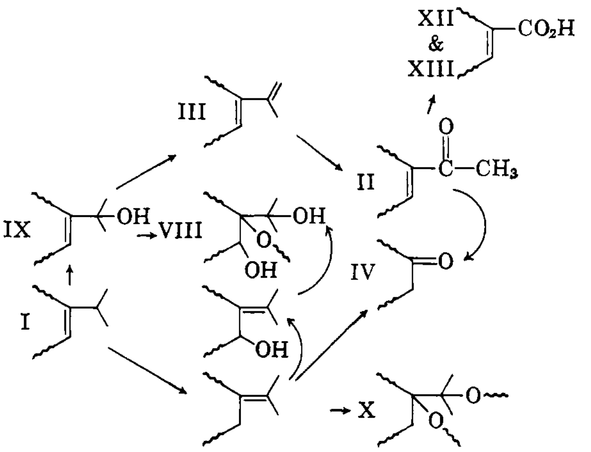
VIII

with diazomethane, they were separated by chromatography on alumina. The first material to be eluted from the column, XIIa, could also be prepared from XIIIa by alkaline isomerization followed by re-esterification. The haloform reaction of IIa, followed by esterification with diazomethane, gave XIIa identical in all respects with that isolated from the ozonolysis experiment. The n.m.r. spectra of XIIa and XIIIa were completely consistent with the suggested structures.



XII, C-15 α-carbomethoxy, R = H; XIIa, R = CH_3
XIII, C-15 β-carbomethoxy, R = H; XIIIa, R = CH_3

It is not possible to offer a detailed mechanism for the unusual ozonolysis observed in this case. However, it does appear likely that Ruzicka's original suggestion of a stepwise oxidation of the isopropyl group is valid. A scheme of oxidation as shown can be visualized.



Peracetic acid, formed by the prolonged action of ozone on the acetic acid solvent, may be the active oxidizing agent. If this were the case, then IV might arise from II *via* a Baeyer–Villiger reaction followed by hydrolysis in the work-up. However, XII and XIII must not arise from II by the action of peracetic acid, since in that case the methyl esters and not the free acids should have been isolated. Ketone IV may arise by a double bond migration to give an isopropylidine group, followed by cleavage of the double bond. Lactones VIII and X also may arise from the same intermediate by hydroxylation followed by lactonization. When a stream of oxygen containing no ozone was passed through an acetic acid solution of Ia under conditions identical to those used in the ozonolysis, no change in Ia occurred.

Experimental

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. Infrared spectra were recorded using a Beckman IR-5 spectrophotometer. Nuclear magnetic resonance spectra were recorded with the Varian A-60 n.m.r. spectrometer, using tetramethylsilane as an internal standard (δ 0) and deuteriochloroform as solvent. Ultraviolet spectra were obtained with the Beckman recording spectrometer, Model DK1.

Ozonolysis of Trimethyl Ester of Maleopimaric Acid (Ia).—The trimethyl ester Ia was prepared as previously described[5] and ozonized as follows. A rapid stream of ozone (approximately 3%) was passed through a solution of 29.8 g. of Ia in 225 cc. of glacial acetic acid for 48 hr. at room temperature. After the addition of 15 cc. of water, the solution was stirred for a short time and then taken to dryness on a steam bath using the water aspirator. The glassy yellow solid thus obtained was then separated into acidic and neutral fractions; it was dissolved in ether and the resulting solution was repeatedly extracted with 5% ice-cold sodium hydroxide solution until the alkaline extract was colorless. The ether layer, after drying over anhydrous sodium sulfate, was concentrated to give 22.7 g. of the yellow neutral fraction.

The aqueous sodium hydroxide extracts were combined, acidified with dilute hydrochloric acid, and extracted with ether. After washing with water and drying over anhydrous sodium sulfate, the combined ether extracts were concentrated to yield 4.52 g. of glassy acidic fraction.

The Ketonic Fraction. Isolation of Ketones IIa and IVa.—A solution of 6.75 g. of previous neutral fraction in 70 cc. of anhydrous methanol containing 2 cc. of glacial acetic acid and 2.7 g. of Girard's T reagent was refluxed for 4 hr. The cooled reaction mixture was then poured into a solution of 2.8 g. of sodium bicarbonate in 280 cc. of water, and this solution was extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, and concentrated to give 1.87 g. of the nonketonic fraction as a viscous gum. The separation of this fraction is described in the section on the nonketonic fraction.

