## 11. *Elaboration Products of Podocarpic Acid.*

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Podocarpic acid has been converted into *trans*-1,2,3,4,9,10,11,12-octahydro-7-methoxy-1,1,12-trimethylphenanthrene thus establishing the absolute stereochemistry of the latter.

The total synthesis of racemic *trans*-1,2,3,4,9,10,11,12-octahydro-7-methoxy-1,1,12-trimethylphenanthrene (VIII; R = Me) has been reported.[1] In view of the value of this compound for terpene syntheses it was obviously desirable to establish the absolute configuration of its enantiomorphs. This has now been achieved by the production of the dextrorotatory enantiomorph from podocarpic acid.

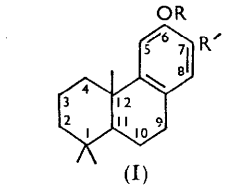
Wolff–Kishner reduction of 1β-formyl-*trans*-1,2,3,4,9,10,11,12-octahydro-1,12-dimethyl-6-methoxyphenanthrene (obtained from podocarpic acid by published procedures) yielded the phenanthrene (I; R = Me, R′ = H) which on nitration could be converted into either the mononitro-compound (I; R = Me, R′ = $NO_2$) or the corresponding dinitrophenol (IV). It was hoped that the methoxyl group in the mononitro-derivative could be replaced by hydrogen *via* the corresponding thiophenol or disulphide. However, we were unable to obtain any useful products from the reaction of the phenanthrene (I; R = Me, R′ = $NO_2$) with sodium sulphide or disulphide, either intractable gums resulting or starting material being recovered.

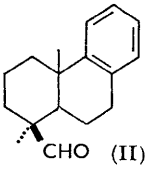
As it was thought that displacement of the toluenesulphonyl group in the derivative (I; R = Ts, R′ = $NO_2$) might take place more readily, the methoxy-compound (I; R = Me, R′ = H) was demethylated with sodamide in piperidine,[2] and the resulting phenol nitrated with cupric nitrate in acetic anhydride, giving (I; R = H, R′ = $NO_2$). All efforts to replace the toluenesulphonyl group in the nitro-toluenesulphonate (I; R = Ts, R′ = $NO_2$) by sodium sulphide again failed. An attempt to remove the phenolic grouping in

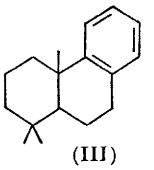
[1] Barltrop and Rogers, *J.*, 1958, 2566.
[2] Brotherton and Bunnett, *Chem. and Ind.*, 1957, 80.

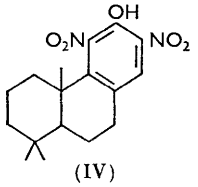
the nitro-compound (I; R = H, R′ = $NO_2$) by conversion into the diethyl phosphate followed by reduction with lithium in ammonia [3] gave the amino-phenol (I; R = H, R′ = $NH_2$).

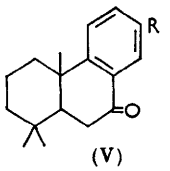
A new approach to the introduction of a substituent in the 7-position was then adopted. *trans*-1,2,3,4,9,10,11,12-Octahydro-1β-hydroxymethyl-1,12-dimethylphenanthrene [4] was oxidised to the corresponding aldehyde (II). Wolff–Kishner reduction of the aldehyde (II) gave the hydrocarbon (III) together with a product corresponding to the azine.

