368. *Sesquiterpenoids. Part XIII.* The Constitution of Zierone.*[1]

By D. H. R. BARTON and G. S. GUPTA.

Zierone has been shown to contain the grouping $-C(Me)=\overset{|}{C}-C(=CMe_2)-CO-$. Based on this evidence and upon the earlier work of others the new constitution (IV; X = O) has been established. The biogenesis of zierone has been briefly discussed.

THE interesting sesquiterpenoid ketone zierone was isolated by Penfold[2] from the essential oil of *Zieria macrophylla* Bonpland. Preliminary work on its chemistry was reported by Bradfield, Penfold, and Simonsen.[3] A more extended study of this ketone was carried out by Birch and his collaborators[4,5] as well as by Hildebrand and Sutherland.[6] Various constitutional suggestions have been entertained of which (I) and (II) are the most recent.[6]

It has been established that zierone is a bicyclic doubly unsaturated ketone of the sesquiterpenoid type. Reduction with lithium aluminium hydride affords zierol which on dehydrogenation gives zierazulene (III). The constitution of this azulene was proved by synthesis by Collins.[7] New evidence which we now present has proved that zierone has, in fact, the constitution (IV; X = O) and that no new arrangement of isoprenoid residues is required in order to explain its biogenesis.

Neither zierone (IV; X = O) nor its semicarbazone (IV; X = N·NH·CO·NH$_2$) shows vinyl hydrogen in the nuclear magnetic resonance spectra. Both compounds show bands characteristic[8] of >CHMe, vinylic methyl, and of $Me_2C=\overset{|}{C}-C(=X)-$ (see Table). Ozonolysis of zierone and of its semicarbazone furnished acetone. There was some uncertainty about this fact in the earlier literature,[3] but our results are in agreement with those recently reported by Hildebrand and Sutherland.[6] Acetone (80%) was also formed on heating zierone with aqueous ethanolic potassium hydroxide. Clearly zierone contains an isopropylidene group which is in conjugation with the ketone group. With alkaline hydrogen peroxide zierone afforded an epoxide. The ultraviolet spectrum of this compound, like that of many other zierone derivatives, is so peculiar [$\lambda_{max.}$ 233 and 303 mμ (ε = 3900 and 540, respectively)] that no conclusion could be reached as to the nature of the conjugation present.

Reduction of zierone with sodium and ethanol gave dihydrozierol (V), purified through its crystalline 3,5-dinitrobenzoate. Oxidation of dihydrozierol with chromic acid–sulphuric acid in acetone[9] afforded dihydrozierone (VI). The latter furnished a crystalline 2,4-dinitrophenylhydrazone. Dihydrozierone had ultraviolet absorption ($\lambda_{max.}$ 294 mμ; ε = 330) indicative[10] of βγ-unsaturation. The parent dihydrozierol, as its 3,5-dinitrobenzoate, showed bands (see Table) indicative of –CHMe$_2$, >CHMe, and vinylic methyl in its nuclear magnetic resonance spectrum. The reduction of the isopropylidene double bond in zierone by sodium–ethanol confirms again that it is conjugated to the ketone

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* Part XII, *J.*, 1960, 2263.

[1] For a preliminary communication see Barton and Gupta, *Proc. Chem. Soc.*, 1961, 308.

[2] Penfold, *J. Roy. Soc. N.S. Wales*, 1926, **60**, 104.

[3] Bradfield, Penfold, and Simonsen, *J. Roy. Soc. N.S. Wales*, 1933, **67**, 200.

[4] Birch, Collins, and Penfold, *Chem. and Ind.*, 1955, 1773.

[5] Birch, Collins, Hildebrand, Penfold, and Sutherland, Chem. Soc. Terpene Symposium, Glasgow, July, 1957.

[6] Hildebrand and Sutherland, *Austral. J. Chem.*, 1959, **12**, 436.

[7] Collins, *J.*, 1959, 531.

[8] Jackman, " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.

[9] Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39.

