

## 192. Podocarpic Acid. Part I.

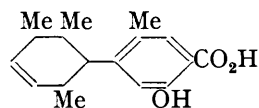
By I. R. SHERWOOD and W. F. SHORT.

The resin acid podocarpic acid,  $C_{17}H_{22}O_3$ , has been shown to be tricyclic and to contain a phenolic nucleus. On dehydrogenation it afforded 6-hydroxy-1-methylphenanthrene and on pyrolysis *p*-cresol and a hydrocarbon  $C_9H_{14}$ . It is inferred that the acid represents a new type of resin acid in which an aromatic nucleus is joined to two isopentane residues through a substituent carbon of the aromatic nucleus. These results, coupled with the abnormal inertness of the carboxyl group, lead to a provisional formula for the acid.

PODOCARPIC acid,  $C_{17}H_{22}O_3$ , was first isolated by Oudemans (*Ber.*, 1873, **6**, 1122; *Annalen*, 1873, **170**, 214; *J. pr. Chem.*, 1874, **9**, 385) from the resin of *Podocarpus cupressinus*, which is endemic to Java. Easterfield and Aston (*Trans. New Zealand Inst.*, 1910, **42**, 53) obtained the same dextrorotatory acid from *Podocarpus dacrydioides* ("kahikatea"), but from *Dacrydium cupressinum* ("rimu") they isolated a levorotatory acid which was considered to be a lower homologue of podocarpic acid (P., 1903, **19**, 190; *Trans. New Zealand Inst.*, 1904, **36**, 483). As the result of a mixed melting point determination and titration values they subsequently concluded (*ibid.*, 1911, **43**, 53) that this acid is identical with podocarpic acid.

Our first experiments were made with the acid obtained from rimu and we confirmed the formula  $C_{17}H_{22}O_3$  but found that the acid was invariably dextrorotatory and that the melting points of a few of its derivatives were very different from those recorded by Oudemans for the corresponding derivatives of podocarpic acid. For example, Oudemans states that methyl podocarpate melts at  $174^\circ$ , whereas the methyl ester of the acid from rimu melted at  $208^\circ$ . Through the kindness of Professor T. H. Easterfield and the Director of the Botanic Gardens, Buitenzorg, we obtained two specimens of the Javanese acid and were able to show that it affords derivatives identical with those prepared from the acid from the New Zealand trees: we are unable to account for the different melting points recorded by Oudemans.

Oudemans showed that podocarpic acid is a monobasic hydroxy-acid capable of nitration and sulphonation. On distillation with zinc dust methanthrene,  $C_{15}H_{12}$  (m. p.  $117^\circ$ ; picrate, m. p.  $117^\circ$ ), was obtained and was believed to be a methylanthracene.



Distillation of the acid or its calcium salt afforded the following products, although in very different proportions: (1) Methanthrol,  $C_{15}H_{12}O$ , m. p.  $122^\circ$ , (2) hydrocarpol,  $C_{16}H_{20}O$ , b. p.  $220^\circ$  "in vacuo," (3) *p*-cresol, (4) carpene,  $C_9H_{14}$ , b. p.  $155-157^\circ$ . As a result of these observations Oudemans suggested that

podocarpic acid has a structure of the annexed type and stated that "the production of

methanthrene is easily explained by this formula if methanthrene is a methylanthracene." At that time (1873) there was still uncertainty regarding the allocation of the linear and angular formulæ to anthracene and phenanthrene.

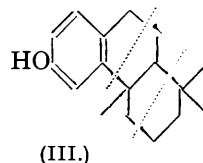
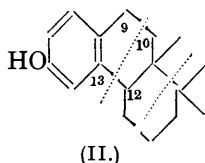
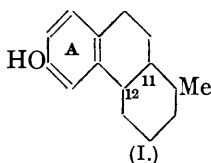
Podocarpic acid resisted esterification by the catalytic method, but esters were readily obtained by the action of alkyl sulphates and alkali or from the acid chloride and an alcohol. *Methyl podocarpate*, m. p. 208°, gave *methyl O-benzoylpodocarpate*, m. p. 143°, by the action of benzoyl chloride and *methyl O-methylpodocarpate*, m. p. 128°, on treatment with excess of methyl sulphate and alkali. The ester group in these compounds was very resistant to hydrolysis and was unaffected by boiling 0.5*N*-alcoholic potassium hydroxide; hydrolysis of methyl *O*-methylpodocarpate with excess of concentrated alcoholic potash at 150°, however, afforded *O-methylpodocarpic acid*, m. p. 157—158°. The ester group was likewise unaffected by boiling with Grignard reagents in toluene solution and it is clear that the carboxyl group in podocarpic acid must occupy a position subject to considerable steric hindrance. The molecular refraction of the acid, determined in quinoline and acetophenone solution, showed that the compound is tricyclic and contains three ethylenic linkages.

