Synthetic Studies on Terpenoids. Part 21.† Synthesis of a Few Perhydro-phenanthrene Derivatives related to Cheilanthatriol and its Degradation Products [1]

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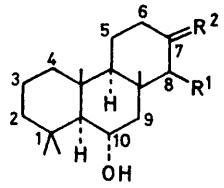
Stereospecific syntheses of 10α-hydroxy-1,1,4aβ,8aβ-tetramethyl-*trans-transoid-trans*-2,3,4,4a,4b,5,7,8,8a,9,-10,10a-dodecahydrophenanthren-6(1*H*)-one (9) and 1,1,4aβ,8aβ-tetramethyl-8β-(3-methylpentanoyl)-2,3,4,4a,-4b,5,7,8,8a,9-decahydrophenanthren-6(1*H*)-one (15), potential intermediates for cheilanthatriol, are described. A few related transformations examined during these studies are discussed.

CHEILANTHATRIOL (1) [2] represents one of the four structural types of tricarbocyclic sesterterpenes, the other three being represented by gascardic acid,[3] ophiobolins [4] and ceroplastols,[5] and heliocide.[6] Recently synthetic studies on sesterterpenes have assumed considerable interest, and the synthesis of the tricyclic framework of ophiobolins has been reported from this [7a] and other laboratories.[7b] We describe here the results of our synthetic studies on cheilanthatriol and its degradation products (2) and (3), culminating in the stereospecific syntheses of (9) and (15) with the desired stereochemistry at each of the five asymmetric centres, along with a few attempts at modifications of ring c with a view to incorporating the remaining functional groups.

The tricyclic ketone (4) [8] was subjected to Wolff–Kishner reduction [9] and the resulting hydrocarbon (5) transformed to the αβ-unsaturated ketone (6) by controlled allylic oxidation with sodium dichromate in acetic acid.[10] Oxidation at the alternative C-9 allylic position is ruled out on steric grounds. The structure of (6) also follows from subsequent investigations, particularly bromination and removal of hydrogen bromide (see later). The unsaturated ketone (6) was obtained in only moderate yield (45%) and was separated from the unchanged hydrocarbon by chromatography. The unsaturated ketone (6) was reduced with lithium in liquid ammonia and the crude product treated with Jones reagent to afford in high yield (7), where the *anti-trans* geometry follows from the mechanistic course of liquid ammonia reduction. It must be mentioned that in one of these experiments, when a slight excess of methanol was used to decompose excess of the Jones reagent, the dimethylacetal (8) was obtained as a by-product. The structure was established from its n.m.r. spectrum which showed two singlets centred at δ 3.1 and 3.19 due to the methoxy protons. This also could be readily converted to (7) on treatment with dilute acids.

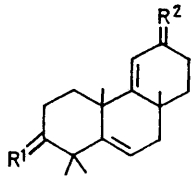
Three of the asymmetric centres at C-4a, -4b, and -8a being well defined, we next turned our attention to incorporate the crucial 10α-hydroxy-function. It was anticipated that the three axially oriented methyl groups would dictate *cis* addition of water from the less hindered α-side, in a hydroboration reaction. After protection of the ketone as the ethylene acetal, the unsaturated ketone (7) was subjected to hydroboration, when, after removal of the protecting group, the alcohol (9) was obtained,



(1) $R^1 = \beta\text{-}[CH_2]_2CMe{=}CH{\cdot}CH_2OH$, $R^2 = \langle^{Me}_{OH}$

(2) $R^1 = \beta\text{-}[CH_2]_2CHMe{\cdot}CH_2Me$, $R^2 = \langle^{Me}_{H}$

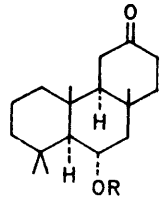
(3) $R^1 = \beta\text{-}[CH_2]_2CHMe{\cdot}CH_2Me$, $R^2 = O$



