Lichens and Fungi. Part XI.[1] Isolation and Structural Elucidation of a New Group of Triterpenes from *Sticta coronata*, *S. colensoi*, and *S. flavicans*

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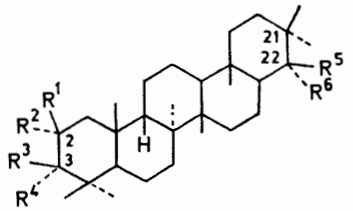
Ten new triterpenes, derived from a new triterpane system for which the name stictane is proposed, have been isolated from the hexane extractives of the lichens named in the title.

In Part I [2] was reported the isolation from *S. coronata* of polyporic acid, calycin, pulvinic lactone, and pulvinic acid, together with a number of neutral compounds which were not investigated. The same four acidic compounds are present in the lichens *S. colensoi* and *S. flavicans*, together with the same neutral compounds.

Ten new triterpenes [(1)—(10)] have now been isolated, by column chromatography supplemented by multiple preparative t.l.c., from the neutral fraction of



	R^1	R^2	R^3	R^4	R^5	R^6
(1)	H	OH	OH	H	H	OH
(2)	H	OAc	OAc	H	H	OAc
(3)	H	OAc	OAc	H	H	OH
(4)	H	OAc	OH	H	H	OH
(5)	H	OH	OAc	H	H	OH
(6)	H	OAc	OAc	H	O	
(7)	H	H	OH	H	H	OH
(8)	H	H	OAc	H	H	OAc
(9)	H	H	OAc	H	H	OH
(10)	H	H	O		H	OH
(11)	H	H	O		O	
(12)	H	OAc	O		O	
(13)	H	H	H	H	H	H
(23)	H	OH	OH	H	H	OAc
(24)	H	H	OH	H	H	OAc
(32)	H	H	H	H	H	OH
(37)	H	OAc	OH	H	H	OAc
(38)	H	OH	OAc	H	H	OAc
(39)	H	OAc	O		H	OAc
(40)	H	H	O		H	OAc
(41)	H	H	O		H	H
(42)	O		OAc	H	H	OAc
(43)	O		H	H	H	OAc
(44)	O		H	H	H	H
(45)	O		H	H	O	
(46)	OH	H	H	H	H	OH
(47)	OH	H	H	H	OH	H

the hexane extractives of the three lichens. Compounds (1), (3), (4), and (5) gave compound (2) on acetylation, and oxidation of compound (3) gave compound (6). Acetylation of compounds (7) and (9) gave compound (8), and oxidation of compounds (7) and (10) gave the same diketone (11). The diketone (11) was related to compound (4) by the reactions outlined in Scheme 1. These inter-relationships established that

$$(4) \xrightarrow{i} (12) \xrightarrow{ii} (11)$$

SCHEME 1

Reagents: i, CrO_3; ii, Ca–liq. NH_3

compounds (1)—(10) were derivatives of the same triterpane, that the ten compounds had the same two carbon atoms oxygenated in each case, and that the third oxygen function in compounds (1)—(6) was attached to the same carbon atom in each.

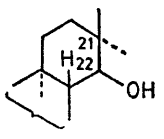
A negative tetranitromethane test, and the absence of any characteristic ethylenic absorption in the i.r., u.v., or ^1H n.m.r. spectra of these compounds showed that they were saturated. Their molecular formulae are consistent with a saturated pentacyclic structure only.

The parent triterpane was obtained by Wolff–Kishner reduction of the diketone (11). The product was different (m.p., g.l.c., n.m.r.) from any of the triterpene hydrocarbons so far reported. The n.m.r. spectrum showed the presence of eight tertiary methyl groups, and the mass spectrum was similar to those of 18α-oleanane, 14α-taraxerane, and gammacerane,[1,3] with a fragment at *m/e* 191 as the most intense peak.[3,4] These n.m.r. and mass spectral data imply that this new triterpane, for which the name strictane (13) is proposed, must have a pentacyclic structure similar to the structures of the foregoing triterpanes.

Compounds (3), (4), (5), (7), (9), and (10) each contain at least one secondary hydroxy-group, and the n.m.r. spectrum of each contains a characteristic doublet [δ 3·09 and 3·19 (1H)]. This hydroxy-group, which the large coupling constant ($J_{ax.ax}$ 10 Hz) defines as equatorial, must be adjacent to a fully substituted carbon atom and a ring junction carrying an axial hydrogen atom, and can only be in ring E, which could have either of the partial structures (14) or (15). The i.r. carbonyl absorption ($\nu_{max.}$ 1700 cm^{-1}) of the oxo-compound (6) supports the contention that ring E is six-membered. Dehydration of this ring E hydroxy-group (C-22 hydroxy-group) should lead to a retro-pinacolinic rearrangement. The alcohol (3) with phos-

