54. *Synthetical Approaches to the Pristimerin Chromophore.*

By J. A. Hill, A. W. Johnson, T. J. King, S. Natori, and S. W. Tam.

Attempts have been made to synthesise 8,8-dialkyl derivatives of 2,8-dihydro-2-oxonaphthalene, the parent chromophoric system of pristimerin. Although such compounds were not obtained, many related intermediates are described and certain rearrangement reactions encountered. The tricyclic terpenoids podocarpic acid and ferruginol were also used as starting materials in projected syntheses of the pristimerin chromophore.

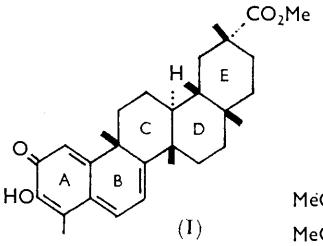
Pristimerin, the colouring matter of the root bark of *Celastrus dispermus*, has been shown [1,2] to have the structure (I), and celastrol from *Celastrus scandens* [3] is the corresponding acid. These substances contain a unique naphthalenoid methylenequinone type of chromophore, which by the action of acids under various conditions, can be rearranged to any of four aromatic structures: a catechol, a 1,2-dihydroxy-4,5-divinylbenzene and two naphthalene-2,3-diols.[2,4–6]

Methylenequinones of the type occurring in celastrol and pristimerin have not been synthesised and we now record some attempts to prepare simple analogues. The first series of reactions investigated had the syntheses of compounds (II; R = OH, R′ = H, OH) as the objectives. These structures are the simplest possible analogues of the AB ring system of pristimerol,[4] the first reduction product of pristimerin, which is readily oxidised back to pristimerin. It is expected that compounds (II; R = OH, R′ = H, OH) will show the same behaviour.

A preliminary approach involved the condensation of veratrole with mesityl oxide [cf.7] as an initial step but when it was found that this did not proceed as expected, an alternative condensation of veratrole with δδ-dimethyl-γ-butyrolactone [cf.8] was investigated. Although a small amount of the presumed 1-tetralone (III) was obtained as the 2,4-dinitrophenylhydrazone, the main product was the uncyclised acid (IV) in rather poor yield. This approach was abandoned in favour of another which had as its basis the observation [9,10] that 2-tetralones can be methylated to the corresponding 1,1-dimethyl-2-tetralones, which in turn can be reduced to 1,1-dimethyl-2-tetralols.

[1] Harada, Kakisawa, Kobayashi, Musya, Nakanishi, and Takahashi, *Tetrahedron Letters*, 1962, 603.
[2] Johnson, Juby, King, and Tam, *J.*, 1963, 2884.
[3] Gisvold, *J. Amer. Pharm. Assoc.*, 1939, **28**, 440; 1940, **29**, 12, 432; 1942, **31**, 529.
[4] Grant and Johnson, *J.*, 1957, 4079.
[5] Grant and Johnson, *J.*, 1957, 4669.
[6] Grant, Johnson, Juby, and King, *J.*, 1960, 549.
[7] Barnes and Buckwalter, *J. Amer. Chem. Soc.*, 1951, **73**, 3858; Campbell and Cromwell, *ibid.*, 1955, **77**, 5169.
[8] Arnold, Buckley, and Richter, *J. Amer. Chem. Soc.*, 1947, **69**, 2322.
[9] Soffer, Stewart, Cavagnol, Gellerson, and Bowler, *J. Amer. Chem. Soc.*, 1950, **72**, 3704.
[10] Lewis, Dickinson, and Archer, *J. Amer. Chem. Soc.*, 1952, **74**, 5321; cf. also Woodward, Patchett, Barton, Ives, and Kelly, *J.*, 1957, 1131.

2,7-Dimethoxynaphthalene was reduced with sodium and ethanol [cf.11] to 7-methoxy-2-tetralone [12] which was methylated with methyl iodide in presence of potassium t-butoxide to form an oily mixture of methylated ketones; this was reduced with lithium aluminium hydride to the corresponding crystalline tetralols. Initially eight moles of methyl iodide were employed in the reaction from which a tetralol was obtained which was further characterised as its benzoate. The corresponding tetralone was also



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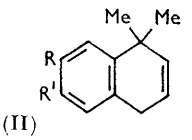

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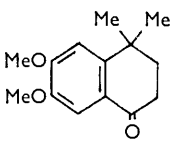

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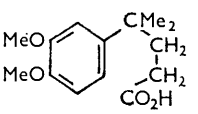

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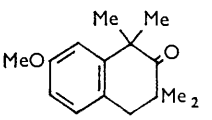

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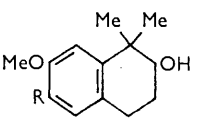


(VI)

demethylated to a crystalline keto-phenol, which in turn was converted by known methods [13,14] into its 2′-benzoyl-4′-nitrophenyl ether and the corresponding 6-hydroxy-ether. At this stage, examination of the nuclear magnetic resonance (n.m.r.) spectra of the compounds of this series showed conclusively that they were all derived, not from the desired 1,1-dimethyl-2-tetralone but from the 1,1,3,3-tetramethyl-2-tetralone (V). The tetramethylation of cyclohexanone itself has been recorded.[15]

It was found that when 7-methoxy-2-tetralone was methylated with five moles of methyl iodide, the main product was the desired tetralone, which was reduced to the crystalline tetralol (VI; R = H). The pure tetralone (it has been obtained recently [16] as a low-melting solid) was obtained by chromic acid oxidation of the tetralol and derivatives of both the tetralol and tetralone were prepared.

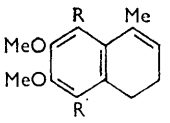
The related tetralol (VI; R = OMe) was obtained from the corresponding monomethyl-tetralone, itself prepared by oxidation of the 3,4-dihydronaphthalene (VII; R = H) with perbenzoic acid by a modification of the method of Howell and Taylor.[17] However, even using modified conditions, we were unable to obtain the 68% yield of the ketone claimed by these authors and the best we observed was of the order of 40%, when only a slight excess of perbenzoic acid was used at 0°. Under more vigorous conditions appreciable amounts of 6,7-dimethoxy-1-methyl-2-naphthol [17] were obtained as a by-product. The use of lead tetra-acetate as oxidising agent was inferior and invariably gave rise to 6,7-dimethoxy-1-methylnaphthalene [18] as a by-product. In spite of the obvious ease with which the 3,4-dihydronaphthalene is dehydrogenated, it reacted with bromine in carbon tetrachloride to give the dibromo-compound (VII; R = Br).

6,7-Dimethoxy-1-methyl-2-tetralone was methylated smoothly with methyl iodide in presence of potassium t-butoxide to the 1,1-dimethyl-ketone which was reduced to 6,7-dimethoxy-1,1-dimethyl-2-tetralol (VI; R = OMe) with lithium aluminium hydride. There was no evidence for the formation of 1,1,3,3-tetramethyl derivatives in this case.

Dehydration of 7-methoxy-1,1-dimethyl-2-tetralol (VI; R = H) with phosphoric or formic acid gave a mixture of benzenoid and styrenoid derivatives, but the product

[11] Cornforth, Cornforth, and Robinson, *J.*, 1942, 689.
[12] Soffer, Cavagnol, and Gellerson, *J. Amer. Chem. Soc.*, 1949, **71**, 3857.
[13] Loudon *et al.*, *J.*, 1950, 55; 1953, 265; Fishman, Tomasz, and Lehman, *J. Org. Chem.*, 1960, **25**, 585.
[14] Hill, Johnson, and King, *J.*, 1961, 4430.
[15] Sobotka and Chanley, *J. Amer. Chem. Soc.*, 1949, **71**, 4138.
[16] Hart, Corbin, Wagner, and Wu, *J. Amer. Chem. Soc.*, 1963, **85**, 3269.
[17] Howell and Taylor, *J.*, 1958, 1248.
[18] Luff, Perkin, and Robinson, *J.*, 1910, **97**, 1131.

obtained from the reaction of (VI; R = H) with phosphorus oxychloride and pyridine has been studied in most detail. It appeared to contain at least three components, the major constituent being the desired 1,4-dihydronaphthalene (II; R = OMe, R′ = H). However, the presence of a product containing a rearranged carbon skeleton was confirmed



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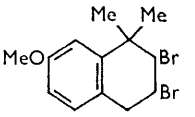

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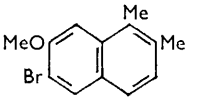
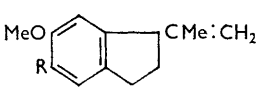


(IX)

when the action of bromine on the dehydration product gave two crystalline bromides (VIII; derived from II; R = OMe, R′ = H) and (IX; derived from 7-methoxy-1,2-dimethylnaphthalene). Nuclear magnetic resonance spectral measurements and analogy with the similar reaction of 6,7-dimethoxy-1,1-dimethyl-2-tetralol (II; R = R′ = OMe) with phosphorus oxychloride and pyridine suggest that the isopropenylindanes (X; R = H or OMe) might also be components of the dehydration mixtures.



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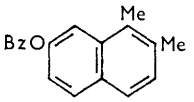

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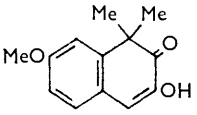


(XII)

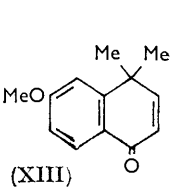
Demethylation of the dehydration product with pyridinium chloride, followed by benzoylation gave the naphthalene (XI).

