New Diterpenoids from *Pterodon emarginatus* Vog.

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Eight new diterpenoids isolated from *Pterodon emarginatus* Vog. have been assigned the following structures and stereochemistry: 6α,7β-diacetoxyvouacapane (1), 7β-acetoxyvouacapane (3), 6α,7β-dihydroxyvouacapan-17β-oic acid (11), methyl 6α,7β-dihydroxyvouacapan-17β-oate (12), methyl 7β-acetoxy-6α-hydroxyvouacapan-17β-oate (14), 6α-acetoxyvouacapano-17β,7β-lactone (16), vouacapane-6α,7β,14β-triol (25), and 6α,7β-diacetoxyvouacap-14(17)-ene (24). Compound (24) was hydrogenated (Pd–C) to 6α,7β-diacetoxy-14-*epi*-vouacapane (20). The same 14-*epi*-diacetate (20) was obtained by reduction with lithium aluminium hydride of the 17-tosylate (18) derived from vouacapane-6α-7β,17-triol (17). 7β-Acetoxyvouacapane (3) has been converted into the parent furohydrocarbon [vouacapane (6)] by Wolff–Kishner reduction of the derived vouacapan-7-one (5). N.m.r. and mass spectra of several compounds are described.

THE oil from the fruits of *Pterodon pubescens* Benth., *P. emarginatus* Vog., and *P. poligalaeflorus* Benth., has protective action [1] against infection by cercaria of *Schistosoma mansoni*. We are engaged in a chemical study of *P. emarginatus* and *P. poligalaeflorus*, and have recently reported preliminary results on the structure and stereochemistry of several diterpenoids isolated from the former.[2] We now describe the structure of two more such compounds [(24) and (25)] obtained from the same source, and give the details of our previous work.

The structures of 6α,7β-diacetoxyvouacapane (1) and 7β-acetoxyvouacapane (3) were mainly derived from n.m.r. evidence (60, 100, and 220 MHz).[2a] Apart from the easily recognized CMe, OAc, and furan α- and β-proton signals, these compounds show characteristic C*H*·OAc absorption which helps to assign the stereochemistry at positions 5—8. Thus the two C*H*·OAc systems at C-6 and C-7 in compound (1) appear as two ABX quartets at δ 5·24 and 4·85 p.p.m., respectively, with J_{AB} 9·0, J_{AX} 11·5, and $J_{BX'}$ 10 Hz, showing that the four protons at C-5, C-6, C-7, and C-8 all occupy axial positions. In the case of the monoacetate (3), the only such proton appears as a doubly split (J 5·5 Hz) triplet (J 10·5 Hz) at δ 4·75 p.p.m. Our assignment of this equatorial acetate to C-7 was confirmed [2b] by comparison of this signal with the C-6 proton signals from the 6α-acetoxy-lactone (16) (δ 5·52), the 6α-acetoxy-ether (22) (δ 5·42), and the 6α,17-diacetoxy-7β-hydroxy-compound (23) (δ 5·24).[3]

The stereochemical assignment at C-14 was derived from 220 MHz spectra of compounds (1) and (3),[2a] where the C-14 proton appears as a quintet showing equal coupling (J 6·5 Hz) with the C-14 methyl group and the C-8 axial proton, and thus revealing its *cis* relationship to the latter.

The monoacetate (3) was related to vouacapane (6) by Wolff–Kishner reduction of the derived ketone (5); a mixture of two isomeric furohydrocarbons was obtained owing to epimerization at C-8. One of the components, m.p. 78—79°, was identical with the furohydrocarbon prepared by King *et al.*[4] Attempts to convert the mono-ol (4) into the corresponding tosylate and to reduce the latter with lithium aluminium hydride afforded only starting material, although there was evidence (i.r.) that the tosylate was formed.

On the other hand, tosylation of the diol (2) in pyridine was not achieved, and attempted tosylation after treatment with sodium hydride in dimethylformamide gave very little of the ditosylate, the main product (30—70%) being the corresponding epoxide (26). Vicinal diols are known to yield epoxides under these conditions,[5] and in the present series the formation of an epoxide is even more favourable on steric grounds. The C-6 and C-7 protons of compound (26) appear in the n.m.r. spectrum as ABX quartets centred at δ 2·9 p.p.m. (J 4·5 and 2·0

[1] W. B. Mors, M. Fascio dos Santos fº. H. J. Monteiro, B. Gilbert, and J. Pellegrino, *Science*, 1967, **157**, 950, and unpublished data obtained by Dr. Pellegrino.

[2] J. R. Mahajan and M. B. Monteiro, *Anais Acad. brasil. Cienc.*, (*a*) 1970, **42** (suppl.), 103; (*b*) 1972, **44**, (suppl.), 51; (*c*) Abstracts 8th International Symposium on the Chemistry of Natural Products, New Delhi, 1972, C-93.

[3] M. Fascio, B. Gilbert, W. B. Mors, and T. Nishida, *Anais Acad. brasil. Cienc.*, 1970, **42** (supl.), 97.