Dehydrogenation of podocarpic acid with selenium or palladium-charcoal produced a hydrocarbon, C<sub>15</sub>H<sub>12</sub> (m. p. 121°; picrate, m. p. 137°) identical with Oudemans's "methanthrene," and this was shown (Radcliffe, Sherwood, and Short, J., 1931, 2293; Sherwood and Short, *Rep. Aust. Assoc. Sci.*, 1932, 21, 38; J., 1936, 318) to be identical with 1-methylphenanthrene (Pschorr, *Ber.*, 1906, 39, 3111; Haworth, J., 1932, 1130; Sherwood and Short, *loc. cit.*; Darzens and Lévy, *Compt. rend.*, 1935, 200, 2187).<sup>\*</sup> The main product of dehydrogenation with selenium and palladium and the sole product of sulphur dehydrogenation was a phenol, C<sub>15</sub>H<sub>12</sub>O, m. p. 161°, and this compound was also produced by sulphur dehydrogenation of methyl podocarpate. Dehydrogenation of methyl *O*-methylpodocarpate afforded the corresponding *methyl ether*, m. p. 87—87.5°. This phenol is identical with Oudemans's methanthrol, for, although he recorded m. p. 122° for the phenol obtained by distillation of podocarpic acid and its calcium salt, repetition of the experiments invariably afforded a compound, m. p. 161°. On distillation with zinc dust this phenol furnished 1-methylphenanthrene, and the possibility of an alkyl migration during the distillation was excluded by the production of the same hydrocarbon by replacing the hydroxy-group successively by an amino-group and an iodine atom and removing the latter by a Grignard reaction. Methanthrol is therefore a hydroxy-1-methylphenanthrene and Oudemans's isolation of *p*-cresol as a distillation product of calcium podocarpate (an observation which we have repeatedly confirmed) suggested that the hydroxyl group is in position 4. A synthesis of 4-hydroxy-1-methylphenanthrene (Higginbottom, Hill, and Short, J., 1937, 264) showed, however, that this supposition is incorrect. The hydroxyl group cannot reside at position 9 or 10, since the *acetate* and the *methyl ether* of the phenanthrol afforded 9 : 10-quinones without loss of the substituent oxygen. We attempted to locate the hydroxyl group by several methods of degradation, but these were all unsuccessful and need not be described. It was therefore necessary to synthesise the seven possible hydroxy-1-methylphenanthenes. This arduous task was recently completed and it was found (Plimmer and Short, this vol., p. 694) that methanthrol is 6-hydroxy-1-methylphenanthrene.

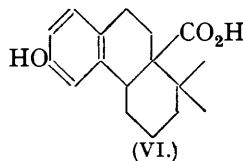
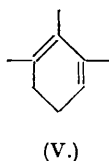
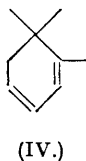
The absorption spectrum of methyl *O*-methylpodocarpate shows a maximum at 2820 Å. and in analogy with observations in the sterol group this indicates that at least two of the double bonds are conjugated and probably, though not necessarily, present in the same ring (Fieser, "Natural Products related to Phenanthrene," 1937, p. 344; Fieser and Campbell, *J. Amer. Chem. Soc.*, 1938, 60, 160; Ruzicka and Sternback, *Helv. Chim. Acta*,

<sup>\*</sup> The "4-methylphenanthrene," m. p. 116° (picrate, m. p. 127—128°; styphnate, m. p. 148°; quinone, m. p. 187°; quinoxaline, m. p. 178°), described by Darzens and Lévy (*Compt. rend.*, 1935, 201, 730) is clearly a slightly impure 1-methylphenanthrene produced by an alkyl migration during the dehydrogenation of 4-methyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene-2-carboxylic acid (compare Haworth, Mavin, and Sheldrick, J., 1934, 455; Akin, Stamatoff, and Bogert, *J. Amer. Chem. Soc.*, 1937, 59, 1268). 4-Methylphenanthrene, its picrate, styphnate, quinone, and quinoxaline melt at 50°, 140—141°, 135°, 187°, and 178°, respectively (Radcliffe and Short, J., 1931, 2296; 1936, 318; Haworth, J., 1932, 1131).

1938, **21**, 568). Although none of the following properties of the acid is completely diagnostic, the weight of the evidence points to the presence of an aromatic nucleus: (1) The acid can be nitrated and sulphonated (Oudemans), (2) the molecular refraction is practically normal, (3) there is no reaction with maleic anhydride or  $\alpha$ -naphthaquinone and the double bonds are not reduced by sodium and alcohol and are inert towards hydrogen in presence of a catalyst which promotes rapid reduction of aliphatic ethylenic linkages, (4) the acid couples readily with diazobenzenesulphonic acid. The properties of the hydroxyl group (ferric chloride coloration and methylation with methyl sulphate and alkali) indicate that this group is attached to the aromatic nucleus. On the basis of this interpretation of the facts, the formula of podocarpic acid may be derived by introducing a methyl and a carboxyl group into the skeleton (I) and the only positions consistent with the dehydrogenation results and the abnormal properties of the carboxyl group are 1, 11, and 12. The three basic carbon skeletons so obtained contain an aromatic nucleus (A) and a  $C_{11}$  residue; one of them is incapable of resolution into *isopentane* units by omitting one carbon atom from this residue, but the other two (II and III) are divisible into *isopentane* units if one carbon atom ( $C_9$  or  $C_4$  from II and  $C_9$  from III) is excluded. Scission of structures (II) and (III) at 9—10 and 12—13 accounts for the production of *p*-cresol, carbon dioxide, and carpane,  $C_9H_{14}$ , by pyrogenic degradation of podocarpic acid and we



find that the properties of carpane are consistent with its formulation as either a 1 : 1 : 2- or a 1 : 2 : 3-trimethylcyclohexadiene (IV or V). In this connexion the probable isolation of (V) from oil of amber (Karoly, *Ber.*, 1914, **47**, 1016) may be significant. Many scissions similar to that indicated above have been observed during the selenium dehydrogenation



of members of the triterpene group (Ruzicka and co-workers, *Helv. Chim. Acta*, 1937, **20**, 1156, and earlier papers).

