## 102. *The Diterpenes of* Xylia dolabriformis.

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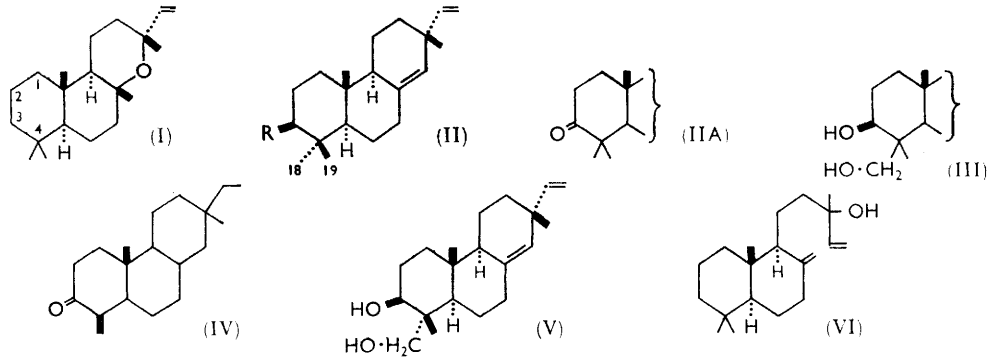
The isolation of the heartwood constituents manoyl oxide, 3-oxomanoyl oxide, sandaracopimaradiene, and sandaracopimaradien-3-one, -3β-ol, and -3β,18-diol * from *Xylia dolabriformis*, and their characterisation, are described.

Pyinkado is an extremely hard, durable timber derived from the tree *Xylia dolabriformis* which grows in association with teak in Burma and parts of India. The present investigation of its extractives was initiated because some samples exuded a petroleum-soluble gum which sometimes crystallised. Extraction of pyinkado sawdust by light petroleum afforded, in 4—8% yield, an oil which was separated by chromatography on alumina into six diterpenes and β-sitosterol. All the diterpenes had infrared absorption bands at or near 3040, 1625, 990, and 910 cm.$^{-1}$ characteristic of a vinyl group, and none showed any ultra violet absorption, indicating the absence of a conjugated system.

The earliest fractions afforded the two known compounds, manoyl oxide [1,2] (I) and sandaracopimaradiene [3] † (II; R = H), both identified by comparison with authentic samples. Manoyl oxide gave a crystalline dihydro-derivative,[4] but sandaracopimaradiene yielded only syrups on hydrogenation, though the related alcohols (see below) gave crystalline di- and tetra-hydro-derivatives. On treatment with hydrogen chloride in chloroform sandaracopimaradiene was isomerised to the $\Delta^{8(9)}$-isomer.[5,6] Sandaracopimaradiene has hitherto been obtained from sandaracopimaric acid, and its racemate has been synthesised,[3] but this is its first isolation from a natural source.




One of the remaining four diterpenes was shown to be 3-oxomanoyl oxide. The carbonyl group, evident from an infrared band at 1695 cm.$^{-1}$ and from 2,4-dinitrophenylhydrazone formation, was converted into methylene by Wolff–Kishner reduction, which yielded manoyl oxide. The compound was different from the known 2-oxomanoyl oxide [7,8] which occurs in *Dacrydium colensoi*, and a 3-oxo-substituent was favoured by the result of a recent nuclear magnetic resonance study [2] and a positive Zimmermann reaction.[9] Reduction of the ketone by potassium borohydride, followed by

* The numbering system of Briggs *et al.* (*J.*, 1962, 1840) is used.

† The authors are indebted to Professor L. H. Briggs for suggesting the identity of this compound.

[1] Hosking and Brandt, *Ber.*, 1935, **68**, 37; Hodges and Reed, *Tetrahedron*, 1960, **10**, 71.
[2] Wenkert and Beak, *Chem. and Ind.*, 1961, 1574.
[3] Ireland and Schiess, *Tetrahedron Letters*, 1960, No. 25, 37.
[4] Hosking and Brandt, *Ber.*, 1934, **67**, 1173.
[5] Church and Ireland, *Tetrahedron Letters*, 1961, No. 14, 493.
[6] Dr. R. E. Ireland, personal communication.
[7] Hosking and Brandt, *Ber.*, 1935, **68**, 286; Grant and Hodges, *Chem. and Ind.*, 1960, 1300.
[8] Grant, *J.*, 1959, 860.
[9] Barton and de Mayo, *J.*, 1954, 887.

