

*The Chemistry of Extractives from Hardwoods. Part XXI.\* The Structure of Eperuic Acid.*

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Eperuic acid, a new bicyclic diterpene carboxylic acid,  $C_{20}H_{34}O_2$ , is the chief constituent (ca. 85%) of an oleo-resin derived from the wallaba tree (*Eperua falcata* and other *Eperua* spp.) of British Guiana. The acid and its principal compounds are liquid.

Selenium dehydrogenation of the methyl ester, which can readily be prepared by the Fischer-Speier method, yields naphthalene derivatives, including 1 : 2 : 5-trimethylnaphthalene. The ozonolysis products of methyl eperuate are formaldehyde, formic acid, and a keto-ester  $C_{20}H_{34}O_3$ , and, when the latter is dehydrogenated, pimanthrene (1 : 7-dimethylphenanthrene) is obtained. These indications of a relation to the manoöl-agathic acid group of diterpenes were substantiated by stepwise oxidation of dihydroeperuic acid, through an acid  $C_{19}H_{34}O_2$  and methyl ketone  $C_{18}H_{32}O$ , to a  $C_{17}$  acid which yielded 1-ethyl-2 : 5-dimethylnaphthalene when aromatised and decarboxylated with selenium. Eperuic acid is therefore 5-(4-carboxy-3-methylbutyl)decahydro-1 : 1 : 10-trimethyl-6-methylenenaphthalene.

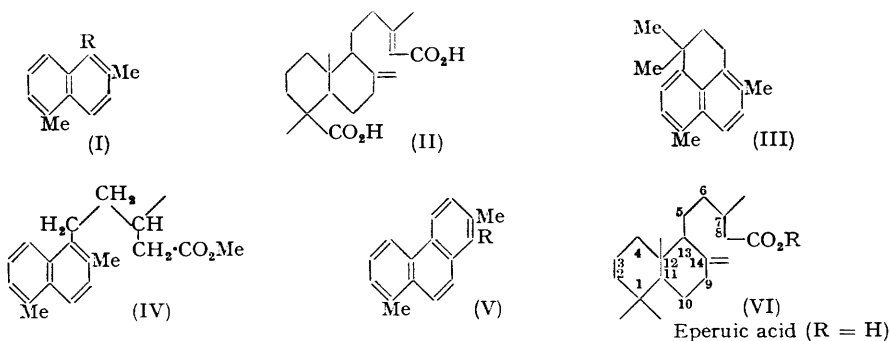
THE tropical American genus *Eperua*, principally *E. falcata*, which occurs extensively in British Guiana, is the source of a highly durable gummy timber commonly known as wallaba. The wood is used locally for constructional purposes and as fuel, and in view of its abundance has been examined for possible commercial applications, e.g., for paper-making (*Bull. Imp. Inst.*, 1928, **26**, 4; 1930, **28**, 411) and as a tanning agent (F. Heim de Balsac, Deforge, and H. Heim de Balsac, *Halle aux Cuirs*, 1930, 369; Spoon, *Nederland Leder. Ind.*, 1941, **53**, 34, 1891). Treatment with boiling alcohol yields considerable amounts of a reddish phenolic resin, as much as 25% of the heartwood being removed in this way (Farmer and Campbell, *J. Soc. Chem. Ind.*, 1948, **67**, 233), but no chemically homogeneous constituent has so far been isolated from the timber or its extractives. From the living tree a further product is obtainable in the form of a pale viscous oleo-resin which is distinct from the phenolic material derivable from the wood by extraction with alcohol. An investigation of this resinous exudate, which was generously provided by Mr. R. S. Greathead, Messrs. Brown and Forth Ltd., London, has shown that approximately 85% is soluble in aqueous sodium carbonate and, as already briefly reported (*Chem. and Ind.*, 1953, 1325), consists of a new monocarboxylic diterpene, eperuic acid. The acid has also been extracted from the wood with boiling light petroleum and therefore appears to be a normal constituent of the tree.

The acid, which is lævorotatory, is conveniently purified through its readily distilled ester, methyl eperuate. Analysis of the acid, of the methyl ester, and of its lithium aluminium hydride reduction product, eperuyl alcohol—all liquids without crystalline derivatives—are consistent with a molecular formula  $C_{20}H_{34}O_2$  for the parent compound. When catalytically reduced, methyl eperuate gives a dihydro-acid yielding a crystalline

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*p*-bromophenacyl ester. Eperuic acid has no marked light absorption above 210  $\mu$ , whence it follows that the ethylenic bond and carboxyl group are not in conjugation. Dihydroeperuic acid,  $C_{20}H_{36}O_2$ , is saturated in the tetranitromethane test; thus the terpene is bicyclic. The ease of esterification of eperuic acid, which occurs under Fischer-Speier conditions, and also of hydrolysis of the resultant ester, is in contrast to the behaviour of the known monocarboxylic diterpenes and the carboxyl group cannot therefore be situated in the usual sterically hindered 1-position.