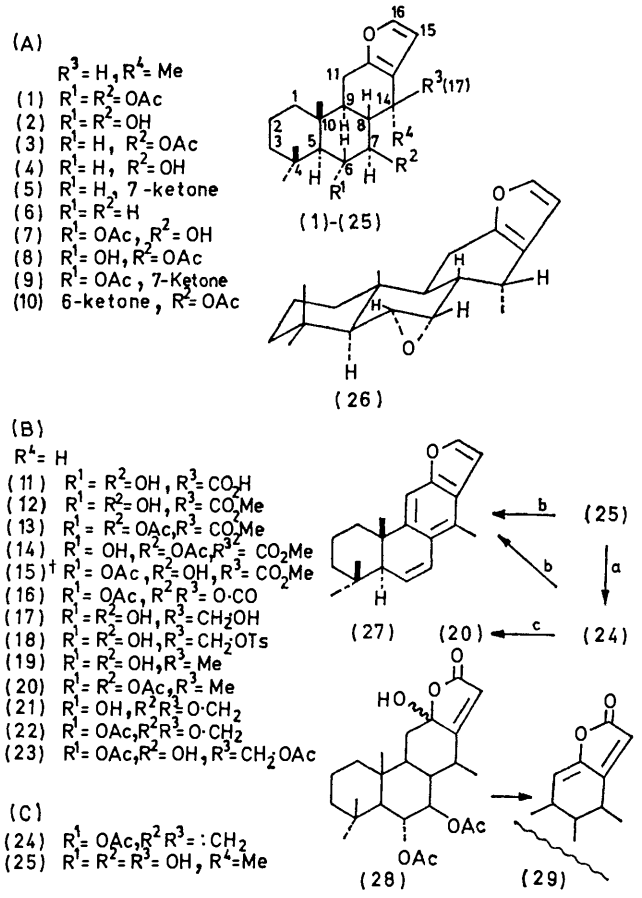
[4] F. E. King, D. H. Godson, and T. J. King, *J. Chem. Soc.*, 1955, 1117.

[5] E. J. Reist, V. J. Bartuska, D. F. Calkins, and L. Goodman, *J. Org. Chem.*, 1965, **30**, 3401.

Hz). The equivalence of J_{AX} and $J_{BX'}$ and their small magnitude (2 Hz) is surprising, but is no doubt due to deformation of ring B.[6]

All efforts to open, isomerize, or deoxygenate this epoxide with various reagents, *e.g.* perchloric acid (70%),[7a] lithium aluminium hydride,[7b] boron trifluoride–ether complex,[7c] lithium–ethylenediamine,[8] triphenylphosphine,[9] *etc.*, were unsuccessful; the epoxide was either recovered unchanged or gave undesirable tarry products.

Mesylation of the diol (2) and subsequent attempts by



Reagents: a, Ac_2O–NaOAc; b, TsOH–$CHCl_3$; c, Pd–C,H_2

† Isolated from *P. poligalaeflorus* (unpublished data).

reduction with lithium aluminium hydride to obtain the corresponding hydrocarbon (6) or mono-ol (4) were also unsuccessful; the diol (2) was recovered along with some epoxide (26).

As the direct elimination of the diequatorial 6,7-diacetate or -diol system was apparently not possible, we attempted to relate compound (1) to the monoacetate (3) or vouacapane (6) through the acetoxy-ketone (9) or (10). Controlled monoacetylation of the diol (2) afforded a mixture of two monoacetates (7) and (8), which were separated by column chromatography (silica gel) and recrystallization. Their identification was based on their n.m.r. spectra (see Experimental section). Solvent shifts in pyridine were also helpful;[10] in the 6α-hydroxy-7β-acetoxyvouacapane (8), the α- and β-methyl groups at C-4 were deshielded by 0·25 and 0·11 p.p.m., respectively, whereas in the isomeric 6α-acetoxy-7β-hydroxyvouacapane (7) the corresponding values were 0·10 and 0·02 p.p.m. only. The extra peak (10—20%) at δ 2·00 may be due to the corresponding hemi-ortho-ester. Oxidation with chromium trioxide–pyridine[11] of the mixture of two hydroxy-acetates gave, however, only the 7-acetoxyvouacapan-6-one (10). Surprisingly, the practically pure 6α-acetoxy-7β-hydroxyvouacapane (7) was very resistant to oxidation in comparison with its isomer, 6α-hydroxy-7β-acetoxy-vouacapane (8). Attempts to eliminate the α-acetoxy-group through reaction with zinc powder in ethanol or acetic acid were unsuccessful, and attempted Wolff–Kishner reduction afforded no identifiable products.

With Jones reagent under controlled conditions, the diacetate (1) was converted to the corresponding lactol (28), which was easily dehydrated to the lactone (29) in conformity with similar reactions of the furan system in methyl vinhaticoate and methyl vouacapenate.[4]

Elucidation of the structures of the rest of the compounds of this series was facilitated by n.m.r. spectral comparisons with each other and with compounds (1) and (3). Thus the similarity of the n.m.r. spectra of compounds (12)—(16) to those of (1) and (3) apart from the disappearance of the C-14 methyl doublet leads to the proposed assignments. The C-14 proton in these compounds is assigned the α-configuration because it shows diaxial coupling with the C-8 proton in compounds (13)—(16) [doublets, with a further fine splitting, at δ 3·40 (J 9 Hz), 3·37 (J 8·5), 3·37 (J 9), and 3·20 (J 11), respectively]. Furthermore, compounds (12)—(16) have been converted, through the common triol (17) and the corresponding monotosylate (18), into the diol (19) and the diacetate (20), which are C-14 epimers of the natural diacetate (1) and the derived diol (2). During the reduction of the tosylate (18) variable amounts of the hydroxy-ether (21) were also produced, along with the diol (19), depending on the reaction temperature and the amount of lithium aluminium hydride employed.

The new compound (24) was identified by the close resemblance of its n.m.r. spectrum to that of the diacetate (1), except for the appearance of signals for two methylene protons and the disappearance of the C-14 methyl doublet. Catalytic hydrogenation over palladium–charcoal (10%) afforded a quantitative yield of 6α,7β-diacetoxy-14-*epi*-vouacapane (20), already synthesized,

[6] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, London, 1969, pp. 272 and 286.

[7] L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' Wiley, New York, 1967, (*a*) p. 796; (*b*) p. 586; (*c*) p. 71.

[8] H. C. Brown, S. Ikegami, and J. H. Kawakami, *J. Org. Chem.*, 1970, **35**, 3243.