[10] Cookson and Wariyar, *J.*, 1956, 2302.

group. The fact that the residual double bond is in a $\beta\gamma$-relation to the ketone requires one of three possible explanations:

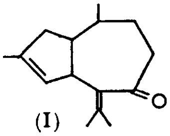
(*a*) $Me_2C{=}C{-}C{=}C{-}CO{-} \longrightarrow Me_2CH{-}C{=}C{-}CH{-}CO{-}$

(*b*) $C{=}C{-}C({=}CMe_2){-}CO{-} \longrightarrow C{=}C{-}CH(CHMe_2){-}CO{-}$

or (*c*) $C{=}C{-}C{-}CO{-}C({=}CMe_2) \longrightarrow C{=}C{-}C{-}CO{-}CH(CHMe_2)$

Since zierone is not a dienone with extended conjugation (*vide* its ultraviolet absorption spectrum) the second or third of these explanations must be correct.

Reduction of zierone with lithium aluminium hydride (see above) gave zierol[4] (VII), which was characterised as a crystalline 3,5-dinitrobenzoate. The latter showed bands in its nuclear magnetic resonance spectrum indicative of >CHMe, as in all other compounds examined, and of three vinylic methyl groups (see Table). The ultraviolet absorption spectrum of zierol is peculiar in showing strong end absorption with shoulders at 226 (ε = 5000) and 233 (ε = 4350) mμ. The subtraction spectrum of cyclohexyl 3,5-dinitrobenzoate from that of the pure zieryl 3,5-dinitrobenzoate gave a curve with similar strong end absorption. These spectra certainly cannot be explained by the absorption of two isolated ethylenic linkages. They are best explained as due to a conjugated diene system of abnormal (overcrowded) type such as is found in photosantonic acid (VIII).[11,12] This evidence excludes part-formula (*c*) (see above) and leaves (*b*) as the unique explanation of the properties of zierone.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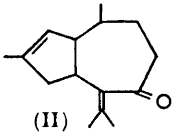
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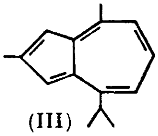
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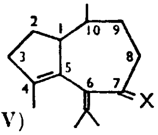
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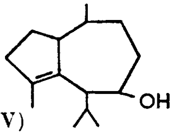
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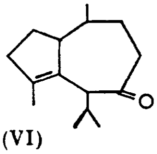
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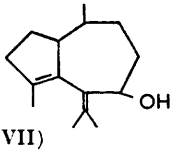
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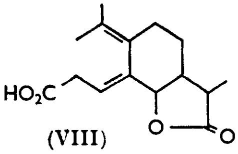
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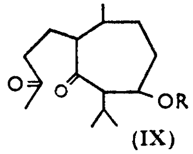
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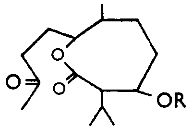
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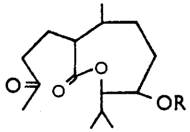
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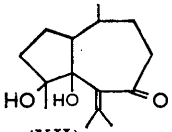
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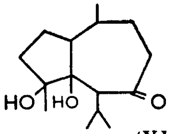
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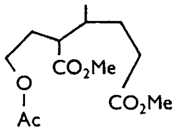
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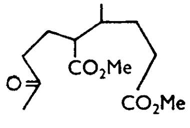
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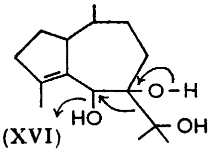
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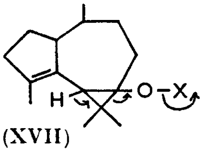
(XVII)

Ozonolysis of dihydrozieryl (V) 3,5-dinitrobenzoate gave two crystalline compounds both of which were methyl ketones. Both compounds gave positive iodoform tests. The expected ozonolysis product (IX; R = 3,5-dinitrobenzoyl) had a band at τ = 7·905 in its nuclear magnetic resonance spectrum indicative of methyl ketone.[8] The second

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[11] van Tamelen, Levin, Brenner, Wolinsky, and Aldrich, *J. Amer. Chem. Soc.*, 1958, **80**, 501.
[12] Barton, de Mayo, and Shafiq, *J.*, 1958, 3314.

product is formulated as (X or XI; R = 3,5-dinitrobenzyl). It showed a band at τ = 8·17 indicative of methyl ketone and had no band due to hydroxyl group in its infrared spectrum. The diketone (IX; R = 3,5-dinitrobenzoyl) was also obtained by ozonolysis of dihydrozierol (V) followed by 3,5-dinitrobenzoylation.