We find that podocarpic acid shows no tendency to lactonise even under drastic conditions and it is improbable that it is a  $\delta$ -hydroxy-acid (carboxyl at  $C_{12}$ ) unless the stereochemical configuration of the molecule with respect to the junction of the rings is unpropitious. The carboxyl group is even more inert than that in abietic acid and we therefore prefer formula (VI) as a working hypothesis.

We are engaged on a detailed examination of carpane.

It seemed possible that podocarpic acid might share some of the physiological properties of oestrone, but Professor E. C. Dodds, who kindly examined the acid for oestrogenic properties, reported that doses of 100 mg. produced no response.

#### EXPERIMENTAL.

*Podocarpic Acid*.—The crude resin was freed from wood and a small amount of an insoluble red powder by solution in hot alcohol. The filtrate was diluted with water until turbid and the precipitate was collected after 2 hours, washed with a little ice-cold 55% alcohol, and recrystallised from the same solvent. Alternatively, the crude alcoholic extract was distilled under reduced pressure, and the fraction, b. p. 296—310°/20 mm., recrystallised from 55% alcohol. The following physical constants were recorded; the rotations were determined in 4% solution in absolute alcohol: (1) Acid from *Podocarpus cupressinus*, m. p. 193°,  $[\alpha]_{578} +144^\circ$ ,  $[\alpha]_{546} +165^\circ$ ; (2) acid from *Dacrydium cupressinum*, m. p. 193.5°,  $[\alpha]_{578} +144^\circ$ ,  $[\alpha]_{546} +165^\circ$ ; (3)

acid from *Podocarpus dactyloides*, m. p. 191°,  $[\alpha]_{578} + 141^\circ$ ,  $[\alpha]_{546} + 161^\circ$ . Admixture of these acids and of the corresponding derivatives caused no depression in m. p. and in these comparisons we included in each case those derivatives and degradation products for which Oudemans records different m. p.'s from those observed by us. Distillation of the acids in a vacuum or recrystallisation from formic acid raised the m. p. by 1—2° in each case, but no change in composition occurred and recrystallisation restored the normal m. p. Analyses of specimens of different origin gave the following results: Found: C, 74.5, 74.4, 74.4, 74.1, 74.4, 74.6, 74.5, 74.5; H, 8.1, 7.8, 7.75, 7.7, 7.8, 8.0, 8.4, 8.2 (Calc. for  $C_{17}H_{22}O_3$ : C, 74.4; H, 8.0%). No satisfactory equivalent could be obtained by titration because the phenolic group affected the end-point. A 7.51% solution of podocarpic acid in quinoline. ( $d_{4}^{41.5^\circ}$  1.0773,  $n_D^{41.5^\circ}$  1.6159) had  $d_{4}^{41.5^\circ}$  1.0872,  $n_D^{41.5^\circ}$  1.6142, and a 4.49% solution in acetophenone ( $d_{4}^{41.5^\circ}$  1.0097,  $n_D^{41.5^\circ}$  1.5240)  $d_{4}^{41.5^\circ}$  1.0324,  $n_D^{41.5^\circ}$  1.5309, whence  $[R_L]_D = 75.59$  (in quinoline) and 76.22 (in acetophenone).  $C_{17}H_{22}O_3$  requires  $[R_L]_D$  75.78. Another specimen in quinoline gave  $[R_L]_D$  75.86. Zerewitinoff determinations showed that the acid contains two atoms of active hydrogen per molecule (Found: 2.03, 1.91) and it gave a green coloration with alcoholic ferric chloride solution. The rotation of the acid was unaltered after  $\frac{1}{2}$  hour's boiling with 2.5% alcoholic hydrogen chloride and no isomerisation occurred. Hydrogen was not absorbed when an acetic acid solution of podocarpic acid was shaken with the gas at 2.5 atms. in presence of a platinum catalyst capable of promoting the rapid reduction of benzaldehyde. Fusion of the acid with 4 parts of potassium hydroxide (1.5 hours at 300°) produced only a trace of oil; almost the whole of the acid was recovered unchanged.

*O-Acetylpodocarpic Acid.*—Podocarpic acid (5 g.), acetic anhydride (7 g.), and anhydrous sodium acetate (1 g.) were boiled for 1 hour, and the excess of anhydride destroyed by warming with water. The crude product was dissolved in ether and washed with dilute aqueous sodium carbonate and water, and the solvent removed. The acetate crystallised from ether in rectangular prisms, which formed a turbid liquid at 173°, clearing at 176° (Found: C, 72.1; H, 7.7. Calc. for  $C_{19}H_{24}O_4$ : C, 72.2; H, 7.6%). A Zerewitinoff determination showed the presence of one active hydrogen atom (Found, 1.1). Oudemans, who prepared the acetate from podocarpic acid and acetyl chloride, states that it softens at 100° and slowly melts between 100° and 152°.