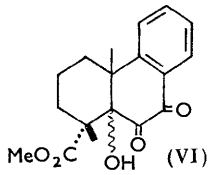


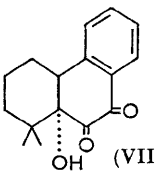


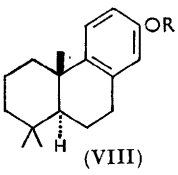


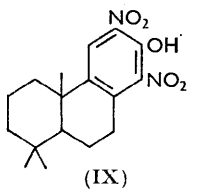


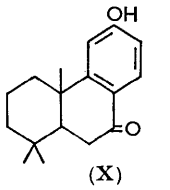













Controlled oxidation of the hydrocarbon (III) produced the expected 9-oxo-derivative (V; R = H) and a substance containing three oxygen atoms. It had infrared and ultraviolet absorptions consistent with its formulation as an α-diketone, and formed a quinoxaline which contained a hydroxyl group (infrared spectrum). In view of the known 5α-hydroxylation of steroids by chromic acid [5] and the suggested formulation of a similarly derived substance (VI),[6] structure (VII) seems the most probable for the by-product.

Nitration of α-tetralone yields [7] a mixture of 7-nitro- and 5-nitro-α-tetralone in the ratio of 93 : 7. Hence, it was expected that nitration of the ketone (V; R = H) would yield almost exclusively (V; R = $NO_2$). Only one product was indeed isolated, which was shown in the sequel to possess the expected structure. Removal of the keto-group was achieved by reduction with sodium borohydride to the corresponding alcohol, followed by acetylation, and reduction with lithium in ammonia to give 7-amino-*trans*-1,2,3,4,9,10,11,12-octahydro-1,1,12-trimethylphenanthrene. The hydrochloride was diazotised, converted into the phenol (VIII; R = H), and thence into (+)-*trans*-1,2,3,4,9,10,11,12-octahydro-7-methoxy-1,1,12-trimethylphenanthrene (VIII; R = Me). In view of the established stereochemistry of podocarpic acid the absolute configuration of (VIII; R = Me) must therefore be represented as shown.

Although precedents were strongly against it, there remained a possibility that the nitration of the ketone (V; R = H) had proceeded to give the corresponding 5-nitro-derivative rather than (V; R = $NO_2$). To procure further evidence on this point the derived phenol was dinitrated. That the product was a 2,6-dinitrophenol (IX) as expected was confirmed by the comparison of its ultraviolet absorption spectrum in the range 320—460 mμ with 2,6- and 2,4-dinitrophenols of known structure, as shown in the Table.

While this work was in progress a new diterpene phenolic ketone nimbiol [8] was reported. The light-absorption data suggested structure (X) for this compound. Accordingly (X)

[3] Kenner and Williams, *J.*, 1955, 522.
[4] Wenkert and Jackson, *J. Amer. Chem. Soc.*, 1958, **80**, 217.
[5] Martin-Smith, *J.*, 1958, 523.
[6] Ohta and Ohmori, *Pharm. Bull. Japan*, 1957, **5**, 91.
[7] Schroeter, *Ber.*, 1930, **63**, 1308.
[8] Sengupta, Choudhury, and Khastgir, *Chem. and Ind.*, 1958, 861.

*Ultraviolet absorption of dinitrophenols in* 0·005N-*sodium hydroxide in* 90% *methanol.*

| | $\lambda_{max.}$ (mμ) | ε | $\lambda_{max.}$ (mμ) | ε |
|---|---|---|---|---|
| 6-Methyl-2,4-dinitrophenol | 371 | 16,600 | 403 | 13,900 |
| 5,6,7,8-Tetrahydro-2,4-dinitro-1-naphthol | 370 | 15,500 | 410 | 14,100 |
| 4-Methyl-2,6-dinitrophenol | | | 447 | 7600 |
| 3,4-Dimethyl-2,6-dinitrophenol | | | 425 | 6300 |
| (IV) | | | 437 | 5300 |
| (IX) | | | 428 | 7100 |

was prepared by the chromium trioxide oxidation of the acetate (I; R = Ac, R′ = H). However, the physical constants of compound (X) conclusively showed that it was not identical with nimbiol, although the two compounds obviously contain similar chromophores.

