

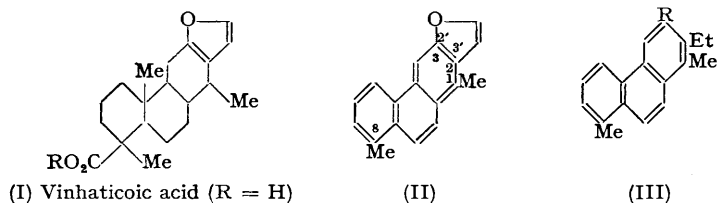
848. *The Chemistry of Extractives from Hardwoods. Part XV.**
The Constitution of Methyl Vinhaticoate.†

By F. E. KING and T. J. KING.

Methyl vinhaticoate, $C_{21}H_{30}O_3$, isolated from the heartwood of *Plathymenia reticulata* (King, King, and Neill, *J.*, 1953, 1055), is a dodecahydrophenanthrofuran (I; R = Me). The furan 4:5-positions were found to be unsubstituted since ozonolysis gave a keto-enolic compound, $C_{20}H_{30}O_4$ (V), which was hydrolysed to the ketone (VI) and formic acid. Selenium dehydrogenation of the ketone gave 1:8-dimethylphenanthrene, and 1:3:8-trimethylphenanthrene after reaction with methylmagnesium iodide, thus indicating the position of the furan oxygen atom. The orientation of the heterocyclic ring with respect to the phenanthrene nucleus was determined by two methods, of which dehydrogenation of an oxidation product (XIV) to 1:2:8-trimethylphenanthrene was the more direct. The methoxycarbonyl and the methyl group at position 1 were located by the usual reactions terminating in the production of a 1-ethylphenanthrene.

The structure (I) does not conform to the isoprene rule, and evidence is presented to show that the 8-methyl group of the various derived phenanthrenes does not arise as a result of the migration of a substituent during dehydrogenation, *e.g.*, from the adjacent angular position 14.

AN introductory account of the heartwood constituents of *Plathymenia reticulata* (King, King, and Neill, *J.*, 1953, 1055) described the isolation of a difficultly hydrolysable ester, methyl vinhaticoate, $C_{21}H_{30}O_3$, in which the presence of a furan ring was demonstrated. From its molecular formula the related acid, $C_{20}H_{28}O_3$, appeared to be a member of the resin acid series of diterpenes; this has been confirmed by further investigations and it is now possible to attribute to the acid the detailed structure (I; R = H). Direct chemical evidence is available for all constitutional features of the molecule except the position of the angular methyl group which is assumed to be situated as in similar diterpenes. The stereochemistry of the ring junctions is unknown, but there is reason to suppose that the methoxycarbonyl and the angular methyl group are in *trans*-relation, as in abietic acid, in contrast to the *cis*-arrangement existing in podocarpic acid and in agathenedicarboxylic acid (agathic acid) (for a discussion of the stereochemistry of the resin acids see Simonsen and Barton, "The Terpenes," Cambridge Univ. Press, 1952, Vol. III, p. 328 *et seq.*).



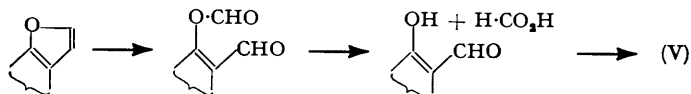
Among the first degradation experiments on methyl vinhaticoate were those involving dehydrogenation. Owing to the unique structure of the ester, however, the resulting phenanthrene derivatives were not capable of ready identification and their isolation did not therefore immediately contribute to a solution of the structural problem. In the dehydrogenation with sulphur a crystalline solid, $C_{18}H_{14}O$, was obtained and characterised by compounds with picric acid and with trinitrobenzene. It was later apparent from the structure (I; R = Me) that the loss of three carbon atoms is due to the elimination of an angular methyl and a tertiary methoxycarbonyl group, and it may therefore be concluded that the product is the dimethylfuranophenanthrene (II). Dehydrogenation with selenium gave two products, $C_{18}H_{18}$ and $C_{18}H_{18}O$, each formula being supported by the analysis

* Part XIV, *J.*, 1953, 3932.

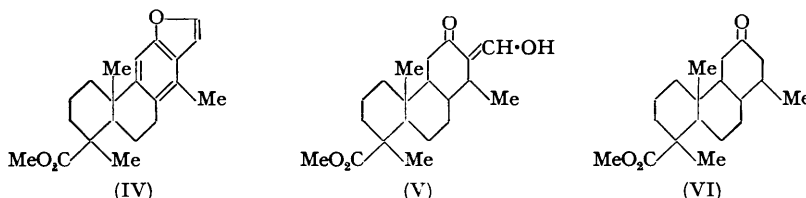
† Presented in summarised form at the 13th Intern. Congr. Pure and Appl. Chem., Stockholm, July 31st, 1953.

of two derivatives. The oxygenated compound was converted into the hydrocarbon, $C_{18}H_{18}$, by zinc dust distillation, and the two products can now be formulated as (III; $R = H$) and (III; $R = OH$). Sulphur dehydrogenation under milder conditions produced a tetrahydro-compound (IV), later the subject of other reactions.

In order to obtain readily identifiable dehydrogenation products it was necessary to devise a method for the prior removal of the furan ring. As a means to this end, partial ozonolysis of the methyl ester (I; $R = Me$) was attempted and by using half the amount of ozone theoretically necessary for the rupture of one double bond, it was to some extent possible to restrict oxidation to the unsubstituted positions of the furan nucleus. The sequence of reactions is as follows, the *O*-formyl group being spontaneously hydrolysed to give the tautomeric hydroxymethylene-ketone (V) :

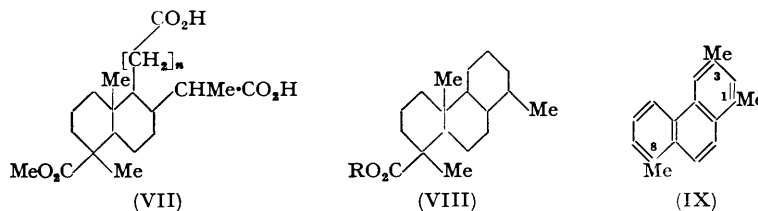


The constitution of the product as a keto-enol compound was shown by its ferric reaction and acidic properties, and by its hydrolysis with alkali to the ketone (VI). The absence of substituents at the carbon atoms of the oxidised bond was apparent from the simultaneous formation with (VI) of a second molecule of formic acid.



The ozonolysis product (V) was invariably accompanied by a dicarboxylic acid, $C_{19}H_{30}O_6$, the sole isolable product when larger quantities of ozone were used. It is presumably formed as a result of the oxidation of both ethylene bonds in the compound (I; $R = Me$), and to it, therefore, the structure (VII; $n = 1$) is attributed.