hydrogenation, afforded dihydro-3β-hydroxymanoyl oxide, with an equatorial hydroxyl group. This compound on dehydration with phosphorus pentachloride gave a product whose ozonolysis yielded acetone and a syrup with an infrared band at 1735 cm.$^{-1}$, characteristic of a carbonyl group in a five-membered ring. Retropinacol rearrangement [10,11] must therefore have occurred at the dehydration stage, which establishes that the oxygen in the ketone and the derived alcohol is in the 3-position. Finally, mild hydrogenation of the ketone gave dihydro-3-oxomanoyl oxide, identical with a sample synthesised by Hodges.[10]

The other three diterpenes were shown to be the 3-oxo-, 3β-hydroxy-, and 3β,18-dihydroxy-derivatives of sandaracopimaradiene, and each was characterised by infrared spectra and the formation of derivatives. Wolff–Kishner reduction of the ketone gave sandaracopimaradiene, and borohydride reduction afforded the 3β-hydroxy-compound. Conversely this alcohol was oxidised to the ketone by chromic acid–pyridine. The ketone gave a positive Zimmermann reaction and confirmation that the carbonyl group was at the 3-position was obtained by reaction of phosphorus pentachloride with the tetrahydro-derivative of the alcohol, which underwent retropinacol rearrangement. Ozonolysis of the product afforded acetone and a syrup with infrared absorption at 1735 cm.$^{-1}$, thus establishing that the naturally occurring ketone is sandaracopimaradien-3-one (IIA). This rearrangement also confirms the equatorial disposition of the hydroxyl group [12] in the alcohol, which is implicit in its preparation by borohydride reduction of the ketone. The alcohol, therefore, is sandaracopimaradien-3β-ol (II; R = OH).

In an attempt to derive the parent hydrocarbon of the diol, the compound was oxidised by chromic acid–pyridine, and the syrupy product was subjected to Wolff–Kishner reduction. Unexpectedly the product obtained was sandaracopimaradien-3β-ol (25% yield), which established the position of one of the hydroxyl groups in the diol. Attempts to isolate the intermediate aldehydo-alcohol were unsuccessful, the only crystalline product obtained being a norketone, $C_{19}H_{28}O$, in 12% yield; similarly the tetrahydro-diol gave a crystalline tetrahydro-norketone, $C_{19}H_{32}O$. The formation of these norketones suggests that the second hydroxyl group of the diol is on one of the *gem*-methyl groups at position 4. This was confirmed by the ability of the diol to form an isopropylidene derivative, but failure to react with periodate. Finally the tetrahydro-diol, when heated with copper bronze, gave formaldehyde and the same $C_{19}$ ketone that was obtained by chromic acid oxidation, a degradation characteristic of partial structure (III).[13] The tetrahydro-norketone is assigned structure (IV) by analogy with the same reaction in the triterpene series.

The above results do not define the stereochemistry at position 4, as models show that an isopropylidene derivative should be formed readily between the 3β-OH and the $-CH_2{\cdot}OH$ group, irrespective of whether the latter is in the 18(equatorial)- or 19(axial)-position. To elucidate the stereochemistry the diol was partially acetylated and the resulting mixture was separated by fractional crystallisation into the two monoacetates. The identity of each was established by chromic acid–pyridine oxidation followed by Wolff–Kishner reduction. In this way 3β-acetoxysandaracopimaradien-18(19)-ol gave sandaracopimaradien-3β-ol *via* the crystalline 3β-acetoxy-18(19)-aldehyde intermediate. On the other hand, 18(19)-acetoxysandaracopimaradien-3β-ol gave a crystalline 18(19)-acetoxy-3-oxo-intermediate, the latter being converted under the strongly alkaline conditions of the reduction into a hydrocarbon $C_{19}H_{30}$, which was also obtained by Wolff–Kishner reduction of the norketone $C_{19}H_{28}O$ described above. The relative instability of the 18(19)-hydroxy-3-oxo-compound, compared with the 3-hydroxy-18(19)-aldehyde compound, suggests that the former is the intermediate in the pyrolysis of the diol, and not the latter as suggested

[10] Hodges, *Tetrahedron*, 1961, **12**, 215.
[11] Ruzicka, Montavon, and Jeger, *Helv. Chim. Acta*, 1948, **31**, 818.
[12] Barton, *Experientia*, 1950, **6**, 316.
[13] Tsuda and Kitagawa, *Ber.*, 1938, **71**, 1604.

