Lichens and Fungi. Part XIII.[1] Comparison of the Nuclear Magnetic Resonance and Mass Spectra of 17,21-Secohopane and 17,21-Secoflavicane Derivatives

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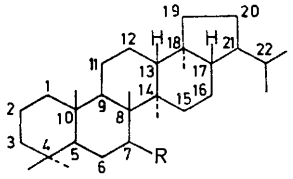
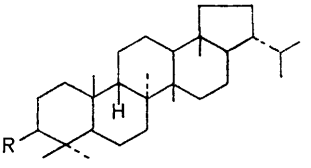
N.m.r. and mass spectral data for derivatives of 17,21-secohopane and 17,21-secoflavicane provide supporting evidence for the structure proposed for flavicane, rings C, D, and E of which are considered to be antipodally related to rings C, D, and E of 21α-*H*hopane.

THE striking similarities in the n.m.r. spectra of 21α*H*-hopane (1a) and flavicane (2a) and their derivatives



(1) a; R = H
b; R = OH
c; R = OAc



(2) a; R = H
b; R = OH
c; R = OAc

were used in elucidating the structure of flavicane (2a) and its parent stictane.[2] In the flavicane structure (2a) rings C, D, and E are identical, but antipodally related about the BC ring junction, to rings C, D, and E of 21α*H*-hopane. In Part XII [1] the preparation of certain flavic-17(21)-ene derivatives was reported, and the n.m.r. spectral similarities between these compounds and those of corresponding hop-17(21)-ene derivatives gave further support to the structure proposed for flavicane. We now report the similar n.m.r. and mass spectral analysis of the seco-diones and -diols prepared by standard methods (Schemes 1 and 2) from hop-17(21)-ene (3a), 7β-acetoxyhop-17(21)-ene (3b), 3β-acetoxyflavic-17(21)-ene (8a), and 2α,3β-diacetoxyflavic-17(21)-ene (8b).

In the hop-17(21)-ene series (Scheme 1), the β-face of the double bond is less hindered than the α-face. The major products of osmylation are assigned the 17β,21β-diol (4a and c) configuration. Cleavage by lead tetra-acetate gave the seco-diones (5a and b), and each of these on reduction gave a mixture of four seco-diols, separable by multiple p.l.c. The isolation of four epimeric seco-diols having axial or equatorial configuration for the hydroxy-group at C-17 and *R*- or *S*-configuration at C-21 has been noted in a parallel series of degradations.[3]

In the secoflavicane series (Scheme 2), it is the α-face of the double bond that is less hindered, and the structures of the seco-derivatives are similar to those of the corresponding secohopane derivatives, except that rings C, D, and E of the two series are antipodally related.

The n.m.r. multiplets produced by the five protons attached to carbon atoms α to the oxo-functions (·C*H*·CO·) in each of the seco-diones [(5a and b) and (10a and b)] are identical.† The protons at C-16 (2), C-20 (2), and C-22 (1) in each of the four diones must have identical stereochemical environments.

Reduction of the seco-diones with sodium borohydride gave, with each dione, four seco-diols, the axial and equatorial epimers at C-17, and for each of these epimers the *R*- and *S*-epimers at C-21. An n.m.r. signal centred at δ *ca.* 3.30 with $W_{\frac{1}{2}}$ 16 Hz is present in all sixteen seco-diols (see Table), and must be from the methine proton (C*H*·OH) at C-21. The C-17 epimeric alcohols can be readily distinguished. The methine proton of the axial alcohols gives a signal at lower field (δ *ca.* 3.58) and with smaller $W_{\frac{1}{2}}$ (7 Hz) than the signal from the equatorial alcohols, which is centred at δ 3.38 ($W_{\frac{1}{2}}$ 12 Hz). In conformity with prediction, the seco-diols with an axial configuration for the C-17 hydroxy-group, had higher R_F values than their C-17 epimers. The absolute configuration at C-21 (*R* or *S*) for each pair of seco-diols, similarly substituted at C-17, cannot be determined on the basis of the present evidence, and for convenience these epimers have been numbered 1 and 2 in order of decreasing R_F value in the Experimental section. The close similarity in the spectra of the seco-diols with an axial hydroxy-group at C-17 and of those with an equatorial hydroxy-group must mean that the hydroxy-groups in the compounds listed have essentially identical stereochemical environments.