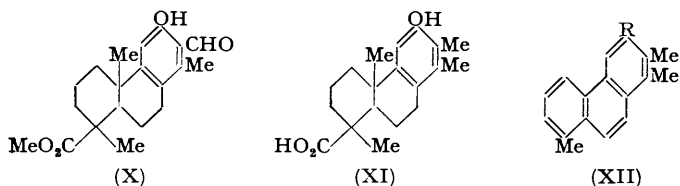
The keto-ester (VI) was reduced by the Wolff-Kishner reaction (Huang-Minlon conditions), with simultaneous hydrolysis of the methoxycarbonyl group, to a perhydrophenanthrene (VIII; $R = H$) which was re-esterified with diazomethane. Dehydrogenation of the reduced ester (VIII; $R = Me$) with selenium gave a hydrocarbon, $C_{16}H_{14}$, easily recognised from its characteristically high melting point as 1 : 8-dimethylphenanthrene. Its identity was confirmed by the preparation of the picrate, phenanthraquinone, and derived quinoxaline, all of which were indistinguishable from specimens obtained from the synthetic hydrocarbon (forthcoming publication). Selenium treatment of the keto-ester (VI) also yielded 1 : 8-dimethylphenanthrene.



The position of the carbonyl group was determined by reaction with methylmagnesium iodide, whereupon dehydrogenation of the resulting alcohol gave a new trimethylphenanthrene, also obtained, in higher yield, when the alcohol was previously dehydrated with acetic anhydride. The derivation of 1 : 8-dimethylphenanthrene from (VI) or from its Wolff-Kishner reduction product (VIII; $R = Me$) determines the orientation of two

of the substituents in the new trimethylphenanthrene and thus limits its possible structures to the two unknown 1:4:8- and 1:3:8-isomers. A synthesis of the latter (forthcoming publication) and direct comparison of the respective hydrocarbons from the two sources and of four of their derivatives proved the dehydrogenation product to be the 1:3:8-trimethylphenanthrene (IX). The furan oxygen atom is thus located at the phenanthrene 3-position, thereby leaving two possible orientations, *viz.*, 2:3 or 3:4, for the heterocyclic component.

The first experiments to determine the position of the furan system attempted to effect dehydrogenation of the keto-enolic compound (V), but they resulted in the elimination of the hydroxymethylene group and formation of 1:8-dimethylphenanthrene. A more suitable intermediate was, however, available from the ozonolysis of methyl tetradehydrovinhaticoate (IV) which with the spontaneous hydrolysis of the *O*-formyl group produces the *o*-hydroxy-aldehyde (X). Reduction by the Huang-Minlon procedure replaced the formyl group by methyl and simultaneously hydrolysed the ester, thus leading to (XI). When dehydrogenated with selenium the product (XI) afforded principally a trimethylphenanthrol (XII; R = OH), converted by zinc dust distillation into a mixture containing 1:2:8-trimethylphenanthrene (XII; R = H) and 1:8-dimethylphenanthrene,

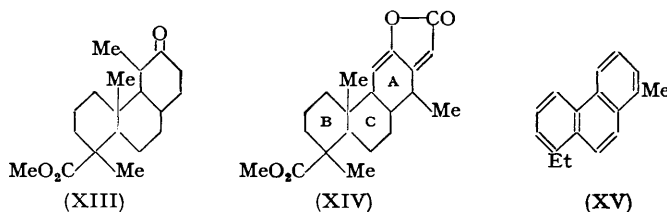


the latter arising from expulsion of the substituent adjacent to the phenolic group. The elimination of an alkyl group under these conditions finds a parallel in the appearance of 1-methylphenanthrene among products similarly derived from 8-methyl-1-*isopropyl*-2-phenanthrol (Short and Wang, *J.*, 1951, 2979). It was not possible to obtain a completely pure specimen of 1:2:8-trimethylphenanthrene from the mixed products but *X*-ray powder photographs prepared by Dr. S. C. Wallwork of the recrystallised substance and of an authentic sample of the trimethylphenanthrene were identical. Consequently, the disposition of the furan ring with respect to the hydrophenanthrene system was decided in favour of the arrangement shown in structure (I) and elsewhere.

In drawing conclusions as to the structures of (I) and of its derivatives from dehydrogenation experiments the drastic conditions involved make it necessary to consider the probability of molecular rearrangements. No examples are known in which substituents in the 2- or 3-position are affected, but the wandering of a methyl group from position 4 to 1 has been observed by Haworth, Mavin, and Sheldrick (*J.*, 1934, 454) in the dehydrogenation of 5:6:7:8:9:10:13:14-octahydro-1:5-dimethylphenanthrene, the product consisting largely of 1:8-dimethylphenanthrene with relatively little of the expected 1:5-compound. Normal dehydrogenation occurred, however, when a 4-methyl group was attached to a doubly bound carbon atom (Haworth *et al.*, *loc. cit.*). For the latter reason the formation of 1:3:8-trimethylphenanthrene was accepted as proof that the keto-ester from which it had been derived was indeed (VI) and not (XIII), since it can be assumed that dehydration of the alcohol obtained by the action of methylmagnesium iodide on (XIII) would largely result in the introduction of a double bond adjacent to the methyl group which would, therefore, be unlikely to migrate. No trace of any isomeric compound was detected in the 1:3:8-trimethylphenanthrene arising from the dehydrogenation.

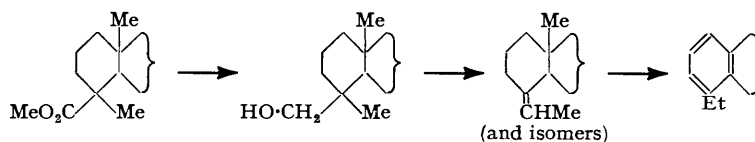
Conclusive proof of the orientation of the furan ring was later provided by selenium dehydrogenation of the lactone (XIV), the anhydro-derivative of a compound obtained from methyl vinhaticoate by perphthalic acid oxidation (see King, King, and Neill, *loc. cit.*). Unlike the material obtained *via* the phenols (XI) and (XII; R = OH), the product readily yielded 1:2:8-trimethylphenanthrene. In view of the experience of Haworth, Mavin, and Sheldrick (*loc. cit.*) it is certain that the formation of the 1:2:8-compound

uncontaminated by any isomer would have been impossible had the methyl group in ring A not occupied the position indicated in structure (XIV).



In the hope of obtaining further information as to the position of the methyl group in ring A, the derivative (XIV) was subjected also to oxidative degradation. Ozonolysis gave mixed products owing to incomplete reaction, and it was therefore not further pursued. With potassium permanganate in acetone an oily acid was obtained which, however, failed to give any solid derivative. When distilled with acetic anhydride it formed a neutral non-ketonic product, $C_{18}H_{26}O_5$, slowly dissolving in aqueous alkalis, and the structure (VII; $n = 0$) is tentatively assigned to the acid.