7-Methoxy-1,1-dimethyl-2-tetralol was not dehydrated by heating it under reflux with a benzene solution of toluene-*p*-sulphonic acid [cf.19] or by heating it with dimethyl sulphoxide.[20] On the other hand, mixtures of products including naphthalenes were obtained by the action of iodine[21] or from an attempt to dehydrobrominate the corresponding bromide prepared by the method of Rydon.[22] As it appeared that all methods of dehydration involving potential carbonium-ion intermediates were likely to afford gross mixtures, we investigated the pyrolytic dehydration of the tetralols. Unresolved mixtures of products, including naphthalenes, were obtained by pyrolysis of 7-methoxy-1,1-dimethyl-2-tetralol with boric acid or by pyrolysis of the tetralol benzoate. However pyrolysis of 6,7-dimethoxy-1,1-dimethyl-2-tetralol (VI; R = OMe) with boric acid gave 6,7-dimethoxy-1,2-dimethylnaphthalene whereas pyrolysis of the benzoate caused the elimination of a methyl group and the formation of 6,7-dimethoxy-1-methylnaphthalene. Although the *O*-ethoxycarbonyl (ethyl carbonate) derivative of (VI; R = H) was unchanged after 6 hours at 180° the corresponding methyl xanthate was converted into a product from which the pure 1,4-dihydronaphthalene (II; R = OMe, R′ = H) could be obtained, and the dimethoxy-analogue (II; R = R′ = OMe) was obtained by a similar method.

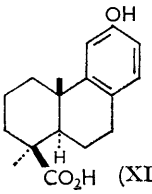
Various attempts have been made to demethylate the methoxy-1,4-dihydronaphthalenes without causing rearrangement, but so far without success. On treatment of 7-methoxy-1,1-dimethyl-1,4-dihydronaphthalene (II; R = OMe, R′ = H) with boron tribromide (cf. ref. 23) at −80° or with pyridinium chloride under various conditions, brown tars were obtained which contained appreciable amounts of naphthalenoid material

[19] Karrer and Eugster, *Helv. Chim. Acta*, 1951, **34**, 1400.
[20] Traynelis, Hergenrother, Livingston, and Valicenti, *J. Org. Chem.*, 1962, **27**, 2377.
[21] Hibbert, *J. Amer. Chem. Soc.*, 1915, **37**, 1748.
[22] Rydon *et al.*, *J.*, 1954, 2281; 1956, 3043.
[23] McOmie and Watts, *Chem. and Ind.*, 1963, 1658.

(spectra). Aqueous nitric acid (50%) gave a small yield of a crystalline yellow solid, m. p. 110—111·5°, which from spectral data was tentatively assigned structure (XII). Treatment with selenium dioxide in dioxan [cf.24] gave a ketone formulated as (XIII) on the basis of its spectral properties and those of the corresponding 2,4-dinitrophenylhydrazone. A similar oxidation of pristimerol dimethyl ether has been recorded.[4]



(XIII)



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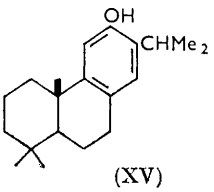
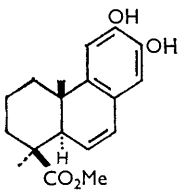


(XV)

As an alternative to the bicyclic systems described above, we have endeavoured to use podocarpic acid (XIV) and ferruginol (XV) as starting materials for the preparation of simple models of the pristimerin chromophore. Methyl podocarpate has been converted [14] into methyl 13-hydroxypodocarpate, incorrectly described previously [14] as the corresponding acid, but which is now formulated as a methyl ester on the grounds of analysis and n.m.r. The crystalline diacetate of this catechol was brominated with *N*-bromosuccinimide and immediately dehydrobrominated with boiling *NN*-dimethylaniline. After reacetylation, the diacetate was crystallised and hydrolysed to the styrene (XVI).

In another approach to (XVI), chromic acid oxidation of the di-*O*-acetyl derivative of methyl 13-hydroxypodocarpate gave the corresponding 7-oxo-compound which was hydrolysed with acid to the corresponding oxo-catechol (XVII; R = OH). Reduction of the 7-oxo-group was achieved by hydrogenation of an acetic acid solution in the presence of perchloric acid and a platinum catalyst, and gave methyl 7,13-dihydroxypodocarpate. Because of the success of the bromination route, this approach was not further pursued.

We were unable to oxidise the catechol (XVI) to a product containing a chromophore corresponding to that of pristimerin and although various yellow non-crystalline products were obtained they appeared (spectra) to contain appreciable amounts of *o*-quinones. Unlike pristimerol which is a derivative of 1,4-dihydronaphthalene, the catechol (XVI) is a derivative of 3,4-dihydronaphthalene and the failure to obtain the pristimerin-type methylenequinone chromophore from this compound, led us to attempt a synthesis of the phenol (XVIII). However, although methyl *O*-methyl-7-oxopodocarpate (methyl ether of XVII; R = H) could be oxidised to the 5,6-dehydro-derivative with selenium dioxide, we have been unable to reduce the keto-group to methylene in this product, *i.e.*, to yield the methyl ether of (XVIII). An attempted desulphurisation of the thioketal caused reduction of the non-aromatic carbon–carbon double bond with the formation of methyl



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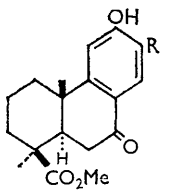

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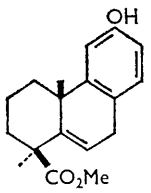

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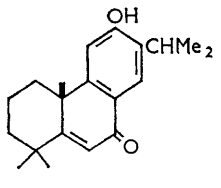

(XIX)

O-methylpodocarpate and Wolff–Kischner reduction of the corresponding hydrazone under varying conditions gave either the azine or intractable mixtures, containing some decarboxylated products.

Ferruginol (XV) has been converted into the benzoate of the corresponding 5-en-7-one,

[24] Duffield, Jefferies, and Lucich, *Austral. J. Chem.*, 1962, **15**, 812.

and the ester was hydrolysed to the free phenol [25] (XIX) on treatment with ethanolic hydrazine. The corresponding methyl ether was again subjected to reduction with a view to replacing the keto-group by methylene but again this was unsuccessful. The azine was the only isolable product when a modified Wolff–Kischner reduction [26] was applied.

Experimental

Melting points were determined on a Kofler hot-stage apparatus. Unless otherwise stated, ultraviolet (u.v.) and visible spectra refer to ethanolic solutions and were determined with a Unicam S.P. 700 spectrophotometer; infrared (i.r.) spectra refer to carbon tetrachloride solutions and were determined with a Unicam S.P. 100 spectrophotometer. N.m.r. spectra were determined with an A.E.I. RS 2 instrument (60 Mc./sec.) with tetramethylsilane as an internal reference and the values quoted are referred to τ values. Light petroleum refers to the fraction of b. p. 60—80°. Alumina used in chromatography was Spence Activated alumina, type " H."

A. *Derivatives of* 1,1-*Dimethyltetralin*-2,7-*diol.*

7-*Methoxy*-1,1-*dimethyl*-2-*tetralol.*—A solution of 7-methoxy-2-tetralone [12] (8·14 g., 1·0 mol.) in t-butyl alcohol (50 ml.) was added to a solution of potassium (4·51 g., 2·5 mol.) in t-butyl alcohol (150 ml.) with stirring under nitrogen at about 40°. After 30 min. at room temperature, a solution of methyl iodide (32·8 g., 5·0 mol.) in t-butyl alcohol (40 ml.) was added dropwise, when potassium iodide began to precipitate almost immediately. The mixture was heated under reflux for 1 hr., and t-butyl alcohol (180 ml.) was then removed. The cooled residue was treated with water (130 ml.), and the mixture was acidified with 3N-hydrochloric acid (100 ml.) and extracted with ether. The ethereal extract was washed and dried ($MgSO_4$), and after evaporation of the ether, the residue distilled as a colourless to pale yellow oil (8·81 g., 94%), b. p. 85—90°/0·03.[cf.16]

A solution of the crude 7-methoxy-1,1-dimethyl-2-tetralone (8·81 g.) in dry ether (100 ml.) was added dropwise, with stirring, to lithium aluminium hydride (3·4 g., 8 mol.) in dry ether (300 ml.), and the mixture was heated under reflux for 1 hr. and stirred for 10 hr. at room temperature. The cooled stirred mixture was decomposed by the dropwise addition of ethyl acetate until there was no further visible reaction. After treatment with water, the mixture was acidified with 5N-sulphuric acid, and the aqueous layer was separated and extracted with ether. The combined ethereal extract was washed with water, dried, and evaporated, giving a red viscous oil which slowly solidified. Crystallisation from light petroleum gave the tetralol (6·28 g., 71%) as needles, m. p. 91—93° (Found: C, 75·8; H, 8·8. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·8%); $\lambda_{max.}$ 221, 282, and 288 mμ (ε, 7560, 1930, and 1780, respectively); $\nu_{max.}$ 1042, 1247, 1286, 1508, 1616, 2945, 2975, and 3648 cm.$^{-1}$. The n.m.r. spectrum contained singlets at τ 8·83 and 8·76 (intensity 3; *C*-methyl groups), 6·39 (3; aromatic *O*-methyl group), a multiplet centred at *ca.* 8·20 (*J*, 6·6 c./sec.; 2; C-3 methylene group), a triplet centred at 7·30 (*J*, 6·6 c./sec.; 2; C-4 methylene group), a singlet at 7·63 (1; hydroxyl proton), a multiplet at *ca.* 6·51 (C-2 proton), and a complex absorption at 3·76—3·27 corresponding to the three aromatic protons.

The *benzoate* was a glass (Found: C, 77·3; H, 7·35. $C_{20}H_{22}O_3$ requires C, 77·4; H, 7·15%). The *toluene*-p-*sulphonate* crystallised from methanol as fine needles, m. p. 110° (Found: C, 66·2; H, 6·1. $C_{20}H_{24}O_4S$ requires C, 66·6; H, 6·7%).