The mass spectra † of the 7β-acetoxysecohopanediols, (6c and d) and (7c and d) are virtually identical, as are those of the secohopanediols (6a and b) and (7a and b). Likewise the mass spectra † of the four 3β-acetoxyseco-flavicanediols (11a and b) and (12a and b) are almost identical with each other in fragmentation pattern and intensity, and with those of the 7β-acetoxysecohopane-diols. This is not unexpected in view of the reported insensitivity [4] of the fragmentation pattern, for fragments of mass greater than *m/e* 189, to the nature and position of a substituent group in rings A and B. Dia-

† Available as Supplementary Publication No. SUP 21724 (4 pp.); for details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.

[1] Part XII, R. E. Corbett and A. L. Wilkins, *J.C.S. Perkin I*, 1976, 857.

[2] W. J. Chin, R. E. Corbett, C. K. Heng, and A. L. Wilkins, *J.C.S. Perkin I*, 1973, 1437.

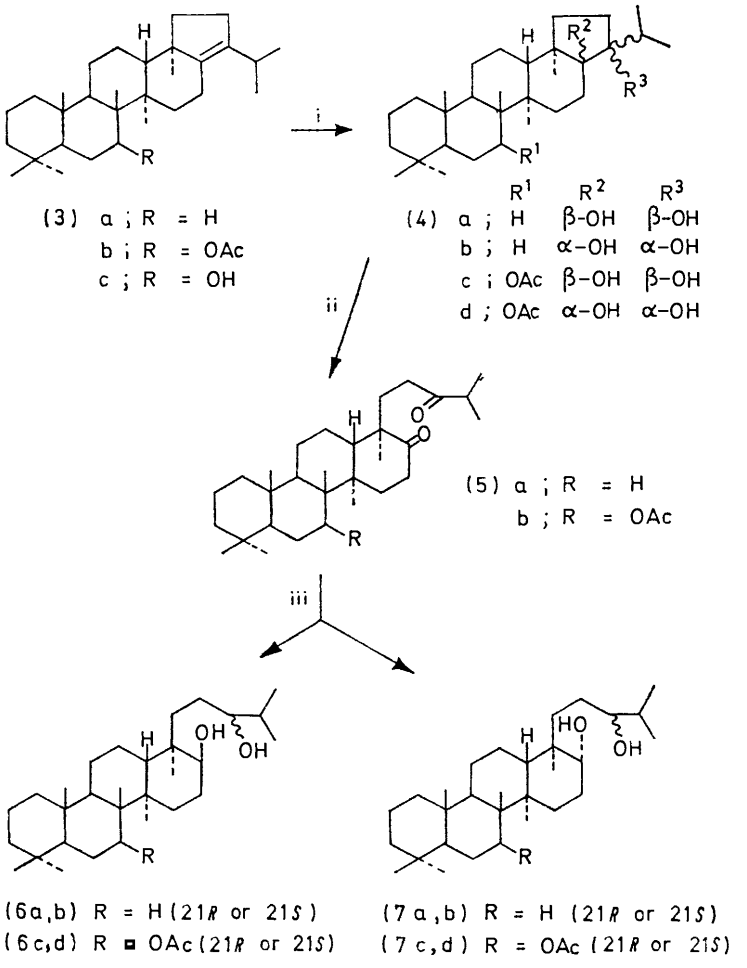
[3] D. H. R. Barton, P. de Mayo, and J. C. Orr, *J. Chem. Soc.*, 1958, 2239; Y. Tsuda and K. Isobe, *Chem. and Pharm. Bull. (Japan)*, 1957, **15**, 797.

[4] H. Budzeckiewicz, J. M. Wilson, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 3688; J. S. Shannon, *Austral. J. Chem.*, 1963, **16**, 683; M. N. Galbraith, C. J. Miller, J. W. L. Rawson, E. Ritchie, J. S. Shannon, and W. C. Taylor, *ibid.*, 1965, **18**, 226; R. E. Corbett and H. Young, *J. Chem. Soc.* (*C*), 1966, 1556, 1564.

grammatic representations of the genesis of these fragments are given in the Supplementary Publication.

Recognition of the characteristic deshielding of the C-8 (0.14 p.p.m.) and C-14 (0.08 p.p.m.) methyl groups of hopane triterpenoids by a 7β-acetoxy-group permitted the specific assignment of all the methyl signals in the two series of secohopanes (see Table). The methyl signals of the secoflavicanes can be identified by direct analogy with those of the secohopanes. In both the series replacement of an equatorial hydroxy-group at C-17 by an axial hydroxy-group has little effect on the C-14 and C-18 methyl signals. On the other hand the C-8 methyl group, which is relatively remote from the C-17 hydroxy-group, is deshielded by an axial but not by an equatorial hydroxy-group at C-17. A methyl group in a 1,3-diaxial relationship to a hydroxy-group is characteristically deshielded by *ca.* 0.25—0.27 p.p.m. The deshielding observed in this case (0.06 p.p.m.) must arise from the usual co-axial effect, much weakened by the inclusion of two additional carbon centres between the interacting groups.