[9] G. Wittig and W. Haag, *Chem. Ber.*, 1955, **88**, 1654.

[10] P. V. Damarco, E. Farkas, D. Doddrell, B. L. Mylari, and E. Wenkert, *J. Amer. Chem. Soc.*, 1968, **90**, 5480.

[11] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 422; R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, 1970, **35**, 4000.

indicating that the hydrogenation had taken place, as expected, from the α-side of the molecule. Treatment of compound (24) in boiling chloroform containing a catalytic amount of toluene-*p*-sulphonic acid, proceeded with the elimination of both acetate groups and gave the partially aromatized compound (27).

The other new compound appeared to be a triol, on the basis of elemental analysis and its i.r. spectrum. On acetylation (acetic anhydride–sodium acetate), it yielded the unsaturated diacetate (24) thus indicating structure (25) for the parent triol. The C-14 hydroxy-group is probably in a quasi-equatorial position, thus favouring elimination of a methyl proton instead of the C-8 axial proton. As expected, the triol (25) also furnished the benzofuran (27) with toluene-*p*-sulphonic acid in refluxing chloroform.

The mass spectra of the foregoing compounds support the proposed structures. Apart from the familiar retro-Diels–Alder reaction involving the furan ring,[12] the main fragmentation modes are depicted in Supplementary Publication No. SUP 20623 (see preamble to Experimental section).

The hydrocarbon fraction of the oil contains several compounds (g.l.c. on DEGS). The major component has been isolated in a pure state and characterized as caryophyllene. The presence of caryophyllene in Pterodon species has been suggested earlier.[13]

EXPERIMENTAL

M.p.s were taken with a Kofler hot-stage apparatus. I.r. spectra (KBr discs) were taken with a Perkin-Elmer 137 instrument. N.m.r. spectra (solutions in CCl_4 or $CDCl_3$) were taken with a Varian A-60D instrument, unless noted otherwise, with tetramethylsilane as standard. When two δ values are quoted for an ABX quartet, these are the mid-points of each A and B part; the centre of the AB system is the average of the two values. The reported values for *J* are the observed separations and not the calculated ones. Mass spectra were run on an A.E.I. MS9 instrument at 70 eV. Optical rotations are for solutions in chloroform. Analyses were performed by Alfred Burnhardt, Germany. Most of the column chromatography was carried out in modified coupled columns,[14] made from three glass tubes (50 cm each) of decreasing diameters, fused in a diminishing sequence. Merck silica gel and alumina were used. All chromatograms were monitored by t.l.c. (silica gel G). G.l.c. was carried on a Varian-Aerograph Autoprep 705 instrument. Anhydrous sodium sulphate was used for drying operations.

I.r. data for compounds (2), (4)—(6), (19), (26), and (29), n.m.r. data for compounds (2), (4), (19), and (29), and mass spectral data for compounds (1), (3), (5), (6), (12)—(14), (16), and (28) are given in Supplementary Publication No. SUP 20623 (18 pp., 1 microfiche).*

Isolation.—The crushed fruits were extracted with petroleum (b.p. 60—80°) in a Soxhlet apparatus, affording (*ca.* 30%) an amber-coloured, viscous oil, with a strong aroma. This slowly deposited 6α,7β-diacetoxyvouacapane (1) (*ca.* 10% of the oil). Chromatography of the remaining oil (A) on silica gel and elution with benzene–ethanol (0—5%) afforded a hydrocarbon fraction (7—9%) followed by 7β-acetoxyvoucapane (3) (2%), 6α,7β-*diacetoxyvouacapane* (1) (another 2—3%), the 6α-acetoxy-lactone (16) (0·1%), and a number of fractions containing several components of similar R_F, which were combined.

The combined fractions were dissolved in ether or hexane and separated into neutral and acidic parts by extraction with Claisen's alkali (KOH–H_2O–MeOH; 35 g : 25 ml : 100 ml). The basic part was acidified with 10% hydrochloric acid and extracted with ether. Attempted extraction of the ethereal solution with saturated sodium hydrogen carbonate precipitated the sodium salt. Acidification and subsequent crystallization from ethyl acetate gave 6α,7β-dihydroxyvoucapan-17β-oic acid (11) (2—3%).

The oil (A) remaining after the removal of the diacetate (1), when submitted to the foregoing treatment, also furnished the dihydroxy-acid (11) as well as the neutral fraction.

A part of the neutral material was chromatographed over silica gel and eluted with petroleum (b.p. 40—60°)–acetone (90 : 10), affording several fractions, of which a few when crystallized from ethanol gave methyl 6α,7β-dihydroxyvouacapan-17β-oate (12) (1%). Rechromatography of another batch of the foregoing fractions with a higher R_F value furnished methyl 7β-acetoxy-6α-hydroxyvouacapan-17β-oate (14) (0·1%).

Repeated chromatography (silica gel) of another portion of the neutral material in benzene–ethanol (1—5%) yielded vouacapane-6α,7β-14β-triol (25) (0·15%), along with several fractions with R_F close to that of the diacetate (1). Rechromatography of the latter on alumina (activity II) and fractional crystallization afforded the diacetate (1) and 6α,7β-diacetoxyvouacap-14(17)-ene (24) (0·2%).

The hydrocarbon fraction showed several components on an analytical DEGS (30%) column run at 160°. The major component was separated on a preparative column and characterized as caryophyllene by comparison of its i.r. and n.m.r. spectra with those of an authentic sample.