(4) $R^1 = O$, $R^2 = H_2$

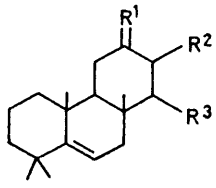
(5) $R^1 = R^2 = H_2$

(6) $R^1 = H_2$, $R^2 = O$



(9) $R^1 = H$

(10) $R^1 = COMe$



(7) $R^1 = O$, $R^2 = R^3 = H$

(8) $R^1 = \langle^{OMe}_{OMe}$, $R^2 = R^3 = H$

(11) $R^1 = O$, $\Delta^{7,8}$ $R^2 = R^3 = H$

(12) $R^1 = R^2 = O$, $R^3 = H$

(13) $R^1 = \langle^{S}_{S}\rangle$, $R^2 = O$, $R^3 = H$

(14) $R^1 = O$, $R^2 = H$, $R^3 = \alpha\text{-}CN$

(15) $R^1 = O$, $R^2 = H$, $R^3 = \beta\text{-}CO{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2Me$

(16) $R^1 = O$, $R^2 = H$, $R^3 = \beta\text{-}CN$

† Part 20, S. Chatterjee, A. Sarkar, and P. C. Dutton, *J.C.S. Perkin I*, 1979, 2914.

albeit in very low yield along with a considerable amount of the ketone (7). The low yield was evidently due to the highly hindred nature of the double bond. The keto-alcohol (9) was converted to the corresponding acetate (10), the n.m.r. spectrum affording evidence of an equatorial acetoxy-group. The C-10 hydrogen appears as a triplet of doublets centred at δ 5.31 (J_1 11, J_2 4.5 Hz), a splitting pattern characteristic of 6α-hydroxy-steroids, arising out of two diaxial and one axial equatorial proton–proton coupling.[11] In the keto-acetate (10), the stereochemistry of the five contiguous asymmetric centres, as found in rings A and B of cheilanthatriol, has thus been fully established.

In view of the poor yield associated with hydroboration, the functionalisation of ring C was left until later in the synthesis. Hence, subsequent experiments centring round ring C were carried out on the unsaturated ketone (7). With a view to introducing a suitable functional group at C-8, (7) was brominated with pyrrolidone hydrotribromide,[12] a specific reagent for bromination at the α position to a carbonyl function in the presence of an olefinic linkage. The bromo-ketone was dehydrobrominated in hexamethylphosphoramide [13] to afford the αβ-unsaturated ketone (11) in satisfactory yield. It must be mentioned here that formation of (11) affords additional evidence for the structure of the allylic oxidation product (6). For the introduction of the six-carbon chain at C-8, copper-catalysed conjugate addition of the corresponding alkyl residue to (11) was considered viable. Although an undesirable axial orientation of the incoming group was a possibility from stereoelectronic considerations, it was thought probable that the bulky nature of the alkyl group would lead to formation of a fair amount of the desired equatorial isomer. However, experiments to carry out the conjugate addition met with little success, evidently due to steric reasons.

Next, the unsaturated ketone (11) was epoxidised under alkaline conditions [14] and the mixture of epoxides subjected to cleavage with methanolic alkali.[15] Hydrolysis of the resulting crude enol ether furnished the diketone (12) in low yield. Attempts were made to alkylate at C-8 with a C_6-chain through the monothioacetal (13) so that the stereochemistry could be modified utilising the C-7 carbonyl group. Because of the greater relative accessibility of the C-6 carbonyl function in the diketone (12), structure (13) has been tentatively assigned to the monothioacetal. As the alkylation did not proceed, further studies on (13) have not been undertaken.

