

*Polyterpenes. IV¹⁾. The Oxidation Products of Thujopsene^{*1, *2}*

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As a result of a recent investigation by Erdtman and Norin²⁾, the sesquiterpene hydrocarbon thujopsene has been shown to possess structure I. In a previous communication³⁾ we described the isolation of the keto acid, together with four other degradation products of thujopsene formed by permanganate oxidation. Now using sodium bichromate these same products were again isolated. On the basis of structure I for thujopsene, we now wish to propose structures for these degradation products (II, III, IV and V)⁴⁾.

Acid II, $C_{15}H_{22}O_4$, on further permanganate oxidation, afforded IV, $C_{14}H_{22}O_5$ ⁵⁾, which was oxidized by sodium hypobromite to the known C_{13} -dicarboxylic acid VI¹⁾. The structure of

the latter was established by Erdtman and Norin²⁾.

Acid II did not show the ultraviolet absorption expected of an α -keto acid; furthermore, its infrared spectrum exhibited a hydroxyl band at 3300 cm^{-1} . However, on esterification a methyl ester was obtained which showed ultraviolet and infrared absorptions consistent with the structure VII ($R=Me$). It therefore appears that, in the solid state, diketo acid II exists in a lactone form. This confirmed by the presence of a band at 1761 cm^{-1} in its infrared spectrum. The compound is therefore formulated as VIII; the alternative structure of IX may be ruled out on the basis of the ultraviolet evidence.

Keto acid IV, on the basis of spectral evidence, exists as a pseudo acid and may therefore be formulated as X. This was confirmed by its dehydration to the enol lactone XI, which on subsequent hydrolysis regenerated the original compound X. The methyl ester of this pseudo acid showed spectral bands in agreement with the structure XII ($R=Me$).

The treatment of II with alkali gave a further acid III, also isolated by the direct oxidation of thujopsene; the assignment of structure III is based on the following reactions. Chromic acid oxidation of III gave the β -diketone XIII, which on further oxidation

1) Part III of this series: H. Kobayashi, S. Nagahama and S. Akiyoshi, *This Bulletin*, **34**, 1123 (1961).

*1 Contribution No. 24 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka.

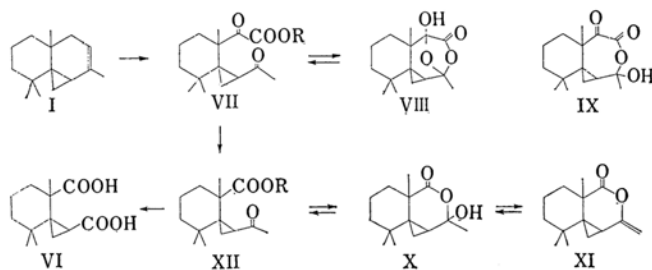
*2 The essential part of this paper was presented before the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

2) H. Erdtman and T. Norin, *Chem. & Ind.*, **1960**, 622; T. Norin, *Acta Chem. Scand.*, **15**, 1676 (1961).

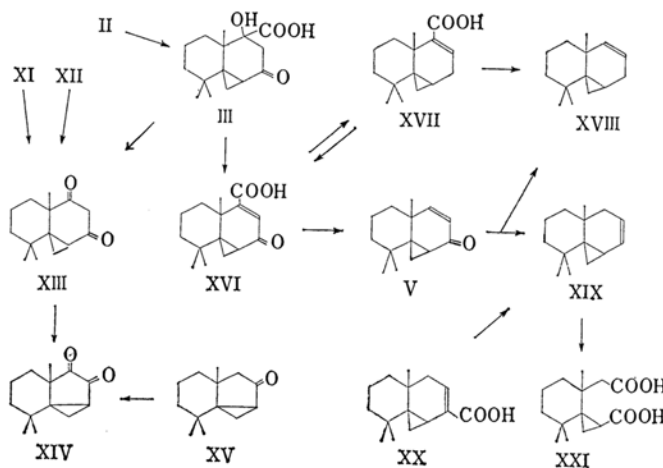
3) S. Akiyoshi and S. Nagahama, *This Bulletin*, **30**, 886 (1957).

