*The Chemistry of Extractives from Hardwoods. Part XXII.** *The Structure of Diterpenes from* Vouacapoua *Species.*

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The diterpene ester, methyl vouacapenate, found by Spoelstra (*Rec. Trav. chim.*, 1930, **49**, 226) in *Vouacapoua americana*, has again been isolated from this source and also from the wood of *V. macropetala* where it occurs with the acetate of vouacapenol, the related carbinol.

Vouacapenic acid contains a furan ring, and its selenium-dehydrogenation products are phenanthrene derivatives previously derived from the dodecahydrophenanthrenofuran, vinhaticoic acid (I*A*; $R = CO_2H$) (King, King, and Neill, *J.*, 1953, 1055; King and King, *ibid.*, p. 4158). Its detailed constitution was ascertained by reduction of the methyl ester $C_{19}H_{27}O{\cdot}CO_2Me$, through vouacapenol and the related aldehyde, to a furano-hydrocarbon $C_{19}H_{27}O{\cdot}Me$, which proved to be identical with the product analogously obtained from methyl vinhaticoate. The two diterpenes are therefore $C_{(1)}$-epimers, the relative optical rotations and hydrolysis rates of their esters indicating that in vouacapenic acid the 1-carboxyl and the 12-methyl group have the *cis*-configuration.

THE genus *Vouacapoua* comprises trees of three species found in tropical South America. From the heartwood of *V. americana*, Spoelstra (*Rec. Trav. chim.*, 1930, **49**, 226) isolated a crystalline compound $C_{21}H_{30}O_3$ consisting of the methyl ester of a new diterpene vouacapenic acid. The ester group was found to be difficultly hydrolysable and is presumably a tertiary substituent; the non-carboxylic oxygen atom proved unreactive and was therefore assumed to be etheric. The presence of two double bonds was also demonstrated, but the principal constitutional features of the molecule remained obscure.

Recently a similar natural product, isomeric with methyl vouacapenate, was discovered in the wood of *Plathymenia reticulata* (King, King, and Neill, *J.*, 1953, 1055). It was shown that this new compound, methyl vinhaticoate, likewise contained two unsaturated bonds and an inert oxygen atom, features which were recognised as the constituents of a furan ring; and, as a result of a more detailed investigation (King and King, *ibid.*, p. 4158), vinhaticoic acid was identified as the dodecahydrophenanthrofuran (I*A*; $R = CO_2H$). The evident similarity of the two diterpenes has therefore led us to renew the study of methyl vouacapenate which has been isolated in these laboratories not only from *V. americana* but also from a second species hitherto unexamined chemically, *viz.*, *V. macropetala*. We record our appreciation of the generous assistance given by the Conservator of Forests, British Guiana, in securing quantities of these two timbers.

Methyl vouacapenate, comprising 3—3½% of the wood, was isolated by Spoelstra from the syrupy benzene extract of *V. americana*. In the present investigation it was first obtained from *V. macropetala*, boiling light petroleum yielding an oil (6·2%) from which

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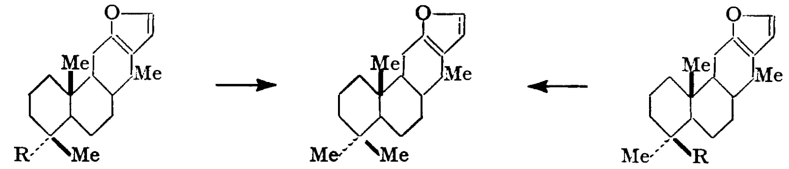
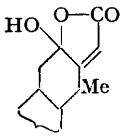
* Part XXI, *J.*, 1955, 658.

the ester was derived by crystallisation, but the method was wasteful, and in order to recover the remainder the oily residue was distilled. After removal of a portion (0·9%) believed to consist of sesquiterpenes, two fractions were collected, the first being principally methyl vouacapenate, m. p. 103—104°, and the second, of slightly higher boiling point, a new compound, $C_{22}H_{32}O_3$, m. p. 114—115°. Mild alkali hydrolysis of the latter yielded a neutral product, $C_{20}H_{30}O_2$, m. p. 131—132°. The diminished molecular formula corresponded to the loss of an acetyl group, and the compound $C_{22}H_{32}O_3$ was in fact regenerated by acetylating the hydrolysis product of m. p. 131—132°, thereby signifying the alcoholic character of the latter. Owing to the similarity of their boiling points it was more convenient to separate the two crystalline constituents by submitting the combined distillate to vigorous hydrolysis with alkali, the solubility of the resulting vouacapenic acid in the reagent then enabling it to be completely removed from the accompanying alcohol. From the weights of the products thus obtained it was shown that 2·5% of methyl vouacapenate and 1·6% of the acetate $C_{22}H_{32}O_3$ were present in the wood sample.

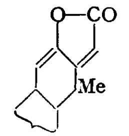
A consideration of the molecular formula of vouacapenic acid ($C_{20}H_{28}O_3$) and of the alcohol, m. p. 131—132° ($C_{20}H_{30}O_2$), suggested the possibility of a carboxylic acid–primary alcohol relationship. This was confirmed when reduction of the methyl ester with lithium aluminium hydride afforded a product identical in respect of melting point, specific rotation, etc., with the natural alcohol, which was accordingly termed vouacapenol. Later, by treatment with light petroleum, methyl vouacapenate was extracted (by Mr. L. C. Manning) from the heartwood of *V. americana* in which it had previously been found by Spoelstra. The presence of cadinene and of free vouacapenic acid has also been demonstrated, but, on the other hand, no trace of vouacapenyl acetate was encountered in this species, nor was any crystalline compound, other than vouacapenic acid, obtained by alkali hydrolysis of the distilled extract.