The aqueous layer, which contained the ketones, was acidified by adding 10 cc. of 6 *N* hydrochloric acid. After standing for 1 hr., ketone IIa crystallized and was collected by filtration, washed with water, and dried to give m.p. 161–163° (3.5 g.). Two recrystallizations from methanol gave m.p. 168–169° (lit.[3] m.p. 168–169°); ν_{max}^{KBr} 1724, 1661, and 1610 cm.$^{-1}$; n.m.r. (p.p.m. downfield from tetramethylsilane), δ 0.50 (3 protons), 1.13 (3), 2.36 (3), and 6.90 (1).

The filtrate remaining after the removal of ketone IIa, on standing open to the atmosphere for 2 weeks, became turbid and then was extracted with ether. After washing with water and drying over anhydrous sodium sulfate, evaporation of the ether gave 1.1 g. of ketone IVa. Recrystallization from methanol gave 0.8 g., m.p. 193–194°; negative tetranitromethane test; ν_{max}^{KBr} 1745, 1740, and 1725 cm.$^{-1}$; n.m.r., δ 0.83 (3), 1.12 (3). This substance exhibited a strongly negative Cotton effect in methanol solution (*c* 0.0565) which was unchanged on the addition of a small amount of hydrochloric acid: $[\alpha]_{589}$ mμ −46°, $[\alpha]_{302}$ −1071°, $[\alpha]_{267}$ + 302°, $[\alpha]_{250}$ −250°.

Anal. Calcd. for $C_{24}H_{34}O_7$: C, 66.33; H, 7.88. Found: C, 66.57; H, 7.95.

Ketone IVa also could be isolated by further acidification of the aqueous filtrate remaining after the removal of ketone IIa.

Alkaline Isomerization of IIa. Preparation of IIb.—A solution prepared by dissolving 0.34 g. of IIa in 10 cc. of methanol and 25 cc. of 2 *N* sodium hydroxide was refluxed for 10 hr. After cooling, it was diluted with water, acidified with dilute hydrochloric acid, and extracted with ether. After washing with water and drying over anhydrous sodium sulfate, the ether extract was concentrated to give the crystalline *trans* acid; after crystallization from aqueous acetic acid it had m.p. 287–289°; ν_{max}^{KBr} 3703–2127, 1709, 1661, and 1626 cm.$^{-1}$.

Treatment of the crystalline *trans* acid with ethereal diazomethane gave IIb as a viscous gum which could not be crystallized; n.m.r., δ 0.50 (3), 1.08 (3), 2.25 (3) and 6.88 (1).

Conversion of IIa into IVa.—A solution of peroxytrifluoroacetic acid was prepared by the dropwise addition of 3 cc. of trifluoroacetic anhydride to a suspension of 0.5 cc. of 90% hydrogen peroxide in 10 cc. of methylene chloride. This solution was added over a period of 15 min. to a stirred suspension of 7.86 g. of dry, finely powdered disodium hydrogen phosphate in a solution of 5.5 g. of ketone IIa in 30 cc. of methylene chloride. After addition was complete, the solution was heated under reflux for 1 hr. The inorganic salts were removed by filtration and washed with methylene chloride. The combined methylene chloride layers were washed with 10% sodium carbonate, dried over anhydrous sodium sulfate, and the solution finally concentrated to give 5.4 g. of crude products.

Two recrystallizations from a mixture of methanol–dioxane gave 3.5 g. (61%) of V, m.p. 208–210°. The analytical sample of V obtained by recrystallization from methanol gave m.p. 210–212°; $\nu_{\max}^{\text{KBr}}$ 1757, 1750, 1727, 1669 cm.$^{-1}$; n.m.r., δ 0.75 (3), 1.13 (3), 2.18 (3), 5.34 (doublet, 1 proton).

Anal. Calcd. for $C_{26}H_{36}O_8$: C, 65.52; H, 7.61. Found: C, 65.41; H, 7.72.

Concentration of the mother liquor from which V was obtained gave a viscous gum which upon the addition of methanol gave 0.55 g. of VI. The analytical sample was obtained by recrystallization from methanol–acetone and had m.p. 268–271°; $\nu_{\max}^{\text{KBr}}$ 3425, 1725 cm.$^{-1}$; n.m.r., δ 0.67 (3), 1.12 (3), 3.05 (3), and 4.10 (doublet which disappears on addition of deuterium oxide).

Anal. Calcd. for $C_{24}H_{34}O_8$: C, 63.98; H, 7.61. Found: C, 64.04; H, 7.55.