4) These correspond to II, III, IV and V respectively in Part I³⁾. The same results for II, III and V have been reported by T. Nozoe et al., *Chem. Pharm. Bulletin*, **8**, 936 (1960).

5) Previously described as an oxyacid $C_{12}H_{14}O_5$ in Ref. 3.



Scheme 1



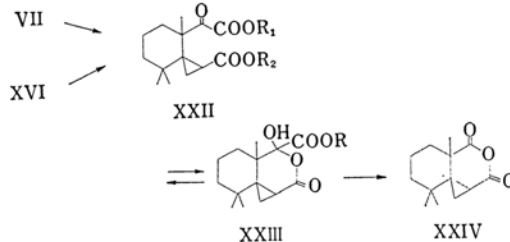
Scheme 2

afforded the yellow α -diketone XIV previously obtained from cycloketone XV¹². The β -diketone XIII was also obtained by treatment of the enol lactone XI or methyl ester XII ($R = \text{Me}$), with methanolic potassium hydroxide. The dehydration of III gave unsaturated keto acid XVI, $\text{C}_{15}\text{H}_{20}\text{O}_3$ ³², which on Huang-Minlon reduction gave the unsaturated acid XVII. XVII could be reoxidized back to XVI. The decarboxylation of XVI, using copper and quinoline, afforded the unsaturated ketone V⁶², which was also obtained by direct oxidation of thujopsene. The Huang-Minlon reduction of V gave a mixture of the two hydrocarbons XVIII and XIX. Compound XVIII was also obtained by the decarboxylation of XVII, whereas hydrocarbon XIX was formed by the decarboxylation of hinokiic acid XX. The oxidation of XVIII with potassium permanganate gave C_{13} -dicarboxylic acid VI, and that of XIX, the known C_{14} -dicarboxylic acid XXII.

Acid II and methyl ester VII ($R = \text{Me}$), on oxidation with sodium hypobromite, gave a dicarboxylic acid formulated as XXII ($R_1 =$

$R_2 = \text{H}$). Different samples of the latter compound, however, exhibited different infrared spectra; this may perhaps be attributed to varying proportions of a lactonoid form such as XXIII ($R = \text{H}$). On methylation, these samples all gave the same dimethyl ester XXII, ($R_1 = R_2 = \text{Me}$).

The acid XXII, ($R = \text{H}$) was also obtained by the ozonolysis of XV and, on chromic acid oxidation, it gave anhydride XXIV corresponding to C_{13} -acid VI.



Scheme 3

The bichromate oxidation of ester VII ($R = \text{Me}$) gave an acid product $\text{C}_{15}\text{H}_{22}\text{O}_5$, m. p. 190°C . Its infrared spectrum showed bands at 3322, 1762 and 1712 cm^{-1} . Therefore, it might be represented by XXIII ($R = \text{Me}$), rather than by XXII ($R_1 = \text{Me}$, $R_2 = \text{H}$). Attempted chromic

6) This derivation was first reported by T. Ozeki, S. Seto and T. Nozoe, at the First Symposium on Perfumery, Terpene and Essential Oil Chemistry, Osaka, November, 1957.

acid oxidation of the dimethyl ester XXII ($R_1=R_2=Me$) gave the same product.

Experimental

Permanganate Oxidation of Thujopsene.—An ice-cooled mixture of thujopsene (100 g.) and acetone (400 cc.) was oxidized with finely powdered permanganate (250 g.).

Separation of Acid Products.—The acid part was obtained as an oil or semisolid. When benzene was added to it, acid III, if produced during separation, was precipitated. The benzene extract was concentrated and ketonic acid was crystallized on cooling. The mother liquor was diluted with petroleum ether and cooled in a refrigerator for several weeks or more, giving acids II and IV. After the second or third crop was obtained, the remaining acid II was converted to acid III, which was easily separable, by treating it with alkali for two or three days.