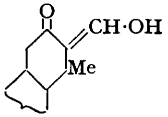
(I*A*) Vinhaticoic acid (R = CO_2H) (IX) (I*B*) Vouacapenic acid (R = CO_2H)



(II, *A* or *B*) *



(III, *A* or *B*) *



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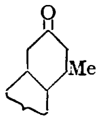

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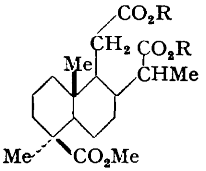
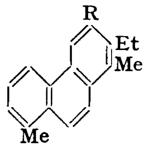


(VI)



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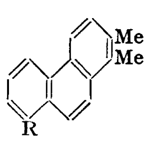
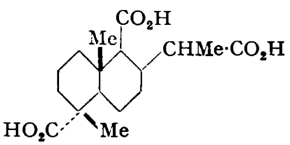


(VIII)



(X)

* Structures II*A* and III*A* are derived from I*A*, and II*B* and III*B* from I*B*. In the present paper the relative configurations at positions 1 and 12 are denoted by heavy and broken bonds with the 12-methyl group arbitrarily placed in front of the plane of the ring (heavy bond) as in the steroid and triterpene convention; ordinary bonds or absence of bonds denote positions of unknown configuration. In Part XV (*loc. cit.*) the formula for vinhaticoic acid (I*A*) was written on the convention that a 1-carboxyl group written to the left in a formula was *trans* relative to the 12-methyl group and that one written to the right was *cis* (cf. Barton, *Quart. Rev.*, 1949, **3**, 36); unfortunately the formula for vinhatoic acid was reversed in this respect in *Annual Reports*, 1953, **50**, 210.

The absorption spectrum of methyl vouacapenate exhibits a maximum at 222 mμ (log ε 3·72), a value virtually coincident with that of methyl vinhaticoate (220 mμ; log ε 3·88). Both esters are somewhat sensitive to acid reagents and it seemed highly probable therefore that methyl vouacapenate also contained a furanoid system. The extent of their resemblance was further apparent from perphthalic acid oxidation experiments which, as already recorded (King and King, *loc. cit.*), with methyl vinhaticoate gave a derivative (II*A*; R = CO_2Me). The spectrum of this compound which in ethanol has no marked absorption >230 mμ, in 0·2N-ethanolic sodium hydroxide was characterised by $\lambda_{max.}$ at 296 mμ (log ε 3·90); the corresponding oxidation product of methyl vouacapenate has $\lambda_{max.}$ at 294 mμ (log ε 3·73). When heated above their melting points, both compounds form anhydro-derivatives, the product (III*A*; R = CO_2Me) from methyl vinhaticoate having $\lambda_{max.}$ 278 mμ (log ε 4·27), which compares very closely with that of the anhydride from methyl vouacapenate, *i.e.*, $\lambda_{max.}$ 274 mμ (log ε 4·5).

Information as to the nature of the furan ring in methyl vinhaticoate (I; R = CO_2Me) was obtained by ozonolysis of the compound which led first to a β-formyl ketone (IV; R = CO_2Me) and then by further loss of carbon monoxide as formic acid to the ketone (V; R = CO_2Me). Qualitatively similar results were observed with methyl vouacapenate but neither product was obtained crystalline. However, as in the case of methyl vinhaticoate (I*A*; R = CO_2Me), a crystalline acid by-product was isolated, isomeric with the corresponding derivative of (I*A*; R = CO_2Me) to which the structure (VI; R = H) has been attributed.

In order to afford further comparison of the two diterpenes, methyl vouacapenate was subjected to dehydrogenation with selenium. Spoelstra (*loc. cit.*) has observed the formation of two dehydrogenation products without, however, recording details of physical constants or other properties. The two compounds produced in our experiments have been identified as the phenanthrenes (VII; R = H and OH) which are already known from their derivation in a similar manner from methyl vinhaticoate. Furthermore, 1 : 2 : 8-trimethylphenanthrene (VIII; R = Me), which was previously obtained from the unsaturated lactone (III*A*; R = CO_2Me), was likewise formed when the analogous derivative of methyl vouacapenate was aromatised with selenium. It follows therefore that the skeletal structures of the diterpenes are identical and that the two compounds differ merely in the distribution of certain substituents, either in a stereochemical sense or in regard to the relative situation of the 1-methoxycarbonyl * and the quaternary 12-methyl group eliminated during aromatisation, which might occupy inverse positions in methyl vouacapenate. The position of the methoxycarbonyl group was accordingly investigated by the usual method of reduction to the carbinol followed by dehydration, whereupon if the substituent occupies the normal position a molecular rearrangement occurs which leads to the appearance of an ethyl group at position 1 in the subsequent dehydrogenation product (see Part XV, *J.*, 1953, p. 4162, for references). Since dehydration requires the employment of acidic reagents, the furan ring had first to be suitably modified, and this was done by peracid oxidation to a lactone of the type previously described, using vouacapenyl alcohol as starting material. The related anhydro-compound, actually (III*B*; R = $CH_2 \cdot OH$), was then pyrolysed with potassium hydrogen sulphate and the oily product dehydrogenated with selenium. This resulted in the formation of 8-ethyl-1 : 2-dimethylphenanthrene (VIII; R = Et), thus locating the original ester group at position 1 and indicating the purely stereochemical nature of the relation between the two diterpenes. The orientation of the new phenanthrene was deduced by performing a similar sequence of reactions on vinhaticol, the lithium aluminium reduction product of methyl vinhaticoate (I*A*; R = CO_2Me), whereupon the identical hydrocarbon was produced.