Treatment of zierone with osmium tetroxide gave a nicely crystalline diol (XII), already described by Birch, Collins, and Penfold.[4] This substance had a nuclear magnetic resonance spectrum in good agreement (see Table) with its constitution, but its ultraviolet absorption is again abnormal ($\lambda_{\text{max.}}$ 246 mμ; ε = 1850). The low intensity of absorption is explained by the overcrowded nature of the molecule. The intensity of the carbonyl absorption band in the infrared region is essentially normal and therefore the low ε of the ultraviolet absorption cannot be explained by intramolecular hemi-ketal formation.

Proton magnetic resonance spectra of zierone and its derivatives
(frequency 56·4 mc/sec.; concn. 10%).

Compound	Solvent	τ Values (relative to $SiMe_4$)	Assignment *
Zierone (IV; X = O)	CCl_4	9·04 doublet	*a*
		8·5 singlet	*b*
		8·35 8·01 {sharp singlets}	*c*
Zierone semicarbazone (IV; X = N·NH·CO·NH_2)	$CDCl_3$	9·06 doublet	*a*
		8·45 singlet	*b*
		8·41 8·24 {sharp singlets}	*c*
Tetrahydrodihydroxyzierone (XIII)	$CDCl_3$	9·06 doublet	*a*
		8·85 singlet	*d*
		8·33 7·97 {sharp singlets}	*c*
Zieryl 3,5-dinitrobenzoate [derivative of (VII)]	$CDCl_3$	9·07 doublet	*a*
		8·35 8·14 {singlets}	*b* and *e*
Dihydrozieryl 3,5-dinitrobenzoate [derivative of (V)]	CCl_4	9·33 doublet	*f*
		9·19 doublet	*a*
		8·52 singlet	*b*

* *a* $>\text{CHMe}$, *b* $=\overset{|}{\text{C}}-\text{Me}$, *c* $\text{Me}_2\text{C}{=}\overset{|}{\text{C}}-\text{CO}-$, *d* $-\text{O}-\text{CMe}<$, *e* $\text{Me}_2\text{C}{=}\text{C}<$, *f* $-\text{CHMe}_2$.

Reaction of dihydrozierol (V) with osmium tetroxide proceeded in an abnormal manner in that the product was tetrahydrodihydroxyzierone (XIII). One must conclude that osmium tetroxide can, in certain cases, oxidise alcohols to ketones; in model experiments cycloheptanol was oxidised similarly to cycloheptanone.

These results require that zierone contains the system $-\text{C(Me)}{=}\overset{|}{\text{C}}-\text{C}({=}\text{CMe}_2)-\text{CO}-$. Since zierone readily forms a hydroxymethylene derivative[3,4] which, on the basis of adequate evidence[4] that need not be recapitulated, must have the hydroxymethylene group α to the carbonyl group one can expand this formula to

$$-\text{C(Me)}{=}\overset{|}{\text{C}}-\text{C}({=}\text{CMe}_2)-\text{CO}-\text{CH}_2-.$$

Placing this group in a skeleton which can afford zierazulene (III) gives (IV; X = O) as the unique constitution for zierone. The migration of the methyl group from position 4 to position 3 on dehydrogenation is not unexpected[13] especially when one has regard to the overcrowded nature of the zierone molecule.

As final confirmation for the correctness of formula (IV; X = O), the ozonolysis of zierone was studied again in order to isolate the expected twelve-carbon fragment. After methylation two compounds were in fact obtained. The first behaved as the dimethyl ester acetate (XIV). The second was a dimethyl ester methyl ketone (XV). This gave

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[13] See, especially, Büchi, Chow, Matsura, Popper, Rennhard, and Wittenau, *Tetrahedron Letters*, 1959, **6**, 14.

a positive iodoform test and afforded a crystalline 2,4-dinitrophenylhydrazone of the expected composition.

The biogenesis of zierone can be accommodated by a slight modification of the norm [14,15] for sesquiterpenoids based on the guaiol skeleton. One can suppose that it is derived from a compound of normal skeleton by a 1 : 2-shift (see XVI; or equivalent) or that it is derived from the fission of a cyclopropane derivative (see XVII, or equivalent; X = departing ion).