N.m.r. and mass spectral data were used to establish [2] and confirm [1] the stereochemical similarities of rings C, D, and E of flavicane and 21α*H*-hopane. The range of these data has been further extended in the present investigation and gives added support to the structures originally proposed for flavicane and stictane.[2]



SCHEME 1 Reagents: i, OsO_4; ii, $Pb(OAc)_4$; iii, $NaBH_4$

EXPERIMENTAL

Experimental procedures are as described in Part VI.[5]

Osmylation of Hop-17(21)-ene (3a).—A solution of the hopene (3a) (1.05 g) in dioxan–pyridine (3 : 2; 50 ml) was stirred with osmium tetraoxide (1 g) for 24 h at room temperature. Saturated aqueous sodium disulphite solution (50 ml) was added, and stirring was continued for a further 2 h. The mixture was worked up in the usual way and the product chromatographed on alumina (40 g). Elution with E–H (1 : 1) (300 ml) gave compound (4a) (0.82 g), and with ether (100 ml) gave (4b) (25 mg). *Hopane-17,21-diol* (4a), the higher R_F component, had m.p. 229—230° (sublimed sample); $\nu_{max.}$ 3 480 cm^{-1} (OH); *m/e* 444 (M^+), 426 (100%), 383, 344, 328, and 191 (Found: C, 80.8; H, 11.6. $C_{30}H_{52}O_2$ requires C, 81.0; H, 11.8%). 17αH,21αH-*Hopane-17,21-diol* (4b), the lower R_F component, had m.p. 216—217° (sublimed sample), $\nu_{max.}$ 3 490 cm^{-1} (OH) (Found: C, 81.2; H, 11.9%).

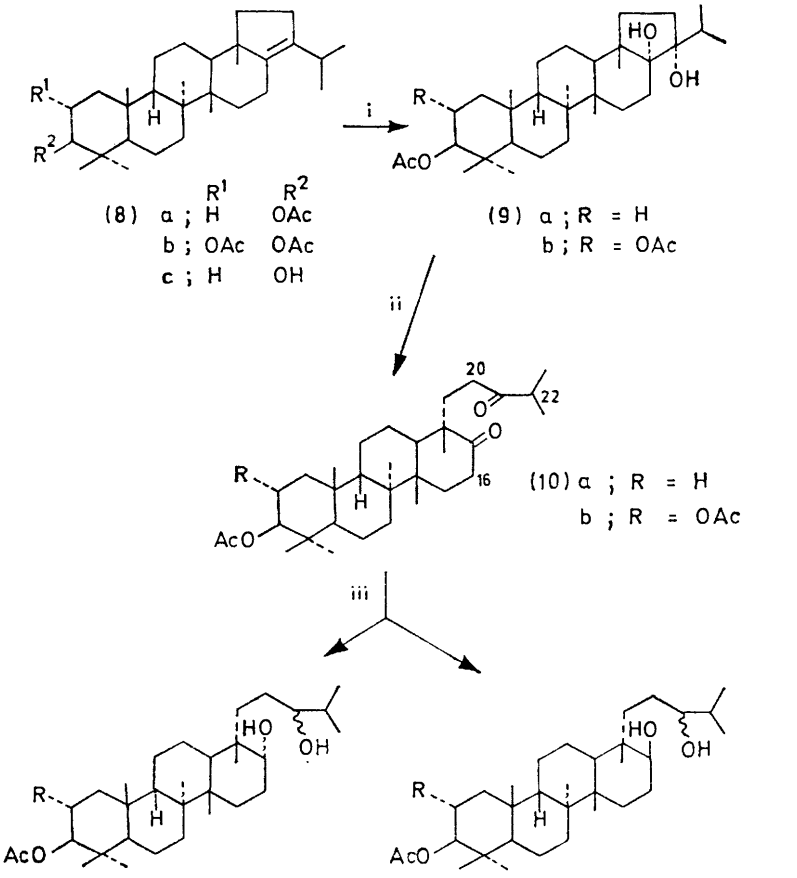
17,21-*Secohopane-17,21-dione* (5a).—A solution of the diol (4a) (400 mg) in benzene–glacial acetic acid (3 : 2; 50 ml) was stirred with lead tetra-acetate (480 mg) for

[5] R. E. Corbett and R. A. J. Smith, *J. Chem. Soc.* (*C*), 1969, 44.