Since stereochemical differences among the principal resin acids are generally connected with the relative disposition of their 1-substituents the further examination of methyl vouacapenate (I*B*; R = CO_2Me) was primarily concerned with the configuration of the molecule at this point. Evidence has already been presented (King and King, *loc. cit.*) to show that in the reactions of its methoxycarbonyl group with phenylmagnesium bromide

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* In this paper the enumeration, common in diterpenes, is that of phenanthrene starting from the *gem*-disubstituted position.

methyl vinhaticoate closely resembles methyl abietate and is appreciably more reactive than methyl podocarpate. A comparison (see Table) of the rates of hydrolysis of these esters and of methyl vouacapenate demonstrates the striking similarity on the one hand of methyl vouacapenate and methyl podocarpate, in which latter the methoxycarbonyl and methyl groups are known to be in *cis*-relation, and of methyl vinhaticoate and the abietic ester in which the respective groups are in the *trans*-configuration. From these data it seemed highly probable that the two phenanthrofurans were epimeric, differing solely in the relative positions of their respective 1-methyl and 1-methoxycarbonyl groups. Consequently, by eliminating the asymmetric centre at position 1 it should be possible to convert both diterpenes into a common derivative, and attempts were accordingly made to test this hypothesis by reactions suitable for the conversion of the methoxycarbonyl group into methyl.

Ester hydrolysis in 0·5N-*ethanolic potassium hydroxide.*

	Time (hr.)	Ester no.		Time (hr.)	Ester no.
Methyl podocarpate	2	0 *	Methyl abietate	2¼	73
Methyl vouacapenate ...	4½	2·2 †	Methyl vinhaticoate	2¼	109

* Campbell and Todd, *J. Amer. Chem. Soc.*, 1942, **64**, 928. † Spoelstra, *loc. cit.*

The reduction of methyl vinhaticoate to the required furano-hydrocarbon (IX) was effected by means of lithium aluminium hydride in two stages, the first leading to the related alcohol (I*A*; R = CH_2·OH), vinhaticol. The concluding phase, *viz.*, hydrogenolysis of the alcohol toluene-*p*-sulphonate, gave a limited yield (30%) of the desired product (IX) which, however, was not obtained entirely pure (m. p. 74—76°). The more sterically hindered toluene-*p*-sulphonyloxy-group in vouacapenyl toluene-*p*-sulphonate either failed to undergo reaction or, when forcing conditions were applied, regenerated the parent alcohol. The action of lithium aluminium hydride on the methanesulphonyl esters of both vinhaticol and vouacapenol resulted in a nearly quantitative recovery of both alcohols.

The investigation then turned to an alternative route involving aldehydes as intermediates. Catalytic hydrogenation of crude vouacapenoyl chloride, although producing hydrogen chloride (70%), was totally unsuccessful in producing the aldehyde. The acid chloride was converted into the dimethylamide (I*B*; R = CO·NMe_2) and this in turn was treated with lithium aluminium hydride, which might have yielded the required material (I*B*; R = CHO) as in the reduction of phthalobisdimethylamide to phthalaldehyde (Weygand and Teitjen, *Ber.*, 1951, **84**, 625), but only vouacapenol and an unrecognised nitrogenous substance were obtained. The desired aldehyde was first derived from vouacapenol by the Oppenauer procedure, using *p*-benzoquinone–aluminium *tert.*-butoxide, but the amount formed in this way (10%) was unsatisfactory. It was afterwards more readily prepared by oxidising the alcohol with chromic oxide in pyridine (Poos, Arth, Beyler, and Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 422) at room temperature. The crystalline product (I*B*; R = CHO), characterised by an oxime, was reduced by the modified Wolff–Kishner reaction to the furano-hydrocarbon (IX) (65%), m. p. 79°, $[\alpha]_D$ +83°. Oxidation of the isomeric alcohol (I*A*; R = CH_2·OH) similarly gave a crystalline aldehyde, vinhatical, and following the procedure used for vouacapenal, it also yielded the hydrocarbon (IX) (70%), m. p. 79°, $[\alpha]_D$ +84°. The epimeric relation of the two esters is thus finally confirmed, and in view of the hydrolysis data presented in the Table, the relative configurations of vinhaticoic and vouacapenic acids at $C_{(1)}$ may be regarded as analogous respectively to those of abietic acid and podocarpic acid. This conclusion gains further support from molecular rotational data (cf. Fieser and Fieser, "Natural Products related to Phenanthrene," Reinhold Publ. Corp., New York, 1949, p. 74), the arithmetical difference between the values of $[M]_D$ for methyl vinhaticoate (+221°) and methyl vouacapenate (+334°), *viz.*, +113°, agreeing very closely with that for methyl 6-methoxydehydroabietate (+243°) and its 1-epimer derived from podocarpic acid (+346°), namely, +103° (Fieser and Fieser, *loc. cit.*). The stereochemistry of the A–C ring junction has not been established, although the foregoing analogies with the abietic–podocarpic acid series suggest that it has the usual *trans*-structure. An attempt was made to determine the configuration by oxidation of the appropriate compound to the dimethyl*cyclo*hexanetricarboxylic acid obtained from abietic acid (cf. Barton and Schmeidler, *J.*, **1948**, 1197), but the action of nitric acid on methyl vinhaticoate failed to effect the desired degradation. The product, a tricarboxylic acid, $C_{17}H_{26}O_{61}$, from which a trimethyl ester was prepared, probably has the constitution (X).

EXPERIMENTAL

Light petroleum used had b. p. 60—80°. Except where otherwise indicated, dried analytical specimens were heated to constant weight at 110° *in vacuo*, and carbon tetrachloride solutions were used for the determination of optical rotations.