*Methyl Podocarpate.*—From silver podocarpate and methyl iodide, Oudemans obtained an ester, m. p. 174°, but records no analysis. Repetition of the experiment gave a low yield of ester, m. p. 208°, and the same compound was obtained from methyl alcohol and the crude chloride prepared from podocarpic acid and thionyl chloride. The best method for the preparation of *methyl podocarpate* was to add methyl sulphate (1.2 mols.) to a well-shaken solution of the acid and sodium hydroxide (1.1 mols.) in 50% alcohol and to complete the reaction by heating on the water-bath for a few minutes. The product was washed with aqueous sodium carbonate and recrystallised from alcohol; m. p. 208° (Found: C, 74.8, 75.0, 75.1; H, 8.1, 8.3, 8.1; OMe, 10.4; *M*, ebullioscopic in acetone, 287.  $C_{18}H_{24}O_3$  requires C, 75.0; H, 8.3; OMe, 10.8%; *M*, 288). We are indebted to Professor W. N. Benson of the University of Otago for the appended description and goniometric measurements.

"Methyl podocarpate forms colourless prismatic crystals.

*Crystal system*: Normal orthorhombic.

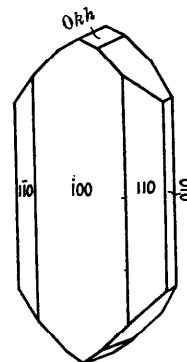
*Axial ratios*:  $a : b : c = 0.99 : 1 : 0.97$ .

*Forms Developed*:  $a$  (100),  $b$  (010),  $m$  (110),  $o$  (011),  $y$  (0 $kh$ ).

The faces of the brachydome (0 $kh$ ) were too poorly developed to admit accurate measurement, but optical tests showed that the substance is definitely biaxial with a small optic axial angle, and this confirms the orthorhombic nature of the crystals."

A Zerewitinoff determination showed that the ester contains one hydroxyl group (Found, 1.11) and treatment with benzoyl chloride and pyridine produced *methyl O-benzoylpodocarpate*, which separated from methyl alcohol in long clustered rods, m. p. 143.5° (Found: C, 76.4; H, 7.1.  $C_{25}H_{30}O_4$  requires C, 76.5; H, 7.1%). The benzoyl derivative was hydrolysed quantitatively by boiling for 2 hours with 0.5N-alcoholic potassium hydroxide with regeneration of methyl podocarpate, m. p. 208° (Found, 1.01 benzoyl group). Methyl podocarpate was recovered unchanged after boiling for 2 hours with 0.5N-alcoholic potassium hydroxide. On dehydrogenation with sulphur (4.5 atoms) for 5 hours at 240° methyl podocarpate afforded 6-hydroxy-1-methylphenanthrene, m. p. 160° (see below).

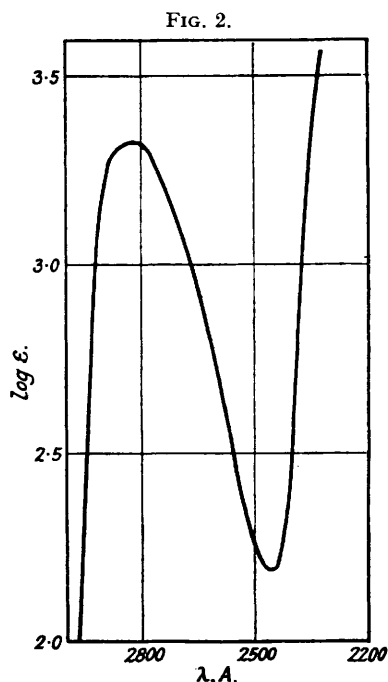
FIG. 1.

*Methyl podocarpate.*

*Ethyl Podocarpate*.—The ester, m. p. 143—146°, prepared by Oudemans from silver podocarpate and ethyl iodide was impure (Found: C, 76.1, 74.8; H, 8.7, 8.6%). A good yield of this ester was obtained by adding ethyl sulphate (1.0 mol.) to a solution of the acid and sodium (0.95 atom) in absolute alcohol and boiling for a few minutes. *Ethyl podocarpate* crystallised from alcohol in stout clustered needles, m. p. 161° (Found: C, 75.5; H, 8.7.  $C_{19}H_{26}O_3$  requires C, 75.5; H, 8.6%).

*p-Nitrobenzyl podocarpate* was readily obtained by refluxing a solution of sodium podocarpate with *p*-nitrobenzyl bromide (1.0 mol.) in 63% alcohol for 15 minutes. The ester separated from alcohol in needles, m. p. 204° (Found: C, 70.2; H, 6.8; N, 3.6.  $C_{24}H_{27}O_5N$  requires C, 70.4; H, 6.6; N, 3.4%).

