

Oxidative Degradation of Resin Acids¹

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Lemieux oxidation of **1b** afforded **3b** in 50% yield, but the Lemieux oxidation of **2b** gave varying yields of **4b** and **5**. Procedures for the exhaustive ozonolysis of **1b** and **2b** have been standardized to afford the important synthetic intermediates, **3b** and **4b**, in 55–60% yields. Partial ozonolysis of **1b** afforded **6**, **8a**, and **10a**. The evidence for structures **8a** and **10a** is presented. RuO₄-NaIO₄ oxidation of **6**, **1b**, and **2b** gave **3b**, **3b**, and **4b** in excellent yields.

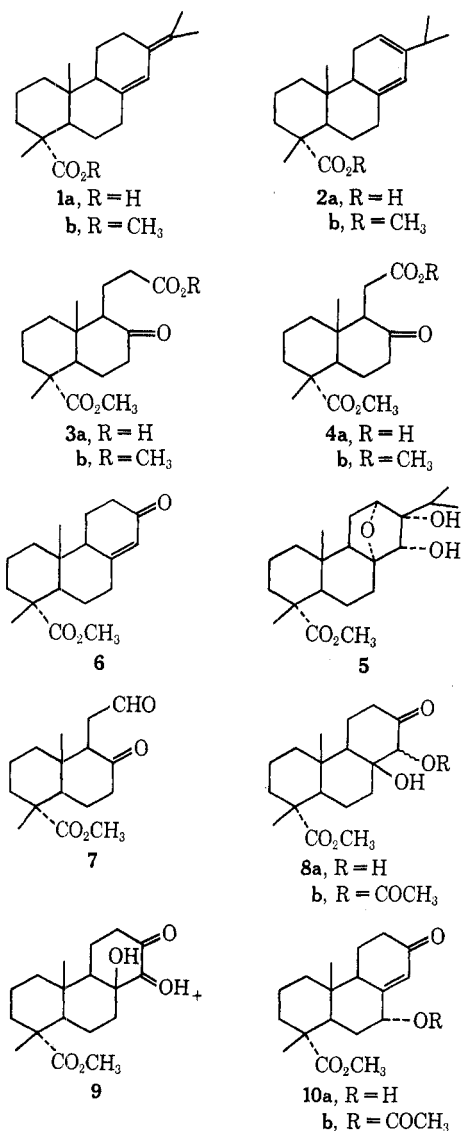
Chemical degradation products of resin acids have proven useful in elucidating the stereochemistry of certain natural products possessing the resin acids A/B ring stereochemistry.² A study of the biosynthesis of resin acids necessitated the development of efficient degradation procedures which could eventually be utilized to locate the labeled atoms in the radioactive resin acids. The quest for a simple method of effecting a one-step cleavage of the conjugated diene system in neobietic acid (**1a**) and levopimaric acid (**2a**) to obtain the important bicyclic keto acids **3a** and **4a**, prompted

us to carry out a systematic investigation of the oxidative degradation of resin acids.

Since the Lemieux-von Rudloff oxidation³ of the enone ester **6** afforded the keto acid ester **3a** in 84% yield,⁴ we were encouraged to study the reaction conditions best suitable for oxidizing **1b** and **2b**. While our work was in progress, Apsimon and coworkers reported⁵ the Lemieux-von Rudloff oxidation of nonconjugated vinyl groups of methyl pimarate and methyl sandaracopimarate. Treatment of **1b** with potassium permanganate-sodium metaperiodate and aqueous dioxane for 48 hr afforded the keto acid ester **3a** in about 50% yields. When **2b** was subjected to the above treatment, varying yields of **4a** and **5**⁶ were obtained. Although the dihydroxy oxide **5** can be converted to **4a** by using Jones reagent, the tedious purification required for the dioxane (see Experimental Section) and the varying yields of the keto acid ester **4a**, suggested a reinvestigation of the ozonolysis of **1b** and **2b**.