30 min at 0 °C. The excess of reagent was destroyed with ethylene glycol and the mixture worked up in the usual way. P.l.c. on silica gel with E–H (1 : 4) gave 17,21-*secohopane*-17,21-*dione* (5a), m.p. 98—99° (sublimed sample); $\nu_{max.}$ 1 700 cm^{-1} (C=O) (Found: C, 81.2; H, 11.0. $C_{30}H_{50}O_2$ requires C, 81.4; H, 11.4%).

Reduction of 17,21-*Secohopane*-17,21-*dione* (5a).—A solution of the dione (5a) (400 mg) in dioxan–methanol–water (4 : 4 : 1; 100 ml) was stirred with sodium borohydride (400 mg) for 30 min at 20 °C. The excess of reagent was destroyed with 2N-hydrochloric acid and the mixture worked up in the usual way. Multiple (× 3) p.l.c. on silica gel with E–H (3 : 2) gave,in order of decreasing R_F value, the diols (6a) (20 mg), (6b) (40 mg), (7a) (140 mg),and (7b) (145 mg). 17,21-*Secohopane*-17β,21ξ-*diol*-1 (6a) had m.p. 162—163° (sublimed sample); $\nu_{max.}$ 3 330 cm^{-1} (OH); *m/e* 446 (M^+), 428 (100%), 426, 413, 410, 385, 345, and 327 (Found: C, 80.9; H, 12.0. $C_{30}H_{54}O_2$ requires C, 80.7; H, 12.2%). 17,21-*Secohopane*-17β,21ξ-*diol*-2 (6b) had m.p. 167—168° (sublimed sample); $\nu_{max.}$ 3 320 cm^{-1} (OH); *m/e* 446 (M^+), 428 (100%), 426, 413, 410, 385, 345, and 327 (Found: C, 80.6; H, 11.9%). 17,21-*Secohopane*-17α,21ξ-*diol*-1 (7a) had m.p. 165—167° (sublimed sample); $\nu_{max.}$ 3 330 cm^{-1} (OH); *m/e* 446 (M^+), 428 (100%); 426, 413, 410, 385, 345, and 327 (Found: C, 81.0; H, 12.1%). 17,21-*Secohopane*-17α,21ξ-*diol*-2 (7b) had m.p. 168—170° (sublimed sample); $\nu_{max.}$ 3 320 cm^{-1} (OH); *m/e* 446 (M^+), 428 (100%), 426, 413, 410, 385, 345, and 327 (Found: C, 80.9; H, 12.0%).

Osmylation of 7β-*Acetoxyhop*-17(21)-*ene* (3b).—Osmylation of the hopene (3b) (1.4 g) as described for (3a) and chromatography of the product on alumina gave, on elution with E–H (3 : 1), the diol (4c) (1.2 g) and, on elution with ether, the diol (4d) (30 mg). 7β-*Acetoxyhopane*-17,21-*diol* (4c) had m.p. 242—244° (sublimed sample); $\nu_{max.}$ 3 490 (OH), 1 730, and 1 250 cm^{-1} (OAc); δ 2.01 (3 H, s, OAc) and 5.13 (1 H, q, C*H*·OAc); *m/e* 502 (M^+, 100%), 484, 442, 424, 386, 343, and 326 (Found: C, 76.6; H, 11.0. $C_{32}H_{54}O_4$ requires C, 76.4; H, 10.8%). 7β-*Acetoxy*-17αH,21αH-*hopane*-17,21-*diol* (4d) had m.p. 238—239° (sublimed sample); $\nu_{max.}$ 3 510 (OH), 1 730, and 1 250 cm^{-1} (OAc); δ 1.94 (3 H, s, OAc) and 5.07 (1 H, q, C*H*·OAc) (Found: C, 76.3; H, 10.7%).



SCHEME 2 Reagents as Scheme 1

7β-*Acetoxy*-17,21-*secohopane*-17,21-*dione* (5b).—Cleavage of the diol (4c) (500 mg) with lead tetra-acetate (500 mg) in benzene–glacial acetic acid (3 : 2; 50 ml) as described for (4a), and p.l.c. on silica gel with E–H (1 : 3) gave 7β-*acetoxy*-17,21-*secohopane*-17,21-*dione* (5b) (460 mg), m.p. 123—124° (sublimed sample); $\nu_{max.}$ 1 705 (C=O), 1 730, and 1 250 cm^{-1} (OAc); δ 1.98 (3 H, s, OAc) and 5.06 (1 H, q, C*H*·OAc) (Found: C, 76.7; H, 10.2. $C_{32}H_{52}O_4$ requires C, 76.8; H, 10.5%).