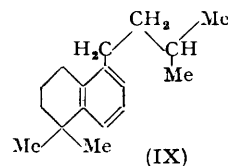
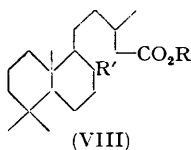
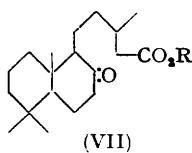
Evidence as to the carbon skeleton of eperuic acid was obtained by dehydrogenation of the methyl ester with selenium, when, at 340–360°, 1 : 2 : 5-trimethylnaphthalene (I; R = Me) was obtained. Under somewhat less drastic conditions two other naphthalene derivatives were formed in which the greater part of the original molecule survived. One, a hydrocarbon  $C_{17}H_{20}$ , now appears to be identical with a product derived from agathic acid (II) (Ruzicka and Hosking, *Annalen*, 1929, 469, 147) and very recently shown by synthesis (Büchi and Pappas, *J. Amer. Chem. Soc.*, 1954, 76, 2963) to be 1 : 1 : 4 : 7-tetramethylperinaphthane (III). The other was an ester and on hydrolysis yielded a crystalline acid,  $C_{18}H_{22}O_4$ ; when the constitution of eperuic acid became known it was possible to assign the structure (IV) to this dehydrogenation product.



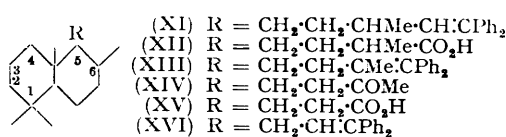
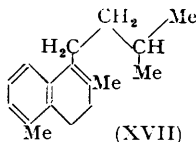
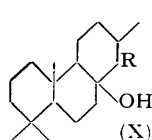
Ozonolysis of methyl eperuate gave a keto-ester,  $C_{20}H_{34}O_3$ , together with formaldehyde and formic acid, thus showing that the double bond terminates in a methylene group. A liquid acid, characterised by a crystalline oxime, was obtained by hydrolysis of the keto-ester. The keto-ester was also the principal product formed by permanganate oxidation of methyl eperuate, being then accompanied by a small quantity of crystalline dicarboxylic acid  $C_{15}H_{24}O_4$ . The constitution of the latter is unknown, and it is not clear whether this by-product is derived from eperuic acid or is the oxidation product of an undetected impurity.

Whereas naphthalene derivatives were obtained from the dehydrogenation of methyl eperuate, the action of selenium on the keto-ester, as well as on the corresponding hydroxy-ester prepared from it with lithium aluminium hydride, gave 1 : 7-dimethylphenanthrene (pimanthrene) (V; R = H) in good yield. This is attributed to the condensation of the keto-ester carbonyl group—or in the case of the hydroxy-ester, of the cation formed during the pyrolysis—with the carbon atom activated by its proximity to the methoxycarbonyl group, and it suggested a relation with the manoöl-agathic acid group of diterpenes. Formula (VI; R = H), bearing, as in agathic acid (II), a carboxyl group at position 19, was therefore tentatively adopted, and subsequently proved to be the correct structure for the new diterpene. Cyclisation of the derived keto-ester (VII; R = Me) and also of the hydroxy-ester (VIII; R = Me, R' = OH) to pimanthrene during dehydrogenation is readily explicable on the basis of this formula. On the other hand, 14-demethyl-dihydro-eperuic acid (VIII; R = R' = H), which was prepared by Wolff-Kishner reduction of the keto-ester (VII; R = Me), under normal conditions of dehydrogenation gave a  $C_{17}$  tetralin, presumably (IX). Further treatment with selenium in a sealed tube at 355° yielded a small amount of fully aromatised material which from the properties of its trinitrobenzene adduct is believed to be 1-ethyl-5-methylnaphthalene.

Attempts were made to establish the position of the carboxyl group in eperuic acid by cyclising the keto-ester (VII; R = Me) to a tricyclic compound. Reduction—for example of carboxyl to methyl—should then avoid possible expulsion of the substituent during dehydrogenation, which, with (VI; R = H) as the structure of the diterpene, should lead ultimately to 1:2:8-trimethylphenanthrene (V; R = Me). The action of boiling acetic



anhydride and sodium acetate on the keto-ester resulted solely in the formation of an enol-acetate, but with sodium methoxide the keto-compound afforded the tricyclic hydroxy-ester (X; R = CO<sub>2</sub>Me) together with an acidic substance having an intense ferric reaction and probably formed by Claisen condensation of the side-chain with one or other of the activated positions adjacent to the carbonyl group. Dehydration with heated potassium hydrogen sulphate gave an unsaturated liquid product which in view of its ultra-violet light absorption seemed to consist of  $\alpha\beta$ -unsaturated ester(s). The hydroxy-ester (X; R = CO<sub>2</sub>Me) was reduced by lithium aluminium hydride to a diol (X; R = CH<sub>2</sub>·OH) which, however, resisted oxidation by the Oppenauer reaction and with chromic anhydride in pyridine gave the acid (X; R = CO<sub>2</sub>H). The attempt to orient the carboxyl group by



this method was therefore abandoned in favour of an alternative, *viz.*, stepwise degradation of the acidic side-chain by the Barbier–Wieland procedure. The diphenylethylene (XI), a liquid prepared from methyl dihydroeperuic acid and excess of phenylmagnesium bromide, was not characterised but oxidised directly to the C<sub>19</sub> acid (XII), also liquid but having a crystalline *p*-bromophenacyl ester. The methyl ester of (XII) yielded a solid diphenylethylene (XIII), and this was oxidised with ozone to a methyl ketone (XIV), thus establishing the relative position of the side-chain methyl group. Further oxidation, with sodium hypoiodite, degraded the ketone (XIV) to a crystalline C<sub>17</sub> acid (XV) from which a solid diphenylethylene (XVI) was obtained in the usual way. The acid (XV), m. p. 134–135°,  $[\alpha]_D^{20}$  –29.9°, is an isomer of that obtained from ambrein by Ruzicka and Lardon (*Helv. Chim. Acta*, 1946, **29**, 912), the latter, m. p. 136–137°, having  $[\alpha]_D^{20}$  +33° (Dr. O. Jeger, personal communication).