Exhaustive ozonolysis of **1b** in ethyl acetate at -70°, followed by work-up according to the procedure of Bailey,⁷ afforded an oil, which on Jones oxidation⁸ gave an acidic fraction in consistent yields of 60–65%. Methylation of this acid fraction with ethereal diazomethane and column chromatography over silica gel afforded the pure keto diester **3b** in 55% yield as a pale yellow oil, C₁₈H₂₈O₅: ν_{\max} 1730 and 1710 cm⁻¹; nmr (CDCl₃) τ 6.3 and 6.33 (two carbomethoxyls), 7.5–7.8 (C-7 methylene), 8.86 (C-4 methyl), and 9.2 (C-10 methyl).

Earlier workers in this laboratory had reported⁹ that drastic ozonolysis of **2b** gave the keto acid ester **4a** in yields varying from 20–45%. However, ozonolysis of **2b** in ethyl acetate at -70°, followed by work-up of Bailey and Jones oxidation, gave an acidic fraction in consistent yields of 60–70%. The acid fraction could be crystallized with some difficulty to afford the pure keto acid ester **4a**, mp 173–175°, but it was easier to purify the acid fraction by methylation with diazomethane and column chromatography over silica gel. The pure keto diester **4b** was obtained in 57–60% yields as a pale yellow oil, C₁₇H₂₆O₅: ν_{\max} 1735 and 1710 cm⁻¹; nmr (CDCl₃) τ 6.29 and 6.32 (two carbomethoxyls), 7.5–7.9 (C-7 methylene), 8.78 (C-4 methyl), and 9.24 (C-10 methyl).



(1) S. W. Pelletier, K. N. Iyer, C. W. J. Chang, and A. Ogiso, *Tetrahedron Lett.*, **35**, 3819 (1968).

(2) See, e.g., K. W. Gopinath, T. R. Govindachari, P. C. Parthasarathy, and N. Vishwanathan, *Helv. Chim. Acta*, **44**, 1040 (1961).

(3) R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).

(4) A. Ogiso and S. W. Pelletier, *Chem. Commun.*, 94 (1967).

(5) J. W. ApSimon, A. S. Y. Chau, W. G. Craig, and H. Krehm, *Can. J. Chem.*, **45**, 1439 (1967).

(6) H. Kanno, W. H. Schuller, and R. V. Lawrence, *J. Org. Chem.*, **31**, 4138 (1966).

(7) P. S. Bailey, *J. Amer. Chem. Soc.*, **78**, 3811 (1956).

(8) K. Bowden, I. M. Hellbron, E. R. H. Jones, and C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(9) S. W. Pelletier, L. B. Hawley, Jr., and K. W. Gopinath, *Chem. Commun.*, 96 (1967).

When the Jones oxidation step is omitted, the yields of **3b** and **4b** are lowered and this decrease in yield is more pronounced in the case of **4b**. It appears that one of the products of ozonolysis may be the ketoaldehyde ester **7** which would afford **4a** on Jones oxidation.

Partial ozonolysis of **1b**, which has been reported¹⁰ to give the enone ester **6** in yields varying from 37–55%, afforded a viscous yellow oil. Purification of this oil by column chromatography over Florisil and preparative thick layer chromatography over silica gel gave the desired enone ester **6**, mp 127–128°, and two more polar products, compounds A and B, respectively.

Efforts to improve the yields of **6** using either potassium iodide–sodium thiosulfate,⁷ or methyl sulfide¹¹ to decompose the ozonide succeeded in affording consistent yields of 60–65% of **6** and the amounts of compounds A and B were significantly reduced.