Extraction of Vouacapoua macropetala *with Light Petroleum.*—(i) The finely shredded heartwood (2800 g.) was extracted with boiling light petroleum (b. p. 60—80°) for 48 hr., evaporation of the solution leaving a clear brown syrup (174 g., 6·2%). Its solution in light petroleum (400 c.c.) deposited a nearly colourless solid from which methyl vouacapenate (32·5 g.) was obtained by crystallisation from methanol and acetone–methanol as prisms, m. p. 103—104°, $[\alpha]_D$ +101° (*c*, 1·5); light absorption in EtOH, max. at 222 mμ (log ε 3·67) (Found, in a specimen dried at 80° *in vacuo*: C, 76·1; H, 9·1. Calc. for $C_{21}H_{30}O_3$: C, 76·3; H, 9·1%); Spoelstra (*loc. cit.*) has recorded m. p. 105° (corr.), $[\alpha]_D$ +101° (*c*, 3·5). A solution of the ester in acetic anhydride and chloroform became deep crimson on the addition of concentrated sulphuric acid. A mixture of methyl vouacapenate and maleic anhydride in benzene failed to give a crystalline adduct.

Distillation of the residual light petroleum extract (140 g.) afforded two principal fractions, (*a*) b. p. 184—188°/0·2 mm. (31 g.), and (*b*) b. p. 193—197°/0·2 mm. (24 g.), the former when crystallised from methanol yielding methyl vouacapenate (8 g.). Similarly (*b*) gave vouacapenyl acetate (9 g.) (see below), m. p. 114—115°.

(ii) A solution of the light petroleum extract (174 g.) in a minimum of methanol yielded methyl vouacapenate (16·5 g., 0·7%) of m. p. 103—104°. The remainder was distilled and, after removal of the portion of b. p. 130—180°/15 mm. (23·3 g.), the bulk of the residue had b. p. 160—190°/0·1 mm. (118·3 g.). The latter was mixed with a solution of potassium hydroxide (40 g.) in ethylene glycol (70 c.c.), and after expulsion of water at 170—195° the mixture was heated under reflux for 1½ hr. Admixture with water (600 c.c.) precipitated vouacapenol which after thorough washing with boiling water and crystallisation from aqueous methanol had m. p. 130—131° (yield 38·5 g., 1·4%). The solid obtained on acidification of the filtrate and crystallisation from ethanol consisted of vouacapenic acid (51·5 g., 1·8%), m. p. 226—229° (sintering at 214°). The pure acid formed colourless prisms, m. p. 227—230° (sintering at 216°), $[\alpha]_D$ +108° (*c*, 2·5) (Found, in a specimen dried at 130° *in vacuo*: C, 75·9; H, 8·8%; equiv., 327. Calc. for $C_{20}H_{28}O_3$: C, 75·9; H, 8·9%; equiv., 316); Spoelstra recorded m. p. 226—229° (sintering at 215°), $[\alpha]_D$ +107—108° (*c*, 3·5). Vouacapenic acid forms a sodium salt crystallising from water in long silky needles, m. p. >340°.

Vouacapenol (*IB*; R = $CH_2{\cdot}OH$).—(i) *Vouacapenyl acetate*, isolated as above by distillation, formed colourless plates (from methanol), m. p. 115°, $[\alpha]_D$ +63°; light absorption in EtOH: max. at 220 mμ (log ε 4·33) [Found, in a dried specimen: C, 76·8; H, 9·3%; *M* (Rast), 325. $C_{22}H_{32}O_3$ requires C, 76·7; H, 9·4%; *M*, 344·5]. The acetate was heated under reflux with 10% alcoholic potassium hydroxide for 1 hr., and the solvent evaporated after the addition of water. The product consisted of *vouacapenol* and crystallised from methanol in prisms, m. p. 130—131°, $[\alpha]_D$ +71° (*c*, 1·8); light absorption in EtOH, max. at 222 mμ (log ε 3·67) (Found, in a dried specimen: C, 79·0; H, 9·9. $C_{20}H_{30}O_2$ requires C, 79·4; H, 10·0%). Acetylation regenerated the acetyl compound, m. p. and mixed m. p. 116°. *Vouacapenyl benzoate*, prepared with benzoyl chloride–pyridine and isolated crystalline by washing with dilute hydrochloric acid, sodium carbonate, and water, separated from ethanol in plates, m. p. 143—145°, after becoming yellow at 110° (Found, in a dried specimen: C, 79·6; H, 8·3. $C_{27}H_{34}O_3$ requires C, 79·8; H, 8·4%).

(ii) Methyl vouacapenate (5 g.), dissolved in ether (100 c.c.), was slowly added to an ethereal solution (50 c.c.) of lithium aluminium hydride (0·4 g.) and, after the initial reaction had subsided, the mixture was refluxed for 45 min. Dilute hydrochloric acid was cautiously added and the product isolated from the ether layer was crystallised from aqueous methanol. Vouacapenol (4 g., 80%) was thus obtained as needles, m. p. alone or mixed with the compound isolated from *V. macropetala*, 131—132°, $[\alpha]_D$ +71° (*c*, 0·8); its acetate had m. p. and mixed m. p. 116°.

Vouacapenol (5·8 g.), toluene-*p*-sulphonyl chloride (5 g.), and dry pyridine (10 c.c.) were heated on a steam-bath for 1 hr. and *vouacapenyl toluene-*p*-sulphonate* isolated by cooling and the addition of methanol (10 c.c.). Crystallisation from acetone–methanol gave prisms (6·7 g., 65%), m. p. 151° (Found, in a dried specimen: C, 71·0; H, 8·0. $C_{27}H_{36}O_4S$ requires C, 71·0; H, 7·95%). The *methanesulphonate* (85%), similarly prepared and precipitated with water, crystallised from methanol in needles, m. p. 164—165° (Found: C, 66·5; H, 8·5. $C_{21}H_{32}O_4S$ requires C, 66·3; H, 8·5%).