Conjugate addition of potassium cyanide to the ketone (11) in hexamethylphosphoramide [16] proceeded smoothly to furnish the ketonitrile (14) in good yield, stereoelectronic considerations suggesting the axial orientation [17] of the cyano-group. This was converted to the ethylenedioxy derivative and treated with 2-methylbutyl-lithium. The resulting crude product was directly subjected to Wolff–Kishner reduction [9] with a view to reducing the intermediate imine. The resulting product was treated with acid to remove the ethylenedioxy-group and purified by extensive chromatography. Benzene–light petroleum afforded the diketone (15) in poor yield. This was formed by simple hydrolysis of the intermediate imine and failed to undergo reduction under the experimental conditions, evidently again due to steric reasons. The orientation of the side chain in the diketone will be equatorial. Subsequent elution of the column with benzene afforded a small amount of a crystalline material and this has been identified as the ketonitrile (16) which has a different melting point from (14). This observation reveals that epimerisation had taken place during the Wolff–Kishner reduction process and that the cyano group had not undergone hydrolysis. Evidently this indirectly supports the assigned equatorial stereochemistry of the C_6-chain in the diketone (15).

EXPERIMENTAL

M.p.s were measured for samples in open capillary tubes using a sulphuric acid-bath. U.v. spectra were recorded with a Beckman DU spectrophotometer for solutions in 95% ethanol. I.r. spectra were taken with a Perkin–Elmer 21 instrument. N.m.r. spectra were measured for solutions in carbon tetrachloride using a Varian T-60 spectrometer, with tetramethylsilane as internal standard. T.l.c. plates were coated (0.2 mm thickness) with silica gel G (200 mesh). Mass spectra were measured with a Hitachi RM-60 spectrometer. Light petroleum refers, unless stated otherwise, to the fraction of b.p. 60—80 °C.

1,1,4aβ,8aβ-*Tetramethyl*-1,2,3,4,4a,6,7,8,8a,9-*decahydrophenanthrene* (5).—A mixture of the ketone (4) (6 g), hydrazine hydrate (70 ml; 95—100%), hydrazine dihydrochloride (19.5 g), and diethylene glycol (280 ml) was heated to 130 °C under nitrogen in a metal bath and maintained at this temperature for 2 h. It was then cooled, potassium hydroxide (25 g) was added, and the temperature raised to 210 °C by distilling off low-boiling materials. The mixture was maintained at this temperature for 2 h then cooled, poured into ice-cold water, and filtered through Supercel. The filtrate was extracted with ether. The extract was washed with cold 2N-hydrochloric acid and water and dried (Na_2SO_4). The hydrocarbon (5) was obtained as an *oil* (4.3 g), b.p. 115 °C at 0.2 mmHg, δ 5.48 (2 H, overlapping t), 1.35 (3 H, s), and 1.15 (6 H, s) (Found: C, 88.6; H, 11.4. $C_{18}H_{28}$ requires C, 88.4; H, 11.5%).

1,1,4aβ,8aβ-*Tetramethyl*-2,3,4,4a,7,8,8a,9-*octahydrophenanthren*-6(1H)-*one* (6).—The hydrocarbon (5) (3 g) was mixed with sodium dichromate (4.5 g), acetic acid (45 ml), and acetic anhydride (3 ml) and the mixture stirred magnetically at room temperature overnight. It was then warmed to 45 °C and kept at this temperature for 3 h. Ethanol (4 ml) was added and the mixture poured into water (120 ml), neutralised with solid sodium carbonate, and extracted with ether. The extract was washed with water and dried over sodium sulphate, and the oil obtained after removal of the ether was chromatographed over alumina (90 g). On elution with light petroleum, unchanged hydrocarbon (1.5 g) was recovered. The fraction eluted with light petroleum–benzene (4 : 1) yielded the αβ-*unsaturated ketone* (6) (1.35 g) as a viscous oil which solidified on scratching, m.p. 55—56° [from light petroleum (b.p. 40—60°)], $\nu_{max.}$ 1 680 and 1 610 cm^{-1}, $\lambda_{max.}$ 240 nm (ε 13 170), δ 5.98 (1 H, t), 1.44 (3 H, s), 1.37 (3 H, s), and 1.13 (3 H, s) (Found: C, 83.5; H, 10.1. $C_{18}H_{26}O$ requires C, 83.6; H, 10.1%). The 2,4-*dinitrophenylhydrazone* had m.p. 190—

191° (from benzene–methanol) (Found: C, 65.8; H, 6.9. $C_{24}H_{30}N_4O_4$ requires C, 65.7; H, 6.9%).