Finally the situation of the quaternary methoxycarbonyl group at position 1 was established by the following series of reactions, first correctly interpreted by Ruzicka, de Graafe, and Müller (*Helv. Chim. Acta*, 1932, **15**, 1300) and Vocke (*Annalen*, 1932, **497**, 247) :



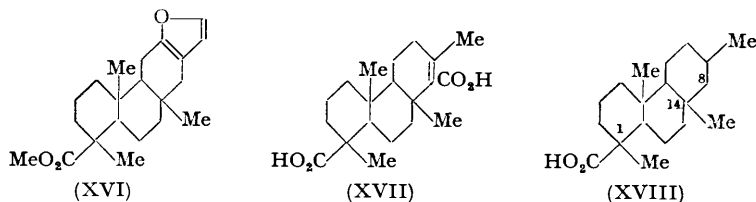
The experiment was performed on the acid (VIII; $R = H$), and the alcohol obtained by lithium aluminium hydride reduction was treated with phosphorus pentachloride in the usual way. The identity of the aromatised product as 1-ethyl-8-methylphenanthrene (XV) was proved by comparison with a synthetic specimen (forthcoming publication).

From a quantitative determination of the rate of hydrolysis of methyl vinhaticoate it is believed, as indicated in the introductory paragraph above, that the stereochemical arrangement of the carboxyl and the angular methyl group is similar to that in abietic acid. Furthermore, methyl vinhaticoate, like methyl dehydroabietate (cf. Zeiss, *J. Amer. Chem. Soc.*, 1947, **69**, 302; 1951, **73**, 497), gave with excess of phenylmagnesium bromide a diphenylcarbinol under conditions similar to those which are without effect on methyl podocarpate (Sherwood and Short, *J.*, 1938, 1006).

The structure emerging from these investigations on methyl vinhaticoate, namely (I; $R = Me$), although apparently well authenticated, is remarkable among diterpenes in containing a carbon skeleton not exclusively constitutable from isoprene units. Further consideration was therefore given to the possible occurrence during dehydrogenation of a molecular rearrangement other than of the type already discussed. The migration of an angular methyl group appeared to offer a possible route through which a carbon atom, unsubstituted in the parent diterpene, might acquire a substituent under the conditions of selenium dehydrogenation. Should this type of migration occur, the structure (XVI), which is theoretically derivable from isoprene units, provides a satisfactory alternative to the expression (I; $R = Me$).

No definite example of the migration of angular methyl to an unsubstituted carbon appears to have been recorded in the diterpene series. A model for studying the possible migration of an angular methyl group adjacent to the 8-position is provided by the acid (XVIII) which Ruzicka and Hosking (*Helv. Chim. Acta*, 1930, **13**, 1402) have prepared by partial decarboxylation and reduction of *isoagathic acid* (XVII). Were the second angular substituent at $C_{(14)}$ a feature of the structure of methyl vinhaticoate, as in (XVI), and hence of its derivatives—including, for example, the tricyclic product otherwise formulated as (VIII; $R = Me$) from which 1:8-dimethylphenanthrene is

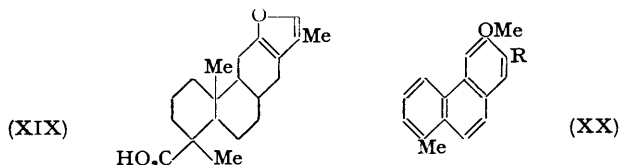
obtained—then the dehydrogenation of (XVIII) also would certainly result in the appearance of 1 : 2 : 8-trimethylphenanthrene. A quantity of the acid (XVIII), prepared by the method of Ruzicka and Hosking and dehydrogenated with selenium, in fact yielded pimanthrene (1 : 7-dimethylphenanthrene), and no trace of the more sparingly soluble 1 : 2 : 8-trimethylphenanthrene was detected. It may therefore be concluded that the 1-methyl group found in the various alkylphenanthrenes derived from vinhaticoic acid



and its transformation products does not come from the neighbouring angular position in these compounds but is indeed originally present in ring A as indicated in formula (I).

Cocker, Cross, Duff, and Holley (*Chem. and Ind.*, 1952, 827) have recently shown that the diterpene marrubiin contains a furan ring; the discovery in vinhaticoic acid of the reduced furanophenanthrene nucleus introduces yet a new ring-system into the terpene series. Evidence will shortly be presented showing that vouacapenic acid also (Spoelstra, *Rec. Trav. chim.*, 1930, 49, 226) is a derivative of this new tetracyclic system.

Details are given in the Experimental section of several transformation processes devised to relate vinhaticoic acid to the resin acids of known constitution when for a time it was believed to contain a hybridised podocarpic-abietic acid skeleton as in (XIX). Thus methylation of the phenol (actually X) obtained by ozonolysis of methyl tetrahydro-



vinhaticoate might on the basis of the alternative structure (XIX) have given methyl 7-acetyl-*O*-methylpodocarpace (Campbell and Todd, *J. Amer. Chem. Soc.*, 1942, 64, 928). Simultaneously, attempts were made to prepare a furano-derivative of methyl podocarpace. For approaching the abietic acid series, methyl tetrahydrovinhaticoate (IV) was hydrogenated to the dihydrofurano-derivative with a view to reductive fission of the furan ring which, with (XIX) as starting point, could lead to methyl 6-hydroxy-7-*isopropyl*-dehydroabietate.

Convincing proof of the non-identity of the vinhaticoic acid and the podocarpic-abietic acid series came from sulphur dehydrogenation which, applied to methyl 7-acetyl-*O*-methylpodocarpace, yielded a ketonic product (7-acetyl-6-methoxy-1-methylphenanthrene) (XX; R = COMe), reduced by the Huang-Minlon conditions to 7-ethyl-6-methoxy-1-methylphenanthrene (XX; R = Et). The vinhaticoic acid derivative, *O*-methyl ether of (X), on the other hand, owing to the greater ease of reduction of aldehyde groups, afforded a non-carbonylic product, which with the establishment of structure (I) is known to be 3-methoxy-1 : 2 : 8-trimethylphenanthrene (XII; R = OMe).