Extraction of V. americana *with Light Petroleum.*—Treatment of the ground wood (4·5 kg.) with boiling light petroleum for 48 hr. and evaporation of the solvent produced a clear brown viscous extract (276 g., 6·14%), and from it a pale yellow aromatic oil (45 g.), b. p. 118—135°/12 mm., was obtained by steam-distillation. Cadinene dihydrochloride was prepared from a portion of the distillate with hydrogen chloride in ether at −20° to −10° (Found: C, 64·9; H, 9·3. Calc. for $C_{15}H_{26}Cl_2$: C, 65·2; H, 9·5%), and from the higher-boiling fraction of the oil, by dehydrogenation with selenium at 200—260° and distillation from sodium, a liquid was prepared which gave a picrate, m. p. 115—116° (cadalene picrate, m. p. 115°) (Found: C, 58·6; H, 4·9. Calc. for $C_{14}H_{16},C_6H_3O_7N_3$: C, 58·1; H, 4·6%). From a solution of the dried non-volatile portion in light petroleum (100 c.c.) diluted with methanol (400 c.c.), crude methyl vouacapenate was obtained which after repeated crystallisation had m. p. 104—105° (yield 60 g.) (Found: C, 75·9; H, 9·2%).

The crystallisation residues (97·6 g.) were distilled and two solid fractions were obtained: (*a*) b. p. 184—195°/0·2 mm. (35·5 g.), and (*b*) b. p. 195—240°/0·2 mm. (25·2 g.). From the former, crude methyl vouacapenate (16 g.), m. p. 98—100°, was obtained which yielded the pure ester, m. p. and mixed m. p. 104—105°, by recrystallisation. From fraction (*b*) vouacapenic acid separated, having m. p. 225—226° (softening at 216°) after crystallisation from methanol or ethyl acetate (yield 4·6 g.) (Found: C, 76·0; H, 8·7. Calc. for $C_{20}H_{28}O_3$: C, 75·9; H, 8·9%), and with diazomethane formed the methyl ester, m. p. 104—105°. A portion (10 g.) of the residue from (*b*), heated with a 20% ethylene glycol solution of potassium hydroxide, gave mainly alkali-soluble material (9 g.), a small unsaponifiable fraction being non-crystalline. The residues from (*a*) were refractionated and methyl vouacapenate was the sole identifiable product.

Oxidation of Methyl Vouacapenate.—(i) *With monoperphthalic acid.* A mixture of the ester (5 g.) in chloroform (50 c.c.) and monoperphthalic acid in ether (100 c.c.) was left at 0° for 50 hr., after which the precipitated phthalic acid was removed and the solution washed with aqueous potassium iodide and sodium thiosulphate. The yellow solid obtained by evaporation was repeatedly washed with boiling water and then kept at 90—100° for 2 hr. Crystallisation from aqueous methanol gave the *lactone* (II*B*; R = CO_2Me) (4·2 g.) as colourless plates, m. p. 208—210° (decomp.), which formed rods from ethyl acetate–light petroleum, m. p. 212—214° (decomp.), light absorption in EtOH, max. at 216 mμ (log ε 4·09); in 0·2N-sodium hydroxide in EtOH, max. at 226 and 294 mμ (log ε 3·89 and 3·73) (Found, in a dried specimen: C, 69·7; H, 8·3%; equiv., 360. $C_{21}H_{30}O_5$ requires C, 69·6; H, 8·3%; equiv., 362). The lactone dissolved in aqueous sodium carbonate and hydroxide, a sodium salt separating in plates from more concentrated solutions, and was recovered by acidification.

When heated at 230—240° for 15 min. the lactone effervesced and was converted into the *anhydro-derivative* (III*B*; R = CO_2Me) which crystallised from methanol in needles, m. p. 197—198°; light absorption in EtOH, max. at 274 mμ (log ε 4·52) (Found, in a dried specimen: C, 73·1; H, 8·2. $C_{21}H_{28}O_4$ requires C, 73·2; H, 8·2%). It was insoluble in aqueous alkali and was recovered on acidification of its solution in cold ethanolic potassium hydroxide.

(ii) *With ozone.* Methyl vouacapenate (7 g.) in ethyl acetate (70 c.c.) at −10° was treated with ozone in excess, and the yellow gum obtained by evaporation of the solvent at 15° was treated with water, first at room temperature for 12 hr. and then for 3 hr. at the b. p. The insoluble product was then dissolved in ether which was extracted with aqueous sodium hydrogen carbonate and with 0·5N-sodium hydroxide. The portion obtained by acidification of the carbonate solution gave *methyl* 6-1′-*carboxyethyl*-5-*carboxymethyldecahydro*-1 : 10-*dimethyl*-1-*naphthoate* (VI; R = H) which crystallised from ethyl acetate–light petroleum as needles (5 g., 70%), m. p., after drying at 150°, 193—194° [Found, in a dried specimen: C, 64·6; H, 8·5%; *M* (Rast), 403; equiv., 191. $C_{19}H_{30}O_6$ requires C, 64·4; H, 8·5%; *M*, 354; equiv., 177]. Treatment with diazomethane in ether gave, after distillation of the product, b. p. 190—210° (bath-temp.)/0·075 mm., the *trimethyl ester* (VI; R = Me) as prisms from light petroleum, m. p. 63—64° (Found: C, 65·8; H, 8·7; OMe, 23·9. $C_{21}H_{31}O_6$ requires C, 65·9; H, 9·0; 3OMe, 24·3%).

The reddish oil (2 g.) precipitated by acid from the sodium hydroxide-soluble ozonolysis product failed to crystallise and yielded a yellow glass on distillation at 0·1 mm. (bath at 150°).