Reduction of 7β-*Acetoxy*-17,21-*secohopane*-17,21-*dione* (5b).

Chemical shifts (δ) of methyl groups

Compound	Chemical shifts (δ) 4β	4α	10β	8β	14α	18α	22* (2 Me)
21α*H*-Hopane (1a)	0.78	0.81	0.84	0.95	0.92	0.64	0.77, 0.87
Hop-17(21)-ene (3a)	0.79	0.84	0.84	0.94	1.05	0.84	0.91, 0.98
21α*H*-Hop-7β-ol (1b)	0.81	0.81	0.87	0.99	1.03	0.67	0.79, 0.89
Hop-17(21)-en-7β-ol (3c)	0.80	0.85	0.85	0.96	1.15	0.83	0.91, 0.99
7β-Acetoxy-21α*H*-hopane (1c)	0.80	0.82	0.87	1.08	1.00	0.64	0.78, 0.88
7β-Acetoxy-hop-17(21)-ene (3b)	0.78	0.83	0.86	1.07	1.13	0.83	0.90, 0.98
Hopane-17,21-diol (4a)	0.80	0.85	0.85	0.92	1.06	1.08	0.89, 0.96
17α*H*,21α*H*-Hopane-17,21-diol (4b)	0.79	0.86	0.86	0.98	0.98	1.13	0.82, 0.88
17,21-Secohopane-17,21-dione (5a)	0.79	0.85	0.85	1.01	1.08	1.04	1.04, 1.04
17,21-Secohopane-17β,21ξ-diol-1 (6a) †	0.79	0.83	0.85	1.01	1.01	0.78	0.90, 0.90
17,21-Secohopane-17β,21ξ-diol-2 (6b) †	0.79	0.83	0.85	1.01	1.01	0.78	0.91, 0.91
17,21-Secohopane-17α,21ξ-diol-1 (7a) ‡	0.79	0.82	0.84	0.95	0.99	0.79	0.92, 0.92
17,21-Secohopane-17α,21ξ-diol-2 (7b) ‡	0.79	0.82	0.84	0.95	0.99	0.79	0.91, 0.91
7β-Acetoxyhopane-17,21-diol (4c)	0.78	0.84	0.86	1.13	1.15	1.08	0.89, 0.96
7β-Acetoxy-17α*H*,21α*H*-hopane-17,21-diol (4d)	0.77	0.86	0.86	1.01	1.11	1.11	0.79, 0.86
7β-Acetoxy-17,21-secohopane-17,21-dione (5b)	0.79	0.87	0.87	1.11	1.16	1.01	1.08, 1.08
7β-Acetoxy-17,21-secohopane-17β,21ξ-diol-1 (6c) †	0.77	0.85	0.86	1.15	1.09	0.77	0.90, 0.90
7β-Acetoxy-17,21-secohopane-17β,21ξ-diol-2 (6d) †	0.77	0.85	0.86	1.15	1.09	0.77	0.90, 0.90
7β-Acetoxy-17,21-secohopane-17α,21ξ-diol-1 (7c) ‡	0.78	0.83	0.86	1.09	1.09	0.79	0.92, 0.92
7β-Acetoxy-17,21-secohopane-17α,21ξ-diol-2 (7d) ‡	0.78	0.83	0.86	1.09	1.09	0.79	0.91, 0.93
Flavicane (2a)	0.81	0.85	0.89	1.13	0.91	0.64	0.78, 0.88
3β-Acetoxyflavicane (2c) [2]	0.86	0.86	0.89	1.14	0.93	0.64	0.78, 0.89
Flavican-3β-ol (2b) [2]	0.78	0.98	0.87	1.14	0.90	0.64	0.79, 0.89
Flavic-17(21)-en-3β-ol (8c) [2]	0.78	0.97	0.91	1.07	0.96	0.80	0.91, 0.98
3α-Acetoxyflavic-17(21)-ene (8a)	0.85	0.85	0.94	1.09	0.96	0.81	0.91, 0.98
3β-Acetoxy-17α*H*, 21α*H*-flavicane-17,21-diol (9a)	0.85	0.85	0.92	1.12	1.03	1.05	0.89, 0.96
3β-Acetoxy-17,21-secoflavicane-17,21-dione (10a)	0.85	0.85	0.96	1.16	1.00	1.00	1.08, 1.08
3β-Acetoxy-17,21-secoflavicane-17α,21ξ-diol-1 (11a) †	0.86	0.86	0.93	1.18	0.93	0.76	0.90, 0.92
3β-Acetoxy-17,21-secoflavicane-17α,21ξ-diol-2 (11b) †	0.86	0.86	0.93	1.18	0.93	0.76	0.90, 0.90
3β-Acetoxy-17,21-secoflavicane-17β-21ξ-diol-1 (12a) ‡	0.86	0.86	0.93	1.11	0.91	0.78	0.90, 0.93
3β-Acetoxy-17,21-secoflavicane-17β,21ξ-diol-2 (12b) ‡	0.86	0.86	0.93	1.11	0.91	0.78	0.89, 0.89
2α,3β-Diacetoxyflavic-17(21)-ene (8b)	0.90	1.05	0.90	1.10	0.97	0.82	0.92, 0.98
2α,3β-Diacetoxy-17α*H*,21α*H*-flavicane-17,21-diol (9b)	0.90	1.03	0.90	1.14	1.03	1.05	0.90, 0.97
2α,3β-Diacetoxy-17,21-secoflavicane-17,21-dione (5b)	0.90	1.06	0.90	1.17	0.99	0.99	1.07, 1.07
2α,3β-Diacetoxy-17,21-secoflavicane-17α,21ξ-diol-1 (11c) †	0.90	1.03	0.89	1.19	0.92	0.77	0.90, 0.92
2α,3β-Diacetoxy-17,21-secoflavicane-17α,21ξ-diol-2 (11d) †	0.90	1.03	0.89	1.19	0.92	0.77	0.90, 0.90
2α,3β-Diacetoxy-17,21-secoflavicane-17β,21ξ-diol-1 and -2 (12c) ‡ and (12d) ‡	0.90	1.03	0.89	1.13	0.91	0.77	0.89, 0.89