*Methyl O-Methylpodocarpate*.—This ether was first prepared by warming a xylene solution of methyl podocarpate with finely divided sodium (1 atom) until the metal dissolved, adding



*Methyl O-methylpodocarpate*.

methyl iodide (1.5 mols.), and boiling for 3 hours. It was obtained in 82—86% yield by adding methyl sulphate (3.0 mols.) to a well-shaken solution of podocarpic acid (1.0 mol.) and sodium hydroxide (3.2 mols.) in 50% aqueous alcohol and boiling for a few minutes. *Methyl O-methylpodocarpate* separated from light petroleum (b. p. 50—60°) in rectangular prisms, m. p. 128° (Found: C, 75.6; H, 8.6; OMe, 20.1.  $C_{19}H_{26}O_3$  requires C, 75.5; H, 8.6; OMe, 20.5%). Dr. D. G. Drummond kindly examined the absorption spectrum of methyl *O*-methylpodocarpate in alcoholic solution and the results are shown in Fig. 2: maximum, 2820 Å.; log ε, 3.33. This ester was recovered unchanged after boiling for 2 hours with 0.5*N*-alcoholic potassium hydroxide or for 6 hours with methylmagnesium iodide or phenylmagnesium bromide in toluene solution. When the ester was submitted to the action of sodium (20—23 atoms) in ethyl-, butyl- or amyl-alcoholic solution, practically the whole of the material was converted into *O*-methylpodocarpic acid and no appreciable reduction occurred. (Mr. W. S. Rapson, M.Sc., who repeated these experiments in 1933 at our request, also found that no reduction occurred.) Dehydrogenation of methyl *O*-methylpodocarpate with sulphur (4.7 atoms) at 220—260° for 5 hours produced a volatile liquid of unpleasant odour (? methyl sulphide), and a 50% yield of 6-methoxy-1-methylphenanthrene, m. p. 89°, (see below) was obtained by vacuum distillation.

*O-Methylpodocarpic Acid*.—Methyl *O*-methylpodocarpate (5 g.) was almost completely hydrolysed when heated at 150° for 4 hours with a solution of potassium hydroxide (5 g.; 5.4 mols.) in alcohol (15 c.c.) and water (5 c.c.). The resulting *O*-methylpodocarpic acid crystallised from methyl alcohol in rectangular prisms, m. p. 158° (Found: C, 75.0; H, 8.4; OMe, 10.9.  $C_{18}H_{24}O_3$  requires C, 75.0; H, 8.3; OMe, 10.8%). The product was soluble in aqueous sodium carbonate and was remethylated to methyl *O*-methylpodocarpate, m. p. 128°, by methyl sulphate and alkali.

*Distillation of Podocarpic Acid with Zinc Dust*.—The distillation was effected from a combustion tube as described by Oudemans. The distillate was dissolved in ether and thoroughly washed with aqueous sodium hydroxide and after removal of the solvent from the dry solution the residue was repeatedly distilled from sodium in a vacuum. The fraction, b. p. 160—185°/2—2.5 mm., solidified and was recrystallised from methyl alcohol to constant m. p. 120.7—121.5° (Found: C, 93.7; H, 6.3. Calc. for  $C_{15}H_{12}$ : C, 93.8; H, 6.25%). The hydrocarbon was converted into (1) a picrate, orange-yellow needles, m. p. 137.5° (Found: C, 59.7; H, 3.8. Calc. for  $C_{15}H_{12}, C_6H_3O_7N_3$ : C, 59.85; H, 3.6%), (2) a *styphnate*, yellow needles, m. p. 152—153° (Found: C, 57.5; H, 3.6.  $C_{15}H_{12}, C_6H_3O_8N_3$  requires C, 57.7; H, 3.4%), (3) a quinone, orange-red needles, m. p. 193—193.5° (Found: C, 80.8; H, 4.5. Calc. for  $C_{15}H_{10}O_2$ : C, 81.1; H, 4.5%), and (4) a quinoxaline, yellow needles, m. p. 177° (Found: N, 9.6. Calc. for  $C_{21}H_{14}N_2$ : N, 9.5%). The constants for this hydrocarbon and its derivatives are slightly lower than those recorded by Pschorr (*loc. cit.*) for 1-methylphenanthrene and its derivatives, but the identity of the two hydrocarbons was established by a direct comparison with synthetic material.

Dr. R. D. Haworth kindly compared our products with 1-methylphenanthrene and its derivatives (which he synthesised by a different method) and reported that no depression in the m. p.'s was observed.

*Dehydrogenation of Podocarpic Acid.*—(i) *With selenium.* Podocarpic acid (36 g.) and selenium powder (45 g.) were heated at 290—310° for 45 hours and the cold mixture was powdered and extracted with ether. The ethereal solution was repeatedly extracted with 10% aqueous sodium hydroxide, dried, and evaporated, and the residue distilled from sodium in a vacuum. The distillate (4 g.) consisted of 1-methylphenanthrene, which was identified as described above. Acidification of the alkaline solution afforded 7 g. of the phenol  $C_{15}H_{12}O$  described below.

(ii) *With sulphur.* A mixture of podocarpic acid (20 g.) and sulphur (10 g.) was heated at 190—250° for 5½ hours and then distilled at 8 mm. The distillate (9·4 g.; m. p. 154—158°) was dissolved in ether and washed with aqueous sodium carbonate to remove a little unchanged podocarpic acid, and the solution extracted with 10% aqueous sodium hydroxide. The residual ethereal solution contained less than 0·5 g. of a sticky oil in which no 1-methylphenanthrene could be detected. Acidification of the alkaline solution gave 6·2 g. of the phenol  $C_{15}H_{12}O$ , m. p. 158—159°.