## Experimental

Rotations were determined in chloroform at room temperature unless otherwise stated. M. p.s were determined on a Kofler block and are corrected. Alumina of activity III was employed for chromatography and the light petroleum used for elution had b. p. 60—80°.

trans-1,2,3,4,9,10,11,12-*Octahydro*-6-*methoxy*-1,1,12-*trimethylphenanthrene* (I; R = Me, R′ = H).—1β-Formyl-*trans*-1,2,3,4,9,10,11,12-octahydro-6-methoxy-1,12-dimethylphenanthrene (23·7 g.) and hydrazine (60 ml.; 60%) were heated under reflux in diethylene glycol (400 ml.) for 90 min. The solution temperature was raised to 200° by distillation, potassium hydroxide (30 g.) was added, and the mixture was kept under reflux for a further 4 hr. The product, in benzene, was filtered through alumina (200 g.) and crystallised from methanol, forming needles (16·2 g.) of the *methoxy-compound* (I; R = Me, R′ = H), m. p. 30·5—31·5°, $[\alpha]_D$ +72° (*c* 2·3) (Found: C, 83·3; H, 9·8; OMe, 11·6. $C_{18}H_{26}O$ requires C, 83·65; H, 10·15; OMe, 12·0%).

trans-1,2,3,4,9,10,11,12-*Octahydro*-6-*methoxy*-1,1,12-*trimethyl*-7-*nitrophenanthrene* (I; R = Me, R′ = $NO_2$).—The methoxy-compound (I; R = Me, R′ = H) (710 mg.), cupric nitrate (355 mg. of trihydrate), and acetic anhydride (20 ml.) were stirred at room temperature for 12 hr. The mixture was poured into water, and the product adsorbed on alumina (30 g.) from light petroleum. Elution with benzene–light petroleum (1 : 1) gave the *nitro-compound* (I; R = Me, R′ = $NO_2$) as needles (260 mg.) (from aqueous methanol), m. p. 133—134·5°, $[\alpha]_D$ +274° (*c* 0·7) (Found: C, 70·9; H, 8·2; N, 4·7. $C_{18}H_{25}O_3N$ requires C, 71·25; H, 8·3; N, 4·6%).

trans-1,2,3,4,9,10,11,12-*Octahydro*-6-*hydroxy*-1,1,12-*trimethyl*-5,7-*dinitrophenanthrene* (IV).—The methoxy-compound (I; R = Me, R′ = H) (1·90 g.), benzene (10 ml.), and nitric acid (8 ml.; 35%) were stirred for 1 hr. at 5°. Extraction from benzene with Claisen's alkali gave a product which was adsorbed from benzene on alumina (100 g.) deactivated with 10% of 10% acetic acid, and eluted with ether. Crystallisation from aqueous methanol gave the *dinitrophenanthrene* (IV) as yellow needles (550 mg.), m. p. 138·5—139·5°, $[\alpha]_D$ +273° (*c* 0·9) (Found: C, 60·85; H, 6·6; N, 8·15. $C_{17}H_{22}O_5N_2$ requires C, 61·05; H, 6·65; N, 8·4%). The alkali-insoluble fraction afforded the mononitro-compound (I; R = Me, R′ = $NO_2$) (80 mg.).

*Demethylation of* trans-1,2,3,4,9,10,11,12-*Octahydro*-6-*methoxy*-1,1,12-*trimethylphenanthrene* (I; R = Me, R′ = H).—The methyl ether (8·9 g.) was heated under reflux with a suspension of sodamide (from 10 g. of sodium) in dry piperidine (60 ml.) for 16 hr. The product crystallised from hexane as needles (7·95 g.) of *trans*-1,2,3,4,9,10,11,12-octahydro-6-hydroxy-1,1,12-trimethylphenanthrene (I; R = R′ = H), m. p. 140—141°.