With the intention of preparing a conjugated diene for the complete oxidative removal of the residual side-chain, the product (XVI) was treated with *N*-bromosuccinimide, but under the usual conditions it entirely failed to react. Selenium dehydrogenation of the acid (XV), however, gave the expected 1-ethyl-2:5-dimethylnaphthalene, as shown by the identity of its trinitrobenzene derivative with an authentic specimen, so confirming the structure attributed to eperuic acid on the basis of its resemblance to the manoöl-agathic acid group of diterpenes.

In the expectation that 2:5-dimethyl-1-isopentyl-naphthalene might be present among the dehydrogenation products of eperuic acid, this hydrocarbon was synthesised from 2:5-dimethyl-1-tetralone (Kipping and Wild, *J.*, 1940, 1238; Hosking and Ruzicka, *Helv. Chim. Acta*, 1930, **13**, 1412). When it was treated with isopentyl-lithium (Gilman, Beel, Brannen, Bullock, Dunn, and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 1499) the dihydronaphthalene (XVII) was obtained which being difficult to dehydrogenate with selenium was oxidised with chloranil in boiling xylene (Campbell and Soffer, *ibid.*, 1942,

64, 422). The product (I; R = isopentyl), a liquid, was characterised as a crystalline trinitrobenzene derivative.

#### EXPERIMENTAL

Unless otherwise stated, specific rotations were determined in  $\text{CHCl}_3$ .

*Eperuic Acid* (VI; R = H).—The wallaba oleo-resin (500 g.), an opaque honey-coloured viscous syrup, was dissolved in ether (2 l.), and the solution was stirred with excess of 0.5N-sodium carbonate. The terpene was then isolated from the aqueous solution, by acidification and ether-extraction, as a nearly colourless thick syrup, distillable in a high vacuum but more conveniently purified as the methyl ester, prepared by refluxing the product for 1 hr. with methanol (1 l.) containing concentrated sulphuric acid (8 c.c.). Most of the unused alcohol was then removed by evaporation from a steam-bath, and the residue was shaken with water and ether, unchanged eperuic acid (20–30 g.) being removed by washing with a solution of sodium carbonate. Distillation of the dried residue gave *methyl eperuate* (VI; R = Me) as a colourless mobile oil (ca. 420 g.), b. p.  $164^\circ/0.4$  mm.,  $[\alpha]_D^{18} -28.2^\circ$  (c, 3.98),  $n_D^{18} 1.4982$ ,  $d 0.979$ ,  $[M_R] 95.5$  (calc., 95.9) (Found: C, 78.7; H, 11.5.  $\text{C}_{21}\text{H}_{36}\text{O}_2$  requires C, 78.8; H, 11.3%).

Hydrolysis of the ester with methanolic 2N-potassium hydroxide for 1 hr., evaporation of the solution, and treatment with mineral acid liberated *eperuic acid*, b. p.  $190^\circ/0.7$  mm. (Found: C, 78.2; H, 11.3.  $\text{C}_{20}\text{H}_{34}\text{O}_2$  requires C, 78.4; H, 11.3%). Its amide, anilide, and phenacyl and *p*-bromophenacyl esters were oily.

The brown gummy fraction of the exudate undissolved by aqueous sodium carbonate yielded a further quantity of eperuic acid (ca. 40 g.) after being refluxed with methanolic N-potassium hydroxide.

*Eperuyl Alcohol*.—Methyl eperuate (9 g.) and lithium aluminium hydride (1.5 g.), dissolved in equal volumes (70 c.c.) of ether, were slowly mixed and then heated under reflux for  $\frac{1}{2}$  hr. Addition of aqueous 2N-sodium hydroxide and evaporation of the ethereal solution yielded *eperuyl alcohol*, a colourless oil (6.5 g., 80%), b. p.  $158^\circ/1$  mm.,  $n_D^{16} 1.5068$ ,  $d 0.953$ ,  $[M_R] 91.18$  (calc., 91.64) (Found: C, 81.4; H, 11.8.  $\text{C}_{20}\text{H}_{36}\text{O}$  requires C, 82.1; H, 12.3%).

A solution of the alcohol in benzene (50 c.c.), stirred with phosphorus tribromide (6.5 g.) for 3 hr. at  $0-5^\circ$ , gave *eperuyl bromide* which was isolated, after washing with sodium carbonate and water, as a colourless syrup, b. p.  $124^\circ/0.14$  mm.,  $n_D^{18} 1.514$  (Found: C, 67.8; H, 9.9.  $\text{C}_{20}\text{H}_{35}\text{Br}$  requires C, 67.6; H, 9.9%).