* Doublets, *J* 6—7 Hz. † 17-H, 3.55—3.57 (m, $W_{\frac{1}{2}}$ 7 Hz); 21-H, 3.26—3.30 (m, $W_{\frac{1}{2}}$ 16 Hz). ‡ 17-H, 3.34—3.39 (m, $W_{\frac{1}{2}}$ 12 Hz); 21-H, 3.28—3.31 (m, $W_{\frac{1}{2}}$ 16 Hz).

—Reduction of (5b) (350 mg) with sodium borohydride (400 mg) in dioxan–methanol–water (4 : 4 : 1; 100 ml) as described for (5a), and separation of the four products by multiple (× 3) p.l.c. on silica gel with E–H (3 : 2), gave, in order of decreasing R_F value, the diols (6c) (15 mg), (6d) (35 mg), (7c) (130 mg), and (7d) (110 mg). 7β-*Acetoxy*-17,21-*secohopane*-17β,21ξ-*diol*-1 (6c) had m.p. 164—165° (sublimed sample); $\nu_{max.}$ 3 380 (OH), 1 735, and 1 246 cm^{-1} (OAc); δ 1.96 (3 H, s, OAc) and 5.07 (1 H, q, C*H*·OAc); *m/e* 504 (M^+), 486, 484, 444, 426 (100%), 383, and 343 (Found: C, 75.8; H, 11.0. $C_{32}H_{56}O_4$ requires C, 76.1; H, 11.1%). 7β-*Acetoxy*-17,21-*secohopane*-17β,21ξ-*diol*-2 (6d) had m.p. 168—169° (sublimed sample); $\nu_{max.}$ 3 380 (OH), 1 735, and 1 245 cm^{-1} (OAc); δ 1.96 (3 H, s, OAc) and 5.07 (1 H, q, C*H*·OAc); *m/e* 504 (M^+), 486, 484, 444, 426 (100%), 383, and 343 (Found: C, 75.8; H, 11.0%). 7β-*Acetoxy*-17,21-*secohopane*-17α,21ξ-*diol*-1 (7c) had m.p. 170—172° (sublimed sample); $\nu_{max.}$ 3 340 (OH), 1 738, and 1 250 cm^{-1} (OAc); δ 1.96 (3 H, s, OAc) and 5.06 (3 H, q, C*H*·OAc); *m/e* 504 (M^+), 486, 484, 444, 426 (100%), 383, and 343 (Found: C, 76.3; H, 11.0%). 7β-*Acetoxy*-17,21-*secohopane*-17α,21ξ-*diol*-2 (7d) had m.p. 168—169° (sublimed sample); $\nu_{max.}$ 3 345 (OH), 1 736, and 1 250 cm^{-1} (OAc); δ 1.96 (3 H, s, OAc) and 5.06 (1 H, q, C*H*·OAc); *m/e* 504 (M^+), 486, 484, 444, 426 (100%), 383, and 343 (Found: C, 76.0; H, 11.2%).