EXPERIMENTAL

M. p.s were taken on the Kofler block. $[\alpha]_D$ were determined in chloroform. Ultraviolet absorption spectra were taken in ethanol unless specified. The term " light petroleum " refers to the fraction of b. p. 40—60°. The alumina for chromatography was standardised according to Brockmann and Schodder.[16] The nuclear magnetic resonance spectra were kindy determined and interpreted by Drs. L. M. Jackman and J. W. Lown, to whom we express our thanks. A Varian Associates spectrometer (56·4 Mc/sec.) was used for the measurements with tetramethylsilane as internal standard.[8]

Zierone.—Zierone semicarbazone (from the collection of the late Sir John Simonsen, F.R.S.) crystallised from methanol as needles, m. p. 179—181°, $[\alpha]_D$ $-142°$ (*c* 2·86), $\lambda_{max.}$ 245 mμ (ε = 17,200) (Found: N, 15·4. Calc. for $C_{16}H_{25}N_3O$: N, 15·3%). This semicarbazone (20·6 g.) was steam distilled with oxalic acid (12·5 g.) in water (500 ml.), and the distillate extracted with ether. Removal of the ether (Na_2SO_4 drying) gave zierone (79%), b. p. 107°/1·25 mm., n_D^{22} 1·5740, $[\alpha]_D$ $-179°$ (*c* 1·32), $\lambda_{max.}$ 245 mμ (ε = 7400), $\nu_{max.}$ (liquid film) 1681 (C=O) and 1600vs (C=C) cm.$^{-1}$.

Zierone, treated with 2,4-dinitrophenylhydrazine in either ethanolic sulphuric or hydrochloric acid, gave, either at room temperature or when warmed, an orange-red 2,4-dinitrophenylhydrazone. Recrystallised from ethanol, this had m. p. 117—120°, $\lambda_{max.}$ 376 mμ (ε = 18,700 in $CHCl_3$) (Found: C, 64·0; H, 6·8; N, 14·6. Calc. for $C_{21}H_{26}N_4O_4$: C, 63·6; H, 6·6; N, 14·1%). Bradfield, Penfold, and Simonsen [3] report m. p. 95—97°; Hildebrand and Sutherland [6] give m. p. 95—96° for a derivative obtained at 0°.

Ozonolysis of Zierone Semicarbazone.—The semicarbazone (200 mg.) in dry methylene dichloride (50 ml.) was ozonised at $-50°$ until a blue colour persisted (45 min.). The issuing gases were passed through water (20 ml.) which was added to the methylene dichloride when the reaction was complete. The combined solvents were distilled into 2,4-dinitrophenylhydrazine reagent and the mixture refluxed. The methylene dichloride was boiled off and the yellow precipitate collected. After chromatography on alumina (Grade III) this was identified as acetone 2,4-dinitrophenylhydrazone (30%) by m. p. and mixed m. p.

Alkaline Hydrolysis of Zierone.—Zierone (224 mg.) and potassium hydroxide (565 mg.) in ethanol (95%; 10 ml.), which had been freed from any carbonyl impurities, was heated under reflux under nitrogen. Ethanol was slowly distilled off (with continous replacement) until no more acetone was evolved (Zimmermann test). The acetone in the distillate was characterised as the 2,4-dinitrophenylhydrazone (m. p. and mixed m. p.). In a separate experiment (33 hr. distillation) the acetone in the distillate was determined colorimetrically [17] (80%).

Zierone Epoxide.—Zierone (250 mg.) in methanol (15 ml.), hydrogen peroxide (6 ml.; 30%), and aqueous sodium hydroxide (4N; 0·75 ml.) was kept at 5° for 4 weeks (ultraviolet spectral control). The methanol was removed *in vacuo* and the product chromatographed (ultraviolet and infrared spectral control of fractions) on alumina (Grade III; 6 g.). Elution with cyclohexane and cyclohexane–ether afforded *zierone epoxide*, b. p. 30—40°/2·94 × 10^{-5} mm., n_D^{25} 1·4960, $[\alpha]_D$ $-106°$ (*c* 1·08), $\lambda_{max.}$ 205, 233, and 303 mμ (ε = 4700, 3900, and 540, respectively), $\nu_{max.}$ (liquid film) 1701 (C=O) cm.$^{-1}$ (Found: C, 77·0; H, 9·5. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%).