It gave with alcoholic ferric chloride an intense purple colour. Shaking its solution in chloroform with ammoniacal cupric acetate gave a deep green copper derivative which after evaporation of the solvent crystallised from aqueous ethanol in plates, m. p. 255—258°. Decomposition with 20% sulphuric acid, however, regenerated the presumed dicarbonyl compound in its original non-crystalline condition. A portion (1 g.) was dissolved in 0·5N-sodium hydroxide (30 c.c.) and hydrolysed under reflux. The precipitated brown gum (0·5 g.), which no longer exhibited a ferric reaction, failed to give crystalline derivatives with the usual ketonic reagents.

Ozonolysis with 50% of the theoretical quantity of ozone, and working up with the addition of zinc dust, resulted in an increased proportion of the less acidic material and a considerable recovery of methyl vouacapenate (50—60%).

Selenium Dehydrogenation of the Anhydro-lactone (III*B*; R = CO_2Me).—A mixture of the anhydro-lactone (3 g.) and selenium (6 g.) was heated for 20 hr. at 300—310° and finally at 330—350° for 4 hr. The ether-soluble product was distilled and the portion, b. p. 140—145° (bath-temp.)/0·2 mm., consisted of 1 : 2 : 8-trimethylphenanthrene which crystallised from methanol in plates, m. p. and mixed m. p. 144—145° (Found: C, 93·1; H, 7·4. Calc. for $C_{17}H_{16}$: C, 92·7; H, 7·3%). The picrate had m. p. 167—168° (sintering at 165°) undepressed by a specimen of m. p. 166—168° (recorded m. p. 162—163°), and the trinitrobenzene derivative had m. p. and mixed m. p. 191—192° (Found: C, 63·9; H, 4·1. Calc. for $C_{17}H_{16},C_6H_3O_6N_3$: C, 63·7; H, 4·4%).

Selenium Dehydrogenation of Methyl Vouacapenate.—The ether-soluble material obtained by heating methyl vouacapenate (5 g.) with selenium (10 g.) at 330—350° for 48 hr. was distilled and the portion of b. p. 120—180° (bath-temp.)/0·07 mm. dissolved in boiling ethanol. The fraction separating at room temperature was recrystallised and formed plates, m. p. 114—115° undepressed when mixed with 2-ethyl-1 : 8-dimethylphenanthrene (VII; R = H) similarly derived from methyl vinhaticoate (I*A*; R = CO_2Me) (King and King, *loc. cit.*) (Found: C, 91·6; H, 7·7. Calc. for $C_{18}H_{18}$: C, 92·3; H, 7·7%); the trinitrobenzene derivative had m. p. and mixed m. p. 167—168°. By evaporating the ethanolic filtrate and crystallising the residue from acetic acid and then light petroleum, 2-ethyl-1 : 8-dimethyl-3-phenanthrol, m. p. 168—169° (decomp.), was obtained identical (mixed m. p.) with a specimen, m. p. 167°, obtained from (I*A*; R = CO_2Me). King and King (*loc. cit.*) found m. p. 164°; the trinitrobenzene derivative had m. p. and mixed m. p. 185—186°.

Vinhaticol (I*A*; R = $CH_2\cdot OH$).—The reduction of methyl vinhaticoate (5 g.) with lithium aluminium hydride followed the method used for the preparation of vouacapenol. The *product* (I*A*; R = $CH_2\cdot OH$) (4 g.) crystallised from aqueous methanol in prisms, m. p. 133°, $[\alpha]_D$ +92° (*c*, 1·33) (Found, in a dried specimen: C, 79·7; H, 10·2. $C_{20}H_{30}O_2$ requires C, 79·4; H, 10·0%). With acetic anhydride–sodium acetate the *acetate* was obtained as leafy plates (from methanol), m. p. 81—82° (Found, in a dried specimen: C, 76·8; H, 9·4. $C_{22}H_{32}O_3$ requires C, 76·7; H, 9·4%).

Vinhaticyl toluene-p-*sulphonate*, prepared in pyridine (yield 60%), formed needles, m. p. 90—91°, from methanol (Found, in a specimen dried at 60° *in vacuo*: C, 71·4; H, 8·1. $C_{27}H_{36}O_4S$ requires C, 71·0; H, 7·95%). The *methanesulphonate*, plates from methanol, had m. p. 117—118° (Found, in a dried specimen: C, 66·0; H, 8·3. $C_{21}H_{32}O_4S$ requires C, 66·3; H, 8·5%).

Perphthalic Acid Oxidation of Vinhaticol and Vouacapenol.—The action of monoperphthalic acid (12 g.) on vinhaticol (I*A*; R = $CH_2\cdot OH$) (10 g.) in ether (250 c.c.) at 0° for 8 days and then 2—3 days at room temperature caused the deposition of solid which was collected and treated with boiling water (5 × 200 c.c.). The pale yellow crystalline residue (9 g.) had m. p. 230°; a small portion recrystallised from methanol formed colourless prisms of the *product* (II*A*; R = $CH_2\cdot OH$), m. p. 242—244° (decomp.) (Found: C, 72·2; H, 8·8. $C_{20}H_{30}O_4$ requires C, 71·8; H, 9·0%). Heating the lactone (2 g.) at 240° for 10 min. yielded a resinous product from which the *anhydro-lactone* (III*A*; R = $CH_2\cdot OH$) (1·7 g.) was obtained as colourless needles, m. p. 180—181°, by crystallisation from methanol (Found: C, 76·1; H, 9·1. $C_{20}H_{28}O_3$ requires C, 75·9; H, 8·9%).