[1] Part X, R. E. Corbett, Susan D. Cumming, and E. V. Whitehead, *J.C.S. Perkin I*, 1972, 2827.
[2] J. Murray, *J. Chem. Soc.*, 1952, 1345.
[3] I. R. Hills, G. W. Smith, and E. V. Whitehead, *Nature*, 1968, **219**, 243.
[4] M. N. Galbraith, C. J. Miller, J. W. L. Rawson, E. Ritchie, J. S. Shannon, and W. C. Taylor, *Austral. J. Chem.*, 1965, **18**, 226.

phoryl chloride in pyridine gave the rearrangement product (16), and a trace of a second compound, which could be the isopropylidene isomer, was detected (t.l.c.). Dehydration of compounds (9) and (10) also



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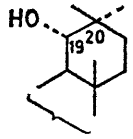

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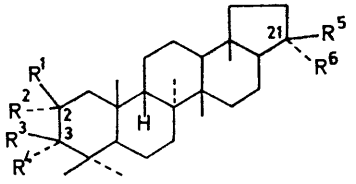
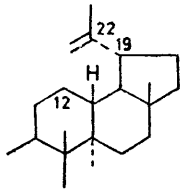


	R^1	R^2	R^3	R^4	R^5	R^6
(16)	H	OAc	OAc	H	H	C(:CH_2)Me
(17)	H	H	OAc	H	H	C(:CH_2)Me
(18)	H	H	O		H	C(:CH_2)Me
(19)	H	H	H	H	H	$CH(Me)_2$
(33)	H	H	H	H	H	C(:CH_2)Me

resulted in a similar contraction of ring E and extrusion of an isopropenyl group, with the formation of compounds (17) and (18). These compounds are named as derivatives of a new triterpane for which the name flavicane (19) is proposed, rather than as 20(21 → 22)-



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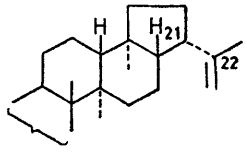
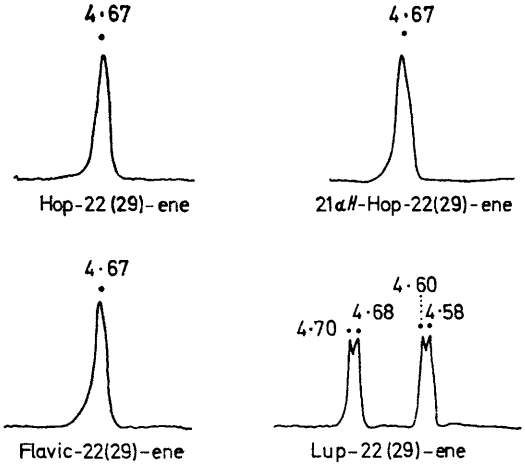


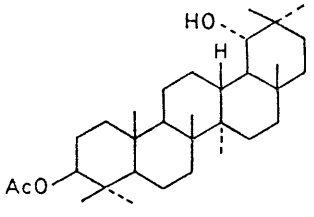
(20)

abeo-strictane derivatives. The numbering proposed for flavicane is identical with that of hopane. The n.m.r. signals from the two vinylic protons in compounds (16)—(18) appear in each case as a broadened singlet (δ 4·67, $W_{\frac{1}{2}}$ 5 Hz), identical with the vinylic proton signal produced by hop-22(29)-ene (20), 21α*H*-hop-22(29)-ene, and their derivatives (Figure). By contrast the vinylic protons of lup-22(29)-ene (21) and its derivatives produce two long-range coupled doublets (typically δ 4·58 and 4·60, and 4·68 and 4·70). Presumably a 21-isopropenyl group in hopane triterpenes (20) has rotational freedom about the C(21)–C(22) bond, whereas the proximity of the two hydrogen atoms at C-12 in lupene triterpenoids inhibits the rotation of a C-19 isopropenyl group. As a consequence of a preferred conformation being adopted in the latter case, unequal ring C anisotropic deshielding of the two vinyclic protons results in each proton having a distinct chemical shift, and in addition long-range coupling effects are observed. On the basis of the identity of the n.m.r. spectral data for the vinylic protons of flavic-22(29)-ene and hop-22(29)-ene and their derivatives, ring E of flavicane is considered to have the hopane configuration rather than that of lupane, and stictane is consequently assigned the configuration for ring E depicted in (14) (or its antipode). Further support for this conclusion is provided by the ease of acetylation of the C-22 hydroxy-group in strictane



Vinylic proton n.m.r. signals (δ values)

derivatives. Compounds (3), (4), (5), (7), (9), and (10) can be acetylated under conditions which are too mild to bring about the acetylation of the equatorial hydroxy-group in 3β-acetoxy-18α-oleanan-19α-ol [5] (22), in which the hydrogen atoms at C-12 sterically hinder the approach of the acetylating reagent.