Compound A [mp 173–174°; $[\alpha]_D$ 11.5°; $C_{18}H_{28}O_5$; ν_{\max} 3525, 3470, 3405, 1740, and 1728 cm^{-1} ; nmr τ 8.94, 8.76 (two C methyls), 6.22 (carbomethoxyl), and 6.15 (one proton on a carbon bearing a hydroxyl group)] exhibited a major peak in its mass spectrum at m/e 323 ($M - 1$) attributable to the stable oxonium ion¹² **9**. The spectral data coupled with the fact that acetylation of compound A afforded only a monoacetate [mp 256–259°; $C_{20}H_{30}O_6$; ν_{\max} 3460, 1755, 1735, 1724, and 1240 cm^{-1}] prompted us to assign structure **8a** to compound A, which may have been formed by epoxidation of the C_8 – C_{14} double bond of **1b**, cleavage of the isopropylidene moiety, and opening of the epoxide. Epoxidation of double bonds during ozonolysis and subsequent opening of the epoxide has ample precedence.¹³

Compound B crystallized from ether–hexane as long needles, mp 153–154°, and exhibited ν_{\max} 3440, 1705, 1680, 1640, 1620, and 1260 cm^{-1} , indicating the presence of a hydroxyl group and a conjugated ketone, whereas the ultraviolet absorption at 241 $m\mu$ and its high extinction coefficient (14,500) suggested the presence of basic enone structure in **6**. That hydroxylation may have occurred at either of the allylic positions at C-7 or C-9 was suggested by an elemental analysis corresponding to a $C_{18}H_{26}O_4$ formula. Evidence for the hydroxyl function at C-7 was obtained from the nmr spectrum, which showed a 1 H doublet at τ 4.03 ($J = 2.5$ cps) attributable to an α proton on a $>C=C-C(=O)-$ function, the hydroxyl proton at τ 5.43 which was successfully exchanged upon deuteration, and the proton geminal to the hydroxyl as a 1 H triplet at τ 5.65. The three proton singlets at τ 9.15, 8.77, and 6.28 could be rationally ascribed to the C-10 methyl, C-4 methyl, and the C-4 carbomethoxyl, respectively. Further evidence for the secondary nature of the hydroxyl group was obtained from the acetate which was obtained under mild conditions, and the nmr spectrum of the acetate which showed a triplet at τ 4.57 ($J = 3$ cps) assignable to the proton geminal to the acetate group. In addition, compound B, which has a deshielded C-14 olefinic proton (τ 4.03) relative to that of **6** (τ 4.31),

has its C-14 proton further downfield (τ 3.92) in the acetate.

Sarett oxidation of compound B gave an oil which exhibited absorption in the ultraviolet at ν_{\max} 261 $m\mu$ characteristic of an emicisoid enedione moiety.¹⁴ On the basis of all this evidence, we propose structures **10a** and **10b** for compound B and its acetate, respectively. Compound B may have arisen from **1b** by an allylic hydroxylation during ozonolysis and work-up. The stereochemistry of the hydroxyl group has been deduced from the nmr spectra of **6**, **10a**, and **10b**. Dreiding models show that the hydroxyl group, with an α -axial configuration has its geminal equatorial proton coupling with the C-6 methylene protons which form dihedral angles of 60° with respect to the C-7 proton. The observed coupling constant of 3 cps does not favor a β -equatorial hydroxyl configuration since an axial C-7 H, axial C-6 H vicinal coupling of 8–14 cps was not observed in the nmr spectrum.

A recent paper by Caspi, *et al.*,¹⁵ utilizing ruthenium tetroxide–sodium metaperiodate in aqueous acetone for the efficient degradation of α,β -unsaturated and cross-conjugated ketones to the corresponding keto acids in high yields prompted us to investigate the utility of this reagent for the oxidative degradation of **6**, **1b**, and **2b**. The RuO_4 – $NaIO_4$ oxidation of **6** proceeded smoothly to afford the keto acid ester **3a** in yields of about 80%. As mentioned previously, it was easier to purify the product as the keto diester **3b**. Oxidation of **1b** and **2b** afforded the keto diesters **3b** and **4b** in 70–77% yield. However, owing to the rather high cost of the ruthenium dioxide used and the tedious work-up, ozonolysis appears to be method of choice for degradation of **1b** and **2b** to the keto acid esters **3a** and **4a**, respectively, on a preparative scale.