Separation of Neutral Products.—About 750 g. of the neutral part was obtained by several runs; it was separated in 5 fractions by distillation. (The yields in this paragraph are shown as percentage of the whole neutral part.) Fraction 1 (b. p. $\sim 119^\circ\text{C}/11\text{ mmHg}$, n_D^{20} 1.5030 \sim 1.5050 28.4%) was mainly unreacted thujopsene containing a small number of isomerized hydrocarbons. Fraction 2 (b. p. $119\sim 130^\circ\text{C}/11\text{ mmHg}$, n_D^{20} 1.5057 \sim 1.5090, 5.9%) was redistilled, and the fraction of maximum refractive index (b. p. $95\sim 100^\circ\text{C}/6\text{ mmHg}$, n_D^{20} 1.5097, 1.6%) was chromatographed on an alumina column. Petroleum ether eluate was hydrocarbon (0.9%), n_D^{20} 1.5111, d_4^{20} 0.9245, $[\alpha]_D^{20} +40.4^\circ$, IR, 1515, 812 cm^{-1} . From a benzene eluate, cycloketone XV was obtained. Fraction 3 (b. p. $130\sim 143^\circ\text{C}/11\text{ mmHg}$, n_D^{20} 1.5018 \sim 1.5030, 5.8%) was redistilled, and the fraction of minimum refractive index (b. p. $125^\circ\text{C}/6\text{ mmHg}$, n_D^{20} 1.4987, 1.5%) was chromatographed. The petroleum ether eluate was a mixture of ketones; one of them was separated as semicarbazone, m. p. $205\sim 206^\circ\text{C}$ (decomp.).

Found: C, 69.21; H, 9.80; N, 15.40. Calcd. for $\text{C}_{16}\text{H}_{27}\text{ON}_3$: C, 69.27; H, 9.81; N, 15.15%.

Another impure semicarbazone, m. p. $201.5\sim 202.5^\circ\text{C}$ (decomp.), was obtained from the mother liquor. Cycloketone XV was obtained successively, and benzene eluate gave a crystalline alcohol, $\text{C}_{15}\text{H}_{26}\text{O}$ m. p. $85.5\sim 86^\circ\text{C}$, which was identified as cedrol by infrared spectrum and mixed melting point tests with an authentic specimen⁷. When petroleum ether was added to the ethyl acetate eluate and the mixture was cooled, it was partly crystallized. This was filtered quickly and recrystallized from petroleum ether, giving crystals of m. p. $116\sim 117.5^\circ\text{C}$ IR, 3330 and 1740 cm^{-1} .

Found: C, 76.27; H, 10.28. Calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_2$: C, 76.22; H, 10.24%.

A similar treatment of fraction 4 (b. p. $143\sim 165^\circ\text{C}/10\text{ mmHg}$, n_D^{20} 1.5060 \sim 1.5100, 18.2%) gave 0.4% of V from petroleum ether and benzene eluate. Ethyl acetate eluate gave an oxyketone, m. p. $68\sim 70.5^\circ\text{C}$, (0.5%) IR, 3384, 3195 and 1702 cm^{-1} (Nujol).

Found: C, 76.15; H, 10.46. Calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_2$: C, 76.22; H, 10.24%.

Semicarbazone of the oxyketone, m. p. 214°C (decomp.).

Found: C, 65.31, 65.37; H, 9.29, 9.24; N, 14.23, 14.31. Calcd. for $\text{C}_{16}\text{H}_{27}\text{O}_2\text{N}_3$: C, 65.49; H, 9.28; N, 14.32%.

Methanol eluate gave a lactone, m. p. $81.5\sim 82.5^\circ\text{C}$ (1.4%) IR, 1795 cm^{-1} .

Found: C, 72.13; H, 8.87. Calcd. for $\text{C}_{15}\text{H}_{22}\text{O}_3$: C, 71.97; H, 8.86%.

Fraction 5 (b. p. $165\sim 180^\circ\text{C}/10\text{ mmHg}$ n_D^{20} 1.5178, 3.3%) gave only ketone V (0.7%) as a crystalline substance.