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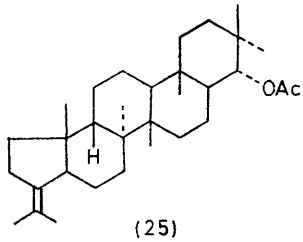

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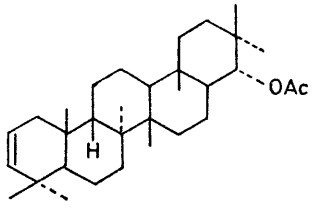

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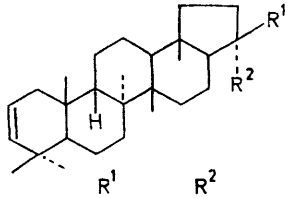


	R^1	R^2
(29)	:C(Me)$_2$	
(30)	H	C(:CH_2)Me
(31)	H	$CH(Me)_2$

The reactions outlined in Scheme 1 are only possible if compound (12) is an α-acetoxy-ketone, and demon-

[5] T. R. Ames, G. S. Davy, T. G. Halsall, and E. R. H. Jones, *J. Chem. Soc.*, 1952, 2868.

strate that in the stictane derivatives which contain three oxygen functions [(1)—(6)] two of the latter are associated with adjacent carbon atoms. The parent of the trisubstituted stictanes (1) must be an α-glycol. Glycol cleavage of compounds (1) and (23) at room temperature with lead tetra-acetate in dry benzene was 50% complete after 24 h (t.l.c.). The slow reaction is consistent with a *trans*-configuration for the hydroxy-groups.[6] The ring A location of the diol system was revealed by a study of the dehydration of compound (24), a partial hydrolysis product of (8). Treatment with phosphorous pentachloride in hexane resulted in a retropinacolinic rearrangement accompanied by extrusion of an isopropylidene group [δ 1·56 and 1·72 (3H each, s, $C{=}CMe_2$)] and gave compound (25). This reaction is only possible if there is a 3β-hydroxy-group in (24), and requires that stictane should have the usual 4,4-dimethyl system with ring A *trans*-fused to ring B.[7] Thus compound (1) must contain a 2α,3β-glycol unit. Reduction of compound (25) with lithium aluminium hydride (LAH) gave 5(4 ⟶ 3)*abeo*-stictan-22α-ol (26).

When phosphoryl chloride in pyridine was used to dehydrate compound (24), the product was 22α-acetoxystict-2-ene (27), which on hydrogenation over Adams catalyst gave 22α-acetoxystictane (28). Dehydration of stictane-3β,22α-diol (7) with phosphoryl chloride in pyridine gave flavica-2,21-diene (29) and flavica-2,22(29)-diene (30). Partial hydrogenation of the latter (30) gave flavic-2-ene (31). In flavic-2-ene and stict-2-ene and their derivatives, coincidental overlap of the C-2 and C-3 olefinic proton signals gives rise to a signal (δ 5·42 ± 0·1) closely similar to that recorded[8] for 8,13-epoxylabd-2-ene (δ 5·38). The dehydration of 3β-hydroxy-triterpenoids with phosphoryl chloride in pyridine to give 2-enes and with phosphorous pentachloride to give 5(4 ⟶ 3)*abeo*-3-enes has been noted by Ourisson *et al.*[9]

The saturated hydrocarbon flavicane (19) was prepared by hydrogenation of the dehydration product, flavic-22(29)-ene (33), of stictan-22α-ol (32), which was itself obtained by Wolff–Kishner reduction of 3-oxostictan-22α-ol (10). Flavicane (19) was different (g.l.c., m.p., and n.m.r.) from lupane, hopane, 21α*H*-hopane, 17α*H*-hopane, and 17α*H*,21α*H*-hopane, but mass (base peak at *m/e* 191) and n.m.r. (six tertiary methyl groups and one isopropyl group) spectral data established that flavicane was structurally related to these triterpanes.

An analysis of the chemical shifts of the eight methyl groups of stictane and appropriate mono- and di-substituted stictane derivatives (Table 1) revealed that in each compound there are three signals that can be associated with the three ring A methyl groups on the basis of established substituent effect data.[1,10] Similarly, three signals for each compound can be associated with the three ring E methyl groups. Two signals, obviously those of two methyl groups remote from ring A and ring E remain relatively constant. In Table 2 the effects of substituents at C-3 on the 4α-, 4β-, 10β-, and 8-methyl chemical shifts of a number of related triterpenes are compared. The chemical shifts of the ring A methyl groups in the stictane derivatives listed (Table 2), with the exception of those of the 3-oxo-derivatives, are typical of 3β-substituted triterpenoids containing a chair ring A. The data for 3-oxostictane derivatives (Tables 1 and 2) indicate that ring A in these compounds does not adopt the usual chair conformation.