*Methyl Dihydroeperuate* (VIII; R = R' = Me).—Methyl eperuate (6 g.), dissolved in acetic acid containing platinum oxide catalyst, readily absorbed hydrogen (430 c.c.; calc. for 1 double bond, 420 c.c.) at N.T.P. When the solution was filtered and distilled, *methyl dihydroeperuate* (5.5 g., 90%), b. p.  $138-140^\circ/0.1$  mm., was obtained as a colourless oil,  $[\alpha]_D^{25} -26.3^\circ$  (c, 3.2),  $n_D^{18} 1.4902$  [Found: C, 78.6; H, 11.8%; M (Rast), 317.  $\text{C}_{21}\text{H}_{38}\text{O}_2$  requires C, 78.2; H, 11.9%; M, 322].

*Dihydroeperuic Acid* (VIII; R = H, R' = Me).—Methyl dihydroeperuate (5 g.) was hydrolysed by refluxing methanolic N-potassium hydroxide (25 c.c.) for 1 hr. The *dihydro-acid* obtained by evaporating the liquid, acidifying and extracting it with ether, was a colourless viscous gum (4.15 g.), b. p.  $186^\circ/0.5$  mm. (Found: C, 78.0; H, 11.9.  $\text{C}_{20}\text{H}_{36}\text{O}_2$  requires C, 77.9; H, 11.8%). The *p*-bromophenacyl ester crystallised from dilute ethanol in plates, m. p.  $71-71.5^\circ$  (Found: C, 66.5; H, 8.0; Br, 15.9.  $\text{C}_{28}\text{H}_{44}\text{O}_3\text{Br}$  requires C, 66.5; H, 8.0; Br, 15.8%).

*Selenium Dehydrogenation of Methyl Eperuate*.—(i) The methyl ester (10 g.) was heated with selenium (10 g.) in a metal bath at  $280-300^\circ$  for 30 hr. Distillation of the product, collected by means of ether, gave three principal fractions, the first (1.9 g.), b. p.  $120-128^\circ/2$  mm., apparently consisting of incompletely dehydrogenated compounds (Found: C, 87.6; H, 11.6%).

The intermediate portion (3.5 g.), b. p.  $140-150^\circ/2$  mm., was heated with 10% methanolic potassium hydroxide for 1 hr. and, after dilution with water, separated into alkali-soluble and insoluble material, the latter being removed in ether. Acidification of the alkaline solution gave 1-(4-carboxy-3-methylbutyl)-2:5-dimethylnaphthalene crystallising as colourless needles (0.15 g.), m. p.  $96^\circ$ , from light petroleum; light absorption in ethanol: max. at 234, 280, 290, 325  $\mu$  ( $\log \epsilon$  4.05, 3.86, 3.92, 3.15) (Found: C, 80.0; H, 7.9%; equiv., 268.  $\text{C}_{18}\text{H}_{22}\text{O}_2$  requires C, 80.0; H, 8.2%; equiv., 270).

The alkali-insoluble liquid gave a picrate which, crystallised from methanol, had m. p.  $133^\circ$  (Found: C, 60.5; H, 4.9; N, 9.2. Calc. for  $\text{C}_{17}\text{H}_{20}\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ : C, 60.9; H, 5.1; N, 9.3%); 1:1:4:7-tetramethylperinaphthane picrate (synthetic, Buchi and Pappas, *loc. cit.*) has m. p.  $135.5-136^\circ$  (*ex agathic acid*, Ruzicka and Hosking, *Helv. Chim. Acta*, 1930, 13, 1402 give

138—139°). A sample of the hydrocarbon, b. p. (bath-temp.) 158°/2 mm., prepared from the re-crystallised picrate had light absorption (in hexane): max. at 235, 290, 326  $\mu$  ( $\log \epsilon$  4.1, 3.84, 2.99).

The third fraction (0.8 g.), b. p. 160—165°/2 mm., dissolved in light petroleum and passed through a column of alumina, also yielded 1:1:4:7-tetramethylperinaphthane (III) (characterised as picrate), followed by a further small amount of ester of which the acid (as IV) (0.05 g.) was the hydrolysis product.

(ii) A mixture of methyl eperuate (5 g.) and selenium (5 g.) at 340—360° for 48 hr. yielded as the sole volatile material an oil (1.3 g.), b. p. 112°/0.05 mm. Its trinitrobenzene derivative formed orange needles (from ethanol), m. p. 154° alone or mixed with a specimen of 1:2:5-trimethylnaphthalene-trinitrobenzene adduct.

*Oxidation of Methyl Eperuate.*—(i) *With ozone.* A solution of methyl eperuate (7 g.) in methylene chloride (100 c.c.) was ozonised at  $-30^\circ$  to  $-40^\circ$  and the issuing gas passed into aqueous 2:4-dinitrophenylhydrazine hydrochloride. The precipitate (0.54 g., 15%), crystallised from methanol, had m. p. 163—164° and was identified with the formaldehyde derivative by mixed m. p. and by paper chromatography (Meigh, *Nature*, 1952, 170, 579).

The reaction mixture was treated with water (100 c.c.), and the methylene chloride removed by means of an air-stream and warming. It was condensed in traps cooled in solid carbon dioxide-alcohol, and washed with water, the washings yielding the crystalline dimedone derivative of formaldehyde, m. p. and mixed m. p. 186—187°. The mixture remaining after evaporation of the original solvent was heated with hydrogen peroxide (20 c.c. of 30%) for 1 hr., and the formic acid isolated by steam-distillation was titrated with sodium hydroxide (required 65% of theory) and characterised as *NN*-di-*p*-tolylformamidine hydrochloride (Whalley, *J.*, 1948, 1015), m. p. and mixed m. p. 264—266°.