Bichromate Oxidation of Thujopsene.—Into a mixture of thujopsene (100 g.) and acetic acid (200 g.), a solution of sodium bichromate (250 g.) in acetic acid (750 g.) was stirred drop by drop over a period of nine hours, and the temperature was kept at $50\sim 70^\circ\text{C}$. After the solution had been left standing overnight, about 250 g. of acetic acid was distilled. The remainder was poured into water (3 l.) and extracted with benzene. The acid part was separated and treated as above. Benzene was removed, and the residue was distilled in vacuo. The fraction of b. p. $140\sim 146^\circ\text{C}/11\text{ mmHg}$ (28 g.) deposited crystals which were identified as ketone V (4.1 g.). The mother liquor was chromatographed on an alumina column, giving ketone V (4.0 g.) and oxyketone (0.2 g.). The results are summarized in Table I.

Oxidation of Acid II.—An acetone solution of II (280 mg. in 15 cc.) was treated with potassium permanganate (420 mg.) in acetone (40 cc.) below 50°C . The reaction mixture was treated in the usual manner, and the product was recrystallized from benzene-petroleum ether or ethanol-water; melting point and mixed melting point with IV, $154.5\sim 156^\circ\text{C}$.

Bichromate Oxidation of Acid IV.—IV (270 mg.) was dissolved in acetic acid (5 cc.), and a solution of sodium bichromate (500 mg.) in acetic acid (5 cc.) was added. The mixture, after being left overnight, showed no color change. Diluted sulfuric acid (5 cc.) was added, and the mixture was left for 2 days. The excess bichromate was decomposed with ethanol, the mixture was diluted with water, and the product was taken into an ether phase. The residue remaining after evaporation of the ether was triturated with benzene, affording a benzene insoluble product (45 mg.) which was identified as C_{13} -dicarboxylic acid VI m. p. $183\sim 185^\circ\text{C}$ (decomp.).

Found: C, 64.94; H, 8.40. Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_4$: C, 64.98; H, 8.39%.

From the benzene solution, the unchanged IV was recovered.

Hypobromite Oxidation of Acid IV.—IV (500 mg.) was treated with a hypobromite solution, and carbon tetrabromide (400 mg.) was isolated. Working up of the acid products afforded C_{13} -diacid VI (100 mg.).

Methyl Ester of Acid II (VII, $R=Me$) and its Saponification.—The methyl ester of II was prepared with diazomethane, m. p. $85\sim 87^\circ$ (from petroleum ether), $[\alpha]_D^{25} -187^\circ$ (c 0.593, ethanol).

⁷ The authors are indebted to Ogawa Perfumery Co., Osaka, for an authentic sample of cedrol.

TABLE I

Substance	Formula	M. p. °C	[α] _D	Yield (g. from 100 g. of thujopsene)	
				KMnO ₄ oxid.	Na ₂ Cr ₂ O ₇ oxid.
Acid part					
Keto acid	C ₁₅ H ₂₄ O ₃	165	−120°	10	0.2
II	C ₁₅ H ₂₂ O ₄	124	− 28.0°	3.5	2.0
III	C ₁₅ H ₂₂ O ₄	193 (d)	+ 21.6°	4.9	0.4
IV	C ₁₄ H ₂₂ O ₃	156	− 85.5°	0.3	4.0
Neutral part					
V	C ₁₄ H ₂₀ O	77	+193.5°	0.6	8.1
Oxyketone	C ₁₅ H ₂₄ O ₂	70.5		0.2	0.2
Lactone	C ₁₅ H ₂₂ O ₃	82.5		0.7	
XV	C ₁₃ H ₂₀ O	121		Trace	
Ketone	C ₁₅ H ₂₄ O ₂	117.5		Trace	

Found: C, 68.41; H, 8.85. Calcd. for C₁₆H₂₄O₄: C, 68.54; H, 8.63%.

When the ester was treated with methanolic potassium hydroxide, acid III was obtained.