The O-*ethoxycarbonyl* derivative was prepared by gradual treatment of a solution of the tetralol (250 mg.) in dry pyridine (3 ml.) at 0° with ethyl chloroformate (1 ml.). The mixture was kept at room temperature for 40 hr. and then poured into a mixture of acetic acid (5 ml.) and water (15 ml.) at 0°. The oil which separated was extracted into ether, the extract washed, and the solvent removed. The residual oil was distilled at 200—210° (bath temp.)/14 mm. to give the carbonate as an oil (150 mg.) (Found: C, 69·2; H, 8·05. $C_{16}H_{22}O_4$ requires C, 69·05; H, 8·0%); $\lambda_{max.}$ 220, 279, and 286 mμ (ε, 8400, 2340, and 2230, respectively); $\nu_{max.}$ 1740 (carbonate C=O) cm.$^{-1}$. The n.m.r. spectrum showed two *C*-methyl singlets at τ 8·67 and 8·72, one methyl triplet centred at τ 8·72 together with one methylene quartet centred at τ 5·84

[25] Bredenburg, *Acta Chem. Scand.*, 1957, **11**, 932.
[26] Cram, Sahyun, and Knox, *J. Amer. Chem. Soc.*, 1962, **84**, 1734.

for the ethyl group of the carbonate; two groups of methylene protons at τ 7·15 (triplet, *J*, 6·3 c./sec.) and 7·93 (multiplet); one proton quartet centred at τ 5·24 (*J*, 6·5 c./sec.) for the proton attached to the same carbon atom as the carbonate group; the aromatic protons corresponded to bands centred at τ 3·08, 3·21, and 3·41 (*J* 8·3 c./sec. for *ortho*-coupling, and 2·7 c./sec. for *meta*-coupling).

The carbonate was unchanged after being heated under reflux at 180° (bath temp.)/14 mm. for 6 hr.

Dehydration of 7-*Methoxy*-1,1-*dimethyl*-2-*tetralol.*—(i) *Xanthate method.* The tetralol (2 g.) and potassium hydroxide (1·2 g.) were heated gently until the alkali melted. The fused mixture was cooled and carbon disulphide (2 ml.) was added with vigorous stirring for 5 min. Ether (40 ml.) was added and the mixture stirred for another 5 min. The yellow solid (1·8 g.) was washed with dry ether. It was purified by dissolution in acetone, filtration, and reprecipitation by addition of ether. The yellow potassium xanthate was dried *in vacuo*, and then suspended in dry benzene (50 ml.) and heated under reflux with methyl iodide (5 ml.) for 4 hr. More methyl iodide (2 ml.) was added and the heating continued for 2 hr. Water was added to the benzene solution and the aqueous layer extracted with ether. The combined organic solution was dried and the solvent removed. The residual oil was heated under reflux at 170° (bath temp.)/15 mm. for 6 hr. and 1,4-*dihydro*-7-*methoxy*-1,1-*dimethylnaphthalene* (1·1 g.) was then obtained as an oil, b. p. 134—136°/19 mm. (Found: C, 82·5; H, 8·55. $C_{13}H_{16}O$ requires C, 82·9; H, 8·6%) $\lambda_{max.}$ 227 and 275 mμ (ε, 8840 and 3100). The n.m.r. spectrum showed a single peak at τ 8·69 (2 *C*-methyl groups) and another at 6·26 (aromatic *O*-methyl), a complex pattern of eight lines in the region 4·0—4·5 for the 2 olefinic protons which form the 2AB protons of an ABX_2 system where the X_2 protons are revealed as a broad envelope about 6·70. The 3 aromatic protons correspond to peaks at τ 3·02 (doublet, J = 8·3 c./sec. for *o*-coupling), 3·12 (doublet, J = 2·6 c./sec. for *m*-coupling), and 3·38 (quartet; J = 8·3 and 2·6 c./sec.).

(ii) *Phosphorus oxychloride in pyridine.* Phosphorus oxychloride (15 ml.) in dry pyridine (35 ml.) was added slowly to the tetralol (5·0 g.) in dry pyridine (35 ml.), and the mixture was heated on the steam-bath for 2 hr. The red solution was cooled to 0° and poured on to finely crushed ice. The resulting mixture was diluted with ether (200 ml.) and acidified with dilute hydrochloric acid. The aqueous layer was separated and extracted with ether (100 ml.), and the combined ethereal extract was washed with dilute hydrochloric acid, water, and dried ($MgSO_4$). Evaporation of the solvent gave a yellow-green oil (4·5 g.) which distilled to give mixture A (3·64 g., 80%) b. p. 78—84°/0·1 mm. (Found: C, 83·0; H, 8·8); $\lambda_{max.}$ 206, 220, 278, and 286 mμ (ε, 12,250, 8980, 2400, and 2080 respectively); $\lambda_{infl.}$ 304 mμ (ε, 642); $\nu_{max.}$ 1049, 1242, 1295, 1498, 1508, 1614, 1671, and 2966 $cm.^{-1}$.

1,4-*Dihydro*-7-*methoxy*-1,1-*dimethyl*-4-*oxonaphthalene.*—The product from the xanthate pyrolysis (200 mg.) in redistilled dioxan (15 ml.) was heated with resublimed selenium dioxide (200 mg.) on the steam-bath for 4 hr. The solid was separated and water was added to the filtrate which was extracted with ether. The solvent was removed from the washed extract and the residue, on distillation from a bulb tube at 140° (bath temp.)/0·5 mm. gave the *product* as an oil (128 mg.) which slowly solidified. It was crystallised from ether–light petroleum and formed prisms, m. p. 93—94° (Found: C, 76·4; H, 6·8. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%); $\lambda_{max.}$ 226, 237, and 337 mμ (ε, 11,100, 10,500, and 9700, respectively); $\nu_{max.}$ 1661 $cm.^{-1}$ (αβ-unsaturated carbonyl). The nuclear magnetic resonance spectrum contained bands at τ 8·56 (singlet for 2 equivalent *C*-methyl groups), 6·06 (singlet for aromatic *O*-methyl), a pair of doublets at τ 2·65 and 3·98 (J = 9·7 c./sec.) for an AX system. The three aromatic protons are shown at τ 2·78 (doublet, J = 8·3 c./sec. for *o*-coupling), 3·00 (doublet, J = 2·4 c./sec. for *m*-coupling) and 3·22 (quartet, J = 8·3 and 2·4 c./sec.). The 2,4-*dinitrophenylhydrazone* crystallised from methanol–chloroform as bright red needles, m. p. 232—233° (Found: C, 59·7; H, 4·75; N, 15·0. $C_{19}H_{18}N_4O_5$ requires C, 59·7; H, 4·75; N, 14·65%); $\lambda_{max.}$ 238 and 408 mu (ε, 23,300 and 36,300); $\lambda_{infl.}$ 255 mμ (ε, 20,600).

Nitric Acid Oxidation of the Xanthate Pyrolysis Product.—The olefin (II; R = OMe, R′ = H; 160 mg.) was stirred with 50% v/v aqueous nitric acid (3 ml.) for 10 min. The oil became a brown gum which was triturated with the aqueous acid for a further 5 min. The aqueous layer was decanted and the gum well washed with water, and after a while it solidified. It was dried, dissolved in ether, and chromatographed on alumina. The solvent was removed from the main yellow band to give a yellow gum; $\lambda_{max.}$ 248 and 373 mμ; $\nu_{max.}$ 3602 (—OH) and 1608 $cm.^{-1}$ (hydrogen bonded and unsaturated carbonyl?). The n.m.r. spectrum showed

singlets at τ 8·95 and 8·52 (*C*-methyl protons), 6·16 (aromatic *O*-methyl), 5·53 (hydroxyl), and 2·31 (olefinic proton at C-4; structure XII). The three remaining aromatic protons are revealed at τ 3·10 (doublet; J = 2·5 c./sec. for *m*-coupling), 2·69 (doublet; J = 8·4 c./sec. for *o*-coupling), and 3·29 (quartet, J = 2·5 and 8·4 c./sec.). After repeated trituration with ether, a small quantity (3 mg.) of a solid was obtained, which after crystallisation from ether gave yellow prisms, m. p. 110—111·5°.

6-Bromo-7-methoxy-1,2-dimethylnaphthalene and 2,3-Dibromo-7-methoxy-1,1-dimethyltetralin.—A solution of the phosphorus oxychloride dehydration product (333 mg.) in carbon tetrachloride (2 ml.) at 0° was treated dropwise, with shaking, with a 2% solution of bromine in carbon tetrachloride until a yellow colour persisted. Evaporation at room temperature under reduced pressure gave a brown gum (500 mg.) which was transferred in benzene–light petroleum (1 : 3) to an alumina column (80 g.). Elution with light petroleum gave a solid (98 mg., 21%) which crystallised from light petroleum as prisms of *6-bromo-7-methoxy-1,2-dimethylnaphthalene* (33 mg., 7%), m. p. 86—88° (Found: C, 58·2; H, 5·2; Br, 29·1. $C_{13}H_{13}BrO$ requires C, 58·4; H, 5·65; Br, 29·9%); $\lambda_{max.}$ 238·5, 261, 272, 283, 293, 324, and 339·5 mμ (ε, 75,800, 3620, 4640, 5060, 3730, 1530, and 1840, respectively). The n.m.r. spectrum (in CH_2Cl_2) showed singlets at τ 7·44 (intensity 6; 2 aromatic *C*-methyl groups) and 6·10 (3; aromatic *O*-methyl group), and a complex absorption at τ 3·28—2·26 (4; aromatic protons).

Elution of the chromatogram with benzene–light petroleum (1 : 1) gave a white solid (181 mg., 29%) which crystallised from light petroleum as prisms of *2,3-dibromo-7-methoxy-1,1-dimethyltetralin* (69 mg., 11%), m. p. 76—79° (Found: C, 45·4; H, 4·9; Br, 47·5. $C_{13}H_{16}Br_2O$ requires C, 44·9; H, 4·6; Br, 45·9%); $\lambda_{max.}$ 281 and 288 mμ (ε, 2360 and 2240); $\lambda_{infl.}$ 220 mμ (ε, 8830). The n.m.r. spectrum contained singlets at τ 8·61 and 8·37 (intensity 3; 2 *C*-methyl groups), 6·24 (3; aromatic *O*-methyl group), and complex absorptions at 6·58—6·41 (2; C-4 methylene group), 5·85 to 5·33 (2; C-2 and C-3 protons), and 3·50—3·09 (corresponding to the 3 aromatic protons).