The c.d. curve of the 3-oxostictane (10) ($\Delta\varepsilon_{284}$ +3·22) exhibited a large-amplitude positive Cotton effect.[11] The tetracyclic triterpenoid, alisol A triacetate,[12] a 3-oxoprotostane[13] derivative, gives a similar c.d. curve ($\Delta\varepsilon_{291}$ +2·57). *X*-Ray structural analysis of alisol A 23,24-acetonide 11-monobromoacetate,[12] which contains a 3-oxo-function, has shown that rings A and B are both in boat conformations. This compound has a *trans-syn-trans* configuration for rings A, B, and C, with a β-H at C-9 and an α-methyl at C-8. The same configuration for rings A, B, and C is proposed for 3-oxostictanes. This configuration will account for the c.d. data and for the anomalous ring A methyl group signals in the n.m.r. spectra of 3-oxostictane derivatives. Irrespective of the conformation adopted by ring A, a 3-oxo-function will deshield the 4α- and 4β-methyl groups (models). On these grounds the two lower-field signals [δ 1·03 and 1·05 (3H each)] are assigned to the 4β- and 4α-methyl groups, respectively, in (10). In a boat conformation a 3-oxo-group will strongly shield the 10β-methyl group, and the singlet at δ 0·77 is assigned to this group. The C-8 methyl group in (10) and other appropriate 3-oxo-compounds (Table 1) is deshielded slightly (δ 1·17—1·19) and this can only be accounted for if ring B is in a boat conformation with the methyl group in the 8α-configuration. For a 3-oxo-compound to adopt a boat ring A conformation is not without precedent. Hemmert *et al.*[14] have reported that in the 4,4-dimethylcholest-5-ene series of compounds with a 3-oxo- or a 2β-substituent ring A has a non-chair conformation whereas with a 2-oxo- or a 2α- or 3β-substituent ring A has the normal chair conformation. Evidence will be introduced later to show that in stictan-2β-ol derivatives ring A appears to adopt a non-chair conformation. Whilst caution

[6] C. Djerassi, D. B. Thomas, A. L. Livingston, and C. R. Thompson, *J. Amer. Chem. Soc.*, 1957, **79**. 5292; G. B. Guise, E. Ritchie, and W. C. Taylor, *Austral. J. Chem.*, 1962, **15**, 314.

[7] D. H. R. Barton, *J. Chem. Soc.*, 1953, 1027.

[8] M. J. A. McGrath, University of Otago, personal communication.

[9] G. Ourisson, P. Crabbé, and O. R. Rodig, 'Tetracyclic Triterpenes,' Hermann, Huddersfield, 1964, p. 36.

[10] H. T. Cheung and D. G. Williamson, *Tetrahedron*, 1969, **25**, 119.

[11] C. Djerassi, 'Optical Rotatory Dispersion,' McGraw-Hill, New York, 1960, pp. 90—96.

[12] T. Murata, M. Shinohara, T. Hirata, K. Kamiga, M. Nishikawa. and M. Miyamoto, *Tetrahedron Letters*, 1968, 103.

[13] T. Hattori, H. Igarashi, S. Iwasaki, and S. Okuda, *Tetrahedron Letters*, 1969, 1023.

[14] F. Hemmert, A. Lablache-Combier, and B. Lacoume, *Bull. Soc. chim. France*, 1966, 982 and references cited therein.

TABLE 1

Chemical shifts (δ) of methyl groups

	4β	4α	10β	8α	14β	18β	21α	21β
Stictane (13)	0·82	0·85	0·89	1·14	0·91	0·68	0·88	0·90
Stictan-22-one (48)	0·83	0·86	0·90	1·17	0·90	0·63	1·01	1·17
Stictan-22α-ol (32)	0·81	0·86	0·91	1·14	0·90	0·73	0·86	0·98
Stictan-22β-ol (49)	0·82	0·85	0·90	1·14	0·92	0·93	0·93	0·93
22α-Acetoxystictane (28)	0·82	0·85	0·89	1·14	0·92	0·82	0·85	0·92
22β-Acetoxystictane (50)	0·81	0·85	0·90	1·15	0·90	0·85	0·90	1·00
Stictan-3-one (41)	1·04	1·05	0·77	1·19	0·92	0·68	0·88	0·90
Stictan-2-one (44)	0·94	1·03	0·94	1·18	0·92	0·70	0·87	0·90
22α-Hydroxystictan-3-one (10)	1·04	1·05	0·77	1·17	0·94	0·74	0·86	1·00
22α-Acetoxystican-2-one (43)	0·94	1·03	0·94	1·16	0·93	0·82	0·85	0·92
Stictane-3,22-dione (11)	1·03	1·05	0·77	1·17	0·94	0·64	1·01	1·20
Stictane-2,22-dione (45)	0·94	1·03	0·94	1·18	0·94	0·62	1·00	1·20
Stictane-3β,22α-diol (7)	0·78	0·97	0·90	1·14	0·90	0·73	0·87	0·97
Stictane-3β,22β-diol (51)	0·78	0·98	0·90	1·15	0·93	0·93	0·93	0·93
Stictane-2β,22α-diol (46)	0·97	0·91	1·06	1·11	0·91	0·73	0·81	0·91
Stictane-2β,22β-diol (47)	0·93	0·91	1·06	1·11	0·91	0·93	0·93	0·93
3β,22α-Diacetoxysticane (8)	0·85	0·85	0·89	1·14	0·93	0·81	0·85	0·93
3β-Acetoxystictan-22α-ol (9)	0·86	0·86	0·89	1·14	0·93	0·74	0·86	0·98
3β-Acetoxystictan-22β-ol (52)	0·85	0·85	0·90	1·14	0·93	0·93	0·93	0·93
22α-Acetoxystictan-3β-ol (24)	0·78	0·97	0·89	1·13	0·89	0·80	0·85	0·92