by Tsuda and Kitagawa.[13] This result is in accordance with the alkali-instability of icterogenin,[9] methyl hederagonate,[9] and 3-oxo-18-iso(α)arjunolic lactone diacetate.[14] The formyl-acetate showed a peak at τ 0·82 in its nuclear magnetic resonance spectrum due to the aldehydic C–H resonance, which is unusually high. It appears, however, that this value is sterically significant as it has been shown [15] that the resonances for the equatorial aldehydes methyl dehydroisopropylidenebassate (τ 1·04) and vinhatical (τ 0·77) are higher than those for the axial aldehydes vouacapenal (τ 0·23) and *O*-methylpodocarpinal [16] (τ 0·33). Though the number of examples is small, the difference in τ value is large enough for a conclusion that the formyl-acetate contains an equatorial aldehyde group. Consequently the diol from which it was derived must be sandaracopimaradiene-3β,18-diol (V).

It is interesting to note that the co-occurring compounds of the manoyl oxide and sandaracopimaradiene series have the same stereochemistry at all asymmetric centres common to both molecules. This is in accord with present biogenetic theory [17] which postulates structure (VI) as one of the intermediates in the formation of diterpenic structures.

In addition to the compounds described above, another unidentified diterpene $C_{20}H_{30}O_2$ was obtained in low yield.

*Note on the Retropinacol Rearrangement.*—Early attempts to carry out the retropinacol rearrangement on the 3β-hydroxy-compounds described above were repeatedly unsuccessful. The reaction was effected by using phosphorus pentachloride in light petroleum, and the product was isolated by passing the filtered reaction mixture through a column of alumina. In no case did the eluted product yield acetone on ozonolysis and the product showed infrared carbonyl absorption at 1700 cm.$^{-1}$. When the product from the phosphorus pentachloride reaction was purified by shaking it with aqueous sodium hydroxide instead of using an alumina column, the syrup obtained gave the desired products (acetone and a syrup with an infrared band at 1735 cm.$^{-1}$) on ozonolysis. The earlier failures must be attributed to a further rearrangement of the exocyclic double bond to an endocyclic position, presumably under the catalytic action of the alumina though in addition a longer reaction time (30 min.) was used. Even under the later conditions the infrared peak at 1700 cm.$^{-1}$ was not entirely absent.

## Experimental

Unless otherwise stated specific rotations were measured for chloroform solutions at room temperature. Light petroleum used had b. p. 40—60°.

*Components of* Xylia dolabriformis.—Heartwood sawdust (2·3 kg.) was extracted by light petroleum (Soxhlet) for 20 hr. Evaporation of the solvent afforded a yellow syrup (92 g.) which was chromatographed on alumina in light petroleum. Elution by light petroleum afforded three crystalline fractions. The first, recrystallised from methanol, gave sandaracopimaradiene (0·24 g.), m. p. 39—39·5°, $[\alpha]_D$ −12·4° (*c* 5) (Found: C, 88·2; H, 11·9. Calc. for $C_{20}H_{32}$: C, 88·1; H, 11·9%). The m. p. was undepressed by an authentic sample,[3] m. p. 40·5—41°, $[\alpha]_D$ −12°, and the compounds had identical infrared spectra. The second fraction, recrystallised from methanol, afforded manoyl oxide (0·72 g.), m. p. 26·5—27°, $[\alpha]_D$ +21° (*c* 1), +18° (*c* 1 in ethanol) (Found: C, 82·7; H, 11·8. Calc. for $C_{20}H_{34}O$: C, 82·7; H, 11·8%), identified, as above, with an authentic sample, m. p. 25·5—26·5°. The third fraction recrystallised from aqueous methanol as leaflets of *sandaracopimaradien*-3-*one* (8·3 g.), m. p. 54—55°. Repeated recrystallisation from small volumes of methanol gave a sample having m. p. 59—60°, $[\alpha]_D$ −56° (*c* 2) (Found: C, 84·2; H, 10·6. $C_{20}H_{30}O$ requires C, 83·9; H, 10·6%), $\nu_{max.}$ 1700 cm.$^{-1}$. The compound gave a deep purple colour in the Zimmermann test [9] and a 2,4-*dinitrophenylhydrazone*,

[14] King, King, and Ross, *J.*, 1954, 3995.
[15] King and Yardley, *J.*, 1961, 4308.
[16] Dr. T. J. King, personal communication.
[17] Barltrop and Rogers, " Progress in Organic Chemistry," Butterworths Scientific Publns., London, 1961, Vol. V, p. 96.

m. p. 176·5—177° (Found: C, 67·0; H, 7·45; N, 11·7. $C_{26}H_{34}N_4O_4$ requires C, 66·9; H, 7·35; N, 12·0%), $\lambda_{max.}$ 368—369 mμ (ε 12,600).