1,1,4aβ,8aβ-*Tetramethyl*-2,3,4,4a,4b,5,7,8,8a,9-*decahydrophenanthren*-6(1H)-*one* (7).—The unsaturated ketone (6) (1.3 g) dissolved in ether was added to a stirred solution of lithium (350 mg) in liquid ammonia. After 10 min it was decomposed by adding solid ammonium chloride. Ammonia was allowed to evaporate off and the residue was diluted with water and extracted with ether. The extract was washed with water, dried over sodium sulphate, and the solvent removed to afford a solid which was treated with Jones reagent in the usual way. Finally it afforded the *ketone* (7) (920 mg), m.p. 86—87° [from light petroleum (b.p. 40—60°)], δ 5.5 (1 H, s), 1.15 (6 H, s), 1.12 (3 H, s), and 1.08 (3 H, s) (Found: C, 82.7; H, 10.6. $C_{18}H_{28}O$ requires C, 73.0; H, 10.8%). The 2,4-*dinitrophenylhydrazone* had m.p. 176—177° (from benzene–methanol).

In one experiment a slight excess of methanol was inadvertently added to decompose excess of the Jones reagent. Work-up and chromatography gave the *acetal* (8) (200 mg) as a first fraction on elution with light petroleum, m.p. 115—116° (from light petroleum), δ 5.42 (1 H, t), 3.19 (3 H, s), 3.1 (3 H, s), 1.31 (3 H, s), 1.1 (3 H, s), 1.02 (3 H, s), and 0.91 (3 H, s), *m/e* 306 (M^+) (Found: C, 78.4; H, 11.0. $C_{20}H_{34}O_2$ requires C, 78.3; H, 11.1%). Heating the acetal (8) with acetic acid (90%) for 1 h on a steam-bath followed by work-up afforded the ketone (7).

10α-*Hydroxy*-1,1,4aβ,8aβ-*tetramethyl*-2,3,4,4a,4b,5,7,8,8a,-9,10,10a-*dodecahydrophenanthren*-6(1H)-*one* (9).—From a mixture of the unsaturated ketone (7) (1 g), ethylene glycol (8 ml), benzene (50 ml), and toluene-*p*-sulphonic acid (70 mg), benzene was distilled off at a very slow rate over 5 h, fresh benzene being added at regular intervals to maintain the initial volume. The product was cooled and the benzene solution washed successively with water, sodium hydrogen carbonate solution (10%), and water. Removal of solvent afforded the acetal (1.2 g) which was used directly in the next step. Diborane, generated by adding sodium borohydride (2 g) in small portions to a stirred mixture of diglyme (40 ml) and boron trifluoride–ether (10 ml) at 45 °C (water-bath), was directly admitted into a solution of the above acetal (600 mg) in tetrahydrofuran (25 ml) at 10—15 °C. The reaction was continued for 5 h. The mixture was cooled. Sodium hydroxide solution (10 ml; 10%) was added followed by hydrogen peroxide (10 ml; 30%) and the suspension so obtained was heated under reflux for 1 h, whereupon two layers separated. The cooled mixture was diluted with ether and the aqueous portion further extracted with ether. The combined extract was washed with water and dried over sodium sulphate. The residue after removal of ether was heated for 1 h with acetic acid (90%) on a steam-bath. Work-up afforded a residue which was chromatographed over alumina (15 g). Elution with light petroleum afforded the unsaturated ketone (7) (350 mg) and subsequently with benzene and ether (9 : 1) yielded the *hydroxy-ketone* (9) (70 mg), m.p. 155—156° (Found: C, 77.8; H, 10.8. $C_{18}H_{30}O_2$ requires C, 77.6; H, 10.8%).