EXPERIMENTAL

1 : 8-Dimethylfuran(3' : 2'-2 : 3)phenanthrene (II).—Methyl vinhaticoate (I; R = Me) (4 g., 1 mol.) and sulphur (2.3 g., 6 atoms) were heated at *ca.* 250° in a boiling "Dowtherm" bath. The evolution of gas ceased after 90 min. and the melt was then cooled, crushed, and thoroughly extracted with ether. The extract was washed with aqueous sodium hydroxide and distilled, the fraction of b. p. below 220° (bath)/0.1 mm. being converted into the *picrate*, which after three crystallisations from benzene separated as orange needles, m. p. 182° (softening

from 170°) (Found: C, 60.8; H, 3.7; N, 9.0. $C_{18}H_{14}O_6C_6H_3O_7N_3$ requires C, 60.6; H, 3.6; N, 8.8%). Regeneration of the *furanophenanthrene* and crystallisation from ethanol gave pale yellow prisms (0.9 g., 30%), m. p. 145—146° (Found: C, 87.8; H, 5.8. $C_{18}H_{14}O$ requires C, 87.8; H, 5.7%). The *trinitrobenzene* derivative separated from ethanol in elongated light orange plates, m. p. 184—185° (Found: C, 63.3; H, 3.9; N, 9.9. $C_{18}H_{14}O_6C_6H_3O_6N_3$ requires C, 62.8; H, 3.7; N, 9.2%). Vinhatocic acid under similar conditions gave a 26% yield of the *furanophenanthrene* (II). Attempted oxidation of (II) to the quinone with chromic acid led to extensive decomposition.

Selenium Dehydrogenation of Methyl Vinhatocic acid.—Methyl vinhatocic acid (2 g.) and selenium (4 g.) were heated at 340—360° (metal-bath) for 48 hr. When cold, the product was dissolved in ether, and the solution filtered (charcoal) and distilled. Two fractions were collected, (a) b. p. 120—140° (bath)/0.2 mm. and (b) b. p. 160—200° (bath)/0.2 mm., of which (a) (100 mg.) crystallised from ethanol in colourless plates consisting of *2-ethyl-1:8-dimethylphenanthrene* (III; R = H), m. p. 113° (Found: C, 92.6; H, 7.7. $C_{18}H_{18}$ requires C, 92.3; H, 7.7%); this gave a *picrate*, orange-red needles (from ethanol), m. p. 148—149° (Found: C, 61.1; H, 5.1. $C_{18}H_{18}C_6H_3O_7N_3C_2H_5O$ requires C, 61.3; H, 5.3. Found, after drying at 100°: C, 62.1; H, 4.2. $C_{18}H_{18}C_6H_3O_7N_3$ requires 62.2; H, 4.6%), and a *trinitrobenzene* derivative, yellow needles (from ethanol), m. p. 167° (Found: C, 64.2; H, 4.6. $C_{18}H_{18}C_6H_3O_6N_3$ requires C, 64.4; H, 4.7%).

Fraction (b) (1.0 g.) rapidly solidified, and crystallisation from acetic acid and then from light petroleum (b. p. 60—80°) gave *2-ethyl-1:8-dimethyl-3-phenanthrol* (III; R = OH) as colourless very long, thin, felted needles, m. p. 164°, sparingly soluble in cold acetic acid and light petroleum, very soluble in alcohol (Found: C, 86.1; H, 7.3. $C_{18}H_{18}O$ requires C, 86.4; H, 7.25%). The *picrate* proved unstable, but the *trinitrobenzene* derivative formed orange leaflets, m. p. 186—187°, from benzene (Found: C, 61.8; H, 4.2. $C_{18}H_{18}O_6C_6H_3O_6N_3$ requires C, 62.2; H, 4.6%). Although the phenanthrol was insoluble in aqueous alkalis its phenolic nature was shown by the formation, with acetic anhydride-sodium acetate, of an *acetate*, plates (from methanol), m. p. 127—128° (Found: C, 82.3; H, 6.8. $C_{20}H_{20}O_2$ requires C, 82.2; H, 6.9%).

After two successive distillations with zinc dust, the crude distillate contained 40% of the ethyldimethylphenanthrene (III; R = H), the remainder being unchanged phenanthrol. The hydrocarbon was readily isolated by passage, in light petroleum solution, through a column of alumina, the more strongly absorbed phenol being eluted, after removal of the hydrocarbon, with benzene containing 5% of methanol.

Methyl 1:4:11:12-Tetradehydrovinhatocic acid (IV).—Methyl vinhatocic acid (10 g.) and sulphur (2 g., approx. 2 atomic proportions) were heated at 250° ("Dowtherm" bath) until the initially brisk evolution of gas had nearly stopped (ca. 1 hr.). The melt was then allowed to cool slightly but while still fluid was poured into light petroleum (b. p. 60—80°). The solution so obtained was decanted from the residual dark resin, which was afterwards exhaustively extracted with boiling light petroleum. The combined extracts (ca. 500 c.c.) were treated with charcoal, evaporated to ca. 25 c.c., and cooled, whereupon *methyl tetradehydrovinhatocic acid* (2.8 g., 28%) separated. A further 0.3 g. was obtained by distillation of the mother-liquors, finally at 0.1 mm., and crystallisation of the distillate from light petroleum.

The main product had a pale yellow colour not removed by crystallisation, but by passing a solution in equal parts of chloroform and carbon tetrachloride through alumina, and recrystallising the eluate from light petroleum and from *isopropanol*, the ester was obtained as lustrous, colourless rods, m. p. 182—184° (Found: C, 77.0; H, 7.7. $C_{21}H_{28}O_3$ requires C, 77.3; H, 8.0%), $[\alpha]_D^{25} + 59.2^\circ$ (c, 5 in $CHCl_3$). Solutions in alcohol and acetic acid showed a marked blue fluorescence.

Alternatively, the cooled melt was dissolved in an equal volume of ether, and after being left in the refrigerator for some hours the crystalline product was collected from the viscous ethereal suspension, though difficulties in filtration and washing of the solid necessitated further recrystallisation (charcoal) of the product.

The tetradehydro-compound (IV) was obtained (yield ca. 7%) when methyl vinhatocic acid was heated with palladised charcoal at 360—380°, the main product being an undistillable resin.

Ozonolysis of Methyl Vinhatocic acid.—Methyl vinhatocic acid (6.6 g., 0.02 mole), dissolved in dry ethyl acetate (60 c.c.), was ozonised at -10° , the concentration of ozone being estimated iodometrically immediately before the reaction. After treatment with 0.01 mole (equiv. to 0.5 double bond), the solvent was removed under reduced pressure at room temperature, and the gummy residue treated overnight with water and zinc dust. The mixture was heated for 1 hr.

on a steam-bath, then cooled, and water removed by decantation. The residue was shaken with ether, and the filtered solution extracted successively with aqueous sodium hydrogen carbonate and 0.5*N*-sodium hydroxide. Acidification of the sodium hydroxide extract gave a yellow gum which rapidly solidified to a friable solid (1.4—1.85 g.). The crude product crystallised from ethanol (*ca.* 4 c.c.), to give the nearly pure *hydroxymethylene-ketone* (V) (0.6—0.85 g., 9—13%) which on further crystallisation gave colourless prisms, *m. p.* 168—169° (Found: C, 71.8; H, 8.9. $C_{20}H_{30}O_4$ requires C, 71.8; H, 9.0%). The ketone was appreciably soluble in organic solvents and freely soluble in dilute sodium hydroxide; its ferric reaction in ethanol is intense purple.