7-Benzoyloxy-1,2-dimethylnaphthalene.—The phosphorus oxychloride dehydration product (above; 3·01 g.) and dry pyridine hydrochloride (14 g.) were heated under reflux under nitrogen for 1 hr. The cooled mixture was poured into water (100 ml.), acidified with dilute hydrochloric acid, and extracted with ether. The ethereal extract was washed with dilute hydrochloric acid, water, and dried. Evaporation gave a brown gum (2·75 g.), which was transferred in benzene to a column of acid-washed alumina (100 g.). Elution with benzene–ether (1 : 1) and then ether gave a dark red gum (2·53 g.), which was dissolved in benzene and transferred to a column of silica (100 g.). Elution with benzene gave two fractions: the first (762 mg.), was a red oil $\nu_{max.}$ 3617 (sharp, strong) cm.$^{-1}$. The second fraction (261 mg.), which was a red gum, $\nu_{max.}$ 3500 and 3620 cm.$^{-1}$ (both sharp, medium), and was discarded. The red oil (762 mg.) distilled (bulb-tube) as a highly viscous phenol (370 mg., 13%), b. p. 114—116° (bath)/0·15 mm. (Found: C, 81·6, 81·7, 81·8; H, 7·9, 7·7, 8·4. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%); $\lambda_{max.}$ 233, 274, and 336 mμ (ε, 23,900, 4500, and 640, respectively); $\lambda_{infl.}$ 265 and 283 mμ (ε, 4130 and 3940); $\nu_{max.}$ 1171, 1181, 1201, 1615, 2936, 2963, 3478, and 3617 cm.$^{-1}$.

In another experiment, the crude product was distilled immediately without chromatography, and the yield of the phenolic product was again 13%.

Benzoylation of the phenol gave *7-benzoyloxy-1,2-dimethylnaphthalene* (26%) as long needles, m. p. 114—117° (Found: C, 82·1; H, 6·0. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%); $\lambda_{max.}$ 232, 266, and 275 mμ (ε, 71,400, 9070, and 8710, respectively); $\lambda_{infl.}$ 282, 298, and 318 mμ (ε, 7440, 3990, and 581). The n.m.r. spectrum contained singlets at τ 7·56 and 7·48 (intensity 3; 2 aromatic *C*-methyl groups) and a complex absorption at 2·74—1·73 corresponding to the aromatic protons.

7-Methoxy-1,1-dimethyl-2-tetralone.—An 8N-chromic acid sulphuric acid solution was added dropwise, with swirling, to a solution of 7-methoxy-1,1-dimethyl-2-tetralol (1·0 g.) in acetone (12 ml.). The mixture was maintained at 5—15° during the addition. When the solution had acquired a persistent pale yellow colour, it was poured into water (100 ml.) and extracted with ether. The ethereal extract was washed with water, dried, and evaporated, giving a yellow oil. Bulb-tube distillation gave the tetralone as a pale yellow oil, b. p. 121—123° (bath)/0·5 mm. (lit.,[16] b. p. 99—101·5°/0·4 mm., m. p. 53·5—54·3°) (Found: C, 76·2; H, 8·0. Calc. for $C_{13}H_{16}O_2$: C, 76·4; H, 7·9%), $\lambda_{max.}$ 206, 220, 282, and 286·5 mμ (ε, 14,800, 7300, 2110, and 1940, respectively); $\nu_{max.}$ 1049, 1270, 1499, 1508, 1617, and 1721 cm.$^{-1}$.

The *semicarbazone* crystallised from ethanol as plates, m. p. 214—216° (Found: C, 64·4;

H, 7·0; N, 16·1. $C_{14}H_{19}N_3O_2$ requires C, 64·3; H, 7·3; N, 16·1%). The *2,4-dinitrophenylhydrazone* formed orange-red needles, m. p. 155—157° (ethanol) (Found: C, 59·1; H, 5·2; N, 14·5. $C_{19}H_{20}N_4O_5$ requires C, 59·4; H, 5·25; N, 14·6%).

7-Methoxy-1,1,3,3-tetramethyl-2-tetralol.—A solution of 7-methoxy-2-tetralone (19·94 g.) in t-butyl alcohol (90 ml.) was added to a solution of potassium (18·5 g., 4 mol.) in t-butyl alcohol (350 ml.) with stirring under nitrogen at 40°. After 30 min. at room temperature, a solution of methyl iodide (58 ml., 8 mol.) in t-butyl alcohol (80 ml.) was added; potassium iodide began to precipitate almost immediately. The mixture was heated under reflux for 2 hr., and t-butyl alcohol (420 ml.) was then removed. The cooled residue was treated with water (50 ml.), and the mixture was acidified with 3N-hydrochloric acid and extracted with ether. The ethereal extract was washed with water, dilute sodium carbonate solution (2 × 200 ml.), dilute sodium thiosulphate solution (4 × 200 ml.), and water again, and dried. After evaporation of the ether, the residue distilled as a pale yellow oil (21·35 g.; 92%), b. p. 103—108°/0·5 mm. In other batches the yields varied from 83 to 96%.

A solution of this methylation product (20·32 g.) in dry ether (180 ml.) was added dropwise, with stirring, to lithium aluminium hydride (8·0 g., 8 mol.) in dry ether (300 ml.), and the mixture was heated under reflux for 20 hr. The cooled mixture was decomposed by the dropwise addition of ethyl acetate, with stirring, until there was no further visible reaction. After similar treatment with water, 5N-sulphuric acid was added to acidify the mixture. The ether layer was separated, the aqueous layer was extracted with ether, and the combined ethereal solutions were washed with water, dried, and evaporated. The oily residue was transferred in light petroleum to an alumina (400 g.) column and the column was eluted with light petroleum, light petroleum–benzene (1 : 1), benzene, and benzene–ethanol (19 : 1). Evaporation of the benzene solution gave a solid (7·32 g., 36%) which crystallised from light petroleum as needles of *7-methoxy-1,1,3,3-tetramethyl-2-tetralol*, m. p. 58—60° (Found: C, 77·2; H, 9·0. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·45%); $\lambda_{max.}$ 220, 281, and 288 mμ (ε, 7380, 2090, and 1960, respectively); $\nu_{max.}$ 1046, 1054, 1253, 1283, 1508, 1615, 2968, and 3647 cm.$^{-1}$. The n.m.r. spectrum showed singlets at τ 9·07, 8·89, 8·68, and 8·61 (intensity 3, *C*-methyl groups), 6·16 (3; *O*-methyl group), 7·41 (2; C-4 methylene group), 7·68 (1; hydroxyl proton), 6·50 (1; C-2 proton), and a complex pattern at 3·37—2·28 for the 3 aromatic protons.

The *benzoate* crystallised from methanol as prisms, m. p. 92—93° (Found: C, 77·6; H, 7·6. $C_{22}H_{26}O_3$ requires C, 78·05; H, 7·7%).

7-Hydroxy-1,1,3,3-tetramethyl-2-tetralone.—The foregoing methylation product (13·56 g.) from 7-methoxy-2-tetralone, and dry pyridine hydrochloride (50 g.) were heated under reflux under nitrogen for 1 hr. The cooled mixture was poured into water (300 ml.), acidified with dilute hydrochloric acid, and extracted with ether (3 × 150 ml.). The combined ethereal extract was washed with dilute hydrochloric acid (2 × 100 ml.), water, and then dilute sodium hydroxide solution (3 × 80 ml.). The alkaline extracts were acidified with dilute hydrochloric acid as rapidly as possible and extracted with ether (3 × 100 ml.). The combined ethereal extract was washed, dried, and evaporated to give a brown gum (9·9 g.). Attempted crystallisations were found to be unsatisfactory, but sublimation at 100°/0·1 mm. gave a white greasy solid which was crystallised from carbon tetrachloride to give prisms of *7-hydroxy-1,1,3,3-tetramethyl-2-tetralone* (3·48 g., 28%), m. p. 140—146°. After sublimation at 100°/0·1 mm. it was obtained as prisms, m. p. 144—146° (Found: C, 76·8; H, 7·75. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%); $\lambda_{max.}$ 220 and 283 mμ (ε, 7130 and 2240, respectively); $\nu_{max.}$ 1045, 1181, 1293, 1715, 2980, 3410, 3467, and 3627 cm.$^{-1}$. The n.m.r. spectrum contained singlets at τ 8·91 and 8·62 (each intensity 6; *gem*-dimethyl groups) and 7·12 (2; C-4 methylene group) and a complex absorption at 3·36—1·54, corresponding to aromatic and phenolic protons.

The *benzoate* crystallised from methanol as long fine needles, m. p. 88—90° (Found: C, 78·2; H, 6·85. $C_{21}H_{22}O_3$ requires C, 78·2; H, 6·9%).

7-(2-Benzoyl-4-nitrophenoxy)-1,1,3,3-tetramethyl-2-tetralone.—The above phenol (2·31 g.), 2-chloro-5-nitrobenzophenone [27] (2·74 g.), and potassium hydroxide (0·67 g.) were heated under reflux in ethanol (75 ml.) for 48 hr. Most of the solvent was then evaporated, and the cooled mixture was diluted with water, acidified with dilute hydrochloric acid, and extracted with ether. The ethereal extract was washed with water, dried ($MgSO_4$), and evaporated, and the residue was transferred to an alumina (120 g.) column in benzene–light petroleum (1 : 1). Elution gave a yellow gum (3·76 g.) which crystallised from chloroform–ethanol to give needles

[27] Fries, *Annalen*, 1927, **454**, 287.

of 7-(2-*benzoyl*-4-*nitrophenoxy*)1,1,3,3-*tetramethyl*-2-*tetralone* (2·76 g., 63%), m. p. 142—149°, raised to 148—150° after recrystallisation from ethanol (Found: C, 72·4; H, 5·5; N, 3·3. $C_{27}H_{25}NO_5$ requires C, 73·1; H, 5·7; N, 3·15%); $\lambda_{max.}$ 205 and 256 mμ (ε, 39,600 and 19,000); $\lambda_{infl.}$ 298 mμ (ε, 12,400); $\nu_{max.}$ 1263, 1277, 1350, 1453, 1479, 1680, and 1714 cm.$^{-1}$.