Elution by benzene–light petroleum, benzene, and ether successively afforded three further crystalline fractions. The first recrystallised from aqueous methanol, to give needles of 3-*oxomanoyl oxide* (3·4 g.), m. p. 99—99·5°, $[\alpha]_D$ +54° (*c* 5) (Found: C, 79·3; H, 10·5. $C_{20}H_{32}O_2$ requires C, 78·9; H, 10·6%), $\nu_{max.}$ 1700 cm.$^{-1}$, giving a deep purple colour in the Zimmermann test and a 2,4-*dinitrophenylhydrazone*, m. p. 178·5° (Found: C, 64·3; H, 7·75; N, 11·5. $C_{26}H_{36}N_4O_5$ requires C, 64·4; H, 7·5; N, 11·6%), $\lambda_{max.}$ 367—369 mμ (ε 15,700). The compound next eluted, recrystallised several times from aqueous methanol, was a flocculent mass of needles of *sandaracopimaradien*-3β-*ol*, m. p. 126·5—127·5°, $[\alpha]_D$ −19·5° (*c* 5) (Found: C, 83·2; H, 10·9. $C_{20}H_{32}O$ requires C, 83·3; H, 11·2%), $\nu_{max.}$ 3610 (sharp) and 3450 (broad) cm.$^{-1}$. The *acetate*, m. p. 102—104·5°, $[\alpha]_D$ +4° (*c* 3) (Found: C, 80·2; H, 10·2. $C_{22}H_{34}O_2$ requires C, 80·0; H, 10·4%), was recrystallised from methanol. The third compound eluted, recrystallised from methanol as needles of β-sitosterol (0·25 g.), m. p. and mixed m. p. 136—137°, $[\alpha]_D$ −33·7° (*c* 3).

Elution of the column with methanol gave a single crystalline fraction which recrystallised from light petroleum (b. p. 80—100°) as blades of *sandaracopimaradiene*-3β,18-*diol* (4·0 g.), m. p. 152—153°, $[\alpha]_D$ −18·5° (*c* 4) (Found: C, 78·85; H, 10·8. $C_{20}H_{32}O_2$ requires C, 78·9; H, 10·6%), $\nu_{max.}$ 3350 (broad) cm.$^{-1}$. The compound formed a *diacetate*, m. p. 131·5°, $[\alpha]_D$ +13·5° (*c* 2) (Found: C, 74·0; H, 9·2. $C_{24}H_{36}O_4$ requires C, 74·3; H, 9·35%). In addition to these crystalline components several intermediate syrupy fractions were obtained.

Another sample of pyinkado heartwood sawdust (3 kg.) gave a syrup (237 g.) which was separated on alumina into four crude fractions by elution with light petroleum, benzene, ether, and methanol. Recrystallisation of the first fraction afforded crude sandaracopimaradien-3-one (42 g.), m. p. 50°; the second remained syrupy; the third gave sandaracopimaradien-3β-ol (17 g.), m. p. 124°, and the final fraction gave sandaracopimaradiene-3β,18-diol (25 g.), m. p. 151°. The evaporated mother-liquor from the recrystallisation of sandaracopimaradien-3β-ol was chromatographed on another column of alumina. Elution by benzene afforded a fraction which recrystallised from methanol as colourless needles (0·19 g.), m. p. 122·5—123°, $[\alpha]_D$ +200° (*c* 1·1) (Found: C, 79·5; H, 10·1. $C_{20}H_{30}O_2$ requires C, 79·5; H, 10·0%) $\nu_{max.}$ 1700 and 1092 cm.$^{-1}$.