From the oxidation of vouacapenol (10 g.) under comparable conditions a somewhat more soluble product was obtained. It crystallised from methanol yielding the *product* (II*B*; R = $CH_2\cdot OH$) as plates, m. p. 240—242° (effervescence), solidifying and remelting at 280—282° (Found: C, 71·8; H, 9·0%). The *anhydro-lactone* (III*B*; R = $CH_2\cdot OH$) formed by heating the oxidation product at 230° for 15 min. was remarkably sparingly soluble, and crystallised from *cyclo*hexanone in needles, m. p. 282—284° (Found, in a specimen dried at 150° *in vacuo*: C, 75·7; H, 8·7%). It dissolved slowly in aqueous-alcoholic potassium hydroxide, the original compound (II*B*; R = $CH_2\cdot OH$), m. p. 238—240° (decomp.), being precipitated on acidification.

Conversion of the Anhydro-lactones (III*A*; R = $CH_2\cdot OH$) *and* (III*B*; R = $CH_2\cdot OH$) *into* 8-*Ethyl*-1 : 2-*dimethylphenanthrene* (VIII; R = Et).—The compound (II*A*; R = $CH_2\cdot OH$) (6 g.) was first heated at 240° and the resulting crude anhydro-compound intimately mixed with potassium hydrogen sulphate (12 g.). The material was then stirred and heated at 230—240° and, after the initially vigorous gas evolution had ceased (30 min.), the melt was cooled and treated with hot water. The undissolved gum was taken up in ether and distilled, the pale yellow viscous distillate (2·9 g.), b. p. 180—210° (bath-temp.)/0·1 mm., partly crystallising after 2—3 weeks (Found, in a redistilled specimen, b. p. 180—190°/0·1 mm.: C, 80·4; H, 8·6. $C_{20}H_{26}O_2$ requires C, 80·5; H, 8·8%).

The dehydrated mixture (1·52 g.) was dehydrogenated with selenium (4 g.) at 330—350° for 40 hr. and the product isolated with ether and distilled. The portion of b. p. 90—180°/0·07 mm. was dissolved in ethanol (3 c.c.) and added to saturated ethanolic trinitrobenzene (5 c.c.). The solid which separated was collected, dissolved in benzene (10 c.c.), and passed through alumina (40 g.). Elution with light petroleum yielded material crystallising from ethanol finally as plates (10 mg.), m. p. 107—108°, and consisting of 8-*ethyl*-1 : 2-*dimethylphenanthrene* (VIII; R = Et) (Found: C, 92·3; H, 7·8. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). The *trinitrobenzene derivative*, orange-red needles from ethanol, had m. p. 169—170° (Found: C, 64·8; H, 4·4. $C_{18}H_{18},C_6H_3O_6N_3$ requires C, 64·4; H, 4·7%).

After preliminary dehydration of the compound (II*B*; R = $CH_2\cdot OH$) (8·5 g.) derived from vouacapenol to the anhydro-compound (III*B*; R = $CH_2\cdot OH$), the product was heated with potassium hydrogen sulphate at 240—250° for 45 min. The mixture obtained by distillation as a pale yellow gum (4·2 g.), b. p. 180—210°/0·1 mm., gradually became semi-solid (Found, in a redistilled specimen, b. p. 150—160°/0·05 mm.: C, 80·5; H, 8·4%). Dehydrogenation of a portion (2 g.) under the conditions used for the isomeric material from (III*A*; R = $CH_2\cdot OH$) yielded 8-ethyl-1 : 2-dimethylphenanthrene, after purification *via* the trinitrobenzene derivative, as plates, m. p. and mixed m. p. 107—108° (Found: C, 92·1; H, 7·6%). The trinitrobenzene derivative, orange-red needles from ethanol, had m. p. and mixed m. p. 169—170° (Found: C, 64·1; H, 4·8%).

NN-*Dimethylvouacapenamide*.—A solution of vouacapenic acid (2·3 g.) in ether (40 c.c.) was treated with thionyl chloride (1 g.) and pyridine (0·2 c.c.) and after 5 hr. the precipitate of pyridine hydrochloride was removed and the liquid quickly washed with 0·2N-sodium hydroxide and dried (Na_2SO_4). Evaporation and heating under reduced pressure at 100° left a light brown gum, supposedly the acid chloride. It was dissolved in xylene (40 c.c.) previously refluxed with Raney nickel and the solution hydrogenated at the b. p. over palladised barium sulphate. Hydrogen chloride (70% of theory) was slowly evolved and evolution ceased only after 50 hr., and evaporation of the filtered solution gave a sparingly-soluble amorphous solid devoid of aldehydic properties.

A specimen of the chloride, prepared as above from 2 g. of acid, was dissolved in aqueous dimethylamine (20 c.c. of 25%) and ethanol (20 c.c.) by warming and after 30 min. at room temperature the solution was diluted with water. The precipitated NN-*dimethylvouacapenamide* crystallised from methanol in plates, m. p. 122—123° (Found, in a dried specimen: C, 76·8; H, 9·5. $C_{22}H_{33}O_2N$ requires C, 76·9; H, 9·7%). Lithium aluminium hydride (0·2 g.), dissolved in ether (10 c.c.), was slowly added to a solution of the amide (0·6 g.) in tetrahydrofuran (5 c.c.), and after 20 hr. the mixture was treated with dilute hydrochloric acid. From the ether vouacapenol (0·1 g.), m. p. and mixed m. p. 130—131°, was isolated; the remaining product, suspended in the aqueous layer, was a nitrogen-containing solid (0·3 g.).

Vouacapenal (I*B*; R = CHO).—(i) The suspension of $CrO_3,2C_5H_5N$ prepared by dissolving chromic anhydride (1 g.) in pyridine (10 c.c.) was mixed with a solution of vouacapenol (1 g.) in pyridine (10 c.c.), and after 1½ hr. at room temperature the dark precipitate was removed and washed with pyridine. The combined pyridine solutions were added to water (300 c.c.) and the mixture shaken with ether (3 × 200 c.c.). When the washed and dried ether extract was isolated it crystallised and separated from methanol finally as colourless plates, m. p. 161—163°, consisting of *vouacapenal* (Found: C, 80·4; H, 9·4. $C_{20}H_{28}O_2$ requires C, 80·0; H, 9·4%). The *oxime*, rods from aqueous ethanol, had m. p. 186—187° (Found: N, 4·5. $C_{20}H_{29}O_2N$ requires N, 4·4%).