3β-*Acetoxy*-21αH-*flavicane*-17α,21-*diol* (9a).—Osmylation of 3β-acetoxyflavic-17(21)-ene (8e) (750 mg) as described for (3a), and chromatography of the product on alumina in ether, gave 3β-*acetoxy*-21αH-*flavicane*-17α,21-*diol* (9a), $\nu_{max.}$ 3 510 (OH), 1 735, and 1 245 cm^{-1} (OAc); δ 2.04 (3 H, s, OAc) and 4.50 (1 H, m, C*H*·OAc); *m/e* 502 (M^+, 100%), 484, 442, 424, 386, 343, and 326 (Found: C, 76.3; H, 10.9. $C_{32}H_{54}O_4$ requires C, 76.4; H, 10.8%).

3β-*Acetoxy*-17,21-*secoflavicane*-17,21-*dione* (10a).—Cleavage of (9a) (256 mg) with lead tetra-acetate (300 mg) in benzene–glacial acetic acid (3 : 2; 40 ml) as described for (4a), and purification of the product by p.l.c. on silica gel with E–H (1 : 2), gave 3β-*acetoxy*-17,21-*secoflavicane*-17,21-*dione* (10a) (240 mg), m.p. 126—128° (sublimed sample); $\nu_{max.}$ 1 703 (C=O), 1 730, and 1 245 cm^{-1} (OAc); δ 2.03 (3 H, s, OAc) and 4.50 (1 H, m, C*H*·OAc) (Found: C, 77.1; H, 10.3. $C_{32}H_{52}O_4$ requires C, 76.8; H, 10.5%).

Reduction of 3β-*Acetoxy*-17,21-*secoflavicane*-17,21-*dione* (10a).—Reduction of the dione (10a) (260 mg) with sodium borohydride (400 mg) in dioxan–methanol–water (4 : 4 : 1; 100 ml) as described for (5a), and separation of the four products by multiple (× 3) p.l.c. on silica gel with E–H (3 : 2), gave in order of decreasing R_F value the diols (11a) (12 mg), (11b) (24 mg), (12a) (130 mg), and (12b) (140 mg). 3β-*Acetoxy*-17,21-*secoflavicane*-17α,21ξ-*diol*-1 (11a) had m.p. 133—134° (sublimed sample); $\nu_{max.}$ 3 380 (OH), 1 735, and 1 245 cm^{-1} (OAc); δ 2.03 (3 H, s, OAc) and 4.50 (1 H, m, C*H*·OAc); *m/e* 504 (M^+), 486, 484, 444, 426 (100%), 383, and 343 (Found: C, 75.9; H, 11.2. $C_{32}H_{56}O_4$ requires C, 76.1; H, 11.1%). 3β-*Acetoxy*-17,21-*secoflavicane*-17α,21ξ-*diol*-2 (11b) had m.p. 138—139° (sublimed sample); $\nu_{max.}$ 3 360 (OH), 1 735, and 1 245 cm^{-1} (OAc); 2.03 (3 H, s,

OAc) and 4.50 (1 H, m, C*H*·OAc); *m/e* 504 (M^+), 486, 484, 444, 426 (100%), 383, and 343 (Found: C, 75.9; H, 10.7%). 3β-*Acetoxy*-17,21-*secoflavicane*-17β,21ξ-*diol*-1 (12a) had m.p. 145—146° (sublimed sample); $\nu_{max.}$ 3 350 (OH), 1 738, and 1 245 cm^{-1} (OAc); δ 2.02 (3 H, s, OAc) and 4.50 (1 H, m, C*H*·OAc); *m/e* 504 (M^+), 486, 484, 444, 426 (100%), 383, and 343 (Found: C, 75.8; H, 11.0%). 3β-*Acetoxy*-17,21-*secoflavicane*-17β,21ξ-*diol*-2 (12b) had m.p. 142—143° (sublimed sample); $\nu_{max.}$ 3 360 (OH), 1 736, and 1 250 cm^{-1} (OAc); δ 2.04 (3 H, s, OAc) and 4.50 (1 H, m, C*H*·OAc); *m/e* 504 (M^+), 486, 484, 444, 426 (100%), 383, and 343 (Found: C, 76.2; H, 10.9%).