*Hydrogenation of* Xylia *constituents*.—3-Oxomanoyl oxide (1 g.) in ethanol (60 ml.) over platinum–charcoal absorbed 91 c.c. of hydrogen at N.T.P. (theor. for 1 mol. 74 c.c.). Crystallisation of the product from aqueous methanol gave dihydro-3-oxomanoyl oxide (0·5 g.), m. p. 70—70·5°, $[\alpha]_D$ +40° (*c* 2) (Found: C, 78·2; H, 11·4. Calc. for $C_{20}H_{34}O_2$: C, 78·4; H, 11·2%). The compound did not depress the m. p. of an authentic sample,[10] m. p. 67—68·5°, and gave a 2,4-*dinitrophenylhydrazone*, m. p. 175—176° (Found: C, 64·2; H, 8·0; N, 11·2. $C_{26}H_{38}N_4O_5$ requires C, 64·2; H, 7·9; N, 11·5%).

Similar hydrogenation of manoyl oxide gave dihydromanoyl oxide, m. p. 19° (lit.,[4,8] 19°); sandaracopimaradien-3-one afforded a *dihydro-derivative*, m. p. 59°, $[\alpha]_D$ −25° (*c* 4) (Found: C, 83·05; H, 11·3. $C_{20}H_{32}O$ requires C, 83·3; H, 11·2%) [2,4-*dinitrophenylhydrazone*, m. p. 183—184·5° (Found: C, 66·95; H, 7·6; N, 11·8. $C_{26}H_{36}N_4O_4$ requires C, 66·7; H, 7·8; N, 12·0%)]. *Dihydrosandaracopimaradien*-3β-*ol*, m. p 132—132·5°, $[\alpha]_D$ +25·5° (*c* 5) (Found: C, 82·6; H, 11·7. $C_{20}H_{34}O$ requires C, 82·7; H, 11·8%), crystallised from aqueous methanol or light petroleum and gave an *acetate*, m. p. 115—116° (Found: C, 79·9; H, 11·0. $C_{22}H_{36}O_2$ requires C, 79·5; H, 10·9%). *Dihydrosandaracopimaradiene*-3β,18-*diol*, m. p. 144—145·5°, $[\alpha]_D$ +25·1° (*c* 3·5) (Found: C, 78·75; H, 11·1. $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·2%), crystallised from light petroleum and gave a *diacetate*, m. p. 103—104° (Found: C, 73·9; H, 9·65. $C_{24}H_{38}O_4$ requires C, 73·8; H, 9·8%). These were prepared in the same way. The infrared bands at 3040, 1625, 990, and 910 cm.$^{-1}$ characteristic of the vinyl group were absent from the spectra of the dihydro-compounds.

Sandaracopimaradien-3β-ol (2 g.) in acetic acid (40 ml.), over a platinum catalyst (from 400 mg. of platinum oxide), absorbed 340 c.c. of hydrogen at N.T.P. (two double bonds require 316 c.c.). Recrystallisation of the product from aqueous methanol gave *tetrahydrosandaracopimaradien*-3β-*ol* (1·6 g.), m. p. 134—135·5°, $[\alpha]_D$ +21·8° (*c* 4) (Found: C, 81·8; H, 12·1. $C_{20}H_{36}O$ requires C, 82·1; H, 12·4%) [*acetate*, m. p. 130—131°, $[\alpha]_D$ +32° (*c* 2) (Found: C, 78·7; H, 11·4. $C_{22}H_{38}O_2$ requires C, 79·0; H, 11·5%)]. Under similar conditions *tetrahydrosandaracopimaradiene*-3β,18-*diol*, m. p. 174—176°, $[\alpha]_D$ +21° (*c* 1) (Found: C, 77·4; H, 11·9. $C_{20}H_{36}O_2$ requires

C, 77·8; H, 11·8%), was obtained after recrystallisation from light petroleum [*diacetate*, m. p. 131·5—133°, $[\alpha]_D$ +44° (*c* 2·3) (Found: C, 73·35; H, 10·1. $C_{24}H_{40}O_4$ requires C, 73·5; H, 10·3%)]. The tetrahydro-diol in ethanol did not consume periodate (triethylammonium periodate reagent [18]).

*Wolff–Kishner Reduction of 3-Oxomanoyl Oxide and Sandaracopimaradien-3-one.*—3-Oxomanoyl oxide (0·5 g.), potassium hydroxide (1·5 g.), and 80% hydrazine hydrate (2·0 ml.) in ethylene glycol (15 ml.) were boiled under reflux for 3 hr. Solvent was then distilled off until the temperature of the vapour reached 185° and boiling was continued for 3 hr. After cooling and dilution with water, the syrupy product was isolated in ether. The syrup was purified by filtration through alumina, and crystallised on cooling to 0° under methanol. Recrystallisation gave manoyl oxide (0·24 g.), m. p. and mixed m. p. 24—25°, with an identical infrared spectrum.