6α,7β-*Diacetoxyvouacapane* (1) formed plates (from ethanol), m.p. 167—168° (Found: C, 71·5; H, 8·6. $C_{24}H_{34}O_5$ requires C, 71·6; H, 8·5%); $[\alpha]_D^{25}$ +88° (*c* 1·0); $\lambda_{max.}$ (EtOH) 218 nm (ε 11,900); $\nu_{max.}$ 1745, 1511, 1370, 1361, 1252, 1229, 1031, 901, and 739 cm^{-1}; δ 0·91, 1·00, and 1·05 (9H, 3 s, Me at C-10 and C-4), 1·00 (3H, d, *J* 7 Hz, Me at C-14), 1·92 (6H, s, 2AcO), 4·85 and 5·24 (2H, each ABXq, J_{AB} 9·0, J_{AX} 11·5, $J_{BX'}$ 10 Hz, H-7 and H-6), and 6·00 and 7·03 (2H, each d, *J* 2 Hz, α- and β-H of furan); δ (220 MHz), 2·45 (2H, 2 ABXq, J_{AB} 16·0, J_{AX} 6·5, J_{BX} 10·5 Hz, C-11 methylene), and a lower field quartet partly superimposed on the multiplet at 2·64 (1H at C-14).

Alkaline hydrolysis gave *vouacapane*-6α,7β-*diol* (2), an amorphous powder (Found: C, 75·2; H, 9·4. $C_{20}H_{30}O_3$ requires C, 75·4; H, 9·5%); $[\alpha]_D^{25}$ +89° (*c* 1·25).

6α-*Acetoxyvouacapan*-7β-*ol* (7).—A mixture of the diol (2) (3·8 g), acetic anhydride (1·1 ml), and pyridine (15 ml) was heated on a water-bath for 4 h. The product (3·5 g),

* For details of Supplementary Publications, see *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (Notice to Authors No. 7).

[12] H. Budzikiewicz, C. Djerassi, D. H. Williams, 'Structure Elucidation of Natural Products by Mass Spectroscopy, vol. II, Holden-Day, San Francisco, 1964, pp. 104 and 152; H. E. Audier, S. Bory, M. Fétizon, and N.-T. Anh, *Bull. Soc. chim. France*, 1966, 4002.

[13] A. Machado and A. S. Peixoto, *Rev. Soc. bras. quim.*, 1938, **7**, 7.

[14] S. M. Partridge and R. C. Brimley, *Biochem. J.*, 1951, **48**, 313.

obtained after the usual work-up, was put on a silica gel (150 g) column and eluted with benzene–ethanol (0—1·5%). Apart from some diacetate and unchanged diol, fractions 4—6 (each 20 ml) (0·24 g) gave a liquid, whereas 7—9 (each 20 ml) (0·75 g) yielded a solid. T.l.c. showed each of these to be contaminated with the other. Although a sharp-melting (138—139°) *sample* was obtained from ethanol, it still contained traces of the other isomer (Found: C, 73·2; H, 9·0. $C_{22}H_{32}O_4$ requires C, 73·3; H, 9·0%); $\nu_{max.}$ 3226, 1742, 1724, and 1256 cm^{-1}; δ 0·95, 1·04, and 1·04 (9H, 2 s, 3 Me), 1·03 (3H, d, *J* 7 Hz, Me), 2·08 (3H, s, OAc), 2·9—3·6 (1H, m, H-7), 5·18 (1H, ABXq, J_{AB} 9·0, J_{AX} 11·5 Hz, H-6), and 6·08 and 7·12 (2H, 2 d, furan H); δ (pyridine) (corresponding values) 0·92, 1·06, and 1·14 (3s), 1·19 (d), 1·98 (10%), and 2·07 (90%) (3H, 2 s, OAc), 3·35—3·95 (m), 5·68 (ABXq), and 6·35 (d).

7β-*Acetoxyvouacapan*-6α-*ol* (8).—The foregoing liquid fractions 4—6 were rechromatographed (silica gel) to furnish a sample containing only traces of the other isomer; a liquid, $\nu_{max.}$ (film) 3460, 1715, and 1250 cm^{-1}; δ 0·98, 1·07, and 1·19 (9H, 3 s, 3 Me), 1·01 (3H, d, *J* 7 Hz, Me), 2·08 (3H, s, OAc), 3·8 (1H, approx. t, *J* 10 Hz, H-6), 4·8 (1H, approx. t, *J* 10 Hz, H-7), and 6·07 and 7·12 (2H, 2 d, *J* 2 Hz, furan H); δ (pyridine) 0·93, 1·18, and 1·44 (3s), 1·24 (d), 2·00 (20%) and 2·06 (80%) (3H, s, OAc), 4·12 (ABXq, J_{AB} 9, J_{AX} 11 Hz), 5·3 (approx. t), and 6·32 (d).

7β-*Acetoxyvouacapan*-6-*one* (10).—The hydroxy-acetate (8) (210 mg) dissolved in pyridine (2 ml) was added dropwise to chromium trioxide (210 mg) in pyridine (2 ml). The mixture was stirred at room temperature for 16 h; dry benzene was then added and solid material was filtered off. The benzene solution was washed with water, dilute hydrochloric acid, and water again to remove pyridine. Drying and evaporation afforded an oil (200 mg), which was chromatographed over silica gel (10 g). Elution with benzene–ethanol (1%) gave an oil (99 mg), $\nu_{max.}$ (film) 1742, 1727, and 1242 cm^{-1}; δ 0·88, 0·98, and 1·31 (9H, 3 s, 3 Me), 1·04 (3H, d, *J* 7·5 Hz, Me), 2·12 (3H, s, OAc), 5·0br (d, *J* 10 Hz, H-7), and 6·10 and 7·15 (2H, 2d, furan H).

The mixture of the hydroxy-acetates (7) and (8) (445 mg), oxidized and worked up under the same conditions, yielded the keto-acetate (10) (115 mg) (identical n.m.r. spectrum) and unchanged 6α-acetoxyvouacapan-7β-ol (7) (120 mg).

The hydroxy-ester (7) (300 mg) treated as above at room temperature, showed almost no reaction (t.l.c.). When the mixture was warmed on a water-bath (60°) for 30 h, work-up and purification gave the keto-acetate (10) (18 mg) and starting material (7) (141 mg).