Experimental Section

General Procedures.—Melting points are corrected and were taken on a hot stage equipped with a microscope and polarizer. Finely powdered samples were placed on the stage 15° below the melting point and the temperature was raised at a rate of about 4°/min. Ultraviolet spectra were determined in 95% ethanol on a Perkin-Elmer Model 202 spectrophotometer and infrared spectra on Perkin-Elmer Model 137, 237, or 457 spectrophotometers. Nuclear magnetic resonance (nmr) spectra were taken on Varian A-60 or HA-100 spectrometers in deuteriochloroform, unless otherwise stated, with tetramethylsilane as an internal standard. Ozonolyses were carried out using a Welsbach Model T-23 laboratory ozonator. Optical rotations were taken on a Perkin-Elmer Model 141 polarimeter. Gas phase chromatography was conducted using a Varian Aerograph 1520 chromatograph. The columns used were 4% QF-1 and 5% SE-30.

Purification of Dioxane.—After commercial dioxane had been purified according to the procedure outlined by Fieser,¹⁶ the purified dioxane was treated at room temperature with small amounts of aqueous potassium permanganate till the solution was not decolorised. Considerable difficulty was encountered with certain batches of dioxane which consumed permanganate at a slow rate over several days and this method proved too tedious for practical use.

Lemieux Oxidation of the Enone Ester 6.—To a solution of 145 mg of the enone ester **6** in 50 ml of dioxane cooled at 15–20° was added a solution of 750 mg of $NaIO_4$, 50 mg of $KMnO_4$, and 25 mg of Na_2CO_3 in 30 ml of water. The mixture was stirred for 45 hr at room temperature. After excess reagent was decomposed by the

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(13) P. S. Bailey, *Chem. Rev.*, **58**, 945 (1958).

(14) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, London, 1964, p 61.

(15) D. M. Piatak, H. B. Bhat, and E. Caspi, *J. Org. Chem.*, **34**, 112 (1969).

(16) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, 1957, p 285.

careful addition of 5% H_2O_2 with ice cooling, the mixture was evaporated to remove the dioxane. The aqueous layer was extracted with chloroform followed by ether and both organic layers were extracted with 5% NaOH. The combined alkaline extract was acidified with concentrated HCl and extracted with ether. Evaporation of the ether gave an oil which was chromatographed on silica gel. Elution with chloroform gave 132 mg of an oil. The oil, the keto acid ester **3a**, and its methyl ester **3b** each showed a single spot on tlc with solvent systems of $CHCl_3$ -MeOH (10:1) and benzene-ethyl acetate (5:1), respectively. The keto acid ester **3a** could not be induced to crystallize. It showed ν_{max} ($CHCl_3$) at 3400-2900 broad, 1715, 1212, 1255 cm^{-1} . Its nmr spectrum showed singlets at τ 9.23, 8.80, and 6.28.

Oxidation of Methyl Neoabietate.—To a solution of methyl neoabietate, derived from 450 mg of neoabietic acid (253 $m\mu$, ϵ 25,600) by the standard methylation with diazomethane in ether, and 250 mg of sodium carbonate in 100 ml of dioxane and 20 ml of water was added a solution of 3.2 g of sodium metaperiodate and 150 mg of potassium permanganate in 50 ml of water at 15-20°. The mixture was stirred for 45 hr at room temperature. The reaction mixture should retain the color of permanganate during the reaction period. After excess reagent was decomposed by the addition of 5% hydrogen peroxide under ice cooling, almost all of the dioxane was evaporated *in vacuo*. The aqueous solution was acidified with concentrated hydrochloric acid and extracted with chloroform followed by ether. The organic layers were extracted with 5% sodium hydroxide. The organic layer was washed with water, dried over sodium sulfate, and evaporated to give 220 mg of a mixture of neutral compounds. The combined alkaline extract was washed with ether, acidified with concentrated hydrochloric acid, and extracted with ether thoroughly. The ether extract was washed with water, dried over sodium sulfate, and evaporated to give 320 mg of an oil. The acidic oil was chromatographed on 5 g of silica gel and elution with chloroform gave 235 mg of the pure keto acid ester **3**. The infrared spectrum and behavior of this product on thin layer chromatography were identical with that of the keto acid ester derived from the enone ester **6**.