TABLE 2

Methyl group chemical shifts

	Skeleton	4β	4α	10β	C-8	Substituent effects (p.p.m.)			
Alkane	Stictane	0·82	0·85	0·89	1·14				
	Hopane	0·78	0·81	0·84	0·94				
	Lupane	0·81	0·84	0·84	1·04				
	Allobetulane	0·81	0·85	0·85	0·99				
	14α-Taraxerane	0·82	0·84	0·88	1·10				
3β-OH	Stictane	0·78	0·97	0·90	1·14	−0·04	+0·12	+0·01	0·00
	Hopane	0·76	0·96	0·83	0·95	−0·02	+0·15	−0·01	+0·01
	Lupane	0·77	0·97	0·84	1·05	−0·04	+0·13	0·00	+0·01
	Allobetulane	0·78	0·97	0·86	0·99	−0·03	+0·12	+0·01	0·00
3β-OAc	Stictane	0·85	0·85	0·93	1·14	+0·03	0·00	+0·04	0·00
	Hopane	0·83	0·83	0·83	0·95	+0·05	+0·02	−0·01	+0·01
	Lupane	0·84	0·84	0·87	1·04	+0·04	0·00	+0·03	0·00
	Allobetulane	0·85	0·85	0·88	0·98	+0·04	+0·00	+0·03	−0·01
3-Oxo	Stictane	1·03	1·05	0·77	1·18	+0·19	+0·20	−0·12	+0·04
	Hopane	1·03	1·07	0·93	1·00	+0·22	+0·26	+0·09	+0·05
	Lupane	1·04	1·08	0·96	1·08	+0·23	+0·24	+0·12	+0·04
	Allobetulane	1·04	1·09	0·98	1·04	+0·23	+0·24	+0·13	+0·05
	14α-Taraxerane	1·04	1·08	0·95	1·10	+0·22	+0·24	+0·07	0·00

must be exercised in extending Hemmert's observations, it is clear that when ring B is subject to steric strain as in 4,4-dimethylcholest-5-ene, or is present in a boat conformation as in protostane derivatives, the stereochemical environment and electronic nature of a ring A substituent could have a significant influence on the conformation adopted by ring A. The evidence described thus far leads to the partial structure (34) for rings A and B of stictane.

The chemical shifts of the four ring D/E methyl groups in flavicane and flavic-22(29)-ene are almost identical with those of the four ring D/E methyl groups in 21α*H*-hopane and 21α*H*-hop-22(29)-ene (Table 3).

TABLE 3

Chemical shifts (δ) of methyl groups

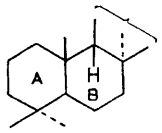
	C-8	C-14	C-18	Other	
21α*H*-Hopane	0·95	0·92	0·64	0·78 *	0·88 *
Flavicane	1·13	0·91	0·64	0·78 *	0·88 *
21α*H*-Hop-22(29)-ene	0·95	0·95	0·68	1·68 †	4·68 †
Flavic-22(29)-ene	1·14	0·93	0·68	1·67 †	4·67 †

* Pr^{i} d, J 6 Hz. † CH_2·CMe.

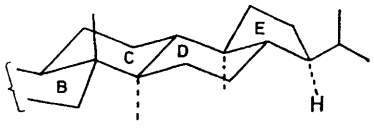
This close similarity strongly implies that rings D and E of flavicane and 21α*H*-hopane have identical configurations and conformations. In addition since the C-14 and C-18 methyl groups in the two series have almost identical chemical shifts it may be concluded that they must have identical structures in the vicinity of C-14. It is therefore postulated that ring D of flavicane is *trans*-fused to ring C and that, as in hopane, a methyl group is located at C-8 in a 1,2-*trans*-diaxial relationship with the methyl group at C-14. Two alternative partial structures, (35) and (36) antipodally related about the B/C ring junction, are possible on this evidence for flavicane. Of these only (36) can be combined with the partial structure (34) to give a total structure for flavicane (19) in which the C-14 methyl group has an environment identical but antipodal to that of 21α*H*-hopane. On the basis of structure (19) for flavicane, stictane must have structure (13).