Treatment with toluene-*p*-sulphonyl chloride in pyridine gave the corresponding *toluenesulphonate*, which crystallised as needles (from methanol), m. p. 72—74°, $[\alpha]_D$ +56° (*c* 0·8) (Found: C, 72·75; H, 7·6. $C_{24}H_{30}O_3S$ requires C, 72·3; H, 7·6%).

trans-1,2,3,4,9,10,11,12-*Octahydro*-6-*hydroxy*-1,1,12-*trimethyl*-7-*nitrophenanthrene* (I; R = H, R′ = $NO_2$).—The hydroxy-compound (I; R = R′ = H) (2·75 g.), cupric nitrate (1·46 g. of trihydrate), and acetic anhydride (30 ml.) were stirred at room temperature for 20 hr., and then diluted with water. Cyrstallisation of the precipitate from aqueous methanol or light petroleum gave (I; R = H, R′ = $NO_2$) as yellow *needles* (2·43 g.), m. p. 113·5—114·5° (Found: C, 70·6; H, 7·45; N, 5·2. $C_{17}H_{23}O_3N$ requires C, 70·55; H, 8·0; N, 4·85%). Attempts to nitrate the toluenesulphonate of (I; R = R′ = H) by this method afforded only starting material.

7-*Amino*-trans-1,2,3,4,9,10,11,12-*octahydro*-1,1,12-*trimethyl*-6-*toluene*-p-*sulphonyloxy*-*phenanthrene* (I; R = Ts, R′ = $NH_2$).—The nitro-compound (I; R = H, R′ = $NO_2$) (1·79 g.), toluene-*p*-sulphonyl chloride (1·25 g.), and pyridine (0·53 ml.) were heated under reflux in dry benzene (50 ml.) for 12 hr. After being washed with water, 2N-sulphuric acid, and sodium hydrogen carbonate solution, the benzene solution was filtered through alumina (70 g.) deactivated with 5% of 10% acetic acid. Evaporation to dryness yielded crude ester (I; R = Ts, R = $NO_2$) as a yellow oil (2·1 g.) which could not be crystallised. This oil (534 mg.) was hydrogenated in benzene (50 ml.), Adams's catalyst (25 mg.) being used. After adsorption from benzene on alumina (50 g.) and elution with ether–methanol (19 : 1), the *ester* (I; R = Ts, R′ = $NH_2$) crystallised as needles (276 mg.) (from light petroleum), m. p. 137—138°, $[\alpha]_D$ +72° (*c* 0·8) (Found: C, 69·7; H, 7·45. $C_{24}H_{31}O_3NS$ requires C, 69·7; H, 7·55%).

7-*Amino*-trans-1,2,3,4,9,10,11,12-*octahydro*-6-*hydroxy*-1,1,12-*trimethylphenanthrene* (I; R = H, R′ = $NH_2$).—The nitro-compound (I; R = H, R′ = $NO_2$) (65 mg.) was subjected to Kenner's deoxygenation procedure. The product would not crystallise from chloroform–light petroleum or aqueous methanol, a gelatinous suspension being formed. However, after sublimation (3 times at 140°/0·003 mm.) it formed fine needles (26 mg.) of the *amine* (I; R = H, R′ = $NH_2$), m. p. 174—176°, $[\alpha]_D$ +86° (*c* 0·15) (Found: C, 78·45; H, 9·65; N, 5·8. $C_{17}H_{25}ON$ C, 78·7; H, 9·7; N, 5·4%).

1β-*Formyl*-trans-1,2,3,4,9,10,11,12-*octahydro*-1,12-*dimethylphenanthrene* (II).—Oxidation of 1β-hydroxymethyl-*trans*-1,2,3,4,9,10,11,12-octahydro-1,12-dimethylphenanthrene (22·7 g.) in acetone (300 ml.) with chromic acid (8N) gave the *aldehyde* (II) which crystallised as flat prisms (17·6 g.) (from methanol), m. p. 106—108°, $[\alpha]_D$ +89° (*c* 1·4) (Found: C, 84·5; H, 8·95. $C_{17}H_{22}O$ requires C, 84·25; H, 9·15%).