When acidified, the sodium hydrogen carbonate extract of the ozonolysis product gave a colourless gum setting to a friable solid and consisting of *methyl 6-1'-carboxyethyl-5-carboxymethyldecahydro-1:10-dimethyl-1-naphthoate* (VII; *n* = 1). It separated from ethyl acetate—light petroleum (*b. p.* 60—80°) as colourless shining leaflets which then readily recrystallised from aqueous methanol (yield, 1.05 g., 19.5%; *m. p.* 203—204°) (Found: C, 64.6; H, 8.3. $C_{19}H_{30}O_6$ requires C, 64.4; H, 8.5%). This was the only isolatable product (yield, 45%) when excess of ozone was used. It was easily soluble in organic solvents except light petroleum, and gave with diazomethane the *trimethyl ester*, which crystallised from aqueous methanol in colourless leaflets, *m. p.* 92—93° (Found: C, 66.1; H, 9.15; OMe, 23.4. $C_{21}H_{34}O_6$ requires C, 65.9; H, 9.0; 3OMe, 24.3%).

In one experiment zinc dust was omitted in the decomposition of the ozonide, and the aqueous phase was acidified (H_2SO_4) and distilled. The acid distillate, which reduced ammoniacal silver nitrate, was neutralised with sodium hydroxide and evaporated to dryness. The residue was identified as sodium formate by its conversion (*cf.* Whalley, *J.*, 1948, 1014) into *NN'*-di-*p*-tolylformamidine hydrochloride, *m. p. ca.* 270° (*decomp.*) alone and mixed with an authentic specimen, *m. p.* 270° (Whalley gives *m. p.* 228—230°), further characterised as the free base, *m. p.* and mixed *m. p.* 139—140° with the authentic amidine (Roberts, *J. Amer. Chem. Soc.*, 1950, 72, 3603) (Found: N, 12.3. Calc. for $C_{15}H_{16}N_2$: N, 12.5%). When *n*-hexane was used as solvent solid ozonide was precipitated and it was unnecessary to estimate the rate of ozone production, the ozonide being collected and the filtrate re-treated until no further precipitation took place. The yield of hydroxymethylene-ketone was, however, unchanged. From the neutral fraction of the ozonolysis varying amounts (up to 1.5 g.) of methyl vinylacetoate could be recovered by crystallisation from methanol.

Methyl Perhydro-1:8:12-trimethyl-6-oxophenanthrene-1-carboxylate (VI).—A solution of the once crystallised ketone (V) (1.7 g.) in a slight excess of 0.1*N*-sodium hydroxide was boiled under reflux for 1 hr. An oil separated which solidified, and was collected from the cooled solution. The filtrate was acidified (sulphuric acid) and distilled, and the volatile acid (91%) present in the distillate shown to be formic acid by conversion into *NN'*-di-*p*-tolylformamidine. The solid consisted of the *ketone* (VI) (1.15 g., 74%) and crystallised from a small volume of ethanol in colourless plates, *m. p.* 125—126° (Found: C, 74.7; H, 10.1. $C_{19}H_{30}O_3$ requires C, 74.5; H, 9.9%). The 2:4-dinitrophenylhydrazone formed orange needles, *m. p.* 206°, from acetic acid (Found: C, 62.1; H, 7.3. $C_{25}H_{34}O_4N_4$ requires C, 61.7; H, 7.0%), and the *semi-carbazone* separated from ethanol in colourless prisms (containing ethanol), *m. p.* 245° (Found: C, 64.4; H, 9.65. $C_{20}H_{33}O_3N_3 \cdot C_2H_6O$ requires C, 64.5; H, 9.6. Found, in a specimen dried at 150° in a vacuum: C, 65.7; H, 9.5. $C_{20}H_{33}O_3N_3$ requires C, 66.1; H, 9.2%).

Dehydrogenation of the ketone with sulphur (6 atomic proportions) at 250° for 3 hr. gave a dark brown gum from which was obtained the original ketone (30%) but no other crystalline product was isolated.

Perhydro-1:8:12-trimethylphenanthrene-1-carboxylic Acid (VIII; R = H).—The mono-ketone (VI) (1.1 g.) was dissolved in ethylene glycol (15 c.c.) containing potassium hydroxide (2 g.) and 90% hydrazine hydrate (1.5 c.c.), and the solution boiled under reflux for 1 hr. After concentration to *b. p.* 188° the liquid was refluxed for a further 3 hr., then poured into water (150 c.c.), and the clear solution was acidified. The amorphous precipitate was collected in ether, and the solution dried (Na_2SO_4) and evaporated, the oily residue of the *keto-acid* (VIII; R = H) (850 mg., 85%) rapidly solidifying and crystallising from ethanol in thick tablets, *m. p.* 182° (Found: C, 77.9; H, 10.9. $C_{18}H_{30}O_2$ requires C, 77.7; H, 10.9%). With diazomethane it gave the *methyl ester* (VIII; R = Me), plates (from methanol), *m. p.* 71—72° (Found: C, 78.2; H, 10.9. $C_{19}H_{32}O_2$ requires C, 78.0; H, 11.0%).

1:8-Dimethylphenanthrene.—(i) The once crystallised ketone (VI) (0.6 g.) was heated for 24 hr. at 330—340° (metal-bath) with excess of selenium (1.5 g.). The product was extracted with ether (charcoal), and the solution filtered and distilled. The principal fraction (250 mg.) sublimed at 150—200° (bath)/0.1 mm., and crystallised from acetic acid and benzene, and from

ethanol in which it is only sparingly soluble, as glistening plates, m. p. 192—193° (lit., 191—192°) (Found: C, 93.0; H, 6.5. Calc. for $C_{16}H_{14}$: C, 93.2; H, 6.8%) undepressed by mixture with an authentic specimen kindly supplied by Dr. J. Walker. The picrate had m. p. and mixed m. p. 152—153° (lit., 151—152°), the corresponding phenanthraquinone m. p. and mixed m. p. 189—190° (lit., 190°), and the derived quinoxaline m. p. and mixed m. p. 190° (sintering at 186°) (Haworth *et al.*, *loc. cit.*, record m. p. 178°) (Found: C, 85.5; H, 5.1. Calc. for $C_{22}H_{16}N_2$: C, 85.7; H, 5.2%).

(ii) When the methyl ester (VIII; R = Me) (0.67 g.) was treated as in (i), the crude product was a pale brown crystalline solid (350 mg., 74%) which was purifiable without distillation.