Lemieux Oxidation of Methyl Levopimarate.—To a solution of methyl levopimarate (obtained from 500 mg of levopimaric acid) in 120 ml of purified dioxane containing 300 mg Na_2CO_3 , was added a solution of 4.9 g of $NaIO_4$ and 250 mg of $KMnO_4$ in 60 ml of water. The mixture was stirred at room temperature for 45 hr. Work-up as for the Lemieux oxidation of methyl neoabietate afforded an acid fraction (140 mg) and a neutral fraction (322 mg).

The acid fraction was methylated and the resulting oil was essentially homogeneous since an injected sample showed a single peak on vpc (4% QF-1). The dimethyl ester was passed through a column of silica gel and eluted with chloroform to afford the keto diester **4a** as a pale yellow oil (126 mg).

The neutral fraction consisted essentially of the dihydroxy ether **5**: mp 182-183°; ν_{max} (Nujol) 3400 (OH), 1725 (CO_2CH_3), 1075 (COC); τ 9.20 and 8.93 (isopropyl), 9.17 (C-10 Me), 6.66 (C-12 H), 5.93 (C-14 H).

Anal. Calcd for $C_{21}H_{34}O_5$: C, 68.82; H, 9.35. Found: C, 68.77; H, 9.32.

Oxidation of the Dihydroxy Oxide 5.—To a solution of 75 mg of the dihydroxy ether **5** in 1 ml of acetic acid was added a solution of 450 mg of lead tetraacetate in 10 ml of acetic acid and 1 ml of water. The solution was allowed to stand overnight at room temperature. The reaction mixture was poured into water and extracted with ether. The ether extract was washed with water, dried over Na_2SO_4 and evaporated to give an oil. The crude oil was oxidized with Jones' reagent to give 25 mg of the keto acid ester **4a**, which was separated by silica gel chromatography and identified by comparison with an authentic sample of **4a** as obtained previously.

Exhaustive Ozonolysis of Methyl Neoabietate.—In typical runs, 1-g batches of neoabietic acid¹⁷ in 25 ml of anhydrous ether were methylated with ethereal diazomethane and the solvent removed by flash evaporation. The resulting methyl ester **1b** in 25 ml of ethyl acetate was ozonized at -70° for 1 hr under the following conditions: 90 V, flow rate 0.02 ft³/min, 5-lb pressure.

The reaction flask was removed from the Dry Ice bath and allowed to come to room temperature. KI solution (10 ml, 1%) was added to decompose the ozonide and the reaction mixture was washed three times with saturated aqueous sodium thiosulfate and once with brine. The organic layer was separated and taken to dryness, and the residue dissolved in acetone. To the cooled

stirred solution, Jones' solution was added dropwise and the reaction was allowed to proceed for 1-2 hr.

Extraction with ether and separation into neutral and basic fractions with cooled 5% aqueous sodium hydroxide yielded neutral fractions weighing 0.28-0.41 g and acidic fractions comprising the keto acid ester **3a** weighing 0.63-0.77 g.

Generally, further purification by chromatography using silica gel (30 g) and chloroform elution was carried out. Homogeneity of the sample was checked by tlc on silica gel G with a solvent system consisting of 10% MeOH in $CHCl_3$ and by gpc of the dimethyl ester on 5% SE-30 and 4% QF-1 columns with a flame ionization detector.