The 2,4-*dinitrophenylhydrazone* crystallised from chloroform–methanol as orange-yellow needles, m. p. 235—237° (Found: C, 62·2; H, 5·5; N, 10·5. $C_{33}H_{29}N_5O_8,CH_3{\cdot}OH$ requires C, 62·3; H, 5·1; N, 10·7. $C_{33}H_{29}N_5O_8$ requires C, 63·55; H, 4·7; N, 11·2%); $\lambda_{max.}$ (i) (in ethanol–chloroform, 9 : 1) 221 and 380 mμ (ε, 39,000 and 28,100), $\lambda_{infl.}$ 295 mμ (ε, 16,900), (ii) (in ethanol–chloroform 9 : 1, made alkaline to 0·01N with sodium hydroxide) 496 mμ (ε, 27,000), $\lambda_{infl.}$ 313 mμ (ε, 15,750); $\nu_{max.}$ (in chloroform) 1715 cm.$^{-1}$ (1680 cm.$^{-1}$ absent).

7-(2-*Benzoyl*-4-*nitrophenoxy*)-6-*hydroxy*-1,1,3,3-*tetramethyl*-2-*tetralone*.—The above ether (1·51 g.) in acetic acid (36 ml.) was treated dropwise during 15 min., with cooling and shaking, with ice-cold concentrated sulphuric acid (58 ml.). After 30 min., the deep red solution was diluted with acetic acid (60 ml.), and 30% hydrogen peroxide (100 ml.) was added dropwise during 20 min., the solution becoming colourless and a solid precipitating. After 30 min. the mixture was poured into water (700 ml.), and the precipitate was collected, washed with water, and dried. The product could not be crystallised and was transferred to an alumina (80 g.) column in benzene–light petroleum (1 : 1). Material eluted with benzene–light petroleum (1 : 1), benzene, and chloroform–benzene mixtures were discarded, but elution with pure chloroform gave the *hydroxy-ether* (1·21 g.) as a yellow transparent glass (Found: C, 70·1; H, 5·3. $C_{27}H_{25}NO_6$ requires C, 70·55; H, 5·5%); $\lambda_{max.}$ 208, 258, and 291 mμ (ε, 47,300, 16,600, and 13,900, respectively); $\nu_{max.}$ 1237, 1277, 1348, 1479, 1633 (bonded C=O), 1717 (C=O), 3312, 3545, and 3578 cm.$^{-1}$.

B. *Derivatives of* 1,1-*Dimethyltetralin*-2,6,7-*triol and Related Compounds.*

4-(3′,4′-*Dimethoxyphenyl*)-4-*methylvaleric Acid*.—δδ-Dimethylbutyrolactone [8] (4·7 g.) in nitrobenzene (5 ml.) was added during 10 min. to a mixture of veratrole (5·7 g.), aluminium chloride (19 g.) and nitrobenzene (30 ml.). The mixture was heated for 3 hr., then cooled, treated with iced water and distilled in steam. The residue was extracted with ether and the ethereal extract shaken with 10% aqueous potassium hydroxide solution. The alkaline extract was acidified and again extracted with ether. The solvent was removed and an oil (2·8 g.), b. p. 160—180°/0·3 mm. obtained. This gave a deep red 2,4-dinitrophenylhydrazone (possibly a derivative of 6-hydroxy-7-methoxy- or 7-hydroxy-6-methoxy-4,4-dimethyl-1-tetralone) (Found: N, 13·8. $C_{19}H_{20}N_4O_6$ requires N, 14·0%). The oil slowly solidified and the main component was 4-(3′,4′-*dimethoxyphenyl*)-4-*methylvaleric* acid which was extracted through aqueous sodium hydrogen carbonate solution and had m. p. 114—115° after crystallisation from ether–light petroleum (Found: C, 66·4; H, 7·8. $C_{14}H_{20}O_4$ requires C, 66·6; H, 8·0%); $\nu_{max.}$ ($CHCl_3$) 1708 (carboxyl carbonyl), 880, 857, and 830 (1,2,4-trisubstituted benzene).

5,8-*Dibromo*-3,4-*dihydro*-6,7-*dimethoxy*-1-*methylnaphthalene*.—6,7-Dimethoxy-1-tetralone [28] [2,4-dinitrophenylhydrazone, scarlet plates, m. p. 247—248°, from chloroform–methanol (Found: C, 55·8; H, 4·4; N, 14·8. $C_{18}H_{18}N_4O_6$ requires C, 55·95; H, 4·7; N, 14·5%); $\lambda_{max.}$ ($CHCl_3$) 250, 309, and 407 mμ (ε, 15,400, 8500, and 25,800, respectively)], was converted into 3,4-dihydro-6,7-dimethoxy-1-methylnaphthalene with methylmagnesium bromide by the method of Howell and Taylor.[17]

A 5% solution of bromine in carbon tetrachloride was added dropwise to a solution of the above styrene in carbon tetrachloride until a red colour persisted. Removal of the solvent gave a brown gum which crystallised on addition of ethanol. Recrystallisation from ethanol gave the *dibromide* as plates, m. p. 123—125° (Found: C, 43·3; H, 3·8; Br, 43·9. $C_{13}H_{14}Br_2O_2$ requires C, 43·1; H, 3·9; Br, 44·15%); $\lambda_{max.}$ 206, 239, and 312 mμ (ε, 22,000, 23,100, and 8770, respectively); $\nu_{max.}$ 1271, 1263, and 1517 cm.$^{-1}$. Aromatic C–H bands at 3015—3080 cm.$^{-1}$ were absent.

6,7-*Dimethoxy*-1-*methyl*-2-*naphthol and* 6,7-*Dimethoxy*-1-*methyl*-2-*tetralone*. (i).—A solution of 6,7-dimethoxy-1-methyl-3,4-dihydronaphthalene (31·1 g.) in chloroform (70 ml.) was treated dropwise at 0—7° during 2 hr. with a solution of perbenzoic acid (22·6 g.; 7% excess) in chloroform (350 ml.). The concentration of the peracid solution was determined by titration. After

[28] Haworth and Mavin, *J.*, 1932, 1486.

16 hr. at 0°, the solution was washed with 4N-sodium hydroxide solution and then water, and evaporated. A solution of the residue in methanol (200 ml.), water (160 ml.), and concentrated sulphuric acid (30 ml.) was heated under reflux for 2 hr. and then concentrated under reduced pressure to *ca.* 300 ml. The cooled solution was diluted with water and extracted with ether, and the ethereal extract was washed with water, dried, and evaporated. The yellow-brown residue (30·25 g.) was boiled with benzene (150 ml.) and cooled. Filtration gave crystalline 6,7-dimethoxy-1-methyl-2-naphthol (2·87 g., 8·5%), m. p. 219—222° (lit.,[17] m. p. 223°). The *benzoate* crystallised from chloroform–methanol as plates, m. p. 191—193° (Found: C, 74·5; H, 5·2. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%); $\lambda_{max.}$ 272, 315, 322, and 329 mμ (ε, 9940, 2950, 2220, and 3640, respectively), $\lambda_{infl.}$ 281 mμ (ε, 8870).

The benzene filtrate was concentrated to *ca.* 100 ml. and the solution was filtered through alumina (400 g.), benzene being used as eluent. Evaporation of the benzene gave a yellow gum (21·3 g.) which crystallised from methanol to give 6,7-dimethoxy-1-methyl-2-tetralone as rods (13·35 g., 40·4%), m. p. 83—87°, raised to 87·5—88·5° (lit.,[17] 87°) after recrystallisation from ether (Found: C, 70·7; H, 7·1. Calc. for $C_{13}H_{16}O_3$: C, 70·9; H, 7·3%); $\lambda_{max.}$ 285 mμ (ε, 3800), $\lambda_{infl.}$ 230 mμ (ε, 7150); $\nu_{max.}$ 1289, 1517, 1722 (C=O), and 2933 cm.$^{-1}$. The semicarbazone, crystallised from methanol as needles, m. p. 195—197° (decomp.) [lit.,[17] m. p. 200° (decomp.)] (Found: C, 60·4; H, 6·7; N, 15·1. Calc. for $C_{14}H_{19}N_3O_3$: C, 60·6; H, 6·9; N, 15·15%).

(ii) A solution of perbenzoic acid (23·0 g.; 52% excess) in chloroform (300 ml.) was added dropwise at 0—8° to a solution of the styrene (21·0 g.) in chloroform (70 ml.), and the solution was kept at 0° for 12 hr. The reaction was completed and worked up as above to give the 2-naphthol (4·94 g., 22%), m. p. 214—222°, and the 2-tetralone (3·2 g., 14%), m. p. 84—87°.

(iii) Lead tetra-acetate (57·0 g.) was added gradually to an ice-cold solution of 3,4-dihydro-6,7-dimethoxy-1-methylnaphthalene (22·2 g.) in acetic acid (250 ml.), and after 20 min. at 0°, the solution was allowed to warm to room temperature. After 2 hr., the solution was poured into water (700 ml.) and extracted with ether. The ethereal extract was washed until neutral and evaporated, and a solution of the residue in ethanol (250 ml.), water (100 ml.), and concentrated sulphuric acid (18 ml.) was heated under reflux for 2 hr. The cooled solution was poured into water (600 ml.) and extracted with ether. The ethereal extract was washed until neutral, dried, and evaporated. Distillation gave a pale yellow oil (9·85 g.), b. p. 133—138°/0·3 mm., which was dissolved in benzene–light petroleum (1 : 4) and transferred to an alumina (120 g.) column. Elution with benzene–light petroleum (1 : 4) gave 6,7-dimethoxy-1-methylnaphthalene (2·14 g., 9%), as plates, m. p. 114—115° (lit.,[18] 114°). Elution with benzene–light petroleum (1 : 1) gave 6,7-dimethoxy-1-methyl-2-tetralone (2·02 g.; 8%) as rods, m. p. 87—88·5°, from ethanol. This sample was identical with that obtained in the previous experiments.