A solution containing 3.37 g. of V, 175 cc. of dioxane, 175 cc. of methanol, and 100 cc. of 6 *N* hydrochloric acid was allowed to stand at room temperature for 10 hr. Addition of 1200 cc. of water yielded 2.95 g. of ketone IVa, m.p. 191–193°. Recrystallization from methanol gave ketone IVa of identical melting and mixture melting point, infrared, and n.m.r. spectra, with IVa obtained by treatment of Ia with ozone.

Alkaline Isomerization of IVa. Preparation of IVb.—A solution prepared by the addition of 0.5 g. of IVa to 10 cc. of methanol, to which was added 15 cc. of 2 *N* sodium hydroxide, was refluxed for 3 hr. After cooling, it was diluted with 100 cc. of water and acidified with dilute hydrochloric acid, then extracted with ether. After washing with water and drying over anhydrous sodium sulfate, the ether extract was concentrated to yield an amorphous solid which was treated directly with an excess of an ethereal solution of diazomethane. The crude product was crystallized from methanol to give 0.41 g. of ketone IVb, m.p. 148–149°; $\nu_{\max}^{\text{KBr}}$ 1730 cm.$^{-1}$; n.m.r., δ 0.80 (3), 1.13 (3).

Anal. Calcd. for $C_{24}H_{34}O_7$: C, 66.33; H, 7.88. Found: C, 66.56; H, 8.03.

The Nonketonic Fraction.—The fraction (1.87 g.) remaining after removal of the ketones with Girard's T reagent was chromatographed on neutral activated alumina (100 g.). Elution with 25% ether–75% benzene gave 1.26 g. of a viscous gum from which was obtained, on crystallization with benzene–*n*-heptane, 40 mg. of compound VIII. Further elution with ether gave 0.34 g. of a viscous gum which could be partially crystallized from aqueous methanol to give 70 mg. of compound IX. Rechromatography of the noncrystalline material (1.08 g.) on 60 g. of neutral activated alumina gave as crystalline material 35 mg. of ketone IVa (which apparently escaped reaction with Girard's T reagent), 10 mg. of a new crystalline compound X, and a further 50 mg. of VIII; these were all eluted with 25% ether–75% benzene. The remainder of the material could not be crystallized, but its ultraviolet spectrum ($\lambda_{\max}^{\text{EtOH}}$ 240 mμ, ϵ 2392) indicated the presence of 15% of the previously reported diene III ($\lambda_{\max}$ 240 mμ, ϵ 17,780).

Compound VIII.—This substance, obtained as described before, after recrystallization from benzene–*n*-heptane and drying at 140° and 1-mm. pressure for 10 hr., had m.p. 220–221° and gave a negative tetranitromethane test; $\nu_{\max}^{\text{KBr}}$ 3448, 1786, and 1712 cm.$^{-1}$; n.m.r., δ 1.10, 1.17, 1.35, 1.47, 3.65, 3.70, 4.35, and 7.36.

Anal. Calcd. for $C_{26}H_{38}O_8 \cdot 0.5H_2O$: C, 64.05; H, 8.06. Found: C, 63.82; 64.12, H, 7.82, 7.99.

Maleopimaric acid and related substances have been shown to hold tenaciously solvents of crystallization and to form hydrates.[12]

Compound IX.—Recrystallization from methanol and drying for 12 hr. at 140° and 1-mm. pressure gave m.p. 194–196° and a positive tetranitromethane test; $\nu_{\max}^{\text{KBr}}$ 3472, 1727, 1638 cm.$^{-1}$; n.m.r., δ 0.62, 1.15, 1.22, 1.33, 3.58, 3.60, 3.67, 5.0 (disappears with deuterium oxide), and 5.70 (doublet, 11 c.p.s.).

Anal. Calcd. for $C_{27}H_{40}O_7 \cdot H_2O$: C, 65.56; H, 8.55. Found: C, 65.83; H, 8.33.

Reaction of IX with Phosphorus Oxychloride.—A solution prepared by dissolving 0.132 g. of IX in 5 cc. of pyridine and 1 cc. of phosphorus oxychloride was heated on the steam bath for 4 hr., then allowed to stand at room temperature for 12 hr. The reaction mixture was diluted with water and then extracted with ether. The ether extract was washed with dilute hydrochloric acid, then with water, and finally dried over anhydrous sodium sulfate. Removal of the solvent yielded 0.070 g. of a glassy product which resisted attempts at crystallization. The infrared spectrum of this material showed no O–H absorption and gave $\lambda_{\max}^{\text{EtOH}}$ 240 mμ (log ϵ 3.84). Reported for diene III, $\lambda_{\max}$ 240 mμ (log ϵ 4.25).