(ii) Vouacapenol (0·9 g., 1 mol.), aluminium *tert.*-butoxide (2·8 g., 2 mols.) and *p*-benzoquinone (2·8 g., 10 mols.) were heated under reflux for 15 hr. in purified benzene (30 c.c.). The dark red solid remaining after steam-distillation was repeatedly extracted with ether, and the ether solution was then washed with 2N-sodium hydroxide until the washings remained colourless. Evaporation of the ether left a red-brown residue which after repeated crystallisation from acetone–methanol (charcoal) formed light brown plates (0·09 g., 10%), m. p. 163—164° alone or mixed with vouacapenal obtained as in (i).

Vinhatical (I*A*; R = CHO).—The oxidation of vinhaticol (2 g.) with chromic anhydride in pyridine as in the preparation of (I*B*; R = CHO) gave the corresponding aldehyde, *vinhatical* (1·3 g., 65%), prisms (from acetone–methanol), m. p. 131—133° (slight decomp.) (Found: C, 80·1; H, 9·3. $C_{20}H_{28}O_2$ requires C, 80·0; H, 9·4%). The *oxime* crystallised from ethanol in prisms, m. p. 205° (Found: C, 76·3; H, 9·1. $C_{20}H_{29}O_2N$ requires C, 76·2; H, 9·3%).

Dodecahydro-1 : 1 : 8 : 12-*tetramethylfurano*(2′ : 3′-6 : 7)*phenanthrene* (IX).—(i) The aldehyde (I*A*; R = CHO) (1·3 g.), potassium hydroxide (8 g.), ethylene glycol (80 c.c.), and hydrazine hydrate (2 c.c. of 90%) were heated under reflux for 2 hr., after which the liquid was concentrated to b. p. 190° and treated with more hydrazine hydrate (1 c.c.). Further heating for 2 hr. and evaporation to b. p. 195° was followed by 6 hours' refluxing, the liquid finally being poured into water (600 c.c.). Ether-extraction yielded a brown oil which was distilled, the product, b. p. 110—130° (bath-temp.)/0·1 mm., then solidifying and forming needles, m. p. 77—78°, from ethanol (0·9 g., 70%). Further crystallisation afforded the *furano-hydrocarbon*, m. p. 79°, $[\alpha]_D$ +84° (*c*, 1·13 in $CHCl_3$) (Found: C, 84·2; H, 10·7. $C_{20}H_{30}O$ requires C, 83·9; H, 10·6%).

(ii) A mixture of vouacapenal (1·67 g.) and the corresponding quantities of reagents used in method (i), refluxed first for 1½ hr. and then after evaporation to b. p. 195° for a further 4 hr., gave the identical furano-hydrocarbon (IX), which was isolated as above and formed needles (1 g., 65%), m. p. and mixed m. p. 79°, $[\alpha]_D$ +83° (*c*, 1·13 in $CHCl_3$) (Found: C, 83·8; H, 10·6%).

(iii) A mixture of vinhaticyl toluene-*p*-sulphonate (3 g.) and lithium aluminium hydride (0·6 g.) was heated under reflux in dioxan (60 c.c.) for 20 hr. Dilute hydrochloric acid was then added and the product ether-extracted. Evaporation of the dried solution and distillation gave the hydrofuranophenanthrene as a gum (0·6 g.), b. p. 110—130° (bath-temp.)/0·1 mm., which solidified in contact with ethanol and was finally obtained by recrystallisation as prisms, m. p. 74—76° (Found: C, 83·4; H, 10·2%).

Reduction of the toluene-*p*-sulphonate of vouacapenol with lithium aluminium hydride led either to recovery of the ester or the formation of vouacapenol which was isolated by chromatography on alumina with benzene–light petroleum. The methanesulphonates of both vinhaticol and vouacapenol gave 90% yields of the parent alcohols when reduced with lithium aluminium hydride.

Oxidation of Methyl Vinhaticoate with Nitric Acid.—When methyl vinhaticoate (20 g.) was treated with small portions of a mixture of nitric acid (225 c.c.; *d* 1·4) and the fuming acid (75 c.c.; *d* 1·52), a vigorous reaction occurred. The clear solution was then cautiously heated to 50°, and 1½ hr. after beginning the experiment the temperature was raised to 100° (oil-bath) and 1 hr. later to 130° for a further 2½ hr. The liquid was then evaporated (50—60°/14 mm.) and the gummy residue dissolved in nitric acid (30 c.c.; *d* 1·42) and the solution left to crystallise for 10 days. The deposited solid was recrystallised from ethyl acetate–light petroleum and formed colourless needles, m. p. 220—222° (decomp.) depressed to 213—214° by the dimethyl*cyclo*hexanetricarboxylic acid, m. p. 218—219°, prepared from abietic acid by oxidation with nitric acid (Barton and Schmeidler, *loc. cit.*) (Found: C, 62·3, 62·5; H, 8·2, 8·2; OMe, nil. $C_{17}H_{26}O_6$ requires C, 62·6; H, 8·0%). The *acid*, believed to be (X), gave with diazomethane a *trimethyl ester*, which after distillation [b. p. 170—190° (bath-temp.)/0·1 mm.] formed rods, m. p. 109—110°, from aqueous methanol (Found: C, 64·9; H, 8·6; OMe, 25·7. $C_{20}H_{32}O_6$ requires C, 65·2; H, 8·8; OMe, 25·2%).

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