(iii) *Catalytic.* A mixture of podocarpic acid (20 g.) and 10% palladium-charcoal (5 g.) was heated for 4¼ hours at 290—350°. The volume of gas evolved was 7·6 l. (21° and 762 mm.) and a trace of 1-methylphenanthrene (picrate, m. p. and mixed m. p. 133·5°) and 5·1 g. of the phenol  $C_{15}H_{12}O$  were isolated from the residue.

*Investigation of the Phenol  $C_{15}H_{12}O$ .*—By the destructive distillation of podocarpic acid or calcium podocarpate Oudemans (*loc. cit.*, pp. 267, 274, 277) isolated a phenol  $C_{15}H_{12}O$ , m. p. 122°, which he termed methanthrol. Repetition of these experiments with either the Javanese or the New Zealand material invariably gave a phenol, m. p. 161°, identical with that obtained in the dehydrogenation experiments. The crude phenol was best purified by successive crystallisation from benzene (charcoal), which yielded an amorphous product, and from chloroform, which afforded white irregular plates, m. p. 161° (Found : C, 86·4, 86·5; H, 5·8, 6·0.  $C_{15}H_{12}O$  requires C, 86·5; H, 5·8%). The product was characterised by the following derivatives : (1) *Picrate*, red needles from alcohol, m. p. 182° (Found : C, 57·5; H, 3·6; N, 9·6.  $C_{15}H_{12}O, C_6H_3O_7N_3$  requires C, 57·7; H, 3·4; N, 9·6%), (2) *acetate*, white plates from alcohol, m. p. 118—119° (Found : C, 81·6; H, 5·7.  $C_{17}H_{14}O_2$  requires C, 81·6; H, 5·6%), (3) *benzoate*, irregular white plates from alcohol, m. p. 147° (Found : C, 84·4; H, 5·2.  $C_{22}H_{16}O_2$  requires C, 84·6; H, 5·1%), and (3) *glycollic ether*, white plates from benzene, m. p. 191° (Found : C, 76·8; H, 5·2.  $C_{17}H_{14}O_3$  requires C, 76·7; H, 5·3%). The methyl ether, prepared either by dehydrogenation of methyl *O*-methylpodocarpate (above) or by methylation of the phenol, separated from methyl alcohol in clustered cream needles, m. p. 87—87·5° (Found : C, 86·6; H, 6·5; OMe, 13·9.  $C_{16}H_{14}O$  requires C, 86·5; H, 6·3; OMe, 14·0%); the *picrate* crystallised from alcohol in vermilion needles, m. p. 140—141·5° (Found : C, 58·65; H, 4·2; N, 9·3.  $C_{16}H_{14}O, C_6H_3O_7N_3$  requires C, 58·5; H, 3·8; N, 9·3%). The methyl ether (0·2 g.) was smoothly demethylated by boiling for 4 hours with acetic acid (9 c.c.) and hydrobromic acid (9 c.c., *d* 1·5) and the phenol so obtained had m. p. 161°. Oxidation of the methyl ether (0·5 g.) in acetic acid (2·5 c.c.) with chromic anhydride (1 g.) in acetic acid (6 c.c.) and water (0·6 c.c.), first at 0° and then for ½ hour at 100°, furnished a golden-brown *quinone*, which separated when the hot solution was poured into water (40 c.c.); purification was effected by solution in hot aqueous sodium bisulphite and crystallisation from acetic acid; m. p. 189° (Found : C, 75·9; H, 5·0.  $C_{16}H_{12}O_3$  requires C, 76·2; H, 4·8%). The corresponding *quinoxaline* crystallised from chloroform in long yellow rods, m. p. 166° (Found : C, 81·4; H, 5·0; N, 8·5.  $C_{22}H_{16}ON_2$  requires C, 81·5; H, 4·9; N, 8·6%). The *acetoxo-quinone*, obtained by the oxidation of the acetate with chromic anhydride (3 mols.) in acetic acid, separated from acetic acid in long orange-yellow needles, m. p. 182·5—183·5° (Found : C, 72·9; H, 4·65.  $C_{17}H_{12}O_4$  requires C, 72·85; H, 4·3%). The acetoxo-quinone was hydrolysed by trituration with *N*-aqueous alcoholic sodium hydroxide, and the product precipitated with acid and recrystallised from alcohol. The *hydroxy-quinone* separated in stout yellow-orange needles, which darkened at 258° when rapidly heated, m. p. 264—265° (decomp.) (Found : C, 75·7; H, 4·4.  $C_{15}H_{10}O_3$  requires C, 75·6; H, 4·2%); it formed a port-wine solution in dilute alcoholic potash and the colour remained unchanged on warming (compare Fieser and Young, *J. Amer. Chem. Soc.*, 1931, 53, 4126). The production of these quinones showed that the phenol  $C_{15}H_{12}O$  was a methylphenanthrol and that the 9—10 positions were unsubstituted. The methyl group was shown to be in position 1 by converting the phenol into 1-methylphenanthrene by the following