trans-1,2,3,4,9,10,11,12-*Octahydro*-1,1,12-*trimethylphenanthrene* (III).—The aldehyde (II) (14·1 g.), hydrazine (50 ml., 60%), and diethylene glycol (250 ml.) were heated under reflux for 1 hr. Potassium hydroxide (15 g.) was added and the temperature raised to 210° by distillation. After 5 hr. the product was extracted with light petroleum, filtered through alumina (300 g.), and crystallised, forming prisms (12·9 g.) of the *hydrocarbon* (III) (from chloroform–methanol), m. p. 16—17°, b. p. 96—97°/18 mm., $[\alpha]_D$ +63° (*c* 3·3) (lit.[9] $[\alpha]_D$ +65°) (Found: C, 89·65; H, 10·55. $C_{17}H_{24}$ requires C, 89·4; H, 10·6%). Further elution with benzene–ether (4 : 1) gave the *azine* (110 mg.) as prisms (from aqueous methanol), m. p. 214—216·5°, $[\alpha]_D$ +223° (*c* 0·6) [Found: C, 84·35; H, 9·0; N, 5·7%; *M* (mass spectrometer), 480 ± 3. $C_{34}H_{44}N_2$ requires C, 84·95; H, 9·25; N, 5·85%; *M*, 480); $\lambda_{max.}$ (hexane) 213 mμ (ε = 37,600); ν (Nujol) 1630 cm.$^{-1}$ (N=N).

trans-1,2,3,4,9,10,11,12-*Octahydro*-1,1,12-*trimethyl*-9-*oxophenanthrene* (V; R = H).—The hydrocarbon (III) (8·13 g.), chromium trioxide (4·78 g.), and acetic acid (120 ml.) were heated at 70—75° for 10 min. The product was freed from acidic material and adsorbed on alumina (300 g.) from light petroleum. Elution with light petroleum gave unchanged hydrocarbon (III) (930 mg.). Elution with benzene gave the *ketone* (V; R = H) as prisms (5·5 g.) (from aqueous methanol), m. p. 82—83·5°, $[\alpha]_D$ +18° (*c* 1·6) (Found: C, 84·55; H, 8·85. $C_{17}H_{22}O$ requires C, 84·25; H, 9·15%), $\lambda_{max.}$ (in methanol) 251 mμ (ε = 10,200). Further elution with methanol gave a yellow oil which was adsorbed from benzene–light petroleum (1 : 1) on alumina (20 g.) deactivated with 5% of 10% acetic acid, and eluted with benzene. Crystallisation from light petroleum–chloroform gave trans-1,2,3,4,9,10,11,12-*octahydro*-11α-*hydroxy*-1,1,12-*trimethyl*-9,10-*dioxophenanthrene* (VII) (52 mg.) as yellow needles, m. p. 167—169°, $[\alpha]_D$ +221° (*c* 0·6) (Found: C, 74·85; H, 7·5. $C_{17}H_{20}O_3$ requires C, 74·95; H, 7·4%); $\lambda_{max.}$ (in methanol) 281 mμ (ε = 6200); ν (in carbon disulphide) 1690 and 1731 cm.$^{-1}$. The quinoxaline derivative crystallised as white needles (from light petroleum), m. p. 208—209° (Found: C, 79·75; H, 7·0; N, 8·55. $C_{23}H_{24}ON_2$ requires C, 80·2; H, 7·0; N, 8·15%).