10α-*Acetoxy*-1,1,4aβ,8aβ-*tetramethyl*-2,3,4,4a,4b,5,7,8,8a,-9,10,10a-*dodecahydrophenanthren*-6(1H)-*one* (10).—Overnight treatment of the hydroxy-ketone (9) (50 mg) with a mixture of acetic anhydride (2 ml), pyridine (4 ml), acetyl chloride (0.5 ml), and ether (20 ml) followed by usual work-up afforded the *acetoxy-ketone* (10) after chromatographic purification through alumina, m.p. 110° (from light petroleum), δ 5.31 (1 H, t of d, J_1 11, J_2 4.5 Hz), 2.02 (3 H, s), 1.24 (3 H, s), 1.03 (3 H, s), 0.95 (3 H, s), and 0.88 (3 H, s) (Found: C, 75.0; H, 10.2. $C_{20}H_{32}O_3$ requires C, 74.9; H, 10.06%).

1,1,4aβ,8aβ-*Tetramethyl*-2,3,4,4a,4b,5,8a,9-*octahydrophenanthren*-6(1H)-*one* (11).—Pyrrolidone hydrotribromide (990 mg) in tetrahydrofuran (3 ml) was added dropwise in the dark to a solution of the unsaturated ketone (7) (520 mg) in tetrahydrofuran (3 ml) containing pyrrolidone (0.08 g). After addition was complete the reaction mixture was set aside for 15 min and then filtered to remove a white solid. Removal of the solvent from the filtrate afforded the crude bromo-ketone as a pale yellow solid. This was mixed with freshly distilled hexamethylphosphoramide (5 ml) and heated in an oil-bath maintained at 130—135 °C for 4 h under nitrogen. The product was cooled, diluted with water, and extracted with ether. The extract was washed with water and dried over sodium sulphate. The solvent was removed and the residue chromatographed over alumina (15 g). Elution with light petroleum afforded the αβ-*unsaturated ketone* (11) (280 mg), m.p. 110—111° (from light petroleum), $\lambda_{max.}$ (224 nm ε 11 910) (Found: C, 83.8; H, 10.1. $C_{18}H_{26}O$ requires C, 83.6; H, 10.1%).

1,1,4aβ,8aβ-*Tetramethyl*-1,2,3,4,4a,4b,5,8,8a,9-*decahydrophenanthrene*-6,7-*dione* (12).—A stirred solution of the unsaturated ketone (11) (450 mg) in methanol (15 ml) was treated simultaneously with hydrogen peroxide (3 ml; 30%) and sodium hydroxide solution (1 ml; 10%), each added dropwise. After stirring for 1 h at 0 °C, the reaction mixture was kept overnight at 5 °C. It was then diluted with water and extracted with ether. The solid mixture of epoxides obtained on removal of the ether was heated under reflux for 18 h with methanol (30 ml) and sodium hydroxide solution (5 ml; 4N). Removal of the solvent and isolation with ether afforded a gummy residue which was hydrolysed with 2N-hydrochloric acid. The isolated product was chromatographed over silica gel (20 g). Elution with benzene afforded the *diketone* (12) (130 mg) as a viscous product, solidifying on careful trituration with light petroleum, m.p. 110—111° (from benzene–light petroleum), $\nu_{max.}$ 1 710 and 1 670 cm^{-1} (Found: C, 78.7; H, 9.4. $C_{18}H_{26}O_2$ requires C, 78.7; H, 9.5%).