Anal. Calcd for $C_{15}H_{23}O_5$: C, 66.64; H, 8.70. Found: C, 66.38; H, 8.92.

Exhaustive Ozonolysis of Methyl Levopimarate (2b).—An ethereal solution of 1 g of levopimaric acid was treated with ethereal diazomethane and the solvent was removed *in vacuo*. The resulting methyl ester **2b** in 25 ml of ethyl acetate was ozonized at -70° for 1 hr under the following conditions: 90 V, flow 0.02 ft³/min, 5-lb pressure.

The reaction flask was removed from the Dry Ice bath and allowed to come to room temperature, 10 ml of 1% KI was added to decompose the ozonide, and then the liberated iodine was removed by washing with sodium thiosulfate. The organic layer was washed with water (four 10-ml portions), dried (Na_2SO_4), and evaporated to dryness. The residue was dissolved in acetone, cooled to 0°, and treated with Jones reagent for 2 hr. Usual work-up followed by separation into acid and neutral fractions with cold 5% NaOH afforded neutral fractions weighing 0.26-0.35 g and acid fractions from 0.62-0.72 g.

The acid fraction was methylated with diazomethane and chromatographed over 20 g of silica gel. Elution with chloroform afforded the pure keto diester (0.57-0.61 g) as a pale yellow oil: ν_{max} 1738, 1710 cm^{-1} ; τ 6.29 and 6.32 (two carbomethoxyls), 7.5-7.9 (C-7 CH_2 -), 8.78 (C-4 Me), 9.24 (C-10 Me).

Anal. Calcd for $C_{17}H_{26}O_5$: C, 65.78; H, 8.44. Found: C, 65.61; H, 8.45.

Partial Ozonolysis of Methyl Neoabietate. Method A.—Four grams of neoabietic acid in 50 ml of anhydrous ether was methylated with diazomethane in ether. After evaporation to dryness the methyl ester **1b** in 75 ml of methylene chloride was subjected to ozonolysis at -70° under the following conditions: 90 V, flow 0.02 ft³/min, 6-lb pressure, 25 min.

The reaction mixture was allowed to come to room temperature, 5 g of powdered zinc and 25 ml of glacial acetic acid were added and the mixture was stirred for 2-3 hr. The zinc dust was collected and washed with methylene chloride, the filtrate carefully neutralized with aqueous saturated sodium bicarbonate and the layers separated. The organic layer was washed with brine and dried over anhydrous sodium sulfate. Evaporation to dryness gave an oil which on standing in ether gave successive crops of crystals of the enone ester **6**, totaling 0.88 g, mp 126-128° (lit.¹⁰ mp 127-128°).

The mother liquor was chromatographed on florisil eluting with chloroform. After the enone ester was eluted, the dihydroxy ketone **8a**, was collected and crystallized as fine needles from hexane-ether: mp 173-174°; $[\alpha]_D +11.5$; for ir and nmr see text. Prominent mass peaks occurred at M^+ 324 (16%) and m/e 323 (84%).

Anal. Calcd for $C_{18}H_{28}O_3$: C, 66.64; H, 8.70. Found: C, 66.33; H, 8.64.

The column was further eluted with 5% methanol in chloroform. The eluent was evaporated to give an oil which was spread on silica gel HF thick-layer plates (2 mm) and developed using 2% MeOH- $CHCl_3$. Separation of the less mobile band relative to the dihydroxy ketone **8a** and washing the adsorbent in a glass sintered funnel with ethyl acetate afforded the hydroxy-enone ester **10a** which crystallized from ether-hexane: mp 153-154°; $[\alpha]_D -101^\circ$ ($CHCl_3$); for nmr and ir see text; λ_{max} (EtOH) 241 $m\mu$ (ϵ 14,500).

Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.56; H, 8.55. Found: C, 70.63; H, 8.66.