Attempted Reactions with the Keto-acetate (10).—(*a*) A mixture of the keto-acetate (10) (100 mg) and zinc dust (200 mg) was refluxed in ethanol (10 ml) for 8 h. Work-up yielded starting material (88 mg) (identical i.r. spectrum). Attempted reactions in absolute ethanol or acetic acid were also unsuccessful, even when freshly activated zinc or zinc amalgam was used.

(*b*) A mixture of the keto-acetate (486 mg), hydrazine hydrate (5 ml), potassium hydroxide (1 g), and ethylene glycol (15 ml) was refluxed for 3 h; it was then distilled until the temperature reached 200° and refluxed for another 12 h. Work-up afforded a gum which gave no identifiable products on attempted purification (chromatography and sublimation).

Tosylation of the Diol (2).—A solution of the diol (2) (318 mg, 1 mmol) in dry ether (20 ml) and dry dimethylformamide (10 ml) was treated with a 20% suspension of sodium hydride in mineral oil (0·3 ml, 2 mmol). After the brisk reaction was over, tosyl chloride (570 mg, 3 mmol) was added; the mixture was kept at room temperature for 12 h then gently refluxed for 15 min. Decomposition with water and extraction with benzene gave the crude product (661 mg), contaminated with mineral oil. Chromatography (silica gel–benzene) of this material afforded a crystalline product (70 mg), m.p. 145—150° (decomp.); $\nu_{max.}$ 1330, 1167, and 905 cm^{-1}. As this product was unstable, it was treated with lithium aluminium hydride (100 mg) in dioxan–ether (1 : 1) and kept at room temperature for 12 h. Work-up and purification gave starting material (58 mg), identified by m.p. and i.r. spectrum. Attempted reduction in refluxing tetrahydrofuran resulted in a complex mixture which did not yield any identifiable product.

Attempted exchange of the ditosylate (60 mg) with potassium iodide (100 mg) and subsequent elimination with zinc dust in boiling ethanol gave a small quantity of the epoxide (26) (9 mg), identified by its i.r. spectrum and m.p., as the only isolable product. T.l.c. of the starting material showed complete absence of the epoxide (26).

6α,7α-*Epoxyvouacapane* (26).—A cooled (ice–salt) solution of the diol (2) (3·18 g, 10 mmol) in dry ether (50 ml) and dry dimethylformamide (50 ml) was treated with a 50% suspension of sodium hydride in oil (1 g, 21 mmol) with magnetic stirring. After the initial brisk reaction, tosyl chloride (2·85 g, 15 mmol) was added slowly and the mixture was kept for 2 days at 0—5°. Work-up furnished a product (4·2 g), which on chromatography (silica gel–benzene) yielded the foregoing tosylate (360 mg) (identical i.r. spectrum; m.p. 150—155°) and 6α,7α-*epoxyvouacapane* (26) (800 mg), rods (from ethanol), m.p. 133—134° (Found: C, 79·9; H, 9·4. $C_{20}H_{28}O_2$ requires C, 80·0; H, 9·4%); δ 0·85, 1·00, and 1·10 (9H, 3s, 3 Me), 1·16 (3H, d, *J* 7 Hz, Me), 2·9 (2H, 2 ABXq, *J* 4·5 and 2·0 Hz, H-7 and H-6), and 6·05 and 7·10 (2H, 2d, furan H).

In another attempt 636 mg of diol (2) afforded 430 mg of 6α,7α-epoxyvouacapane (26).

Mesylation of the Diol (2).—An ice-cold solution of the diol (2) (318 mg, 1 mmol) in dry dimethylformamide (6 ml) was treated with oil-free sodium hydride (48 mg, 2 mmol) in the same solvent. After addition of methanesulphonyl chloride (345 mg, 3 mmol), the mixture was kept at 0° for 24 h. Work-up gave a yellow foam (447 mg), which still showed some i.r. hydroxy-absorption. Reduction with lithium aluminium hydride in tetrahydrofuran and subsequent purification gave the starting diol (2) (300 mg), identified by its i.r. spectrum and t.l.c.

Mesylation in pyridine at room temperature for 5 h and subsequent reduction with lithium aluminium hydride gave a mixture of products, which on chromatography (silica gel) yielded a small quantity of the epoxide (26).

Attempted Reactions of 6α,7α-*Epoxyvouacapane* (26).—(*a*) The epoxide (26) (60 mg) dissolved in dioxan (2 ml) was added to lithium aluminium hydride (40 mg) in the same solvent (3 ml) and the mixture was refluxed for 6 h. T.l.c. at this stage revealed traces of a material which might have been a mono-ol. More lithium aluminium hydride (40 mg) was added and refluxing was continued for another 12 h. Work-up yielded a semi-solid (46 mg), which on purification over silica gel gave starting material (25 mg) along with traces of a hydroxy-compound. Attempted reductions in ether and in tetrahydrofuran were also unsuccessful.

(*b*) Boron trifluoride–ether complex (2 drops) was added to a solution of the epoxide (26) (50 mg) in benzene (2·5 ml).

After a few min at room temperature, the solution became orange-yellow and a semi-solid separated. Decomposition with sodium hydrogen carbonate and extraction with ether yielded a resin, insoluble in ethanol, showing a streak on t.l.c.

(*c*) The epoxide (20 mg), mixed with triphenylphosphine (50 mg), was heated at 180—190° for 2 h, in the presence of a crystal of hydroquinone. The mixture was chromatographed over alumina in benzene; starting material was recovered.

Similarly, treatment of the epoxide with perchloric acid polymerized it. Treatment with lithium in ethylenediamine gave no reaction.