Isomerization of Acid II to Acid III.—A solution of II in a 5% sodium hydroxide solution was left at room temperature overnight. Acidification and working up in the usual manner gave III. From ethanol or ether solution of II containing hydrogen chloride, only the starting material was recovered.

Huang-Minlon Reduction of Acid XVI.—A mixture made from XVI (2.55 g.), hydrazine hydrate (2 cc.), potassium hydroxide (2.5 g.), and diethylene glycol (25 cc.) was refluxed for 4 hr. The reaction mixture was diluted with water and acidified, giving precipitates (XVII, 1.54 g.) which were recrystallized three times from ethanol, m. p. 171~172°, [α]_D²⁰ -21.2° (c 1.19 chloroform).

Found: C, 76.82; H, 9.53. Calcd. for C₁₅H₂₂O₂: C, 76.88; H, 9.46%.

This shows a marked melting point depression when mixed with hinokiic acid (XX).

Permanganate Oxidation of Acid XVII.—To a solution of XVII (186 mg.) in a 3% potassium hydroxide solution (4 cc.), a 2% potassium permanganate solution (10 cc.) was added. The mixture was stirred for 1.5 hr. and was then treated with sodium bisulfite after acidification. The precipitate was recrystallized from ethanol-water, giving acid XVI, melting point and mixed m. p. 206°C and superimposable infrared spectra.

Found: C, 72.59; H, 8.14. Calcd. for C₁₅H₂₀O₃: C, 72.55; H, 8.12%.

Permanganate Oxidation of Hinokiic Acid (XX).—Hinokiic acid (2.4 g.) was dissolved in acetone (20 cc.) and treated with permanganate (5.0 g.) in acetone for 1.5 hr. The acetone was removed, and the remainder was dissolved in ether and extracted with a sodium bicarbonate solution. The neutral part crystallized (120 mg.) was identified as C₁₃-anhydride XXIV. From the acid part, C₁₄-diacid XXI (200 mg.), m. p. 206~211°C, was separated. The mother liquor was treated with diazomethane, giving a product (1.03 g.) which was absorbed onto an alumina column. Elution with petroleum ether-benzene (1:1) afforded C₁₃-diacid dimethyl ester (165 mg.).

Decarboxylation of Hinokiic Acid (XX), Acid XVII and Acid XVI.—A mixture of hinokiic acid (1.05 g.), copper powder (1.05 g.) and quinoline (10 cc.) was heated in a distillation flask at 230~250°C for 2 hr. The copper was removed and the filtrate, combined with the distillate, was diluted with ether and extracted with hydrochloric acid. The ether layer was washed with a sodium bicarbonate solution and water, and, after it was dried over potassium carbonate the ether was removed. The solid residue (320 mg.) was distilled in vacuo, and the distillate was recrystallized from methanol three times, m. p. 47°C, [α]_D²⁰ -135° (c 0.933 ethanol) (XIX).

One gram of acid XVII was treated similarly and afforded an oily product (XVIII), n_D^{20} 1.5042, [α]_D²⁰ -114° (c 0.957 ethanol), which solidified on cooling, m. p. 12~14°C.

Treatment of acid XVI in a similar manner gave ketone V.

Huang-Minlon Reduction of Ketone V.—Ketone V (5 g.) was reduced with a mixture of hydrazine hydrate (3.3 cc.), potassium hydroxide (4.8 g.), and diethylene glycol (50 cc.). The waxy product was recrystallized several times from methanol, using a methanol-dry ice mixture as a cooling agent, m. p. 33~35°C, (2.85 g.). This was shown to be a mixture of XVIII and XIX by the infrared spectrum.

Permanganate Oxidation of Hydrocarbon XVIII and XIX.—To a solution of XIX (550 mg.) in acetone (10 cc.), a solution of permanganate (2 g.) in acetone (50 cc.) was added; the mixture was then stirred for 1.5 hr. below 40°C. After being left overnight, it was worked up as usual. The product was recrystallized from ethanol-water, m. p. 210~211.5°C, (60 mg.). Admixture with authentic C₁₄-diacid (XXI, m. p. 209.5~210.5°C) showed m. p. 210~211°C.