Methyl Perhydro-6-hydroxy-1 : 6 : 8 : 12-tetramethylphenanthrene-1-carboxylate.—The ketone (VI) (1.0 g.) in dry ether (25 c.c.) was added to an ethereal solution of methylmagnesium iodide prepared from 0.7 g. (1.5 mol.) of methyl iodide, and the mixture left overnight at room temperature and finally boiled for 1 hr. It was then treated with ice and dilute hydrochloric acid, and the semi-solid product from the ethereal solution crystallised from light petroleum (b. p. 60—80°). The alcohol thus obtained formed colourless prisms (0.3 g., 29%), m. p. 140—142° (Found: C, 74.8; H, 10.8. $C_{20}H_{34}O_3$ requires C, 74.5; H, 10.6%).

1 : 3 : 8-Trimethylphenanthrene (IX).—The crude semi-solid product from the preceding Grignard reaction was treated with Girard's reagent T in the usual way and the non-ketonic fraction was heated for 1 hr. with boiling excess of acetic anhydride. The product, presumably mixed olefins, was isolated as an oil (0.6 g.) which was heated with excess of selenium (2 g.) at 330° (metal-bath) for 18 hr. The product soluble in benzene was distilled, thus affording an oil (0.4 g.), b. p. ca. 150° (bath)/0.3 mm., which thereafter solidified. Crystallisation from ethanol gave pure *1 : 3 : 8-trimethylphenanthrene* (0.32 g.) as colourless needles, m. p. 116° (Found: C, 92.8; H, 7.2. $C_{17}H_{16}$ requires C, 92.7; H, 7.3%). The picrate crystallised from ethanol in orange needles, m. p. 174—175° (Found: C, 61.1; H, 4.1. $C_{17}H_{16}, C_6H_3O_7N_3$ requires C, 61.5; H, 4.3%); the trinitrobenzene derivative formed lemon-yellow needles (from ethanol), m. p. 188° (Found: C, 64.0; H, 4.4. $C_{17}H_{16}, C_6H_3O_6N_3$ requires C, 63.7; H, 4.4%); the corresponding phenanthraquinone formed orange needles, m. p. 179—180°, from acetic acid (Found: C, 81.6; H, 5.6. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.6%), and the derived quinoxaline formed pale yellow long needles, m. p. 146—147°, from ethanol or acetic acid (Found: C, 85.3; H, 5.6. $C_{23}H_{18}N_2$ requires C, 85.7; H, 5.6%). Mixed m. p.s with the corresponding synthetic compounds showed no depression.

The hydrocarbon (yield, 38%) was also prepared by dehydrogenation of the alcohol without previous dehydration. Examination (by chromatography on alumina) of residues from its crystallisation did not show the presence of any other purifiable hydrocarbon.

Ozonolysis of Methyl Tetradehydrovinhaticoate.—Methyl tetrahydrovinhaticoate (2.6 g.) was ozonised in carbon tetrachloride (80 c.c.) at 0°. As soon as excess of ozone was detected (acidified potassium iodide bubbler) the reaction was stopped, and the solvent removed in a vacuum at room temperature. Water and zinc dust were added to the residue, and after 12 hr. the mixture was heated under reflux for 15 min. Extraction with ether gave a gum which, when crystallised from a small quantity of methanol, consisted of the pure phenolic aldehyde (X) (30—35% yield), colourless prisms, m. p. 132—133° (Found: C, 72.3; H, 7.8. $C_{20}H_{26}O_4$ requires C, 72.7; H, 7.9%). The phenol dissolved in hot aqueous 2N-sodium hydroxide to a yellow solution and was recovered unchanged on acidification; its ferric reaction in alcohol is bright greenish-blue. The sparingly soluble 2 : 4-dinitrophenylhydrazone separated from 2-ethoxyethanol as very small yellow needles, m. p. 290° (decomp.) (Found: C, 61.2; H, 5.3; N, 10.5. $C_{26}H_{28}O_7N_4$ requires C, 61.4; H, 5.5; N, 11.0%).

Ozonolysis of the tetradehydro-compound, previously freed from sulphuretted impurities by boiling in benzene solution with Raney nickel, enabled the ozonide to be decomposed reductively (hydrogen-platinum), but the yield of phenolic aldehyde was unchanged, and no other crystalline compound could be isolated. Decomposition of the ozonide in the absence of zinc and distillation gave formic acid (47%), identified as *NN'*-di-*p*-tolylformamide.

Methylation of the phenol (X) with diazomethane was incomplete after 24 hr. (ferric chloride colour), but treatment for 12 hr. with excess of methyl iodide-potassium carbonate in acetone gave the *O*-methyl ether (72%), isolated by distillation from the filtered solution as a brittle resin, b. p. 205—210° (bath)/0.05 mm. (Found: C, 72.8; H, 8.1; OMe, 17.4. $C_{21}H_{28}O_4$ requires C, 73.2; H, 8.2; OMe, 18.0%). The oxime also was non-crystalline but the very sparingly soluble 2 : 4-dinitrophenylhydrazone separated from ethanol as orange needles, m. p. 275° (decomp.) (Found: C, 62.0; H, 6.2; OMe, 11.1. $C_{27}H_{30}O_7N_4$ requires C, 62.1; H, 5.8; OMe, 11.8%).

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydro-6-hydroxy-1 : 7 : 8 : 12-tetramethylphenanthrene-1-carboxylic Acid (XI).—The phenol (X) (1.4 g.) was reduced in the manner described for the reduction of the ketone (VI). The crude oily phenolic acid (XI) (1.2 g.) so obtained crystallised from aqueous methanol as the monohydrate in colourless tablets, m. p. 120° (effervescence) (Found : C, 70.7; H, 9.1. $C_{19}H_{26}O_3 \cdot H_2O$ requires C, 71.2; H, 8.8%). When crystallised from dry benzene it separated in tablets which frothed at ca. 110°, resolidified, and finally had m. p. 198° (Found : C, 75.8; H, 8.6. $C_{19}H_{26}O_3$ requires C, 75.5; H, 8.7%). The *acetate*, prepared with acetic anhydride-sodium acetate, separated from benzene-light petroleum or methanol as needles, m. p. 208—209° (Found, after drying at 150° : C, 72.8; H, 8.35. $C_{21}H_{28}O_4$ requires C, 73.2; H, 8.2%).

3-Hydroxy-1 : 2 : 8-trimethylphenanthrene (XII; R = OH).—The phenolic acid (XI) (1 g.) was heated at 310—340° (metal-bath) with excess of selenium (2 g.) for 24 hr. The product extracted with chloroform was distilled giving two fractions, (a) b. p. 120—140° (bath)/0.5 mm. (50 mg.) and (b) b. p. 180—220° (bath)/0.5 mm. (550 mg.). Fraction (b) crystallised from chloroform in colourless prisms or plates of the *phenanthrol* (XII; R = OH), m. p. 203° (Found : C, 86.4; H, 6.9. $C_{17}H_{16}O$ requires C, 86.4; H, 6.8%), very sparingly soluble in aqueous alkali. Methylation with methyl iodide-potassium carbonate in acetone gave the methoxyphenanthrene (m. p. and mixed m. p.) (below) prepared by dehydrogenation of the *O*-methyl ether of the aldehydo-phenol (X).