Jones Oxidation of 6α,7β-*Diacetoxyvouacapane* (1).—Jones reagent (0·5 ml) was added dropwise to a solution of compound (1) (402 mg) in acetone (5 ml), with stirring and cooling. After completion of the reaction, the solution was decanted from the precipitate and evaporated at room temperature. The residue was treated with cold water; the resulting solid was taken up in benzene and the solution was washed free of acid, dried, and evaporated to afford a crystalline solid (396 mg). Washing with cold ether gave the lactol (28) as fine needles, m.p. 252—255°; $\nu_{max.}$ 3400, 1754, 1739, 1250, and 1031 cm^{-1}; δ 0·92, 0·95, and 1·02 (9H, 3s, 3 Me), 1·24 (3H, d, *J* 7 Hz, Me), 2·02 and 2·05 (6H, 2s, 2 AcO), 4·8—5·6 (2H, m, H-7 and H-6), and 5·68 (1H, s, H-15).

The lactol (28) was heated to its m.p. and then kept at 200° for 20 min. Crystallization from ethanol gave the anhydro-compound (29) as fine needles, m.p. 211—212°; $\nu_{max.}$ 1786, 1745, 1674, 1619, 1235, 1217, and 1027 cm^{-1}.

7β-*Acetoxyvouacapane* (3).—This formed plates (from ethanol), m.p. 147—148° (Found: C, 76·5; H, 9·3. $C_{22}H_{32}O_3$ requires C, 76·7; H, 9·4%); $[\alpha]_D^{23}$ +73° (*c* 1·0); $\lambda_{max.}$ (EtOH) 218 nm (ε 11,000); $\nu_{max.}$ 1730, 1502, 1252, 1034, 901, and 730 cm^{-1}; δ 0·88, 0·96, and 0·96 (9H, 2s, 3 Me), 0·94 (3H, d, *J* 7 Hz, Me), 2·00 (3H, s, OAc), 4·75 (1H, dt, *J* 5·5 and 10·5 Hz, H-7), and 6·05 and 7·08 (2H, 2d, *J* 2 Hz, furan H); δ (220 MHz) 2·45 (2H, 2 ABXq, J_{AB} 16, J_{AX} 6·5, J_{BX} 10·5 Hz, C-11 methylene), and 2·79 (1H, quintet, *J* 6·5 Hz, H-14).

Alkaline hydrolysis gave *vouacapan*-7β-*ol* (4), needles (from ethanol), m.p. 72—80° (Found: C, 79·2; H, 10·2. $C_{20}H_{30}O_2$ requires C, 79·4; H, 10·0%); $[\alpha]_D^{22}$ +92° (*c* 1·25).

Vouacapan-7-*one* (5).—Pyridine–chromium trioxide (Sarett) oxidation of the mono-ol (4) (794 mg) and subsequent chromatography (silica gel–benzene) afforded the *ketone* (5) (503 mg), needles (from ethanol), m.p. 98—99° (Found: C, 80·0; H, 9·5. $C_{20}H_{28}O_2$ requires C, 80·0; H, 9·4%); $[\alpha]_D^{23}$ +112° (*c* 1·0); δ 1·03, 0·92, and 0·92 (9H, 2s, 3 Me), 0·97 (3H, d, *J* 7 Hz, Me), 3·00—3·50 [1H, m (irradiation decouples the C-14 methyl doublet), H-14], and 6·07 and 7·08 (2H, 2d, furan H).

Wolff–Kishner Reduction of the Ketone (5).—A mixture of the ketone (5) (300 mg), ethylene glycol (8 ml), hydrazine hydrate (1 ml), and potassium hydroxide (300 mg) was refluxed for 5 h. More potassium hydroxide (500 mg) was then added and the mixture was distilled to raise its temperature to 200° and maintained there for another 10 h. Work-up furnished a thick liquid (200 mg). Chromatography over silica gel and elution with benzene–petroleum (b.p. 60—80°) yielded a solid with melting range 60—110°. Repeated fractional sublimation and subsequent recrystallization afforded: (i) vouacapane (6), needles, m.p. and mixed m.p.[4] 78—79°; $\nu_{max.}$ 1661, 1639, 1550, 1499, 1377, 1361, 1096, 898, 726, and 704 cm^{-1} (identical with that of the authentic sample); $[\alpha]_D^{23}$ +72° (*c* 1·0) (lit.,[4] +83°) (it was not possible to obtain a sufficient quantity of the sample free from its isomer for satisfactory optical rotation determination); (ii) 8-*epi*-vouacapane, rods (ethanol), m.p. 122—123°; $[\alpha]_D^{23}$ −45° (*c* 1·0).

Tosylation of the Mono-ol (4).—The mono-ol (4) (302 mg, 1 mmol), dissolved in dry ether (20 ml) and dry dimethylformamide (7 ml), was treated with sodium hydride in oil (20%; 0·15 ml, 1 mmol). After the brisk reaction, tosyl chloride (286 mg, 1·5 mmol) was added and the mixture was kept at room temperature for 12 h. T.l.c. then showed the presence of only starting material. Benzene (10 ml) was then added and the mixture was refluxed for 6 h. Work-up and chromatography (silica gel) of the crude product, afforded an oil (200 mg) having strong tosylate absorption [$\nu_{max.}$ (film) 1342 and 1163 cm^{-1}]. Reduction of this oil with lithium aluminium hydride in refluxing tetrahydrofuran yielded only the starting mono-ol (4) (144 mg); no evidence was obtained for the formation of the corresponding hydrocarbon.