trans-1,2,3,4,9,10,11,12-*Octahydro*-1,1,12-*trimethyl*-7-*nitro*-9-*oxophenanthrene* (V; R = $NO_2$).—A mixture of nitric acid (2·51 ml.; 70% w/w) and sulphuric acid (4·2 ml.) was added dropwise to a stirred solution of the ketone (V; R = H) (9·6 g.) in sulphuric acid (10 ml.) maintained at 0°. After being stirred for 10 min. the mixture was poured on ice, and the product crystallised from methanol, forming plates (10·67 g.) of the *nitro-ketone* (V; R = $NO_2$), m. p. 169·5—170°, $[\alpha]_D$ +36° (*c* 1·0) (Found: C, 70·7; H, 7·25; N, 4·95. $C_{17}H_{21}O_3N$ requires C, 71·05; H, 7·35; N, 4·85%); $\lambda_{max.}$ (in methanol) 237 (ε = 25,400), 268 mμ (ε = 10,250).

trans-1,2,3,4,9,10,11,12-*Octahydro*-9-*hydroxy*-1,1,12-*trimethyl*-7-*nitrophenanthrene*.—The

[9] Ohta and Ohmori, *Pharm. Bull. Japan*, 1957, **5**, 96.

nitro-ketone (V; R = $NO_2$) (380 mg.) was reduced with sodium borohydride (100 mg.) in dioxan (10 ml.) for 1 hr. at room temperature. Acetic acid and water were added, and the product was crystallised from aqueous methanol, giving needles (340 mg.) of trans-1,2,3,4,9,10,11,12-*octahydro*-9-*hydroxy*-1,1,12-*trimethyl*-7-*nitrophenanthrene*, m. p. 145—147·5°, $[\alpha]_D$ +115° (*c* 0·8) (Found: C, 70·85; H, 7·7; N, 4·8. $C_{17}H_{23}O_3N$ requires C, 70·55; H, 8·0; N, 4·85%).

9-*Acetoxy*-trans-1,2,3,4,9,10,11,12-*octahydro*-1,1,12-*trimethyl*-7-*nitrophenanthrene*.—The 9-hydroxy-derivative (168 mg.), acetic anhydride (5 ml.), and sodium acetate (200 mg.) were heated under reflux for 3 hr. The product, isolated by precipitation with water, crystallised from methanol as flat prisms (152 mg.) of 9-*acetoxy*-trans-1,2,3,4,9,10,11,12-*octahydro*-1,1,12-*trimethyl*-7-*nitrophenanthrene*, m. p. 104—105·5°, $[\alpha]_D$ +79° (*c* 0·7) (Found: C, 68·65; H, 7·8. $C_{19}H_{25}O_4N$ requires C, 68·85; H, 7·6%).

7-*Amino*-trans-1,2,3,4,9,10,11,12-*octahydro*-1,1,12-*trimethylphenanthrene*.—9-Acetoxy-*trans*-1,2,3,4,9,10,11,12-octahydro-1,1,12-trimethyl-7-nitrophenanthrene (8·14 g.) in ether (50 ml.) was added to liquid ammonia (250 ml.). Lithium (5 g.) was added, the mixture stirred for 10 min., and the excess of lithium destroyed by the addition of ammonium chloride. The product was isolated as the amine hydrochloride (5·3 g.), precipitated from ether by hydrogen chloride. Acetylation gave 7-*acetamido*-trans-1,2,3,4,9,10,11,12-*octahydro*-1,1,12-*trimethylphenanthrene*, crystallising as long prisms, m. p. 151—154°, $[\alpha]_D$ +75° (*c* 1·1), from chloroform–light petroleum (Found: C, 80·35; H, 9·6; N, 5·55. $C_{19}H_{17}ON$ requires C, 79·95; H, 9·55; N, 5·6%).

trans-1,2,3,4,9,10,11,12-*Octahydro*-7-*hydroxy*-1,1,12-*trimethylphenanthrene* (VIII; R = H).—Sodium nitrite (33 mg.) in sulphuric acid (0·25 ml.) was added dropwise to a stirred solution of 7-amino-*trans*-1,2,3,4,9,10,11,12-octahydro-1,1,12-trimethylphenanthrene hydrochloride (128 mg.) in acetic acid (2 ml.) at 0°. After the mixture had been stirred for 30 min., ice (10 g.) was added, and the mixture was poured into a solution of sulphuric acid (20%) and sodium sulphate in water maintained at 120° under reflux. The product was extracted from benzene with Claisen's alkali, adsorbed from petrol on alumina (20 g.) deactivated with 10% of 10% acetic acid, eluted with benzene–light petroleum (2 : 3), and crystallised from light petroleum, giving needles of the *phenol* (VIII; R = H) (44 mg.), m. p. 132—134°, $[\alpha]_D$ +61° (*c* 1·3) (Found: C, 83·05; H, 10·3. $C_{17}H_{24}O$ requires C, 83·55; H, 9·9%).