Compound X.—Compound X, eluted from alumina with 15% ether–85% benzene, had m.p. 264–265° after recrystallization from benzene–*n*-hexane and drying for 10 hr. at 60° and 1 mm., and gave a negative test with tetranitromethane; $\nu_{\max}^{\text{KBr}}$ 3401, 1739, 1718, and 1691 cm.$^{-1}$; n.m.r., due to the small size of sample available, a strong spectrum could not be obtained, but there were no signals at field higher than δ 1.0.

Anal. Calcd. for $C_{26}H_{38}O_7$: C, 67.50; H, 8.28. Found: C, 67.43; H, 8.01.

The Acid Fraction. Isolation of Tetraesters XIIa and XIIIa.—The glassy acidic fraction (4.52 g.) obtained as described earlier was treated with an excess of an ethereal solution of diazomethane. After the usual work-up, the crude ester mixture (4.7 g.) was chromatographed directly on 200 g. of neutral activated alumina. Crystallization of the glassy fraction, eluted with 10% ether–90% benzene, gave 160 mg. of XIIa, m.p. 155–156° (lit.[3] m.p. 152–153°); $\nu_{\max}^{\text{KBr}}$ 1724, 1709 and 1634 cm.$^{-1}$; n.m.r., δ 0.50 (3), 1.10 (3), 3.57 (3), 3.64 (3), 3.70 (3), 3.74 (3), and 6.93 (1). The remainder of the noncrystalline material eluted from the column was rechromatographed on neutral alumina. Elution with ether–benzene and crystallization from benzene–hexane gave an additional 60 mg. of pure XIIa and 340 mg. of pure XIIIa. Recrystallization of XIIIa from *n*-hexane–benzene gave m.p. 177–178°; $\nu_{\max}^{\text{KBr}}$ 1754, 1712, and 1628 cm.$^{-1}$; n.m.r., δ 0.53 (3), 1.11 (3), 3.49 (3), 3.52 (3), 3.64 (3), 3.75 (3), and 6.92 (1).

Anal. Calcd. for $C_{26}H_{36}O_8$: C, 65.52; H, 7.61. Found: C, 65.93; H, 7.68.

The rest of the material eluted in the chromatography could not be crystallized. Infrared spectra of the noncrystalline fractions indicated the presence of hydroxyl-containing compounds and γ-lactones.

Preparation of XIIa and XIIIa by Alkaline Isomerization.—A solution prepared by mixing 40 mg. of XIIIa, 5 cc. of methanol, and 10 cc. of 2 *N* sodium hydroxide was refluxed for 8 hr. The cold reaction mixture was diluted with 50 cc. of water, acidified with dilute hydrochloric acid, and extracted with ether. The ether layer, after drying over anhydrous sodium sulfate, was concentrated to give a white solid, which was immediately esterified with a solution of diazomethane in ether. Evaporation of the ether and crystallization of the residue from ether–*n*-hexane gave 34 mg. of XIIa, m.p. 155–156° identical in all respects with that obtained as already described.

Preparation of XIIa from IIa by the Haloform Reaction.—Using the procedure reported by Ruzicka and Kaufmann[3] ketone IIa was oxidized with sodium hypobromite. The crude acid product was esterified directly with ethereal diazomethane to yield XIIa, m.p. 155–156°, m.m.p. 155–156° (lit.[3] m.p. 152–153°), identical in all respects with XIIa isolated as described earlier.

Alkaline Isomerization of Ia. Preparation of Ib.—A solution prepared by dissolving 0.30 g. of Ia in 10 cc. of methanol and 25 cc. of 2 *N* sodium hydroxide, was refluxed for 10 hr., then cooled, diluted with 150 cc. of water, acidified with dilute hydrochloric acid, and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, and concentrated to give the crystalline acid. Recrystallization from aqueous acetic acid gave m.p. 252–253°, with previous melting at 190–210°, followed by resolidification.[12] This substance was identical in mixture melting point and infrared spectrum with the product obtained from the Diels–Alder reaction of abietic acid and fumaric acid.[12]

Treatment of the acid with ethereal diazomethane gave Ib as a viscous gum which could not be crystallized. The n.m.r. spectra of Ia and Ib were almost identical, the C-10 methyl protons appearing at δ 0.60, and the C-14 vinylic proton at δ 5.34.

---

(12) L. H. Zalkow and M. L. Corser, *Proc. Oklahoma Acad. Sci.*, **42**, 190 (1962).