6,7-*Dimethoxy*-1,1-*dimethyl*-2-*tetralone*.—A solution of 6,7-dimethoxy-1-methyl-2-tetralone (13·55 g., 1·0 mol.) in t-butyl alcohol (270 ml.) was added to a solution of potassium (2·65 g., 1·1 mol.) in t-butyl alcohol (160 ml.) with stirring under nitrogen at 35°. After the addition the mixture was stirred for 10 min. at room temperature, and then a solution of methyl iodide (18 g., 2·0 mol.) in t-butyl alcohol (120 ml.) was added dropwise. The mixture was stirred for 1 hr., heated under reflux for 1·5 hr., and t-butyl alcohol (420 ml.) was then removed. The cooled mixture was treated with water (100 ml.), acidified with 5N-hydrochloric acid (300 ml.), and extracted with ether. The ethereal extract was washed with water, dried, and evaporated giving 6,7-*dimethoxy*-1,1-*dimethyl*-2-*tetralone* (13·76 g., 95%) as a yellow oil. A sample distilled (bulb-tube) as a pale yellow viscous oil, b. p. 129—132° (bath)/0·1 mm. (Found: C, 71·8; H, 7·9. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·75%); $\lambda_{max.}$ 205 and 286 mμ (ε, 30,100 and 3260, respectively), $\lambda_{infl.}$ 227 mμ (ε, 7100); $\nu_{max.}$ 1080, 1261, 1277, 1468, 1521, and 1720 cm.$^{-1}$. The 2,4-*dinitrophenylhydrazone* crystallised from chloroform–methanol as orange-yellow needles, m. p. 197—199° (Found: C, 57·8; H, 5·0; N, 13·1. $C_{20}H_{22}N_4O_6$ requires C, 57·95; H, 5·35; N, 13·5%); $\lambda_{max.}$ 232, 269, and 365 mμ (ε, 24,300, 11,350, and 23,800, respectively).

The *semicarbazone* crystallised from methanol as prisms, m. p. 171—173° (Found: C, 62·1; H, 7·65. $C_{15}H_{21}N_3O_3$ requires C, 61·85; H, 7·3%).

6,7-*Dimethoxy*-1,1-*dimethyl*-2-*tetralol*.—A solution of the above tetralone (13·75 g.) in dry ether (300 ml.) was added dropwise, with stirring to lithium aluminium hydride (7·0 g., 8 mol.) in dry ether (450 ml.) and the mixture was heated under reflux for 2 hr. and stirred for 14 hr. at room temperature. The cooled stirred mixture was decomposed by the dropwise addition of ethyl acetate until there was no further visible reaction. After treatment with water, the

mixture was acidified with 7N-sulphuric acid, and the aqueous layer was separated and extracted with ether. The combined ethereal solution was washed with water, dried, and evaporated, giving a brown viscous gum (13·53 g.). Crystallisation from ether–light petroleum gave the *tetralol* (7·73 g., 56%) as needles, m. p. 75—79°. After evaporation, the residual product was transferred to an alumina (100 g.) column in benzene–light petroleum (1 : 3). All material eluted with light petroleum, benzene–light petroleum (1 : 1), and benzene was discarded, and elution with benzene–ethanol (19 : 1) gave a yellow gum (2·86 g.) which crystallised from ether–light petroleum to give the tetralol (1·96 g.), m. p. 74—79°. The total yield of tetralol was 70% (9·69 g.). A sample recrystallised from ether–light petroleum as needles, m. p. 78—79° (Found: C, 70·7; H, 8·4. $C_{14}H_{20}O_3$ requires C, 71·15; H, 8·5%); $\lambda_{max.}$ 209, 224, 283, and 286 mμ (ε, 18,500, 7960, 3540, and 3540, respectively); $\nu_{max.}$ 1082, 1268, 1469, 1523, 2940, 2970, and 3640 cm.$^{-1}$. The n.m.r. spectrum contained singlets at τ 8·74 and 8·68 (intensity 3; 2 *C*-methyl groups), 6·16 and 6·11 (3; aromatic *O*-methyl groups), a quartet centred at 8·05 (*J*, 6·6 c./sec.; 2; C-3 methylene group), a triplet centred at 7·16 (*J*, 6·6 c./sec.; 2; C-4 methylene group), a singlet at 7·58 (hydroxyl proton), a multiplet about 6·37 (C-2 proton), and 2 singlets at 3·44 and 3·17 (aromatic protons).

The *benzoate* crystallised from methanol as cubes, m. p. 82—83° (Found: C, 74·0; H, 6·7. $C_{21}H_{24}O_4$ requires C, 74·1; H, 7·1%).

A mixture of the tetralol (660 mg.) and potassium hydroxide (0·6 g.) was heated gently until it melted. The fused product was stirred vigorously; after cooling, carbon disulphide (1 ml.) was added and the stirring continued for 5 min. Ether (20 ml.) was then added and the mixture stirred for a further 5 min. The *xanthate* separated as a yellow powder and was purified by dissolution in the minimum amount of acetone followed by precipitation with ether. It was dried *in vacuo* (Found, on a sample dried at 100° *in vacuo* over phosphorus pentoxide: C, 50·1; H, 5·35; S, 15·3. $C_{15}H_{19}KO_3S_2,\frac{1}{2}H_2O$ requires C, 50·1; H, 5·6; S, 17·8%).

1,4-*Dihydro*-6,7-*dimethoxy*-1,1-*dimethylnaphthalene*.—The foregoing xanthate (950 mg.) was suspended in dry benzene (30 ml.), methyl iodide (3 ml.) was added, and the mixture was heated under reflux for 4 hr. More methyl iodide (2 ml.) was added and the heating continued for another 12 hr. Water was then added and the benzene layer separated. The aqueous layer was extracted with ether and the organic solutions combined. Removal of the solvent gave the methyl xanthate as a yellow gum which was heated in a metal-bath at 170—190°/12 mm. for 4 hr. Distillation of the product gave the *dihydronaphthalene*, b. p. 160—162°/13 mm. which was purified by chromatography through alumina and redistillation at 150—160° (bath temp.)/0·6 mm.; the product was obtained as a liquid (Found: C, 76·6; H, 8·25. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%); $\lambda_{max.}$ 225, 282, and 284·5 mμ (ε, 11,000, 4210, and 4260, respectively). The n.m.r. spectrum showed a singlet at τ 8·66 (2 equivalent *C*-methyl groups), singlets at 6·19 and 6·16 (aromatic *O*-methyl), singlets at 3·51 and 3·17 (aromatic protons at C-5 and C-8), and a complex pattern of eight lines between 4·56 and 4·10 for the 2 AB olefinic protons of an ABX_2 system where the X_2 protons were revealed as a broad envelope centred at τ 6·68.

6,7-*Dimethoxy*-1,2-*dimethylnaphthalene*.—A mixture of 6,7-dimethoxy-1,1-dimethyl-2-tetralol (502 mg., 1·0 mol.) and boric acid (147 mg., 1·1 mol.) was heated under reflux under nitrogen in a bath maintained at 250—280° for 1·5 hr. The cooled mixture was taken up in ether (70 ml.) and water (50 ml.), and the slightly fluorescent ethereal solution was washed with dilute sodium carbonate solution (100 ml.), water (100 ml.), and dried ($MgSO_4$). Evaporation gave a yellow gum (442 mg.), which crystallised (twice) from methanol as colourless plates of 6,7-*dimethoxy*-1,2-*dimethylnaphthalene* (104 mg., 22%), m. p. 127—128° (Found: C, 77·5; H, 7·85. $C_{14}H_{16}O_2$ requires C, 77·75; H, 7·5%); $\lambda_{max.}$ 236, 266, 275, 284, 294, 314, 321, and 329 mμ (ε, 66,000, 4190, 4740, 4630, 3310, 2430, 1820, and 3530, respectively); $\nu_{max.}$ 1163, 1269, 1426, 1468, 1497, 1519, and 1523 cm.$^{-1}$. The n.m.r. spectrum contained singlets at τ 7·54 and 7·46 (intensity 3; aromatic *C*-methyl groups), 6·02 and 5·98 (3; aromatic *O*-methyl groups), and a complex absorption at 3·10—2·58 corresponding to the aromatic protons. The *picrate* crystallised from ethanol as orange-red needles, m. p. 126—127° (Found: C, 54·3; H, 4·5. $C_{20}H_{19}N_3O_9$ requires C, 53·95; H, 4·3%).

6,7-*Dimethoxy*-1-*methylnaphthalene*.—2-Benzoyloxy-6,7-dimethoxy-1,1-dimethyltetralin (516 mg.) was heated under reflux for 2 hr. under nitrogen in a bath at 350—360°. The cooled product was dissolved in ether (50 ml.), and the solution was washed and dried ($MgSO_4$). Evaporation gave a brown solid (328 mg.), which was dissolved in benzene and filtered through

alumina (10 g.). Evaporation of the benzene eluate gave a solid (287 mg.), which crystallised from methanol to give 6,7-dimethoxy-1-methylnaphthalene (124 mg., 37%) as plates, m. p. 114—115° (lit.[18] 114°) (Found: C, 76·6; H, 7·4. Calc. for $C_{13}H_{14}O_2$: C, 77·2; H, 7·0%). The m. p. was not depressed on admixture with a sample prepared by oxidation of 3,4-dihydro-6,7-dimethoxy-1-methylnaphthalene (above); $\lambda_{max.}$ 236, 243, 264, 273, 281, 292, 311, 318, and 325 mμ (ε, 60,100, 41,000, 3890, 4530, 4670, 3250, 2050, 1450, and 3110, respectively). The infrared spectra of the two samples were also identical The picrate crystallised from ethanol as long orange needles, m. p. 124—125° (lit.,[28] m. p. 116—117°).