8α-*Cyano*-1,1,4aα,8aβ-*tetramethyl*-2,3,4,4a,4b,5,7,8,8a,9-*decahydrophenanthren*-6(1H)-*one* (14).—To a stirred solution of the unsaturated ketone (11) (100 mg) in hexamethylphosphoramide (6 ml) was added at room temperature sodium cyanide (31 mg) dissolved in a few drops of water. Stirring was continued for 2 h and then the mixture was diluted with water. Any alkaline material was destroyed through treatment with 6N-hydrochloric acid in the cold. The mixture was extracted with ether and the extract washed with water and dried. After removal of the solvent the residue was chromatographed over acidic alumina (3 g). Elution with benzene afforded the crystalline *nitrile* (14) (85 mg), m.p. 180° (from benzene–light petroleum), $\nu_{max.}$ 2 240 and 1 720 cm^{-1} (Found: C, 79.8; H, 9.5. $C_{19}H_{27}ON$ requires C, 79.9; H, 9.5%).

1,1,4aβ,8aβ-*Tetramethyl*-8β-(3-*methylpentanoyl*)-2,3,4,4a,-4b,5,7,8,8a,9-*decahydrophenanthren*-6(1H)-*one* (15).—From a mixture of the ketonitrile (14) (250 mg), ethylene glycol (2 ml), benzene (30 ml), and toluene-*p*-sulphonic acid (20 mg), benzene was distilled off at a very slow rate over 5 h, fresh benzene being added at regular intervals to maintain the initial volume. The product was cooled and the benzene solution washed with water, sodium hydrogen carbonate solution (10%), and more water. On removal of

the benzene the ethylenedioxy-derivative was obtained which was directly used in the next step. 2-Methylbutyl bromide (1 g) in ether (10 ml) was added dropwise to lithium pieces (10 mg) in ether (20 ml) under nitrogen at −10 °C. Stirring was continued for a number of hours and finally for ½ h at room temperature. The mixture was cooled to 0 °C and a solution of the above ketonitrile in ether (10 ml) was added dropwise. The reaction mixture was stirred for 3 h at 0 °C and 1 h at room temperature. It was decomposed with a mixture of saturated ammonium chloride solution and ammonia and extracted with ether. The product obtained on removal of the ether was mixed with hydrazine hydrate (3 ml), hydrazine dihydrochloride (100 mg) (care was taken to see that the resulting mixture was alkaline), and diethylene glycol (20 ml). It was heated to 130 °C under nitrogen in a metal-bath and maintained at this temperature for 2 h. It was then cooled, potassium hydroxide (15 g) added, and the temperature raised to 210 °C by distilling off low boiling materials and kept at this temperature for 2 h. The product was cooled, poured into water (60 ml), and extracted with ether. The extract was washed with water and dried over sodium sulphate. The residue after removal of the ether was dissolved in acetic acid (5 ml; 80%) heated on a steam-bath for 1 h and the mixture neutralised with sodium carbonate and extracted with ether. The gummy residue left after removal of the ether was chromatographed over neutral alumina (10 g). Elution with benzene–petroleum (1 : 4) afforded a small amount of the crystalline diketone (15) (30 mg), m.p. 186—187° (from benzene–light petroleum), $\nu_{max.}$ 1 720 cm^{-1} (Found: C, 80.6; H, 10.3. $C_{24}H_{38}O_2$ requires C, 80.3; H, 10.6%). Continued elution of the column with benzene afforded another crystalline solid, identified as the *keto-β-nitrile* (16) (85 mg), m.p. 161—163° (from benzene–light petroleum) (Found: C, 79.7; H, 9.4%), mixed m.p. with the keto-α-nitrile (14), 145—147°.

We thank Dr. Nitya Nand, Central Drug Research Institute, Lucknow, for mass and n.m.r. spectral data, Mrs. C. Dutta for microanalyses, Mr. A. Ghosal for u.v. spectra, and the N.I.H. (U.S.A.) for financial assistance. Thanks are also due to Professor U. R. Ghatak for his kind interest.

[8/1627 *Received*, 12*th September*, 1978]

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