1 : 2 : 8-Trimethylphenanthrene (XII; R = H).—(i) Crystallisation of fraction (a) obtained in the preceding experiment from ethanol yielded plates, m. p. 140—141° raised to 142—143° by admixture with an authentic specimen of 1 : 2 : 8-trimethylphenanthrene of m. p. 143—144°, kindly supplied by Professor R. D. Haworth; the picrate had m. p. 162—163° (lit., 162—163°). Analyses of the small quantity of hydrocarbon available were unsatisfactory; the yield was not increased by variation in the dehydrogenation conditions.

(ii) The phenanthrol (XII; R = OH) (0.4 g.) was distilled with zinc dust, and the yellow distillate extracted with light petroleum and purified by passage of the solution through an alumina column. The hydrocarbon (150 mg.) so obtained had m. p. 136° after several recrystallisations, eventually raised abruptly to 182°, obviously owing to the content of 1 : 8-dimethylphenanthrene. Purification through the picrate, m. p. 162—163°, again yielded the phenanthrene of maximum m. p. 138° (trinitrobenzene derivative, m. p. 187°; lit., 192°), undepressed by authentic 1 : 2 : 8-trimethylphenanthrene. The *X*-ray powder photographs of the hydrocarbon and of an authentic specimen were indistinguishable.

(iii) The lactone (XIV) (1 g.) was dehydrogenated with selenium at 310—330° for 24 hr. and the product worked up by distillation. The fraction of b. p. 120—140° (bath)/0.5 mm. (0.5 g.) readily crystallised from methanol, to give 1 : 2 : 8-trimethylphenanthrene as glistening plates, m. p. and mixed m. p. 144—145° (Found : C, 92.9; H, 7.4. Calc. for $C_{17}H_{16}$: C, 92.7; H, 7.3%). The picrate, orange needles from ethanol, had m. p. 164—165°, and the trinitrobenzene derivative, m. p. 191—192° (Found : C, 63.9; H, 4.3. Calc. for $C_{17}H_{16} \cdot C_6H_3O_6N_3$: C, 63.7; H, 4.4%).

Oxidation of the Lactone (XIV).—(i) When ozone was passed into a solution of the lactone (XIV) (2 g.) in ethyl acetate (60 c.c.) a solid was precipitated, and, after evaporation of the solvent at room temperature, the total residue was treated with water and zinc dust. The product soluble in ether gave (a) with sodium hydrogen carbonate a solid sodium salt (50 mg.) of a non-crystalline acid, and (b) neutral material isolated by evaporation of the ether and resolved by crystallisation from methanol into a *substance* separating in colourless needles (110 mg.), m. p. 171° (Found : C, 70.0; H, 7.8. $C_{21}H_{28}O_5$ requires C, 70.0; H, 7.8%), and a pale yellow oily *ketone* (110 mg.), b. p. 150° (bath)/0.1 mm., isolated from the filtrate by Girard's reagent T (Found : C, 73.1; H, 9.2%), and giving a 2 : 4-dinitrophenylhydrazone as orange leaflets from acetic acid, m. p. 237—238° (Found : C, 61.2; H, 6.15; N, 11.8%).

(ii) The lactone (3.5 g.) was refluxed in acetone with potassium permanganate (8.5 g.) and when oxidation was complete the solution was cooled and filtered. The only appreciable product was an oily non-ketonic acid (2.6 g.) obtained by extracting the precipitate with water and acidifying the solution. The *S*-benzylthiuronium and benzylammonium salts and the *p*-bromophenacyl ester failed to crystallise. Distillation from acetic anhydride gave the acid *anhydride*, b. p. 130—140° (bath)/0.05 mm., slowly soluble in aqueous alkali (Found : C, 67.6; H, 8.0. $C_{18}H_{26}O_5$ requires C, 67.1; H, 8.1%).

Perhydro-1-hydroxymethyl-1 : 8 : 12-trimethylphenanthrene.—The acid (VIII; R = H) (0.85 g.), dissolved in dry ether (15 c.c.), was added slowly to an ethereal solution of lithium aluminium hydride (ca. 0.5 g.), and the solution boiled for 2 hr. The excess of hydride was decomposed

with ethyl acetate, and the solution worked up by addition of cold dilute hydrochloric acid. The ethereal layer was washed with alkali, dried, and distilled to give *perhydro-1-hydroxy-methyl-1 : 8 : 12-trimethylphenanthrene* as a colourless resin (0.77 g.), b. p. 130° (bath)/0.1 mm. (Found: C, 81.9; H, 11.8. $C_{18}H_{32}O$ requires C, 81.8; H, 12.1%), which formed an α -*naphthylurethane* separating from methanol in woolly needles, m. p. 147—148° (Found: C, 80.1; H, 9.2. $C_{29}H_{38}O_2N$ requires C, 80.3; H, 9.1%).

1-Ethyl-8-methylphenanthrene (XV).—The alcohol (750 mg.) derived from (VIII; R = H) was treated in ether (50 c.c.) with phosphorus pentachloride (600 mg., 1 mol.), and after being set aside overnight the mixture was refluxed for 2 hr. Ice-water was then added and the ethereal layer washed with sodium carbonate solution and distilled. The product was a fuming oil, b. p. 110—150° (bath)/0.1 mm., still containing chlorine, and it was therefore boiled with quinoline (5 c.c.) for 10 min., the olefinic *hydrocarbon* being isolated after washing with hydrochloric acid as an oil (400 mg.) which when redistilled from sodium had b. p. 120—125° (bath)/0.1 mm. (Found: C, 87.7; H, 11.9. $C_{18}H_{30}$ requires C, 87.7; H, 12.3%).

The olefin (360 mg.) was heated with selenium (1 g.) at 330—350° for 24 hr., and the product isolated by ether-extraction and distillation. The fraction of b. p. 120° (bath)/0.1 mm. rapidly solidified, and crystallisation from ethanol or methanol gave the *1-ethyl-8-methylphenanthrene* (240 g.) as shining plates, m. p. 106—107° (Found: C, 92.2; H, 7.2. $C_{17}H_{16}$ requires C, 92.7; H, 7.3%). The *picrate* formed orange needles, m. p. 124—125°, from ethanol (Found: C, 61.7; H, 4.6. $C_{17}H_{16}, C_6H_3O_7N_3$ requires C, 61.5; H, 4.3%), and the *trinitrobenzene* derivative crystallised from ethanol in slender yellow needles, m. p. 146—147° (Found: C, 63.6; H, 4.2. $C_{17}H_{16}, C_6H_3O_6N_3$ requires C, 63.7; H, 4.4%), m. p.s being unaffected by authentic specimens.