Dihydrozierol.—Zierone (250 mg.) in ethanol (15 ml.) was treated under reflux with sodium (1·5 g.; small pieces) until all the sodium had dissolved (1 hr.). The excess of ethanol was removed *in vacuo* and the product isolated in the usual way as a viscous oil, n_D^{20} 1·5090.

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[14] Barton and de Mayo, *Quart. Rev.*, 1957, **11**, 189.

[15] Hendrickson, *Tetrahedron*, 1959, **7**, 82.

[16] Brockmann and Schodder, *Ber.*, 1941, **74**, 73.

[17] Lapin and Clark, *Analyt. Chem.*, 1951, **23**, 541.

3,5-Dinitrobenzoylation by the method of Brewster and Ciotti,[18] followed by chromatography over alumina (Grade III) and elution with benzene, gave (from methanol–ether) *dihydrozieryl* 3,5-*dinitrobenzoate*, m. p. 103—106°, $\lambda_{max.}$ 208 mμ (ε = 34,300), λ_{sh} 227 mμ (ε = 23,100), $\nu_{max.}$ (in $CHCl_3$) 1724 (ester) cm.$^{-1}$ (Found: C, 63·6; H, 7·0. $C_{22}H_{28}N_2O_6$ requires C, 63·4; H, 6·8%).

This 3,5-dinitrobenzoate (130 mg.) in methanolic sodium hydroxide (15 ml.; 4%) was refluxed for 1 hr. under nitrogen. The methanol was removed *in vacuo* and the product chromatographed over alumina (Grade III), being eluted with benzene. After sublimation *in vacuo dihydrozierol* was obtained as a colourless viscous oil, n_D^{23} 1·5030, $[\alpha]_D$ +42° (*c* 1·12), $\lambda_{max.}$ 209 mμ (ε = 4350), $\nu_{max.}$ (in $CHCl_3$) 3448 and 1012 (hydroxyl) cm.$^{-1}$ (Found: C, 81·3; H, 11·7. $C_{15}H_{26}O$ requires C, 81·0; H, 11·8%).

Dihydrozierone.—Dihydrozierol (100 mg.) in acetone (30 ml.; "AnalaR," redistilled over potassium permanganate) was treated under nitrogen with the theoretical amount of chromium trioxide in aqueous sulphuric acid (0·11 ml.) at 10—15° for 5 min. Chromatography of the product on alumina (Grade III; 3·5 g.) and elution with light petroleum gave dihydrozierone (75 mg.) as an oil, n_D^{25} 1·4980, $[\alpha]_D$ ±0° (*c* 0·26), $\lambda_{max.}$ 206 and 294 mμ (ε = 5500 and 330, respectively), λ_{sh} 227 mμ (ε = 2200), $\nu_{max.}$ (in $CHCl_3$) 1685 (C=O) cm.$^{-1}$. The derived 2,4-*dinitrophenylhydrazone*, chromatographed over 1 : 1 bentonite : Celite and eluted with light petroleum–benzene, crystallised from ethanol as yellow needles, m. p. 129—131°, $\lambda_{max.}$ 368 mμ (ε = 25,800 in $CHCl_3$) (Found: C, 62·75; H, 7·1; N, 13·4. $C_{21}H_{28}N_4O_4$ requires C, 63·0; H, 7·05; N, 14·0%).