Under identical conditions sandaracopimaradien-3-one (0·5 g.) afforded sandaracopimaradiene (0·27 g.), m. p. 33—34·5°. Repeated recrystallisation from methanol gave a sample with m. p. 39·5—40°, $[\alpha]_D$ −14° (*c* 2), identified by mixed m. p. and infrared comparison.

*Interconversion of Sandaracopimaradien-3-one and -3-ol.*—Sandaracopimaradien-3-one (0·5 g.) in methanol (25 ml.) was added to a suspension of potassium borohydride (0·5 g.) in methanol (25 ml.), and the mixture was kept at room temperature overnight. A few drops of acetic acid were then added and the solvent was evaporated. Water was added and the solid was isolated in ether and purified by filtration through alumina in ether–light petroleum (1 : 4). Recrystallisation from aqueous methanol gave sandaracopimaradien-3β-ol (0·3 g.), m. p. 123—124°. Repeated recrystallisation gave a pure sample, m. p. 125·5—126·5°, $[\alpha]_D$ −20° (*c* 5), identified by mixed m. p. and infrared comparison.

Sandaracopimaradien-3β-ol (0·2 g.) in pyridine (2 ml.) was added to the complex of chromic acid (0·2 g.) in pyridine (2 ml.), and the mixture was kept at room temperature overnight. The product, obtained by dilution with water and extraction with ether, recrystallised from aqueous methanol, giving sandaracopimaradien-3-one (0·08 g.), m. p. and mixed m. p. 56—58°, $[\alpha]_D$ −53° (*c* 2).

*Rearrangement of Sandaracopimaradiene.*—Dry hydrogen chloride was passed through an ice-cold solution of sandaracopimaradiene (0·38 g.) in dry chloroform (40 ml.) for 50 min. Evaporation at reduced pressure gave a syrup which recrystallised from methanol, to give $\Delta^{8(9)}$-sandaracopimaradiene (0·13 g.), m. p. 50—51° (lit.,[6] 52—53°), $[\alpha]_D$ +117° (*c* 3) (Found: C, 88·1; H, 11·6. Calc. for $C_{20}H_{32}$: C, 88·15; H, 11·85%).

*Chromic Acid Oxidation of Sandaracopimaradiene-3β,18-diol.*—The diol (2·5 g.) in pyridine (25 ml.) was added to the complex of chromic acid (2·5 g.) in pyridine (25 ml.), and the mixture was kept at room temperature for 19 hr. Dilution with water and extraction by ether afforded a brown syrup (2·38 g.) which was divided into two parts.

Wolff–Kishner reduction of one portion (0·95 g.) with potassium hydroxide (3 g.), 100% hydrazine hydrate (3 ml.), and ethylene glycol (30 ml.) was carried out as described before. The syrupy product was chromatographed on alumina in light petroleum; elution by light petroleum gave a colourless syrup (0·16 g.), and further elution by ether afforded crystals (0·23 g.), recrystallising from aqueous methanol to afford sandaracopimaradien-3β-ol, m. p. and mixed m. p. 127·5—128·5° (identity confirmed by infrared spectrum).

The second portion of the syrup (1·43 g.) was chromatographed on alumina in benzene–light petroleum (1 : 1). Elution by this solvent gave crystals (0·17 g.) of 18-*norsandaracopimaradien-3-one*, m. p. 53—55° (from aqueous methanol), $[\alpha]_D$ −19° (*c* 2) (Found: C, 83·65; H, 10·35. $C_{19}H_{28}O$ requires C, 83·75; H, 10·3%), $\nu_{max.}$ 1700 cm.$^{-1}$ [2,4-*dinitrophenylhydrazone*, m. p. 194—195° (Found: C, 66·1; H, 7·1; N, 12·5. $C_{25}H_{32}N_4O_4$ requires C, 66·35; H, 7·1; N, 12·4%)]. Further elution of the column gave only syrups.

Chromic acid oxidation of tetrahydrosandaracopimaradiene-3β,18-diol (1 g.) by the same procedure afforded *tetrahydro-18-norsandaracopimaradien-3-one* (0·2 g.), m. p. 74—76°, $[\alpha]_D$ +30° (*c* 1·6) (Found: C, 82·3; H, 11·35. $C_{19}H_{32}O$ requires C, 82·5; H, 11·7%), $\nu_{max.}$ 1697 cm.$^{-1}$ [2,4-*dinitrophenylhydrazone*, m. p. 192° (Found: C, 65·7; H, 7·8; N, 12·0. $C_{25}H_{36}N_4O_4$ requires C, 65·7; H, 7·95; N, 12·3%)].