A similar treatment of XVIII (710 mg.) gave C₁₃-diacid VI, (170 mg.).

Permanganate Oxidation of Acid XVI.—XVI (290 mg.) was oxidized in an alkaline permanganate solution in the usual manner. From the neutral part, C₁₃-anhydride XXIV (76 mg.) was obtained and recrystallized three times from petroleum ether, m. p. 211~212°C.

Found: C, 70.42; H, 8.59. Calcd. for C₁₃H₁₈O₃: C, 70.24; H, 8.16%.

Permanganate Oxidation of Ketone V.—To ketone V a solution of permanganate (4.27 g.) in water (100 cc.) was added. The oxidation was allowed to proceed for 2.5 hr. below 70°C, and the product was then treated as usual. The acid part contained C₁₃-diacid VI (90 mg.), and the neutral part, the corresponding anhydride (XXIV) m. p. 206~207°C (165 mg.).

Bichromate Oxidation of Acid III.—To a mixture of III (30 g.) and acetic acid (450 cc.) (not a complete solution) a solution composed of sodium bichromate (12 g.) and acetic acid (50 cc.) was added; the mixture was left at room temperature for one week. The insoluble material (7.84 g.) was identified to be the starting material, m. p. 205.5~207°C (decomp.). The filtrate was concentrated to about 1/3 of the original volume and was poured into water (1 l.). The precipitate filtered and triturated with hot benzene gave an insoluble product which was recrystallized from ethanol to give XIII, m. p. 218~221°C (4.0 g.), $[\alpha]_D^{25} +272^\circ$ (c 0.93, ethanol).

Found: C, 75.91; H, 9.12. Calcd. for C₁₄H₂₀O₂: C, 76.32; H, 9.15%.

The benzene extract contains a mixture of yellow diketone XVI and C₁₃-diacid anhydride XXIV. From the acid part, C₁₃-diacid VI (440 mg.) was obtained. The amount of sodium bichromate (20 g.) relative to III (15 g.) was increased and the yield of XIII was diminished, but a larger amount (8 g.) of a mixture of XIV and XXIV was obtained.

Bichromate Oxidation of Diketone XIII.—XIII (1.34 g.) was dissolved in acetic acid (40 cc.), and a solution of sodium bichromate (1.75 g.) in acetic acid (10 cc.) was added. The mixture was kept below 50°C for 5 hr., and then concentrated to 1/2 volume. The yellow precipitates obtained upon dilution with water were dissolved in benzene and freed from acids. Recrystallization from methanol-water gave yellow crystals of diketone XIV, m. p. 175~180°C (960 mg.). Chromatography on an alumina column gave a sample, m. p. 179.5~180°C and mixed melting point with XIV prepared from cycloketone XV¹, 181~182.5°C.

Methyl Ester XII (R=Me) and its Saponification.—Treatment of acid IV with diazomethane gave crystals, m. p. 69~71°C. $[\alpha]_D -211^\circ$ (c 0.78, ethanol).

Found: C, 71.40; H, 9.80. Calcd. for C₁₅H₂₄O₃: C, 71.39; H, 9.59%.

The product (140 mg.) was refluxed with 5% methanolic sodium hydroxide for 2 hr. and then poured into water and acidified. The precipitates, on trituration with petroleum ether, were crystallized. Recrystallization from ethanol-water gave β -diketone XIII (5 mg.) as the first crop, m. p. 219~220°C (decomp.). From the second crop, acid IV was obtained.

Enol Lactone XI and its Saponification.—Treatment of acid IV with acetic anhydride in pyridine gave the anhydroderivative XI, m. p. 80.5~83°C (from ethanol).

Found: C, 76.29; H, 9.39. Calcd. for C₁₄H₂₀O₂: C, 76.32; H, 9.15%.