6α,7β-*Dihydroxyvouacapan*-17β-*oic Acid* (11).—This formed *rods* (from ethanol), m.p. 272—274° (Found: C, 68·8; H, 8·1. $C_{20}H_{28}O_5$ requires C, 68·9; H, 8·1%); $\nu_{max.}$ 3448, 1715, 1508, 1057, 904, 747, and 687 cm^{-1}; sparingly soluble in most organic solvents. Esterification with diazomethane gave *methyl* 6α,7β-*dihydroxyvouacapan*-17β-*oate* (12), also isolated from the oil as fine needles, m.p. 204—206° (Found: C, 69·5; H, 8·3. $C_{21}H_{30}O_5$ requires C, 69·6; H, 8·3%); $[\alpha]_D^{23}$ −6° (*c* 1·0); $\nu_{max.}$ 3521 and 1724 cm^{-1}; δ 1·00, 1·07, and 1·16 (9H, 3s, 3 Me), 3·73 (3H, s, CO_2Me), 3·1—3·9 (3H, m, H-14, H-7, and H-6), and 6·15 and 7·22 (2H, 2d, *J* 2 Hz, furan H).

Acetylation in refluxing acetic anhydride–sodium acetate afforded *methyl* 6α,7β-*diacetoxyvouacapan*-17β-*oate* (13), needles (from ethanol), m.p. 206—207° (Found: C, 67·0; H, 7·5. $C_{25}H_{34}O_7$ requires C, 67·2; H, 7·7%); $[\alpha]_D^{22}$ −11° (*c* 1·0); $\nu_{max.}$ 1748, 1733, and 1247 cm^{-1}; δ 0·98, 0·98 and 1·12 (3 Me), 1·96 and 2·00 (2 AcO), 3·40 (1H, dm, *J* 9 Hz, H-14), 3·7 (CO_2Me), 4·97 and 5·44 (2H, 2 ABXq, J_{AB} 9·5, J_{AX} 11, $J_{BX'}$ 10 Hz, H-7 and H-6), and 6·13 and 7·25 (2H, 2d, *J* 2 Hz, furan H).

6α-*Acetoxyvouacapano*-17β,7β-*lactone* (16).—The hydroxy-acid (11) (500 mg) was refluxed in acetic anhydride–sodium acetate for 6 h to afford the acetoxy-lactone (16) as fine *needles* (400 mg) (from ethanol), m.p. 279—280° (Found: C, 70·8; H, 7·7. $C_{22}H_{28}O_5$ requires C, 70·9; H, 7·6%); $[\alpha]_D^{24}$ +27° (*c* 1·0); $\nu_{max.}$ 1802, 1724, 1242, and 949 cm^{-1}; δ 1·00, 1·08, and 1·08 (3 Me), 2·10 (OAc), 3·20 (1H, dm, *J* 11 Hz, H-14), 4·13 and 5·52 (2H, s ABXq, J_{AB} 9·5, J_{AX} = $J_{BX'}$ = 10·5 Hz, H-7 and H-6), and 6·60 and 7·30 (2d, furan H).

Methyl 7β-*Acetoxy*-6α-*hydroxyvouacapan*-17β-*oate* (14).*—This formed *crystals*, m.p. 210—212°; $[\alpha]_D^{23}$ −21° (*c* 1·0); $\nu_{max.}$ 3460, 1745, 1724, 1263, 1042, and 723 cm^{-1}; δ 1·03, 1·07 and 1·17 (3 Me), 2·05 (OAc), 3·37 (1H, dm, *J* 8·5 Hz, H-14), 3·73 (CO_2Me), 3·7—4·1 (1H, m, H-6), 4·84 (1H, ABXq, J_{AB} 9, J_{AX} 10·5 Hz, H-7), and 6·12 and 7·23 (2H, 2d, furan H). Acetylation afforded the corresponding diacetate (13).

Vouacapane-6α,7β,17-*triol* (17).—A solution of the dihydroxy-ester (12) (724 mg, 2 mmol) in tetrahydrofuran

* The positional isomer (15) of this hydroxy-acetate has been isolated from *P. poligalaeflorus* (unpublished data). For comparison: δ 5·23 (H-6, ABXq, *J* 9 and 11·5 Hz).

(10 ml) was added dropwise to a suspension of lithium aluminium hydride (500 mg) in the same solvent (10 ml), and the whole was refluxed for 4 h. Work-up and extraction with chloroform afforded a solid (675 mg), which crystallized from ethanol as *rods*, m.p. 180—182° (Found: C, 71·8; H, 8·7. $C_{20}H_{30}O_4$ requires C, 71·8; H, 9·0%); $\nu_{max.}$ 3280, 1653, 1508, 1012, 903, and 724 cm^{-1}. Acetylation gave the corresponding *triacetate*, m.p. 171—172° (Found: C, 67·9; H, 8·0. $C_{26}H_{36}O_7$ requires C, 67·8; H, 7·9%); $\nu_{max.}$ 1739, 1245, 1052, and 756 cm^{-1}.

The same triol (17) was obtained by reduction with lithium aluminium hydride of the acetoxy-lactone (16), the diacetoxy-ester (13), or the monoacetoxy-compound (14), under similar conditions.