2α,3β-*Diacetoxy*-21αH-*flavicane*-17α,21-*diol* (9b).—Osmylation of 2α,3β-diacetoxyflavic-17(21)-ene (8b) (350 mg) as described for (3a) and chromatography of the product on alumina in ether gave 2α,3β-*diacetoxy*-21αH-*flavicane*-17α,21-*diol* (9b) (330 mg), m.p. 253—254° (sublimed sample); $\nu_{max.}$ 3 520 (OH), 1 738, and 1 245 cm^{-1} (OAc); δ 1.97 and 2.03 (3 H, each, s, OAc), 4.73 (1 H, d, C*H*·OAc), and 5.17 (1 H, sextet, C*H*·OAc) (Found: C, 73.0; H, 10.4. $C_{34}H_{56}O_6$ requires C, 72.8; H, 10.1%).

2α,3β-*Diacetoxy*-17,21-*secoflavicane*-17,21-*dione* (10b).—Cleavage of the diol (9b) (300 mg) with lead tetra-acetate (300 mg) in benzene–glacial acetic acid (3 : 2; 40 ml) as described for (4a), and p.l.c. on silica gel with E–H (1 : 2), gave 2α,3β-*diacetoxy*-17,21-*secoflavicane*-17,21-*dione* (10b) (380 mg), m.p. 120—121° (sublimed sample); $\nu_{max.}$ 1 704 (C=O), 1 730, and 1 245 cm^{-1} (OAc); δ 1.98 and 2.04 (3 H each, s, OAc), 4.74 (1 H, d, C*H*·OAc), and 5.17 (1 H, sextet, C*H*·OAc) (Found: C, 73.0; H, 9.9. $C_{34}H_{54}O_6$ requires C, 73.1; H, 9.8%).

Reduction of 2α,3β-*Diacetoxy*-17,21-*secoflavicane*-17,21-*dione* (10b).—Reduction of the dione (10b) (460 mg) with sodium borohydride (500 mg) in dioxan–methanol–water (4 : 4 : 1; 100 ml) as described for (5a), and separation of the four products by multiple (× 3) p.l.c. on silica gel with E–H (3 : 2), gave, in order of decreasing R_F value, the diols (11c) (12 mg), (11d) (20 mg), (12c) (95 mg), and (12d) (160 mg). 2α,3β-*Diacetoxy*-17,21-*secoflavicane*-17α,21ξ-*diol*-1 (11c) had m.p. 98—99° (sublimed sample); $\nu_{max.}$ 3 380 (OH), 1 739, and 1 250 cm^{-1} (OAc); δ 1.98 and 2.04 (3 H each, s, OAc), 4.74 (1 H, d, C*H*·OAc), and 5.17 (1 H, sextet, C*H*·OAc) (Found: C, 72.4; H, 10.2. $C_{34}H_{58}O_6$ requires C, 72.6; H, 10.4%). 2α,3β-*Diacetoxy*-17,21-*secoflavicane*-17α,21ξ-*diol*-2 (11d) had m.p. 97—98° (sublimed sample); $\nu_{max.}$ 3 380 (OH), 1 735, and 1 250 cm^{-1} (OAc); δ 1.98 and 2.03 (3 H each, s, OAc), 4.74 (1 H, d, C*H*·OAc), and 5.17 (1 H, sextet, C*H*·OAc) (Found: C, 72.4; H, 10.7%). 2α,3β-*Diacetoxy*-17,21-*secoflavicane*-17β,21ξ-*diol*-1 (12c) had m.p. 101—103° (sublimed sample); $\nu_{max.}$ 3 320 (OH), 1 735, and 1 245 cm^{-1} (OAc); δ 1.98 and 2.03 (3 H each, s, OAc), 4.74 (1 H, d, C*H*·OAc), and 5.17 (1 H, sextet, C*H*·OAc) (Found: C, 72.4; H, 10.7%). 2α,3β-*Diacetoxy*-17,21-*secoflavicane*-17β,21ξ-*diol*-2 (12d) had m.p. 99—100° (sublimed sample); $\nu_{max.}$ 3 320 (OH), 1 735, and 1 250 cm^{-1} (OAc); δ 1.98 and 2.03 (3 H each, s, OAc), 4.74 (3 H, d, C*H*·OAc), and 5.17 (3 H, sextet, C*H*·OAc) (Found: C, 72.9; H, 10.5%).

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