The principal ozonolysis product—which was collected in ether, washed with aqueous sodium carbonate, and distilled—consisted of the liquid *keto-ester* (VII; R = Me) (5 g.), b. p. 141°/0.05 mm.,  $n_D^{16}$  1.4940 (Found: C, 74.7; H, 10.3.  $C_{20}H_{34}O_3$  requires C, 74.5; H, 10.6%). Hydrolysis by refluxing it with methanolic 2*N*-potassium hydroxide for 2 hr. gave the parent acid characterised by an *oxime*, which crystallised from ethanol in needles, m. p. 223°,  $[\alpha]_D^{20}$   $-79.4^\circ$  (*c*, 0.91 in dioxan) (Found: C, 70.7; H, 10.3; N, 4.3.  $C_{19}H_{33}O_3N$  requires C, 70.5; H, 10.3; N, 4.3%).

The *keto-ester* (7 g.), sodium acetate (5 g.), and acetic anhydride (50 c.c.) were heated for 4 hr. under reflux. The mixture was evaporated under reduced pressure, treated with water, and extracted with ether. After the extract had been washed with aqueous sodium hydroxide and water, it was dried and evaporated, and the residue treated with Girard reagent  $\tau$ . The non-ketonic residue (3.4 g.), b. p. 185—190°/0.3 mm., consisted of *ester enol-acetate* (Found: C, 71.8; H, 10.2.  $C_{22}H_{36}O_4$  requires C, 72.5; H, 10.0%) from which the corresponding *acid*, b. p. 165—170°/0.1 mm., was obtained by hydrolysis with methanolic *N*-potassium hydroxide (Found: C, 71.4; H, 9.7%; equiv., 334.  $C_{21}H_{34}O_4$  requires C, 72.0; H, 9.8%; equiv., 350).

(ii) Methyl eperuate (25 g.) in refluxing acetone (300 c.c.) was oxidised by the gradual addition (Soxhlet) of potassium permanganate until reaction ceased (36 hr.). The precipitate was collected, the filtrate evaporated, and the residue shaken with a mixture of ether and water containing sulphur dioxide. *Keto-ester* (18 g.), b. p. 152°/0.2 mm.,  $n_D^{18}$  1.4940, was isolated from the ether layer; a small fraction of higher b. p. deposited solid which was separated by addition of methanol and consisted of hydroxy-ester (X; R =  $CO_2Me$ ) (below), m. p. 184—185°.

The precipitate collected from the reaction mixture was stirred with warm water (100 c.c.) which was then filtered and acidified with sulphur dioxide. Hydrolysis of the ether-extracted product with boiling aqueous 2*N*-sodium hydroxide afforded an *acid*, which crystallised from ethyl acetate in needles (0.7 g.), m. p. 218—219° (Found: C, 67.4; H, 9.4.  $C_{15}H_{24}O_4$  requires C, 67.2; H, 9.0%). The *dimethyl ester*, prepared by the action of diazomethane in ether, was a viscous liquid, b. p. 115°/0.1 mm. [Found: C, 69.0; H, 9.7%; *M* (Rast), 322.  $C_{17}H_{28}O_4$  requires C, 68.9; H, 9.5%; *M*, 296].

*Decahydro-6-hydroxy-5-(4-methoxycarbonyl-3-methylbutyl)-1:1:10-trimethylnaphthalene* (VIII; R = Me, R' = OH).—Ethereal solutions of the *keto-ester* (VII; R = Me) (4.5 g.) and of lithium aluminium hydride (0.72 g.) were heated together under reflux for 1 hr., and the product isolated after the addition of dilute hydrochloric acid gave the *hydroxy-ester* (VIII; R = Me, R' = OH) as a colourless oil (2.8 g., 70%), b. p. 160—162°/0.1 mm.,  $n_D^{18}$  1.500 (Found: C, 74.2; H, 11.2.  $C_{20}H_{36}O_3$  requires C, 74.0; H, 11.2%).

*Cyclisation of the Keto-ester* (VII; R = Me).—A solution of the *keto-ester* (10 g.) in toluene (100 c.c.) was gradually mixed with alcohol-free sodium methoxide (1.7 g.), and after 2 hr. at room temperature, was heated under reflux for 2 hr. After cooling, the product was treated

with ice-water, and the toluene solution separated, washed with aqueous sodium hydroxide, and evaporated. The residue of *methyl perhydro-14-hydroxy-1 : 1 : 7 : 12-tetramethylphenanthrene-8-carboxylate* (X; R = CO<sub>2</sub>Me) crystallised from methanol in needles (2.4 g.), m. p. 184—185° (Found: C, 74.6; H, 10.3. C<sub>20</sub>H<sub>34</sub>O<sub>3</sub> requires C, 74.5; H, 10.6%). When the orange-yellow aqueous solution and alkali washings were acidified, a brownish oil was obtained which exhibited a strong, purple ferric reaction. It formed a chloroform-soluble copper complex, but the recovered carbonyl compound neither distilled nor gave crystalline derivatives.