methods: (1) The phenol (5 g.) and zinc dust (200 g.) were distilled from a combustion tube and the resulting pasty yellow solid (2.4 g.) was distilled from sodium in a vacuum. The solid white distillate (1.5 g.; m. p. 112—115°), recrystallised from light petroleum (b. p. 40—50°), had m. p. 120—121°, undepressed by 1-methylphenanthrene. There was no depression in m. p. when the picrate was mixed with that of 1-methylphenanthrene. (2) Attempts to convert the methylphenanthrol into the corresponding amine by the Bucherer method were unsuccessful, but the corresponding *acetamido*-compound was obtained in 58% yield by heating the phenol at 290° for 10 hours with sodium acetate (4.4 mols.), ammonium chloride (4.8 mols.), and acetic acid (5.7 mols.). The product was dissolved in ether and washed with aqueous sodium hydroxide; it crystallised from methyl alcohol in greyish-white rhombs, m. p. 197.5—198° (Found: C, 82.0; H, 6.1; N, 5.7.  $C_{17}H_{15}ON$  requires C, 81.9; H, 6.0; N, 5.6%). The corresponding amine was obtained in 79% yield by heating the acetyl derivative (15.2 g.), hydrochloric acid (66 c.c.), water (61 c.c.), and acetic acid (152 c.c.) on the water-bath for 5 hours. The hydrochloride separated from water in small plates, which began to decompose at 260° and melted at 270—272° when slowly heated. The *amine*, liberated with ammonia, crystallised from ligroin in large plates, m. p. 151° (Found: C, 86.9; H, 6.6; N, 6.7.  $C_{15}H_{13}N$  requires C, 87.0; H, 6.3; N, 6.8%). Diazotisation of the amine was effected by the method of de Miltz and Zandt (*J. Amer. Chem. Soc.*, 1936, **58**, 2044): a solution of the amine (5.0 g.) in pyridine (24 c.c.) was stirred mechanically at -10° and a solution of sodium nitrite (3.7 g.) in concentrated sulphuric acid (36 c.c.) and water (18 c.c.) was added during 1 hour. After being stirred for 1 hour longer, the solution was diluted to 500 c.c. with water, treated with a solution of urea (2.5 g.) in water (62 c.c.), and stirred for 1 hour. A solution of potassium iodide (4.8 g.) in water (13 c.c.) was added and, after 12 hours, the mixture was heated on the steam-bath for 2 hours. The black solid was collected and extracted with benzene, and the solution washed with aqueous sodium bisulphite, dried, and evaporated. The *iodomethylphenanthrene* was isolated from the fraction, b. p. ca. 200°/2 mm., and recrystallised from benzene-light petroleum (b. p. 40—60°), forming long clustered rods, m. p. 144.5—145° (Found: C, 56.4; H, 3.6.  $C_{15}H_{11}I$  requires C, 56.6; H, 3.5%). Yield, 29%. When the diazonium solution was boiled, the methylphenanthrol was regenerated, m. p. and mixed m. p. 161°, so that the amino-group occupied the same position as the hydroxyl group replaced. Solutions of the above iodo-compound (2.0 g.) in benzene (15 c.c.) and of ethyl bromide (0.5 c.c.) in dry ether (3.3 c.c.) were added simultaneously during  $\frac{1}{2}$  hour to magnesium (0.3 g.) covered with boiling ether (4.7 c.c.). The mixture was boiled in an atmosphere of dry nitrogen for 2 hours, cooled, and decomposed with ice-cold dilute sulphuric acid. The ethereal solution was washed, dried, and evaporated, and the residue distilled from sodium in a vacuum. The distillate (0.65 g.; b. p. ca. 180°/10 mm.) had m. p. 117—120° and recrystallisation from methyl alcohol gave 1-methylphenanthrene, m. p. and mixed m. p. 120—121°.

Attempts to locate the hydroxyl group in the 1-methylphenanthrol by degradation were vitiated by the stability of the compound and the destruction of the hydroxylated ring when a reaction occurred. The compound was recovered unchanged when heated to 250° with potassium hydroxide and lead dioxide (compare Graebe and Kraft, *Ber.*, 1906, **39**, 794). The methyl ether was either unchanged or totally destroyed on heating with aqueous selenious acid (compare I.G. Farbenind. A.-G., D.R.-P. 347,743; Cook, J., 1932, 1476). Oxidation of the methoxy-quinone with hydrogen peroxide resulted in extensive disruption with the production of a number of compounds which could not be separated, and distillation with soda-lime did not yield a substituted diphenyl (compare Graebe, *Ber.*, 1873, **6**, 63).

Only two of the seven possible hydroxy-1-methylphenanthrenes possess constants similar to those of the compound from podocarpic acid and the following comparison showed that the latter is 6-hydroxy-1-methylphenanthrene:

	Methyl ether, m. p.	Picrate of methyl ether, m. p.
(1) 3-Hydroxy-1-methylphenanthrene, * m. p. 161° .....	90°	147°
(2) 6-Hydroxy-1-methylphenanthrene, † m. p. 161° .....	87—87.5	140—141.5
(3) Phenanthrol from podocarpic acid, m. p. 161° .....	87—87.5	140—141.5

\* Hill, Short, Stromberg, and Wiles, J., 1937, 512.

† Plimmer, Short, and Hill, this vol., p. 694.

Admixture of the corresponding pairs (1) and (3) caused 10—20° depressions in the m. p.'s, but no depressions were caused by admixture of the pairs (2) and (3).