Saponification. a) XI (46 mg.) in a 5% sodium hydroxide solution (5 cc.) was refluxed for an hour;

12 mg. of acid IV was isolated. b) XI (85 mg.) in a methanolic potassium hydroxide solution was refluxed for two hours, and about a half of the methanol was removed. The remainder was poured into water, and the precipitates were purified, giving the ester XII (R=Me). The filtrate was acidified and a small amount of β -diketone XIII was obtained. Both were identified by their infrared spectra.

Hypobromite Oxidation of Ester XII (R=Me).—A solution of XII (R=Me) (450 mg.) in dioxane (22 cc.) was treated with a hypobromite solution (20 cc.) for 30 min. Water (30 cc.) was added and extracted with ether. The acid product was recrystallized from aqueous methanol, giving C₁₃-diacid monomethyl ester (168 mg.) m. p. 139~141°C. The infrared spectrum was identical with an authentic sample¹².

Hypobromite Oxidation of II.—Fine crystals of II (680 mg.) were added to a hypobromite solution (20 cc.) and left for 2.5 hr. When sodium bisulfite and hydrochloric acid were added, the whole solution became a gel. A crude material obtained from air-dried gel showed infrared bands at 3390 and 1690 cm⁻¹ (broad). The gel was shaken with ether. Evaporation of ether left fine needles, which were recrystallized from a mixture of ether-petroleum ether, m. p. 178~180°C (decomp.). IR, 3378, 1745 and 1667 cm⁻¹.

Found: C, 62.49; H, 7.66. Calcd. for C₁₄H₂₀O₃: C, 62.67; H, 7.51%.

Alternatively the gel-product was treated with an alkaline hydrogen peroxide solution overnight and then acidified. The precipitates were dissolved in methanol-water. An oil separated and solidified on standing, then needles were crystallized from the solution. The needles, m. p. 178~180°C, show infrared bands at 3408, 3155 and 1721 cm⁻¹. The solidified oil shows infrared bands at 3333, 1727 and 1675 cm⁻¹ (Nujol). With diazomethane both of them gave the same dimethyl ester (XXII, R=Me) m. p. 80.5~82.5°C, which was identical with the dimethyl ester obtained from the gel without hydrogen peroxide treatment.

Found: C, 64.91; H, 8.39. Calcd. for C₁₆H₂₄O₃: C, 64.84; H, 8.16%.

Ozonolysis of Acid XVI.—To a solution of XVI (1.1 g.) in a carbon tetrachloride-chloroform mixture (1:1, 80 cc.), ozone was passed for three hours while the solution was cooled in an ice-bath. The solvent was removed, and the residue was taken up in ether, from which the acid product was extracted. The product (air-dried gel) was identified as acid XXIII by infrared spectral comparison.

Chromic Acid Oxidation of Acid XXIII.—XXIII (90 mg.) was dissolved in acetic acid (3 cc.), and a solution composed of chromic acid (200 mg.) and concentrated sulfuric acid (3 drops) was added. The mixture was kept for 24 hr. and diluted with water. C₁₃-anhydride XXIV (20 mg.) m. p. 208°C was obtained.

Bichromate Oxidation of Ester VII (R=Me).—To an acetic acid solution (2 cc.) of VII (500 mg.), a solution of sodium bichromate (2.0 g.) in acetic acid (3 cc.) was added. Four drops of concentrated sulfuric acid was added, and the mixture was left

for a few minutes. The precipitates occurring were recrystallized from a benzene-petroleum ether mixture and sublimed under reduced pressure, giving XXIII ($R=Me$), m. p. $188\sim190^{\circ}C$.

Found: C, 64.03; H, 8.03. Calcd. for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85%.

Attempted Oxidation of Ester XXII ($R_1=R_2=Me$).—The ester was treated with chromic acid in a mixture of acetic and sulfuric acid for 1.5 hr. Water was added, and the resulting precipitates were filtered. They contain mostly the starting material, besides a small amount of a petroleum ether-insoluble material, which was recrystallized from benzene, m. p. $187\sim190^{\circ}C$, and was shown

to be identical with the XXIII ($R=Me$) obtained from VII ($R=Me$).

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