The hydroxy-ester (0.3 g.) was heated with fused potassium hydrogen sulphate (1.5 g.) at 200—210° for  $\frac{1}{2}$  hr., and water and ether were added to the cooled product. The ether-soluble material gave when distilled (bath-temp. 130°/0.05 mm.) an *anhydro-ester*,  $n_D^{17}$  1.5180. Light absorption in ethanol: 240 m $\mu$  (log  $\epsilon$  3.44) (Found: C, 78.7; H, 10.0. C<sub>20</sub>H<sub>32</sub>O<sub>2</sub> requires C, 78.9; H, 10.6%).

*Selenium Dehydrogenation of the Keto-ester* (VII; R = Me).—Dehydrogenation of the ester (15 g.) with selenium (20 g.) at 300—340° for 45 hr. and ether-extraction of the product gave a brown gum which was decolorised by passing its solution in light petroleum through alumina, and then distilled. The first fraction (2.5 g.), b. p. <95°/0.05 mm.,  $n_D^{17}$  1.5158, contained incompletely dehydrogenated products and failed to give crystalline derivatives. The portion of b. p. 115—120°/0.05 mm. (3.5 g.) solidified and crystallised from methanol in plates, m. p. 83—84° undepressed by a specimen of pimanthrene (V; R = H) kindly provided by Professor R. D. Haworth, F.R.S. (Found: C, 92.8; H, 7.1. Calc. for C<sub>16</sub>H<sub>14</sub>: C, 93.2; H, 6.8%). The picrate had m. p. 131—132° (lit., 132°) and the styphnate, m. p. 155.5° (lit., 159°). The intermediate fraction (4 g.), b. p. 96—115°/0.05 mm., was liquid, and a sample gave pimanthrene picrate (yield, ca. 90%) when mixed with alcoholic picric acid.

Dehydrogenation of the hydroxy-ester (VIII; R = Me, R' = OH) (2.5 g.) under similar conditions to the above keto-ester (VII; R = Me) gave a yellow oil (1.3 g.) which after distillation was crystallised from methanol and had m. p. 82—83° alone or mixed with authentic pimanthrene. The trinitrobenzene derivative also was identical with the corresponding pimanthrene compound of m. p. 158°.

*Dihydro-14-demethyleperuic Acid* (VIII; R = R' = H).—A mixture of the keto-ester (VII; R = Me) (10 g.), potassium hydroxide (7 g.), and 90% hydrazine hydrate (4 g.) in diethylene glycol (50 c.c.) was refluxed for  $1\frac{1}{2}$  hr., and then concentrated to b. p. 195° and further refluxed for 4 hr. The product was precipitated from the diluted ether-washed solution by acidification, and after being collected in ether was distilled. *Dihydro-14-demethyleperuic acid* (6.5 g., 71.5%), b. p. 168—170°/0.2 mm., slowly crystallised and had m. p. 38—40°,  $[\alpha]_D^{18}$  -32° (c, 1.73) (Found: C, 76.9; H, 11.1%; equiv., 292. C<sub>19</sub>H<sub>34</sub>O<sub>2</sub> requires C, 77.5; H, 11.5%; equiv., 294.5). Its *p-bromophenacyl ester*, plates (from aqueous ethanol), had m. p. 68—69° (Found: C, 66.0; H, 8.1; Br, 16.0. C<sub>27</sub>H<sub>36</sub>O<sub>2</sub>Br requires C, 66.0; H, 8.0; Br, 16.3%).

*Perhydro-14-hydroxy-8-hydroxymethyl-1 : 1 : 7 : 12-tetramethylphenanthrene* (X; R = CH<sub>2</sub>·OH).—The ester (X; R = CO<sub>2</sub>Me) (0.5 g.), dissolved in ether-tetrahydrofuran (25 c.c. of 1 : 1 mixture), was heated under reflux with a solution of lithium aluminium hydride (0.5 g.) in ether for 1 hr. Treatment when cold with dilute hydrochloric acid and evaporation of the ether layer gave the *diol* (X; R = CH<sub>2</sub>·OH) which crystallised from aqueous methanol as leaflets (0.39 g. 86%), m. p. 144—145° (Found: C, 77.2; H, 11.2. C<sub>19</sub>H<sub>34</sub>O<sub>2</sub> requires C, 77.5; H, 11.2%).

The diol (0.8 g.), dissolved in pyridine (8 c.c.), was oxidised overnight at room temperature with chromic anhydride-pyridine (Poos, Arth, Beyler, and Barrett, *J. Amer. Chem. Soc.*, 1953, 75, 427). The mixture was filtered, and the filtrate treated with water and ether-extracted. The extracted solid crystallised from acetone in needles (0.65 g.), m. p. 250° (decomp.), consisting of the *hydroxy-acid* (X; R = CO<sub>2</sub>H) (Found: C, 74.1; H, 10.7. C<sub>19</sub>H<sub>32</sub>O<sub>3</sub> requires C, 74.0; H, 10.5%) characterised by reaction with diazomethane to give the ester (X; R = CO<sub>2</sub>Me), m. p. and mixed m. p. 184°. When the diol (0.65 g.) was heated under reflux with benzoquinone (2.4 g.) and aluminium *tert.*-butoxide (2.55 g.) in benzene, and the product remaining after acidification and steam-distillation chromatographed in benzene on alumina (20 g.), the principal fraction consisted of unchanged diol (0.45 g.), m. p. 144—145°, which was eluted with benzene-ether (1 : 1). A minute fore-run removed with benzene was uncrystallisable.