Method B.¹⁸—Ozone was bubbled through a solution of methyl neoabietate (1 g) in 25 ml of ethyl acetate at -75° for 6 min. The reaction mixture was allowed to attain room temperature. The ozonide was decomposed by the addition of 25 ml of a 1% solution of potassium iodide and a few drops of acetic acid. The organic layer was then washed with a solution of sodium thiosul-

(17) V. M. Loeblich and R. V. Lawrence, *J. Org. Chem.*, **21**, 610 (1956).

(18) We thank Mr. S. W. Page for conducting these experiments.

fate, and then with brine. The sodium sulfate-dried organic extract afforded 1.048 g of an oil which was dissolved in 4 ml of chloroform and spread on a 4-mm thick 200 × 400 mm silica gel plate. Development of the plate with chloroform and visualization by a uv lamp showed 3 main bands. The least polar compound, the enone ester **6**, was obtained as a crystalline solid, mp 126–127°, in 65% yield. Compounds **8a** and **10a** were isolated in 3 and 0.6%, respectively.

Method C.¹⁸—The ozonolysis was conducted exactly as in method B but the ozonide was treated at –75° with 3 ml of methyl sulfide and the resulting mixture was stirred at room temperature for 3 hr. Removal of solvent afforded an oil (1.026 g) which on preparative thick layer chromatography afforded the enone ester **6**, mp 125–127°, in a 67% yield. Compounds **8a** and **10a** were found to be present in very small amounts (from tlc) and were not isolated.

Acetylation of the Ketodiol Ester (8a).—To an ice-cooled flask containing 40 mg of the ketodiol ester suspended in 1 ml of acetic anhydride (98%) was added 0.5 ml of pyridine (dried over KOH). After the diol had dissolved, the flask was removed from the ice bath and kept at room temperature for 17 hr. The crystals were collected, washed with water, and dried to give 30 mg of the monoacetate **8b**, mp 241–248°. The filtrate was extracted with ether and this fraction yielded an additional 10 mg, mp 247–253°.

The analytical sample was recrystallized from methylene chloride–carbon tetrachloride: mp 258–259°; ν_{\max} 3460 (OH), 1755 (ketone flanked by acetoxy), 1735 (ester), 1724, 1240 (acetate) cm^{-1} .

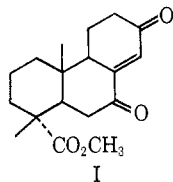
Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_6$: C, 65.55; H, 8.25. Found: C, 65.62; H, 8.39.

Acetylation of the Hydroxyenone Ester.—To 30 mg of hydroxy–enone ester **10a** dissolved in 0.6 ml of acetic anhydride (98%) and cooled in an ice bath was added 0.02 ml of pyridine. After standing overnight (22 hr) the mixture was poured onto ice. Extraction with ether and drying (Na_2SO_4) the ether extract, followed by evaporation to dryness *in vacuo* yielded an oil. Dry benzene was added and the oil was evaporated to dryness again to remove residual pyridine and acetic acid.

Preparative thick layer chromatography on silica gel HF, eluting with 2% $\text{MeOH}-\text{CHCl}_3$, gave the acetate–enone ester **10b** as the more mobile band. The acetate–enone ester **10b** obtained as an oil, 20 mg, was crystallized from hexane–ether: mp 143–144°; ν_{\max} (CCl_4) 1740, 1685, 1635, 1230 cm^{-1} ; nmr absorptions appeared at τ 9.12 (C-10 Me), 8.79 (C-4 Me), 6.31 (CO_2Me), 3.92 [doublet, $J = 25$ cps, $\text{C}=\text{CHC}(=\text{O})-$], 5.65 (triplet, $J = 3$ cps, $-\text{CHO}-$), 7.92 (OAc).

Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{O}_5$: C, 68.94; H, 8.10. Found: C, 68.95; H, 8.33.