trans-1,2,3,4,9,10,11,12-*Octahydro*-7-*methoxy*-1,1,12-*trimethylphenanthrene* (VIII; R = Me).—The potassium salt of the above phenol (800 mg.), prepared with molecular potassium in benzene, was methylated with methyl iodide. The product, in light petroleum, was filtered through alumina (50 g.) and crystallised from methanol, forming plates (644 mg.) of the *methyl ether* (VIII; R = Me), m. p. 86—88°, $[\alpha]_D$ +54° (*c* 1·7) (Found: C, 83·45; H, 10·4; OMe, 11·6. $C_{18}H_{26}O$ requires C, 83·65; H, 10·15; OMe, 12·0%).

trans-1,2,3,4,9,10,11,12-*Octahydro*-7-*hydroxy*-1,1,12-*trimethyl*-6,8-*dinitrophenanthrene* (IX).—Nitric acid (0·0087 ml.; 70% w/w) was added to a solution of *trans*-1,2,3,4,9,10,11,12-octahydro-7-hydroxy-1,1,12-trimethylphenanthrene (23 mg.) in acetic anhydride (2 ml.) at room temperature. The mixture was heated to 70° for 10 min. and then poured into water, and the product filtered off. Adsorption on alumina (5 g.) deactivated with 10% of 10% acetic acid, followed by elution with benzene gave the *dinitro-compound* (IX) (6 mg.) as yellow needles, m. p. 110—112°, from aqueous methanol (Found: C, 61·05; H, 6·7; N, 8·3. $C_{17}H_{22}O_5N_2$ requires C, 61·05; H, 6·65; N, 8·4%).

trans-1,2,3,4,9,10,11,12-*Octahydro*-6-*hydroxy*-1,1,12-*trimethyl*-9-*oxophenanthrene* (X).—*trans*-1,2,3,4,9,10,11,12-Octahydro-6-hydroxy-1,1,12-trimethylphenanthrene (115 mg.) was heated under reflux with sodium acetate (200 mg.) and acetic anhydride (5 ml.) for 1 hr. The crude product, in acetic acid (10 ml.), was treated with chromium trioxide (60 mg.) at 70—75° for 10 min. Extraction with light petroleum, washing with sodium hydrogen carbonate solution, and adsorption on alumina (20 g.) followed by elution with ether gave the crude ketone (X). This was purified by chromatography on alumina deactivated with 5% of 10% acetic acid, the product being obtained as needles (24 mg.), m. p. 217—219°, $[\alpha]_D$ +28° (*c* 1·0), from aqueous methanol (Found: C, 78·65; H, 8·65. $C_{17}H_{22}O_2$ requires C, 79·05; H, 8·6%); $\lambda_{max.}$ (in methanol) 230 ($\varepsilon$ = 11,550) and 286 m$\mu$ ($\varepsilon$ = 12,950). Nimbiol has $\lambda_{max.}$ 231 and 286 m$\mu$ ($\varepsilon$ = 11,800 and 11,500). The *dinitrophenylhydrazone* of our product formed needles, m. p. 266—268°, from methanol (Found: C, 63·25; H, 5·75. $C_{23}H_{26}O_5N_4$ requires C, 63·0; H, 6·0%); $\lambda_{max.}$ (in methanol): 400 m$\mu$ ($\varepsilon$ = 23,000).

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