*Selenium Dehydrogenation of Dihydro-14-demethyleperuic Acid* (VIII; R = R' = H).—Treatment of the acid (VIII; R = R' = H) (8 g.) with selenium (10 g.) at 300—340° for 48 hr. yielded an oil which was dissolved in light petroleum and passed through alumina. The bulk of the eluate had b. p. 88—90°/0.2 mm.,  $n_D^{20}$  1.5148, and apparently consisted of 1 : 2 : 3 : 4-*tetrahydro-1 : 1-dimethyl-5-isopentyl-naphthalene* (IX) (5.1 g.) (Found: C, 87.8; H, 11.5. C<sub>17</sub>H<sub>26</sub> requires C, 88.6; H, 11.4%) which failed to give crystalline products with picric acid or trinitro-

benzene. Further treatment of the tetralin with selenium at 340—360° for 48 hr., or in a sealed tube at 310°, was without effect. Finally, dehydrogenation of the tetralin (1.7 g.) was carried out with selenium (2 g.) for 35 hr. at 355° (electric furnace) in a sealed tube. Two fractions were thus obtained of which that of b. p. 185°/15 mm.,  $n_D^{21}$  1.5185, appeared to be largely the original tetralin (0.45 g.). The portion of b. p. 155°/15 mm. (0.3 g.),  $n_D^{21}$  1.5480, however, gave a *trinitrobenzene derivative*, yellow needles, m. p. 145—146°, from ethanol (Found : C, 59.9; H, 4.3; N, 11.3.  $C_{13}H_{14}, C_6H_5O_6N_3$  requires C, 59.5; H, 4.5; N, 11.0%).

*5-3'-Carboxybutyldecahydro-1 : 1 : 6 : 10-tetramethylnaphthalene* (XII).—Methyl dihydroperuuate (30 g.) in ether (150 c.c.) was slowly added to Grignard reagent prepared from bromobenzene (34 g.) and magnesium (5 g.), and the mixture set aside overnight. The pasty mass was then heated under reflux for 1 hr. and the product worked up with ice and aqueous ammonium chloride. Unchanged ester was removed by heating with methanolic *N*-potassium hydroxide, and of the residue the portion dissolved after 2 hours' refluxing in acetic acid (100 c.c.), consisting of a viscous liquid (22 g.), b. p. 206—208°/0.03 mm.,  $n_D^{18}$  1.5520, was regarded as the diphenylethylene (XI).

A solution of this product (21 g.) in chloroform (20 c.c.) and acetic acid (150 c.c.) was treated below 30° with acetic acid (40 c.c.) and water (15 c.c.) containing chromic anhydride (25 g.). After being stirred for a further  $\frac{1}{2}$  hr., the solution was cooled to 5° and excess of reagent destroyed with sulphur dioxide. Treatment with water and concentration at reduced pressure on a steam-bath to remove acetic acid was followed by ether-extraction, the product being isolated from the extract with aqueous sodium carbonate. Acidification precipitated the *derivative* (XII) (12 g.), a viscous oil, b. p. 168—170°/0.2 mm.,  $n_D^{17}$  1.5010 (Found : C, 77.9; H, 11.4%; equiv., 294.  $C_{19}H_{34}O_2$  requires C, 77.5; H, 11.6%; equiv., 294.5). The *p*-bromophenacyl ester crystallised in leaflets, m. p. 86—87°, from aqueous alcohol (Found : C, 66.0; H, 8.4.  $C_{22}H_{39}O_3Br$  requires C, 66.0; H, 8.0%). In later preparations the acetic acid solution of crude product was oxidised without isolation of the phenylethylene, the yield of acid (XII) from (III; R = R' = Me) being 52%.

*Decahydro-1 : 1 : 6 : 10-tetramethyl-5-3'-oxobutylnaphthalene* (XIV).—The methyl ester (8.5 g.), b. p. 134—136°/0.2 mm., of (XII) and Grignard reagent from bromobenzene (8.6 g.), under conditions used for the preparation of the diphenylethylene (XI), gave the lower *homologue* (XIII), which crystallised from the reaction product as leaflets, m. p. 116°,  $[\alpha]_D^{18}$  -24.4° (c, 2.5). Light absorption in chloroform : max. at 208, 244  $m\mu$  (log  $\epsilon$ , 4.38, 4.17) (Found : C, 89.9; H, 10.0.  $C_{19}H_{32}$  requires C, 89.8; H, 10.2%).

A solution of the hydrocarbon (XIII) (9 g.) in ethyl acetate (75 c.c.) was ozonised at 0° and then treated with water and zinc dust. After evaporation of the original solvent at room temperature the aqueous mixture was heated under reflux for 1 hr. and filtered, and the product isolated in ether. Traces of acidic material were removed with aqueous sodium carbonate, and the residue left after evaporation of the ether was treated with excess of Girard reagent *T*. The ketone (XIV) was thus obtained as a mobile liquid (ca. 3.7 g., 65%), b. p. 128°/0.05 mm., characterised by a *semicarbazone*, needles, m. p. 195°, from aqueous ethanol (Found : C, 71.4; H, 10.7; N, 12.8.  $C_{19}H_{35}ON_3$  requires C, 71.0; H, 11.0; N, 13.1%).