CrO₃–Pyridine Oxidation of 10a.—A solution of 30 mg of **10a** in 1 ml of pyridine was added to a cooled solution of 35 mg of CrO_3 in 1 ml of pyridine and the reaction mixture was allowed to stand at room temperature for 18 hr. The reaction was terminated by the addition of 2 ml of 2 *N* sulfuric acid and 5 ml of a saturated solution of sodium bisulfite. The mixture was diluted with 25 ml of water and extracted with ether (five 10-ml portions). The ether extract was washed with water (three 5-ml portions), dried over sodium sulfate, and evaporated to dryness *in vacuo* to give an oil whose tlc showed the presence of starting material and a less polar compound. The less polar compound was obtained by preparative chromatography. The compound (5.5 mg) failed to crystallize, ν_{\max} 1735 and 1685 cm^{-1} , λ_{\max} 260 $\text{m}\mu$. On the basis of these spectral characteristics the oxidation product appears to be the enedione (**I**).



RuO₄–NaIO₄ Oxidation of the Enone Ester (6).—A solution of 500 mg of the enone ester **6** in 25 ml of acetone was added dropwise to a stirring yellow suspension of ruthenium tetroxide (generated by adding a solution of 1.0 g of sodium metaperiodate in 20 ml of water to a black suspension of 100 mg of ruthenium dioxide in 45 ml of acetone). Small portions of a solution of 4 g of NaIO_4 in 50 ml of aqueous acetone were added at periodic intervals when the reaction mixture turned dark in color. The reaction mixture was stirred at room temperature for 24 hr and the reaction was terminated by the addition of 15 ml of isopropyl alcohol. The dark colored mixture was filtered through a well-packed column (150 × 40 mm) of Celite 545. In later experiments we found that a column of sand worked efficiently. The column was washed well with 150–175 ml of acetone to ensure complete recovery of organic material. The clear filtrate and washings were combined and evaporated to dryness *in vacuo*. The residue was taken up in 100 ml of water and extracted five times with 30-ml portions of ether. The combined ether extract was washed with 5% sodium hydroxide (five 15-ml portions), and then with water six 20-ml portions). The ether extract was dried over sodium sulfate and evaporated to dryness *in vacuo* to afford a neutral fraction (48 mg) whose tlc indicated that it is a complex mixture.

The combined 5% NaOH extract was acidified with 6*N* hydrochloric acid and the product was taken up in ether (six 35-ml portions). The ether extract was washed with water (four 20-ml portions), dried over magnesium sulfate, and evaporated to dryness *in vacuo* to obtain the acidic fraction (476 mg). The acidic fraction was methylated with ethereal diazomethane and the resulting ester was purified by column chromatography using silica gel. The pure keto diester **3a** was obtained as a pale yellow oil (424 mg) identical in all respects with the product of exhaustive ozonolysis of **1b**.

RuO₄–NaIO₄ Oxidation of Methyl Neoabietate (1b).—A solution of 516 mg of methyl neoabietate in 30 ml of acetone was added dropwise to a stirring yellow suspension of RuO_4 (generated by adding a solution of 1.8 g of NaIO_4 in 20 ml of water to a black suspension of 200 mg of RuO_2 in 45 ml of acetone). The experiment was conducted as the oxidation of **6**. Usual work-up afforded pure **3b** in 72–75% yield. The neutral fraction (10–15%) was a complex mixture (from tlc) and was not investigated further.

RuO₄–NaIO₄ Oxidation of Methyl Levopimarate (2b).—The experimental conditions used were similar to those used in the oxidation of **1b**. Thus, 515 mg of **2b** afforded 76–79% of pure **4b** and 10–12% of a neutral fraction which was essentially the dihydroxy oxide **5**.

Registry No.—**1b**, 3310-97-2; **2b**, 3513-69-7; **3b**, 25594-16-5; **4b**, 25594-17-6; **5**, 25594-18-7; **8a**, 25594-19-8; **8b**, 25565-15-5; **10a**, 25594-20-1; **10b**, 25594-21-2.

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