The compounds described in the following section were prepared in connexion with various

degradation experiments, and, owing to the fixation of the bonds in the phenanthrene system, reaction is assumed to have occurred at position 5.

*5-Bromo-6-hydroxy-1-methylphenanthrene*.—A solution of bromine (8.5 g.) in chloroform was added to a cold solution of 6-hydroxy-1-methylphenanthrene (10.4 g.) in the same solvent (300 c.c.). After standing overnight, the solvent was removed, finally under diminished pressure, and the residual black solid was repeatedly extracted with hot ligroin. The solution, which was decanted from a small amount of oil which separated on cooling slightly, deposited *5-bromo-6-hydroxy-1-methylphenanthrene* in white plates (7.5 g.), m. p. 124° (Found : C, 62.8; H, 4.0; Br, 28.2.  $C_{15}H_{11}OBr$  requires C, 62.7; H, 3.8; Br, 27.9%). Methylation with methyl sulphate and alkali afforded the *methyl* ether, which separated from ligroin in elongated plates, m. p. 129—130° (Found : Br, 26.4.  $C_{16}H_{13}OBr$  requires Br, 26.6%). The bromo-ether would not react with magnesium in dry ether.

*1-Methyl-5 : 6-phenanthraquinone*.—A solution of sulphanilic acid (4.2 g.), sodium hydroxide (0.8 g.), and sodium nitrite (1.4 g.) in water (20 c.c.) was added to a mixture of concentrated hydrochloric acid (5 c.c.), water (8 c.c.), and ice (20 g.) and the resulting diazo-suspension was added at 0° to a mechanically stirred solution of 6-hydroxy-1-methylphenanthrene (4.2 g.) and sodium hydroxide (2.4 g.) in water (60 c.c.). After the mixture had been stirred for 10 minutes the suspension of the red azo-dye was reduced by addition of powdered sodium hydrosulphite (10 g.) at 80—90°. The flocculent precipitate was collected and repeatedly extracted with boiling dilute (1 : 25) hydrochloric acid containing sulphur dioxide. Addition of concentrated hydrochloric acid precipitated the amine hydrochloride, which was purified by solution in a mixture of alcohol and concentrated hydrochloric acid (1 : 1). *5-Amino-6-hydroxy-1-methylphenanthrene hydrochloride* melted at 243—245° (decomp.) when rapidly heated (Found : N, 5.3; Cl, 13.9.  $C_{15}H_{13}ON.HCl$  requires N, 5.4; Cl, 13.7%). Yield, 87%. The free base was unstable. A solution of chromic anhydride (1.7 g.) in water (1.6 c.c.) was added to a suspension of the amine hydrochloride (4.1 g.) in acetic acid (40 c.c.) at 10°. The temperature rose to a maximum of 35° and after a few minutes the solution was poured into water (170 c.c.). The crude product contained a black impurity which was difficult to remove, but crystallisation from chloroform ultimately afforded *1-methyl-5 : 6-phenanthraquinone* as a red powder, m. p. 176—177° (decomp.) when rapidly heated (Found : C, 80.7; H, 4.8.  $C_{15}H_{10}O_2$  requires C, 81.1; H, 4.5%).

*5 : 6-Diacetoxy-1-methylphenanthrene*.—The quinone (0.2 g.), dissolved in acetic anhydride (2.0 c.c.) and pyridine (6 drops), was stirred with zinc dust (0.3 g.) until the solution became pale yellow. The mixture was diluted with acetic acid (2.0 c.c.), filtered from excess of zinc, and diluted with water, and the solid collected. The *diacetate* separated from benzene-light petroleum in colourless plates, m. p. 154.5—155° (Found : C, 73.9; H, 5.3.  $C_{19}H_{16}O_4$  requires C, 74.0; H, 5.2%).

*Distillation of Calcium Podocarpate*.—Distillation of anhydrous calcium podocarpate (from 100 g. of the acid) as described by Oudemans (*loc. cit.*, p. 249) gave 67—74 g. of a tar, which was steam-distilled. The distillate was exhaustively extracted with ether and separated into neutral and acid portions. The acid fraction (6.6 g.), most of which had b. p. 200—202°, would not solidify and was identified by the preparation of the following compounds, which caused no depression in the m. p.'s of the corresponding derivatives of *p*-cresol : (1) *p*-tolyl benzoate, m. p. 70° (Found : C, 79.2; H, 5.8. Calc. for  $C_{14}H_{12}O_2$  : C, 79.25; H, 5.7%), (2) *p*-tolylloxyacetic acid, m. p. 135° (Found : C, 65.2; H, 6.2. Calc. for  $C_9H_{10}O_2$  : C, 65.1; H, 6.0%)\*. The neutral product (12.5 g.) was purified by distillation from sodium in a vacuum; the distillate (7.2 g.) had b. p. 154—155°/754 mm., which agrees with the b. p. of carpine recorded by Oudemans (Found : C, 88.3; H, 11.4. Calc. for  $C_9H_{14}$  : C, 88.5; H, 11.5%).

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AUCKLAND UNIVERSITY COLLEGE, NEW ZEALAND.  
THE COLLEGE OF TECHNOLOGY, MANCHESTER.

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