C. *Podocarpic Acid Derivatives.*

Methyl 1,2,3,4,4a,9,10,10a-*Octahydro*-6-*methoxy*-1,4a-*dimethyl*-9-*oxophenanthrene*-1-*carboxylate* (*Methyl* O-*Methyl*-7-*oxopodocarpate*).—Methyl *O*-methylpodocarpate[29] (2·1 g.) was dissolved in acetic acid (50 ml.) and powdered chromic acid (1·5 g.) was added. The mixture was heated on the steam-bath for ½ hr. and then kept at room temperature for 48 hr. Water was then added until the solution became turbid; crystals (1·9 g.) of the oxidation *product* were slowly deposited. Crystallisation from light petroleum gave the keto-ester as needles, m. p. 111—112° (Found: C, 72·2; H, 7·6; OMe, 21·6. $C_{19}H_{24}O_4$ requires C, 72·1; H, 7·65; 2OMe, 19·6%); $\lambda_{max.}$ 226 and 277 mμ (ε, 13,000 and 14,400, respectively); $\nu_{max.}$ in the carbonyl region at 1686 (ketone) and 1735 (ester) cm.$^{-1}$.

Methyl 1,2,3,4,4a,9-*Hexahydro*-6-*methoxy*-1,4a-*dimethyl*-9-*oxophenanthrene*-1-*carboxylate* (*Methyl* O-*Methyl*-7-*oxo*-5,6-*dehydropodocarpate*).—The foregoing keto-ester (1·9 g.) in acetic acid (70 ml.) was heated with selenium dioxide (1·0 g.) on the steam-bath for 7 hr. and then kept at room temperature overnight. The suspension was filtered, and water was added to the filtrate. Crystals of the *unsaturated ketone* (1·73 g.) separated and were crystallised from methanol, giving rods, m. p. 176—177° (Found: C, 72·3; H, 6·7; OMe, 16·9. $C_{19}H_{22}O_4$ requires C, 72·6; H, 7·05; 1 OMe, 19·75%); $\lambda_{max.}$ 202, 242, and 302 mμ (ε, 24,200, 15,300, and 11,300, respectively); $\nu_{max.}$ in the carbonyl region at 1660 (αβ-unsaturated ketone) and 1737 (ester) cm.$^{-1}$. The n.m.r. spectrum showed peaks at τ 8·78 and 8·52 (*C*-methyls), 6·37 (ester methyl), 6·14 (aromatic methoxyl), 3·51 (singlet, olefinic proton at C-10), 3·05 (singlet, aromatic proton at C-5), a pair of doublets centred at 3·17 and 2·00 (J = 8·6 c./sec.) (AB system of the two aromatic protons at C-7 and C-8).

The *hydrazone* was crystallised from aqueous ethanol and formed rectangular plates, m. p. 130—131° (Found: C, 69·7; H, 7·05; N, 8·55; OMe, 13·15. $C_{19}H_{24}N_2O_3$ requires C, 69·5; H, 7·35; N, 8·5; 1OMe, 18·8%); $\lambda_{max.}$ 244 and 319 mμ (ε, 14,400 and 8000, respectively); $\nu_{max.}$ 3411 (NH_2), 1735 (ester carbonyl), and 1648 (C=N) cm.$^{-1}$. The n.m.r. spectrum was similar to that of the parent ketone: the olefinic proton was revealed as a singlet at τ 3·31, and the aromatic protons corresponded to peaks at τ 3·20 (singlet, for that at C-5); and a pair of doublets centred at τ 2·12 and 3·33 (J = 8·9 c./sec.) (AB system for those at C-7 and C-8).

The *thioketal* was prepared by adding a mixture of ethane-1,2-dithiol (1·2 ml.) and boron trifluoride etherate (2 ml.) dropwise to an ice-cooled solution of the unsaturated ketone (3·14 g.) in acetic acid (50 ml.). The product (2·2 g.) crystallised after 3 days at room temperature and more (0·7 g.) was obtained by addition of water to the filtrate. Sublimation or recrystallisation from chloroform–ethanol gave cubes of the *thioketal*, m. p. 176—177° (Found: C, 64·8; H, 6·35; S, 16·7; OMe, 16·1. $C_{21}H_{26}O_3S_2$ requires C, 64·6; H, 6·7; S, 16·4; 1OMe, 15·9%); $\lambda_{max.}$ none; $\nu_{max.}$ 1735 (ester carbonyl) cm.$^{-1}$.

Methyl O-*Methylpodocarpate*.—The above thioketal (800 mg.) in ethanol (100 ml.) was heated under reflux with Raney nickel (W-2, *ca.* 2 g.) for 16 hr. The metal was separated and the solvent evaporated. The yellow oily residue was chromatographed on alumina and afforded only one fraction of solid (240 mg.). Crystallisation from aqueous ethanol gave prisms of methyl *O*-methylpodocarpate, m. p. and mixed m. p. 127—128° (lit.,[29] 128°). The u.v. and i.r. spectra of the product were identical with those of an authentic sample.

Azine of Methyl 1,2,3,4,4a,9-*hexahydro*-6-*methoxy*-1,4a-*dimethyl*-9-*oxophenanthrene*-1-*carboxylate*.—Nitrogen was bubbled through a mixture of resublimed potassium t-butoxide (1 g.) and dimethyl sulphoxide (5 ml.). The above hydrazone (50 mg.) was gradually added to the mixture during 40 min., and the nitrogen stream maintained for another 1 hr. (cf. ref. 26). Methylene dichloride and water were added and shaken with the reaction mixture; the organic

[29] Sherwood and Short, *J.*, 1938, 1006.

layer was separated and washed with water, dried, and evaporated. The residual brown gum was chromatographed through alumina and one fraction of yellow solid (23 mg.) was obtained. Crystallisation from methanol gave yellow needles of the *azine*, m. p. 264—266° (Found: N, 4·9. $C_{38}H_{44}N_2O_6$ requires N, 4·5%); $\lambda_{max.}$ 243, 296, and 368 mμ (ε, 24,000, 18,600, and 18,500, respectively); $\nu_{max.}$ 1639 (C=N) and 1736 (ester carbonyl) cm.$^{-1}$.

Methyl 6,7-*Diacetoxy*-1,2,3,4,4a,9,10,10a-*octahydro*-1,4a-*dimethylphenanthrene*-1-*carboxylate* (*Diacetate of Methyl* 13-*Hydroxypodocarpate*).—Methyl 13-hydroxypodocarpate [cf.14] m. p. 242—244° (Found: C, 70·7; H, 7·5. $C_{18}H_{24}O_4$ requires C, 71·0; H, 7·95%) was acetylated with acetic anhydride and pyridine at room temperature. The diacetate crystallised from methanol as needles, m. p. 130—132° (Found: C, 68·2; H, 7·3. $C_{22}H_{28}O_6$ requires C, 68·0; H, 7·3%); $\lambda_{max.}$ 271 and 277 mμ (ε, 1320 and 1350); $\nu_{max.}$ 1171, 1173, 1199, 1218, 1734 (ester carbonyl), and 1779 (aromatic acetate carbonyl) cm.$^{-1}$. The n.m.r. spectrum contained singlets at τ 8·99 and 8·76 (intensity 3; *C*-methyl groups), 7·77 (6; 2 acetate methyl groups), 6·38 (3; ester methyl group), 3·16 and 2·98 (1; aromatic protons).

Methyl 6,7-*Diacetoxy*-1,2,3,4,4a,9,10,10a-*octahydro*-1,4a-*dimethyl*-9-*oxophenanthrene*-1-*carboxylate* (*Diacetate of Methyl* 13-*Hydroxy*-7-*oxopodocarpate*).—A solution of chromic acid (644 mg.; 2·5 mol.) in 80% aqueous acetic acid (3 ml.) was added dropwise, with shaking, to a solution of the above diacetate (1·0 g.; 1 mol.) in glacial acetic acid (10 ml.) at 0°. The mixture was kept at room temperature for 5 days, and then poured into water (150 ml.) and extracted with ether. The ethereal extract was washed and dried; evaporation gave a solid which crystallised from methanol to give the *ketone* as prisms (647 mg., 62%), m. p. 142—150° raised to 150—152° by recrystallisation (Found: C, 65·8; H, 6·05. $C_{22}H_{26}O_7$ requires C, 65·7; H, 6·5%); $\lambda_{max.}$ 209, 253, and 293 mμ (ε, 22,500, 11,900, and 2130, respectively); $\nu_{max.}$ 1146, 1176, 1208, 1281, 1373, 1697 (aryl ketone carbonyl), 1736 (ester carbonyl), and 1788 (aryl acetate carbonyl) cm.$^{-1}$.

Variations in the method of preparation gave the following yields of the ketone: (*a*) oxidation with 2 mol. of chromic acid at room temperature for 48 hr. (49%); (*b*) 3 mol. of chromic acid at room temperature for 6 days (60%); (*c*) 1·5 mol. of chromic acid at 100° for 30 min. (54%); (*d*) 2 mol. of chromic acid at 100° for 1 hr. (57%).

Methyl 1,2,3,4,4a,9,10,10a-*Octahydro*-6,7-*dihydroxy*-1,4a-*dimethyl*-9-*oxophenanthrene*-1-*carboxylate* (*Methyl* 13-*Hydroxy*-7-*oxopodocarpate*; XVII, R = OH).—A solution of the above ketone (200 mg.) in ethanol (8 ml.) and 2N-hydrochloric acid (8 ml.) was heated under reflux under nitrogen for 2 hr. The cooled solution was poured into water (100 ml.) and extracted with ether. The ethereal extract was washed and dried; removal of the solvent gave a solid residue (153 mg.), which gave the *keto-catechol* as pale yellow prisms (from methanol), m. p. 278—279° (decomp.) (Found: C, 66·6; H, 7·0; OMe, 13·8. $C_{18}H_{22}O_5,\frac{1}{2}CH_3{\cdot}OH$ requires C, 66·45; H, 6·9; OMe, 13·9. $C_{18}H_{22}O_5$ requires C, 67·9; H, 7·0; OMe, 9·75%); $\lambda_{max.}$ 211, 237, 283, and 320 mμ (ε, 15,800, 16,500, 10,500, and 7440, respectively); $\nu_{max.}$ 1215, 1296, 1304, 1313, 1453, 1659 (aryl ketone carbonyl), 1714 (ester carbonyl), and 3401 (hydroxyl) cm.$^{-1}$.