*5-2'-Carboxyethyldecahydro-1 : 1 : 6 : 10-tetramethylnaphthalene* (XV).—The ketone (1.5 g.), dissolved in dioxan (60 c.c.) to which aqueous sodium hydroxide (12.5 c.c. of 10%) was added, was treated at 60° with iodine-potassium iodide solution until the mixture remained yellow for 5 min. It was then cooled, diluted with water (200 c.c.), filtered, treated with a small quantity of sodium hydrogen sulphite, and finally acidified. The gummy precipitate was taken up in ether, and the ethereal solution extracted with alkali to yield the *acid* (XV) which crystallised from aqueous methanol in needles, m. p. 134°,  $[\alpha]_D^{17}$  -29.9° (c, 1.5) (Found : C, 76.3; H, 10.7%; equiv., 266.  $C_{17}H_{30}O_2$  requires C, 76.6; H, 11.4%; equiv., 266.4).

*5-(3 : 3-Diphenylprop-2-enyl)decahydro-1 : 1 : 6 : 10-tetramethylnaphthalene* (XVI).—The product obtained from the methyl ester of (XV), b. p. 125° (bath-temp.)/0.1 mm. (1.3 g.), and phenylmagnesium bromide (from bromobenzene, 2.25 g., and magnesium, 0.35 g.) as in the preparation of (XI), was finally heated for 3 hr. in acetic acid (12 c.c.), and the soluble portion was isolated and eluted from alumina in light petroleum. Evaporation of the solution gave the *hydrocarbon* (XVI) (1.46 g.), crystallising from acetone in plates, m. p. 118—119°. Light absorption in hexane : max., 250  $m\mu$  (log  $\epsilon$  4.18) (Found : C, 89.9; H, 10.3.  $C_{29}H_{38}$  requires C, 90.1; H, 9.9%).

A mixture of the diphenylethylene (XVI) (1.46 g.) and *N*-bromosuccinimide (0.73 g.) in carbon tetrachloride (30 c.c.) containing a trace of benzoyl peroxide was irradiated with ultra-violet light during 1 hour's refluxing. The filtered solution was treated with diethylaniline

(4 c.c.) and after evaporation of the carbon tetrachloride was heated to boiling for 10 min. Acidification and ether-extraction followed by purification in light petroleum on alumina (30 g.) led to the recovery of the colourless hydrocarbon (XVI) (0.93 g.), m. p. 115—116° undepressed by an authentic specimen.

*Dehydrogenation of 5-2'-Carboxyethyldecahydro-1:1:6:10-tetramethylnaphthalene* (XV).—The distillable product obtained by heating the acid (XV) (1.5 g.) with selenium (4.5 g.) for 40 hr. at 340—360° was a liquid (0.6 g.) ( $n_D^{18}$  1.563) which yielded a picrate, orange needles, m. p. 83—84°, from methanol (Found: C, 57.6; H, 4.7; N, 10.5.  $C_{14}H_{16}C_6H_3O_7N_3$  requires C, 58.1; H, 4.6; N, 10.2%). Ruzicka, Ehmann, and Mörgeli (*Helv. Chim. Acta*, 1933, 16, 268) record m. p. 82° for 1-ethyl-2:5-dimethylnaphthalene picrate but no analysis. The *trinitrobenzene compound* crystallised from ethanol in yellow needles, m. p. 118—119° (Found: C, 60.1; N, 10.7.  $C_{14}H_{16}C_6H_3O_6N_3$  requires C, 60.4; H, 4.8; N, 10.5%). A specimen synthesised from 2:5-dimethyl-1-tetralone had m. p. and mixed m. p. 118—119°.

*2:5-Dimethyl-1-isopentylnaphthalene* (I; R =  $CH_2 \cdot CH_2 \cdot CHMe_2$ ).—A solution of isopentyl bromide (1.2 g.) in ether (5 c.c.) was mixed with lithium (0.25 g.) and ether, and the reaction controlled by ice-cooling. After being stirred for an hour the solution was filtered under nitrogen, mixed with 2:5-dimethyl-1-tetralone (1 g.), and heated under reflux for 1 hr. Next day water was added and the product contained in the ether was fractionated with Girard's reagent T. The non-ketonic portion (0.8 g.), distilled twice from sodium, was an oil,  $n_D^{17}$  1.5508, which when dehydrogenated with selenium had  $n_D^{18}$  1.5920, but failed to give homogeneous crystalline derivatives. The dihydronaphthalene (XVII) (1.1 g.) was then heated in boiling xylene (8 c.c.) with chloranil (1.4 g.) for 20 hr., the mixture afterwards being diluted with light petroleum, filtered, washed with sodium hydroxide and dithionite, dried, and distilled. The distillate (0.8 g.), b. p. 135° (bath-temp.)/0.05 mm.,  $n_D^{20}$  1.5642, of 2:5-dimethyl-1-isopentylnaphthalene gave a *trinitrobenzene derivative* crystallising from ethanol in yellow needles, m. p. 91—92° (Found: C, 63.1; H, 5.7.  $C_{17}H_{22}C_6H_3O_6N_3$  requires C, 62.8; H, 5.7%).

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