Reaction of Methyl Vinhaticoate with Phenylmagnesium Bromide.—Methyl vinhaticoate (I; R = Me) (3.3 g.) in dry ether was added to a solution of phenylmagnesium bromide (from 3.5 g. of bromobenzene) in ether, and the mixture refluxed for 2 hr. After removal of the ether and further heating on a steam-bath (2 hr.) the product was cooled and treated with ice-cold dilute sulphuric acid. Steam-distillation removed traces of volatile material and the residue consisted of a pale yellow gum which when triturated with methanol fell to an amorphous powder. This slowly crystallised from a small volume (5 c.c.) of acetic acid in very large trigonal tablets (1.8 g., 40%) which when crystallised from ethanol gave the pure *alcohol*, m. p. 145—147° (Found: C, 84.9; H, 8.7. $C_{32}H_{38}O_2$ requires C, 84.5; H, 8.4%).

Dehydrogenation of Dihydronorisoagathic Acid (XVIII).—Dihydronorisoagathic acid (XVIII) has been obtained crystalline from acetic acid (and no other common solvent); it forms laths, m. p. 166° (slow heating) (Found: C, 72.2; H, 10.4. $C_{19}H_{32}O_2, C_9H_4O_2$ requires C, 71.6; H, 10.3. Found, on specimen dried at 100° in vacuum: C, 78.3; H, 10.7. $C_{19}H_{32}O_2$ requires C, 78.6; H, 10.4%). The acid (1 g.) was heated with selenium at 330—350° for 36 hr. The product (600 mg.) after distillation and one crystallisation from methanol had m. p. 85°, undepressed by an authentic specimen of pimanthrene, and gave a *picrate*, m. p. 131—132° (lit., 132°). No 1 : 2 : 8-trimethylphenanthrene could be detected in the crude reaction mixture.

Methyl O-Acetylpodocarpate.—Methyl podocarpate (5.5 g.) was heated for 4 hr. in acetone (50 c.c.) containing bromoacetone (2.9 g., 1.1 mols.) and excess of potassium carbonate. The cooled mixture was filtered and the filtrate evaporated to an oil which crystallised slowly from methanol (5 c.c.), giving the *acetyl* derivative as rhombs (2.75 g., 42%), m. p. 75—76° (Found: C, 73.2; H, 8.1. $C_{21}H_{28}O_4$ requires C, 73.2; H, 8.2%). The action of sulphuric acid, sulphuric-acetic acid, and zinc chloride under various conditions failed to give the corresponding 2-methylfuran.

Reduction of Methyl Tetrahydrovinhaticoate (IV).—The tetrahydro-compound (IV) (3.5 g.), from which traces of sulphur had been removed by refluxing in benzene solution with Raney nickel, was hydrogenated at ordinary temperature and pressure in acetic solution in the presence of Adams platinum catalyst (absorption after 36 hr., 230 c.c.; theor., 240 c.c.). The solution, now no longer fluorescent, was filtered and evaporated, and the residue crystallised first from light petroleum and then from ethanol, from which the *dihydro*-compound (2.55 g.) separated as glistening rods, m. p. 137° (Found: C, 76.7; H, 8.35. $C_{21}H_{28}O_3$ requires C, 76.8; H, 8.6%); $[\alpha]_D^{20} + 52.1^\circ$ (c, 10 in $CHCl_3$). Attempts to open the hydrofuran ring in this compound with solutions of hydriodic acid or of potassium iodide in 95% phosphoric acid (cf. *Org. Synth.*, 1950, 30, 33) followed by zinc-hydrochloric acid reduction gave unpurifiable products.

7-Acetyl-6-methoxy-1-methylphenanthrene (XX; R = COMe).—Methyl 7-acetyl-O-methylpodocarpate (Campbell and Todd, *loc. cit.*) (2 g.), from methyl O-methylpodocarpate kindly supplied by Dr. W. F. Short, was dehydrogenated with sulphur (0.77 g., 4 atomic equivs.) in a boiling "Dowtherm" bath for 4 hr. The product extracted with ether was distilled,

the fraction, b. p. 240—280° (bath)/0.2 mm., crystallising from ethanol in yellow needles, m. p. 138—140°. Further crystallisation from ether, redistillation, and crystallisation from ethanol gave almost colourless needles of the *acetylphenanthrene* (260 mg.), m. p. 144—145° (Found: C, 81.9; H, 6.1. $C_{18}H_{16}O_2$ requires C, 81.8; H, 6.1%). The *picrate* separated from ethanol in orange leaflets, m. p. 144—145° (Found: C, 58.4; H, 3.9. $C_{18}H_{16}O_2, C_6H_3O_7N_3$ requires C, 58.4; H, 3.9%). The 2:4-*dinitrophenylhydrazone* was an orange powder, m. p. 239° (decomp.) (Found: C, 64.9; H, 4.9. $C_{24}H_{20}O_5N_4$ requires C, 64.9; H, 4.5%). Chromatographic treatment of the crystallisation residues gave but very small quantities of other products which were not identified.

7-*Ethyl-6-methoxy-1-methylphenanthrene* (XX; R = Et).—The ketone (XX; R = COMe) (150 mg.) was heated under reflux for 1 hr. in ethylene glycol (5 c.c.) containing potassium hydroxide (0.5 g.) and hydrazine hydrate (0.5 c.c. of 90%). The solution was then concentrated to b. p. 190° and again refluxed for a further 3 hr. The product was poured into water (50 c.c.), and the material extracted with ether was crystallised from ethanol, thus giving 7-*ethyl-6-methoxy-1-methylphenanthrene* (100 mg.) in colourless rods, m. p. 83—84° (Found: C, 86.1; H, 6.9. $C_{18}H_{18}O$ requires C, 86.4; H, 7.2%) [*picrate*, light orange needles (from ethanol), m. p. 168—169° (Found: C, 60.2; H, 4.6. $C_{18}H_{18}O, C_6H_3O_7N_3$ requires C, 60.1; H, 4.4%)].

3-*Methoxy-1:2:8-trimethylphenanthrene* (XII; R = OMe).—The methyl ether of the phenol (X) (1.0 g.) was heated with the calculated amount of sulphur (0.38 g.) (boiling "Dowtherm" bath) for 3 hr. Distillation of the product gave an oil which was purified as the *picrate*, unstable in alcoholic solvents but separating from benzene in solvated red leaflets, m. p. 168—172° (Found: C, 63.9; H, 5.0. $C_{18}H_{18}O, C_6H_3O_7N_3, C_6H_6$ requires C, 64.6; H, 4.9%). Decomposition of the *picrate* and crystallisation of the product from ethanol gave the 3-*methoxy-1:2:8-trimethylphenanthrene* in colourless needles (100 mg.), m. p. 122—123° (Found: C, 86.1; H, 7.2. $C_{18}H_{18}O$ requires C, 86.4; H, 7.2%). No appreciable amount of other crystalline compound could be isolated.

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