Methyl 1,2,3,4,4a,9,10,10a-*Octahydro*-6,7,9-*trihydroxy*-1,4a-*dimethylphenanthrene*-1-*carboxylate* (*Methyl* 7,13-*Dihydroxypodocarpate*).—A solution of the above ketone (20 mg.) in glacial acetic acid (8 ml.) and perchloric acid (5 drops) was hydrogenated in the presence of Adams catalyst (10 mg.). After 12 hr., the solution was treated in the usual way giving a gum which crystallised from ether–carbon tetrachloride to give the *hydroxy-catechol* as needles, m. p. 228—231° (Found: C, 68·0; H, 6·9. $C_{18}H_{24}O_3$ requires C, 67·5; H, 7·55%); $\lambda_{max.}$ 225 and 286 mμ (ε, 9520 and 3900); $\nu_{max.}$ ($CHCl_3$) 1298, 1726 (ester carbonyl), 3282, 3564, and 3610 (hydroxyls) cm.$^{-1}$.

Methyl 6,7-*Diacetoxy*-1,2,3,4,4a,10a-*hexahydro*-1,4a-*dimethylphenanthrene*-1-*carboxylate* (*Diacetate of Methyl* 13-*Hydroxy*-6,7-*dehydropodocarpate*).—A small quantity of benzoyl peroxide was added to a mixture of methyl 6,7-diacetoxy-1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethylphenanthrene-1-carboxylate (2·35 g., above, 1 mol.) and freshly purified *N*-bromosuccinimide (1·128 g., 1·05 mol.) in dry carbon tetrachloride (100 ml.), and the mixture was heated under reflux for 90 min. The cooled mixture was filtered, the filtrate was evaporated to dryness, and the oily residue was heated under reflux for 3 hr. with freshly distilled *NN*-dimethylaniline (40 ml.). The yellow solution was cooled, poured into water (400 ml.), and acidified with 2N-hydrochloric acid. The mixture was extracted with ether, and the ethereal extract was washed, dried, and evaporated, giving a yellow gum. A solution of the yellow gum in dry pyridine (25 ml.) and acetic anhydride (25 ml.) was kept at room temperature for 12 hr., and was then heated at 100° for 2 hr. The cooled mixture was poured into water (400 ml.), acidified with 2N-hydrochloric acid, and extracted with ether. The ethereal extract was

washed and dried and, after evaporation of the solvent, the solid residue was crystallised from methanol to give the *diacetoxy-styrene* derivative (1·632 g., 70%) as prisms, m. p. 140—146° raised to 145—147° by recrystallisation (Found: C, 68·2; H, 7·0. $C_{22}H_{26}O_6$ requires C, 68·4; H, 6·8%); $\lambda_{max.}$ 220, 269, and 300 mμ (ε, 24,000, 11,200, and 1990, respectively); $\nu_{max.}$ 1188, 1200, 1217, 1737 (ester carbonyl), and 1780 (aryl acetate carbonyl) cm.$^{-1}$.

Methyl 1,2,3,4,4a,10a-*Hexahydro*-6,7-*dihydroxy*-1,4a-*dimethylphenanthrene*-1-*carboxylate* (*Methyl* 13-*Hydroxy*-6,7-*dehydropodocarpate*).—A solution of the foregoing diacetate (500 mg.) in ethanol (20 ml.) and 2N-hydrochloric acid (20 ml.) was heated under reflux under nitrogen for 2 hr. The cooled red solution was poured into water (300 ml.), and extracted with ether. The ethereal extract was washed with water, dried, and evaporated giving a brown solid. Attempted crystallisation were found to be unsatisfactory, but sublimation at *ca.* 180° (bath)/0·1 mm. gave the *catechol* (360 mg., 92%) as a pale yellow solid, m. p. 203—207°. A sample resublimed at 170°/0·1 mm. as prisms, m. p. 205—207° (Found: C, 71·5; H, 7·5. $C_{18}H_{22}O_4$ requires C, 71·5; H, 7·3%); $\lambda_{max.}$ 224, 281, 305, and 315 mμ (ε, 21,700, 7030, 4690, and 4160, respectively; $\nu_{max.}$ (KBr disc) 1220, 1230, 1244, 1699 (intermolecular bonded ester carbonyl), 3360, and 3400 (hydroxyls) cm.$^{-1}$.

D. *Ferruginol Derivatives.*

6-*Benzoyloxy*-1,2,3,4,4a,9,10,10a-*octahydro*-1,1,4a-*trimethyl*-7-*isopropyl*-9-*oxophenanthrene* (7-*Oxoferruginol Benzoate*).—Powdered chromic acid (500 mg.) was added to a solution of ferruginol benzoate [30] (1 g.) in acetic acid (50 ml.) and the mixture heated on the steam-bath for 3/4 hr. and then kept at room temperature for 48 hr. Water was then added to precipitate the crude product (0·9 g.) which was extracted into ether. The ethereal solution was washed with sodium hydrogen carbonate solution, dried, and evaporated. Crystallisation of the residue from methanol gave needles of the *keto-ester*, m. p. 180—181° (Found: C, 80·4; H, 8·25. $C_{27}H_{32}O_3$ requires C, 80·2; H, 8·0%); $\lambda_{max.}$ 257 mμ (ε, 13,700), $\lambda_{infl.}$ 240 and 293 mμ (ε, 13,300 and 2920); $\nu_{max.}$ in the carbonyl region at 1738 (benzoate C=O), 1683 (ketone C=O) cm.$^{-1}$.

6-*Benzoyloxy*-1,2,3,4,4a,9-*hexahydro*-7-*isopropyl*-1,1,4a-*trimethyl*-9-*oxophenanthrene* (7-*Oxo*-5,6*dehydroferruginol Benzoate*).—The above keto-benzoate (110 mg.) in acetic acid (5 ml.) was heated with selenium dioxide (50 mg.) on the steam-bath for 7 hr. The suspension was filtered, water was added to the filtrate, and the precipitate (78 mg.) dissolved in ether and filtered through a column of alumina. Evaporation of the solvent and recrystallisation from methanol gave prisms of the *product*, m. p. 181·5—182·5° (Found: C, 80·6; H, 7·4. $C_{27}H_{30}O_3$ requires C, 80·6; H, 7·5%); $\lambda_{max.}$ 234, and 260 mμ (ε, 19,900 and 15,200); $\nu_{max.}$ in the carbonyl region at 1742 (benzoate C=O), and 1660 (αβ-unsaturated C=O) cm.$^{-1}$.

1,2,3,4,4a,9-*Hexahydro*-6-*hydroxy*-7-*isopropyl*-1,1,4a-*trimethyl*-9-*oxophenanthrene* (7-*Oxo*-5,6-*dehydroferruginol*, XIX).—The foregoing benzoate (70 mg.) in methanol (7 ml.) was heated under reflux with hydrazine hydrate (0·3 ml.) for 4 hr. Water was added, and the precipitate (46 mg.) was crystallised from methanol forming needles, m. p. 283—284° (lit.,[25] 287—289°). The u.v. and i.r. spectra of the product were identical with those of an authentic specimen.

The phenol (150 mg.) in methanol (10 ml.) was heated under reflux with potassium carbonate and dimethyl sulphate (0·3 ml.) for 3 hr. The product (110 mg.) in ether was chromatographed through alumina. Subsequent crystallisation from ether or sublimation gave prisms of the O-*methyl* derivative, m. p. 155—156° (Found: C, 80·9; H, 8·7; OMe, 10·3. $C_{21}H_{28}O_2$ requires C, 80·7; H, 9·0; 1 OMe, 9·9%); $\lambda_{max.}$ 222, 244, and 310 mμ (ε, 12,600, 15,500, and 9940); $\nu_{max.}$ 1660 (αβ-unsaturated C=O) cm.$^{-1}$. The n.m.r. spectrum showed three singlet protons at τ 2·05, 3·06, and 3·60; one aromatic *O*-methyl singlet at 6·05; three *C*-methyl singlets at 8·70, 8·64, and 8·48 and a pair of *C*-methyl doublets centred at 8·76 and 8·74 split by the α-proton of the isopropyl group which itself is revealed as a multiplet centred at 7·32 (J = 6·6 c./sec.).

Azine of 1,2,3,4,4a,9-*Hexahydro*-7-*isopropyl*-6-*methoxy*-1,1,4a-*trimethyl*-9-*oxophenanthrene*.—Reduction of the hydrazone of the foregoing keto-methyl ether was attempted by the method employed for the podocarpic acid derivative (above). The hydrazone (150 mg.), m. p. 124—126°, of the *O*-methyl derivative afforded one crystallisable product (47 mg.), the *azine*, as yellow needles, m. p. 279—280° (Found: C, 81·7; H, 9·2%. *M* (Rast), 577. $C_{42}H_{56}N_2O_2$ requires C, 81·25; H, 9·1%; *M*, 621); $\lambda_{max.}$ 250, 290, and 376 mμ (ε, 20,300, 13,900, and 27,700); $\nu_{max.}$ 1635 (C=N) cm.$^{-1}$.

1,1-*Dimethyl*-2-*tetralol*.—A solution of lithium aluminium hydride (0·9 g.) in ether (150 ml.)

[30] Brandt and Neubauer, *J.*, 1939, 1031.

was added gradually to a solution of 1,1-dimethyl-2-tetralone [9] (2·15 g.) in dry ether (50 ml.). The mixture was heated under reflux for 1 hr. and then treated with water (50 ml.) and then dilute sulphuric acid (10%; 100 ml.). The ethereal layer was separated, washed, and dried, and the solvent removed. The residue was dissolved in light petroleum and chromatographed on alumina. Elution with benzene afforded a main fraction which gave needles of the *tetralol*, (1·6 g.), m. p. 89—91° after crystallisation from cyclohexane (Found: C, 81·5; H, 9·2. $C_{12}H_{16}O$ requires C, 81·8; H, 9·2%).

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