Ozonolysis of Dihydrozierol and of its 3,5-*Dinitrobenzoate.*—The 3,5-dinitrobenzoate (310 mg.) in dry methylene dichloride (15 ml.) was ozonised at −20° until the tetranitromethane (1 hr.) test was negative. Water (10 ml.) was added and the reaction mixture heated on the steam-bath (removal of the methylene dichloride) for 1 hr. The neutral product (acid fraction negligible) was chromatographed on alumina (Grade III; 8 g.) and eluted with light petroleum–benzene, benzene, and then benzene–ether (15 fractions). From the earlier fractions the *keto-ester* (X or XI; R = 3,5-dinitrobenzoyl) (needles from ethanol–ether) was isolated, m. p. 166—168°, $[\alpha]_D$ +87° (*c* 0·93), and gave a positive (m. p. and mixed m. p.) iodoform test (Found: C, 56·9; H, 6·1. $C_{22}H_{28}N_2O_9$ requires C, 56·9; H, 6·1%). From the later fractions the *diketo-ester* (IX; R = 3,5-dinitrobenzoyl) was obtained (plates from ethanol), m. p. 129—131°, $[\alpha]_D$ +5° (*c* 0·95), $\nu_{max.}$ (in $CHCl_3$) at 1726 and 1710 (3,5-dinitrobenzoate and methyl ketone, respectively), ν_{sh} 1702 (cycloheptanone) cm.$^{-1}$ (Found: C, 59·1; H, 6·4. $C_{22}H_{28}N_2O_8$ requires C, 58·9; H, 6·3%). It gave a positive (m. p. and mixed m. p.) iodoform test.

Dihydrozierol (regenerated from its 3,5-dinitrobenzoate; 300 mg.) in dry methylene dichloride (20 ml.) was ozonised at −20° until a tetranitromethane test was negative (2½ hr.). Water (10 ml.) was added and the mixture processed as above. The resultant hydroxy-diketone did not crystallise. It was 3,5-dinitrobenzoylated and the product chromatographed over alumina to give the same diketo-ester (m. p., mixed m. p., $[\alpha]_D$, infrared spectrum) as described above.

Zierol and its 3,5-*Dinitrobenzoate.*—Zierone (407 mg.) in dry ether (20 ml.) was refluxed with lithium aluminium hydride (300 mg.) in the same solvent (25 ml.) for 1 hr. Working up in the usual way but avoiding any treatment with acidic reagents gave zierol as a thick oil, n_D^{22} 1·5150, $\lambda_{max.}$ 207 mμ (ε = 9500), λ_{sh} 226 and 233 mμ (ε = 5000 and 4350, respectively), $\nu_{max.}$ (liquid film) 3448 and 1010 (hydroxyl) cm.$^{-1}$. Zierol (100 mg.) in dry benzene (1 ml.) was treated with 3,5-dinitrobenzoyl chloride (135 mg.) in the same solvent (1 ml.) with addition of dry pyridine (0·06 ml.) at room temperature for 3 hr. Working up in the usual manner but avoiding any treatment with acidic reagents and keeping the temperature of all operations at <50°, furnished *zieryl* 3,5-*dinitrobenzoate.* After crystallisation from methanol–ether or from light petroleum, this had m. p. 108—110° (decomp. above this temp.), $\nu_{max.}$ (in $CHCl_3$) 1720 (ester) cm.$^{-1}$ (Found: C, 63·5; H, 6·5. $C_{22}H_{26}N_2O_6$ requires C, 63·75; H, 6·3%). There was a marked m. p. depression on admixture with dihydrozieryl 3,5-dinitrobenzoate (see above). The difference curve between the ultraviolet absorption of zieryl 3,5-dinitrobenzoate and cyclohexyl 3,5-dinitrobenzoate was as follows: ε (213 mμ) 4220, ε (217 mμ) 3900, ε (222 mμ) 3150, ε (227 mμ) 1870, and ε (233 mμ) 1060.

Reaction of Zierone with Osmium Tetroxide.—Zierone (200 mg.) in dry dioxan (2 ml.) was treated with osmium tetroxide (271 mg.) in the same solvent (2 ml.) with addition of dry

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[18] Brewster and Ciotti, *J. Amer. Chem. Soc.*, 1955, **77**, 6214.