Monotosylate of the Triol (17) *and Reduction of the Product.*—Tosyl chloride (460 mg, 2·4 mmol) was slowly added with stirring to an ice-cold solution of the triol (17) (530 mg, 1·6 mmol) in dry pyridine (10 ml) and the whole was kept at 0—5° for 48 h. T.l.c. then revealed that the reaction was essentially over. The mixture was taken up in chloroform and washed with dilute hydrochloric acid and water till neutral. The solvent was evaporated off at *ca.* 40° to leave a yellow powder (740 mg); $\nu_{max.}$ 3333, 1344, and 1167 cm^{-1}. This material, dissolved in benzene (2 ml) and tetrahydrofuran (5 ml), was added, with stirring and cooling, to lithium aluminium hydride (130 mg) in the same solvent (5 ml), and the mixture was heated (24 h) on a water-bath kept at 50°. Work-up furnished a solid (507 mg), which on chromatography over silica gel in benzene–ethanol (1—5%) gave the starting triol (150 mg) and 7β,17-*epoxy-vouacapane*-6α-*ol* (21) (320 mg), m.p. 173—175° (from ethanol) (Found: C, 75·8; H, 8·9. $C_{20}H_{28}O_3$ requires C, 75·9; H, 8·9%); $\nu_{max.}$ 3425, 1610, 1502, 1100, 1036, 952, 899, and 722 cm^{-1}. Acetylation yielded the corresponding *acetoxy-ether* (22), rods, m.p. 262—264° (Found: C, 73·7; H, 8·4. $C_{22}H_{30}O_4$ requires C, 73·7; H, 8·4%); $\nu_{max.}$ 1724 and 1239 cm^{-1}; δ 1·00, 1·04, and 1·07 (3 Me), 2·12 (OAc), 3·4—3·9 (2H, m, OCH_2), 4·36 (1H, t, *J* 7·5 Hz, H-7), 5·42 (1H, ABXq, *J* 9 and 10·5 Hz, H-6), and 6·2 and 7·3 (2H, 2d, 2 Hz, furan H).

In another attempt the monotosylate (18) (460 mg) was treated with lithium aluminium hydride (150 mg) in tetrahydrofuran at room temperature for 16 h, with stirring. Work-up gave a powder (310 mg), which on chromatography as before afforded the 14-epi-*vouacapane*-6α,7β-*diol* (19) (153 mg) [followed by the triol (17)]. Recrystallization from methanol gave needles, m.p. 114—115° (Found: C, 75·2; H, 9·6. $C_{20}H_{30}O_3$ requires C, 75·4; H, 9·5%). Acetylation in refluxing acetic anhydride (NaOAc) afforded 6α,7β-*diacetoxy*-14-epi-*vouacapane* (20), fine needles (from ethanol), m.p. 179—181° (Found: C, 71·5; H, 8·6. $C_{24}H_{34}O_5$ requires C, 71·6; H, 8·5%); $[\alpha]_D^{22}$ +46° (*c* 1·0); $\nu_{max.}$ 1733, 1504, 1250, 1043, 1032, 1020, 741, and 726 cm^{-1}; δ 0·97, 0·97, and 1·06 (9H, 2s, 3 Me), 1·17 (3H, d, *J* 6·5 Hz, Me), 2·01 and 2·05 (6H, 2s, 2 AcO), 5·02 (1H, t, *J* 9 Hz, H-7), 5·44 (1H, ABXq, *J* 9 and 11·5 Hz, H-6), and 6·2 and 7·23 (2H, 2d, *J* 2 Hz, furan H).

6α,7β-*Diacetoxyvouacap*-14(17)-*ene* (24).—This formed *rods* (from benzene–ethanol), m.p. 157—158° (Found: C, 71·9; H, 8·1. $C_{24}H_{32}O_5$ requires C, 72·0; H, 8·1%); $[\alpha]_D^{22}$ +112° (*c* 1·12); $\nu_{max.}$ 1742, 1658, 1513, 1250, 1045, 1028, 901, 883, and 725 cm^{-1}; δ 0·95, 1·03, and 1·12 (9H, 3s, 3 Me), 1·98 and 2·04 (6H, 2s, 2 AcO), 2·5—1·9 (3H, ABXq superimposed on a multiplet, C-11 methylene and H-8), 4·90 and 5·06 (2H, 2d, *J* 2 Hz, $=CH_2$; partly superimposed on signals from H-7), 5·50 (1H, ABXq, *J* 9 and 10 Hz, H-6; the upfield part overlapped with signals from H-7), and 6·42 and 7·25 (2H, 2d, *J* 2 Hz, furan H). Hydrogenation of compound (24) (80 mg) in ethanol, containing a few drops of acetic acid, over palladium–charcoal (10%) for 2 h, yielded the C-14 epimeric diacetate (20) (72 mg), identified by mixed m.p. and i.r. and n.m.r. spectra.

1,2,3,4,4aα,11b-*Tetrahydro*-4,4,7,11bβ-*tetramethylphenanthro*[3,2-b]*furan* (27).—The diacetoxyvouacapene (24) (60 mg) was refluxed for 1·5 h in chloroform containing a catalytic amount of toluene-*p*-sulphonic acid. The cooled solution was washed with sodium hydrogen carbonate solution and evaporated. The resulting oil (41 mg) was purified over silica gel to give an oil (27 mg), $\nu_{max.}$ (film) 1613, 1587, 1534, 1389, 1368, 1140, 855, 783, and 717 cm^{-1}; δ 0·98, 1·07, 1·07 (9H, 3s, 3 Me), 2·47 (3H, s, Me), 2·10 (1H, t, *J* 3 Hz, H-5), 6·03 and 6·88 (2H, 2dd, *J* 3 and 10·5 Hz, H-6 and H-7, partly superimposed on furan H at 6·7), 7·23 (1H, approx. d, aromatic H-11), and 7·53 (1H, d, *J* 2 Hz, furan α-H).

Vouacapane-6α,7β,14β-*triol* (25).—This formed *crystals*, m.p. 218—222° (Found: C, 71·7; H, 8·9. $C_{20}H_{30}O_4$ requires C, 71·8; H, 9·0%); $\nu_{max.}$ 3413, 1653, 1506, 1075, 1041, 905, 729, and 687 cm^{-1}. Acetylation of 86 mg in refluxing acetic anhydride (2 ml) containing fused sodium acetate, gave a product (80 mg) which was purified over silica gel (10 g) in benzene. The product (24) (27 mg) crystallized from ethanol, m.p. and mixed m.p. 155—157°; i.r. spectrum identical with that of authentic compound (24).

The triol (25) gave the same hydrocarbon (27) as obtained from the diacetoxyvouacapene (24) under the conditions already described.

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