*Isopropylidene Derivative of Sandaracopimaradiene-3β,18-diol.*—A solution of the diol (0·5 g.) in acetone (50 ml.) containing concentrated sulphuric acid (1 drop) was kept at room temperature overnight and then shaken with anhydrous potassium carbonate for 1 hr. The filtered solution was evaporated to a solid which was purified by isolation in light petroleum

[18] Reddaway, *Analyst*, 1959, **82**, 506.

and recrystallisation from acetone to give the *isopropylidene derivative* (0·27 g.), m. p. 126—127°, $[\alpha]_D$ −26° (*c* 2) (Found: C, 80·1; H, 10·5. $C_{23}H_{36}O_2$ requires C, 80·2; H, 10·5%).

*Pyrolysis of Tetrahydrosandaracopimaradiene-3β,18-diol.*—A mixture of the diol (1 g.) and copper bronze (3 g.) was heated at 65 mm. under a stream of nitrogen. The temperature of the mixture was raised to 280° and maintained thus for 10 min. The issuing gases were passed through a solution of dimedone in aqueous alcohol; unchanged dimedone, precipitated during the reaction, was filtered off; the filtrate, when kept for several hours, deposited crystals of formaldehyde dimedone (110 mg.), m. p. and mixed m. p. 188—190°. The copper bronze mixture was cooled and leached with ether, and the brown syrup obtained was chromatographed on alumina in light petroleum. Elution by benzene–light petroleum (1 : 1) gave crystals which recrystallised from aqueous methanol (charcoal), to give tetrahydro-18-norsandaracopimaradien-3-one (0·4 g.), m. p. and mixed m. p. 73—74·5°.

*Dihydro-3β-hydroxymanoyl Oxide.*—3-Oxomanoyl oxide (2 g.) in methanol (200 ml.) was stirred with potassium borohydride (2 g.) at room temperature for 2 hr. The resulting solution was evaporated and the residue, after having been dissolved in ether and washed with water, recrystallised from aqueous methanol as leaflets of *3β-hydroxymanoyl oxide* (1·4 g.), m. p. 83—84°, $[\alpha]_D$ +17° (*c* 1·8) [Found: C, 76·4; H, 11·0. $C_{20}H_{34}O_2,\frac{1}{2}CH_3{\cdot}OH$ requires C, 76·3; H, 11·2%. Found (in a sample fused at 150°/45 mm.): C, 78·3; H, 11·1. $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·2%]; the *acetate*, m. p. 128—129°, $[\alpha]_D$ +31° (*c* 2) (Found: C, 76·0; H, 10·7. $C_{22}H_{36}O_3$ requires C, 75·8; H, 10·4%), crystallised from methanol.

3β-Hydroxymanoyl oxide (1·3 g.) in ethanol (40 ml.) over platinum–charcoal absorbed 117 c.c. at N.T.P. of hydrogen (theor. for 1 mol. 95 c.c.). The product, purified on an alumina column, was eluted with ether–light petroleum (1 : 1) and recrystallised from aqueous methanol as needles of *dihydro-3β-hydroxymanoyl oxide*, m. p. 83—84°, $[\alpha]_D$ +4° (*c* 4) (Found, in a sample fused at 120°/60 mm.: C, 77·7; H, 12·2. $C_{20}H_{36}O_2$ requires C, 77·9; H, 11·8%).

*Dehydration of Tetrahydrosandaracopimaradien-3β-ol.*—Phosphorus pentachloride (2 g.) was shaken with a solution of tetrahydrosandaracopimaradien-3β-ol (1·25 g.) in light petroleum (100 ml.) at room temperature for 5 min. The solution was filtered, shaken with 2N-sodium hydroxide, then water, dried ($Na_2SO_4$), and evaporated to a syrup (1·18 g.). The infrared spectrum of the syrup was devoid of hydroxyl and C–Cl absorption bands.