An equatorial C-22 substituent in stictane will have the α-configuration, and bears the same conformational relationship to the 21,21-dimethyl system as a 3β-

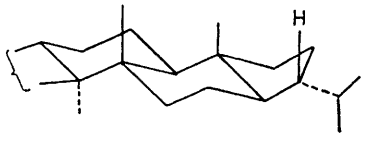
substituent does to the 4,4-dimethyl system in a 4,4-dimethylcholestane. This analogy permits the chemical shifts of the two C-21 methyl groups, and consequently



(34)



(35)



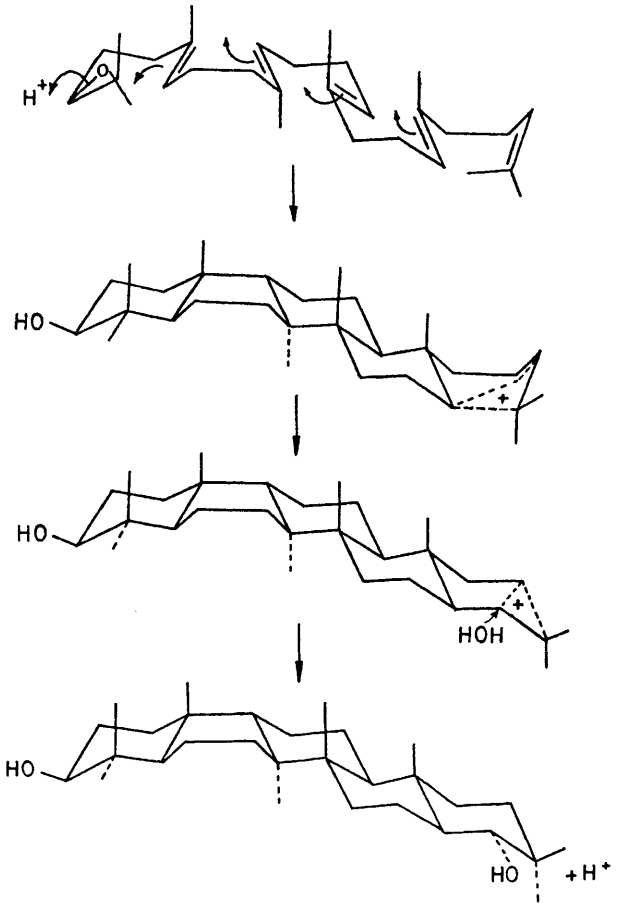
(36)

of the third ring E methyl group, to be assigned. Conversion of the 22α-hydroxy-group into the axial 22β-epimer results in marked deshielding of one of the ring E methyl groups. The extent of the deshielding (0·25 p.p.m.) is characteristic of a methyl group in a 1,3-diaxial relationship with a hydroxy-group, and confirms the location of an axial methyl group at C-18.

The stictane and flavicane derivatives listed in Tables 1 and 3 were prepared by standard methods from the ten triterpenoids isolated from the lichens. Deacetoxylation of 2α,22α-diacetoxystictan-3-one (39) with calcium in liquid ammonia gave 22α-acetoxystictan-3-one (40) and a minor product, stictan-3-one (41); similar deacetoxylation of 3β,22α-diacetoxystictan-2-one (42) gave 22α-acetoxystictan-2-one (43) and stictan-2-one (44) as a minor product. The isolation of the ketones (41) and (44) indicated that to a limited extent deacetoxylation of the isolated 22α-acetoxy-group had occurred in these reactions. Rothman and Wall [15] have reported a similar deacetoxylation of an acetoxy-group not adjacent to an oxo-group.

Reduction of 22α-acetoxystictan-2-one (43) and of stictane-2,22-dione (45) with lithium aluminium hydride gave stictane-2β,22α-diol (46) and stictane-2β,22β-diol (47), respectively. Since metal hydride reduction of a 4,4-dimethylcholestan-2-one invariably gives the axial 2β-ol, and since there is no n.m.r. evidence to suggest that ring A in the 2-oxo-compounds is other than a normal chair, it was concluded that the C-2 hydroxy-group in these compounds is axially oriented. The chemical shifts of the three ring A methyl groups in these compounds are not typical of those reported for other 4,4-dimethylcholestan-2β-ols. Ring A must be considerably flattened, or exist in a boat or twist conformation, to minimize the strong 1,3-diaxial interactions of the 2β-hydroxy-group with the 4β- and 10β-methyl groups. This deviation of ring A from a classical chair conformation in certain stictane derivatives has already been referred to and compared with the observations of Hemmert *et al.*[14] The ring A methyl group assignments made for these two compounds are tentative and are based on the reasonable argument [14] that even in a non-chair ring A conformation a 2β-hydroxy-group will still deshield the axial 4β- and 10β-methyl groups to a greater degree than the equatorial 4α-methyl group.