pyridine (2 drops) and kept in the dark at room temperature for 7 days. The osmic ester was decomposed with dry hydrogen sulphide and the product in methanol was filtered through Celite to give dihydrodihydroxyzierone (70%) as prisms from light petroleum–ether, m. p. 127—128°, $[\alpha]_D$ +165° (*c* 0·23), $\lambda_{max.}$ 246 mμ (ε = 1900), $\nu_{max.}$ (in CCl_4) 1698 (C=O) and 1647 (C=C; abnormally intense), $\nu_{max.}$ (in Nujol) similar (Found: C, 71·5; H, 10·0; active H, 0·8. Calc. for $C_{15}H_{24}O_3$: C, 71·4; H, 9·6; active 2H, 0·8%). The diol consumed 0·9 mol. of periodic acid to give an oily triketone. This had $[\alpha]_D$ +7° (*c* 0·22), $\lambda_{max.}$ 240 mμ (ε = 5500), $\nu_{max.}$ (in $CHCl_3$) 1718 (CH_3–CO), 1672 (C=C), and 1600 (C=C) cm.$^{-1}$. It gave a positive iodoform test (m. p. and mixed m. p.).

Reaction of Dihydrozierol with Osmium Tetroxide.—Dihydrozierol (170 mg.) in dry dioxan (2 ml.) was treated with osmium tetroxide (232 mg.) in the same solvent (3 ml.) with addition of dry pyridine (3 drops) at room temperature in the dark for 15 days. The osmic ester was decomposed with hydrogen sulphide and the product chromatographed over alumina (Grade III; 5 g.). Elution with chloroform afforded *tetrahydrodihydroxyzierone* (XIII) (40%) as plates (from benzene or chloroform), m. p. 170—171°, no ultraviolet light absorption, $\nu_{max.}$ (in $CHCl_3$) 3521 (hydroxyl) and 1704 (C=O) cm.$^{-1}$ (Found: C, 70·7; H, 10·9. $C_{15}H_{26}O_3$ requires C, 70·8; H, 10·3%). The compound consumed 1·06 mol. of periodic acid.

In a model experiment cycloheptanol (400 mg.) in dry dioxan (11 ml.) and dry pyridine (0·3 ml.) containing osmium tetroxide (920 mg.) was kept in the dark at room temperature. After 3 days gas chromatography showed that 9% of cycloheptanone had been formed. After 8 weeks conversion was substantially complete.

Ozonolysis of Zierone.—Zierone (561 mg.) in dry methylene dichloride (25 ml.) was ozonised at −20° for 1·5 hr. Water (7 ml.) was added and the ozonide decomposed by heating it on the steam-bath (removal of the methylene dichloride). The product was separated into an acidic (sodium hydrogen carbonate) and a neutral fraction; the latter (70 mg.) was not investigated further. The acidic fraction (550 mg.) was treated with excess of redistilled diazomethane in ether, and the esterified product chromatographed over alumina (Grade III; 12 g.) with infra-red spectral control. Elution with light petroleum and distillation of the eluate gave the *acetoxy-diester* (XIV), b. p. 44—50°/1·08 × 10^{-4} mm., n_D^{25} 1·4518, $[\alpha]_D$ −7° (*c* 1·25), no ultra-violet-light absorption, $\nu_{max.}$ (liquid film) 1730 (ester C=O) cm.$^{-1}$ (Found: C, 5·71; H, 8·5. $C_{13}H_{22}O_6$ requires C, 56·9; H, 8·1%). This compound gave a negative iodoform test.

Elution with benzene and with benzene–ether and distillation of the eluate gave the keto-diester (XV) as a thick oil, b. p. 55—65°/1·08 × 10^{-4} mm., $\nu_{max.}$ (liquid film) 1727 (C=O) cm.$^{-1}$. It gave a positive (m. p. and mixed m. p.) iodoform test. This keto-diester (100 mg.) was converted into its 2,4-*dinitrophenylhydrazone* in the usual way. Purified by chromatography over bentonite–Celite (1 : 1; 10 g.) and elution with chloroform, this crystallised from ethanol as yellow needles (88 mg.), m. p. 111—112°, $\lambda_{max.}$ 365 mμ (ε = 19,500 in $CHCl_3$) (Found: C, 52·25; H, 5·85; N, 12·85. $C_{19}H_{26}N_4O_6$ requires C, 52·05; H, 6·0; N, 12·8%)

A similar ozonolysis of zierone (100 mg.) and steam distillation into 2,4-dinitrophenyl-hydrazine in diluted sulphuric acid as with zierone semicarbazone (see above) gave acetone 2,4-dinitrophenylhydrazone (m. p. and mixed m. p.).

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