The syrup (1·06 g.) in acetic acid (50 ml.) was treated with a stream of ozonised oxygen (1·25 moles of ozone) during 80 min. Water and zinc dust were then added and steam was passed through the whole. The aqueous distillate, on treatment with aqueous 2,4-dinitrophenylhydrazine reagent, gave acetone 2,4-dinitrophenylhydrazone (0·45 g.), m. p. and mixed m. p. 124—125°. The non-volatile syrupy residue, collected in ether and washed with aqueous sodium hydroxide, had an infrared band at 1735 $cm.^{-1}$ with a less intense band at 1700 $cm.^{-1}$.

Similar treatment of dihydro-3β-hydroxymanoyl oxide (0·9 g.) gave acetone 2,4-dinitrophenylhydrazone (0·39 g.) and a non-volatile syrup with an infrared band at 1735 $cm.^{-1}$ and a less intense band at 1700 $cm.^{-1}$

*Partial Acetylation of Sandaracopimaradiene-3β,18-diol.*—The powdered diol (5 g.) was shaken with acetic anhydride (100 ml.) and pyridine (10 drops) at room temperature for 3·5 hr. Addition of water gave a solid which was chromatographed in light petroleum on alumina. Elution with benzene gave the diacetate (0·9 g.), m. p. and mixed m. p. 131—132°, and elution by benzene–ether (4 : 1) gave a syrup (4·38 g.). Crystallisation of the syrup from aqueous methanol at 0° gave leaflets of *3β-acetoxysandaracopimaradien-18-ol* (0·82 g.), m. p. 108—109° $[\alpha]_D$ −37·4° (*c* 2·1) (Found: C, 76·35; H, 10·05. $C_{22}H_{34}O_3$ requires C, 76·2; H, 9·9%). Addition of more water precipitated crystals (2·27 g.), m. p. 65—80°. Several recrystallisations from a small volume of light petroleum gave *18-acetoxysandaracopimaradien-3β-ol* (0·74 g.), m. p. 79—81°, $[\alpha]_D$ −35·4° (*c* 1·9) (Found: C, 76·8; H, 10·0%). Both hydroxy-acetates gave the diacetate, m. p. 131—132°, on acetylation.

*Oxidation of the Hydroxy-acetates.*—The hydroxy-acetates were oxidised by the chromic acid–pyridine method (described above). 3β-Acetoxysandaracopimaradien-18-ol afforded *3β-acetoxysandaracopimaradien-18-al*, m. p. 123—124°, $[\alpha]_D$ ±0° (Found: C, 76·4; H, 9·6. $C_{22}H_{32}O_3$ requires C, 76·7; H, 9·4%); 18-acetoxysandaracopimaradien-3β-ol gave *18-acetoxysandaracopimaradien-3-one*, m. p. 94—95°, $[\alpha]_D$ −42° (*c* 2) (Found: C, 76·35; H, 9·5%); each sample was recrystallised from aqueous methanol.

In a later experiment the syrupy mixture of hydroxy-acetates (4·0 g.) was oxidised by chromic acid–pyridine, and the product was chromatographed on alumina. Elution with

benzene–light petroleum (1 : 1) gave 18-norsandaracopimaradien-3-one (0·07 g.), m. p. and mixed m. p. 55°; elution by benzene–light petroleum (4 : 1) gave 3β-acetoxysandaracopimaradien-18-al (1·15 g.); and elution by benzene–ether (20 : 1) gave 18-acetoxysandaracopimaradien-3-one (0·52 g.). Later syrupy fractions were not identified.

18-Acetoxysandaracopimaradien-3-one (0·52 g.), potassium hydroxide (1·5 g.), and 100% hydrazine hydrate (4 ml.) in ethylene glycol (15 ml.) were allowed to react as described before. The syrupy product was chromatographed on alumina; elution by light petroleum gave 18-norsandaracopimaradiene (0·36 g.), $[\alpha]_D$ −23° (*c* 2·5), $n_D^{20}$ 1·5195 (Found: C, 88·15; H, 11·8. $C_{19}H_{30}$ requires C, 88·3; H, 11·7%), as a colourless syrup. Wolff–Kishner reduction of 18-norsandaracopimaradien-3-one gave a colourless syrup, $[\alpha]_D$ −7° (*c* 2), $n_D^{20}$ 1·5169. The infrared spectra of the two syrups were identical, though the latter showed a trace of carbonyl impurity at 1700 cm.$^{-1}$.

3β-Acetoxysandaracopimaradien-18-al (0·52 g.), similarly reduced, gave a solid; recrystallised from aqueous methanol, it yielded sandaracopimaradien-3β-ol (0·26 g.), m. p. and mixed m. p. 124—125·5°.

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