The stictane structure can be derived from squalene by acceptable biogenetic steps. The presence of ring A and ring E oxygen functions at C-3 and C-22 suggests that cyclisation is initiated in the usual manner by protonation of squalene 2,3-epoxide and terminated without backbone rearrangements by hydration of the resulting ring E cation (with loss of a proton). Scheme 2 depicts the possible biogenetic pathway to stictane-



SCHEME 2

3β,22α-diol. Since C-22 substitution has been established, a 1,2-Wagner–Meerwein shift in ring E is indicated.

Degradative studies in which flavic-17(21)-ene and

[15] E. S. Rothman and M. E. Wall, *J. Amer. Chem. Soc.*, 1957, **79**, 3228.

17,21-secoflavicane-17ξ,21ξ-diols and their derivatives are compared with hop-17(21)-ene and 17,21-secohopane-17ξ,21ξ-diols and their derivatives provide further support for the structures proposed. This work will be described in subsequent papers.

EXPERIMENTAL

Experimental procedures are as described in Part VI.[16]

Extraction of the Lichens.—The lichens *S. colensoi* and *S. coronata* were collected in the beech forests on the shores of Lake Hauroko, Southland, and *S. flavicans* was collected from the slopes of Ben Lomond, above Queenstown, Central Otago, in January 1968. Samples collected from other localities at different times of the year yielded the same compounds.

In a typical extraction of *S. flavicans*, the air-dried lichen (325 g) was ground to a fine powder in a Wiley mill and extracted (Soxhlet) with hexane (4 l) for 40 h. Fractional concentration of the hexane extract, as described by Murray,[2] gave crops of the acidic pigments (3·0 g total), polyporic acid, pulvinic acid, calycin, and pulvinic lactone, and a neutral fraction (3·2 g).

The neutral fraction (3·2 g) was chromatographed on alumina (100 g; Spence grade H). Elution with hexane gave a mixture of aliphatic hydrocarbons (0·20 g) (these will be reported elsewhere); elution with benzene and benzene–ether mixtures changing to ether–ethanol (3 : 1) gave fractions containing mixtures from which the triterpenoids were separated and purified by multiple preparative layer chromatography (p.l.c.) on silica gel.

3β,22α-*Diacetoxystictane* (8) (0·22 g) had m.p. 281—283° (from acetone); $[\alpha]_D^{20}$ −14·7° (*c* 0·47); $\nu_{max.}$ 1730 and 1245 cm^{-1} (OAc); δ 2·03 and 2·04 (3H each, s, OAc), 4·50 (1H, m, C*H*·OAc), and 4·70 (1H, d, C*H*·OAc) (Found: C, 77·2; H, 10·6. $C_{34}H_{56}O_4$ requires C, 77·2; H, 10·7%).

2α,3β,22α-*Triacetoxystictane* (2) (0·45 g) had m.p. 274° (from acetone); $[\alpha]_D^{20}$ −55·1° (*c* 0·88), $\nu_{max.}$ 1730 and 1240 cm^{-1} (OAc); δ 0·81 (3H), 0·85 (3H), 0·89 (9H), 0·93 (3H), 1·02 (3H), and 1·15 (3H) (Me groups), 1·97, 2·03, and 2·03 (3H each, s, OAc), 4·69 (1H, d, C*H*·OAc), and 4·74 (1H, d, C*H*·OAc), and 5·16 (1H, sextet, C*H*·OAc) (Found: C, 74·0; H, 10·0. $C_{36}H_{58}O_6$ requires C, 73·7; H, 10·0%).

2α,3β-*Diacetoxystictan*-22-*one* (6) (0·03 g) had m.p. 263—264° (from acetone); $[\alpha]_D^{20}$ −32·8° (*c* 0·92), $\nu_{max.}$ 1740, 1245 (OAc), and 1700 cm^{-1} (C=O); δ 0·62 (3H), 0·90 (9H), 1·01 (3H), 1·03 (3H), and 1·19 (3H) (Me groups) 1·97 and 2·03 (3H each, s, OAc), 4·73 (1H, d, C*H*·OAc), and 5·16 (1H, sextet, C*H*·OAc) (Found: C, 75·6; H, 10·0. $C_{34}H_{54}O_5$ requires C, 75·2; H, 10·0%).

3β-*Acetoxystictan*-22α-*ol* (9) (0·25 g) had m.p. 243—244° (sublimed sample), $[\alpha]_D^{20}$ −12·2° (*c* 0·95); $\nu_{max.}$ 3420 (OH), 1730, and 1245 cm^{-1} (OAc), δ 2·04 (3H, s, OAc), 3·14 (1H, d, C*H*·OH), and 4·51 (1H, m, C*H*·OAc) (Found: C, 78·9; H, 10·9. $C_{32}H_{54}O_3$ requires C, 79·0; H, 11·2%).

2α,3β-*Diacetoxystictan*-22α-*ol* (3) (0·29 g) had m.p. 231—232° (from acetone), $[\alpha]_D^{20}$ −1·5° (*c* 1·0); $\nu_{max.}$ 3550 (OH), 1735, 1715, 1225, and 1255 cm^{-1} (OAc); δ 0·72 (3H), 0·86 (3H), 0·90 (6H), 0·91 (3H), 0·98 (3H), 1·04 (3H), and 1·15 (3H) (Me groups), 1·97 and 2·03 (each 3H, s, OAc), 3·14 (1H, d, C*H*·OH), 4·72 (1H, d, C*H*·OAc), and 5·16 (1H, sextet, C*H*·OAc) (Found: C, 74·7; H, 10·5. $C_{34}H_{56}O_5$ requires C, 75·0; H, 10·4%).

Stictane-3β,22α-*diol* (7) (0·10 g) had m.p. 283° [from chloroform–acetone (1 : 1)]; $[\alpha]_D^{20}$ +12·3° (*c* 1·1); $\nu_{max.}$ 3560 and 3450 (OH) cm^{-1}; δ 3·14 (1H, d, C*H*·OH) and 3·26 (1H, m, C*H*·OH) (Found: C, 81·1; H, 11·9. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%).

3β-*Acetoxystictane*-2α,22α-*diol* (5) (0·23 g) had m.p. 227° (sublimed sample); $[\alpha]_D^{20}$ −58·2° (*c* 0·62): $\nu_{max.}$ 3450, 3440 (OH), 1735, and 1250 cm^{-1} (OAc); δ 0·73 (3H), 0·87 (9H), 0·91 (3H), 0·96 (3H), 0·98 (3H), and 1·16 (3H) (Me groups), 2·12 (3H, s, OAc), 3·14 (1H, d, C*H*·OH), and 3·83 (1H, sextet, C*H*·OH), and 4·50 (1H, d, C*H*·OAc) (Found: C, 76·3; H, 10·9. $C_{32}H_{54}O_4$ requires C, 76·4; H, 10·9%).

2α-*Acetoxystictane*-3β,22α-*diol* (4) (0·28 g) had m.p. 215—216° (from ethanol); $[\alpha]_D^{20}$ −42·0° (*c* 0·36); $\nu_{max.}$ 3580, 3440 (OH), 1730, and 1250 cm^{-1} (OAc); δ 0·73 (3H), 0·86 (6H), 0·91 (3H), 0·98 (3H), 0·99 (3H), 1·04 (3H), and 1·14 (3H) (Me groups), 2·05 (3H, s, OAc), 3·14 (1H, d, C*H*·OH), 3·18 (1H, d, C*H*·OH), and 5·01 (1H, sextet, C*H*·OAc) (Found: C, 76·2; H, 10·8. $C_{32}H_{54}O_4$ requires C, 76·4; H, 10·8%).

Stictane-2α,3β,22α-*triol* (1) (0·04 g) had m.p. 276° (from acetone); $[\alpha]_D^{20}$ +15·2°; $\nu_{max.}$ 3500—3340 cm^{-1} (OH) (Found: C, 78·0; H, 11·2. $C_{30}H_{52}O_3$ requires C, 78·2; H, 11·4%).

S. coronate and *S. colensoi* could be collected more readily in kilogram quantities than *S. flavicans*, and bulk quantities of the stictane triterpenoids were extracted from these lichens. In typical extractions *S. coronata* gave acidic pigments (7·8%) and triterpenoids (3·0%) and *S. colensoi* gave acidic pigments (3·4%) and triterpenoids (3·2%). Compound (10), which could be detected (t.l.c.) in the *S. flavicans* extractives, was isolated from the other two lichens.

22α-*Hydroxystictan*-3-*one* (10) had m.p. 216° (from acetone); $[\alpha]_D^{20}$ +129° (*c* 1·0); $\nu_{max.}$ 3500 (OH) and 1700 cm^{-1} (C=O); δ 3·14 (1H, d, C*H*·OH) (Found: C, 81·4; H, 11·4. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%).

Acetylation of Compounds (1), (3), (4), *and* (5).—Acetic anhydride (5 ml) was added to the alcohol (50 mg) in pyridine (5 ml) and the solution was kept for 48 h at room temperature. Work-up gave in each case 2α,3β,22α-acetoxystictane (2) (mixed m.p.)

Acetylation of Compounds (7) *and* (9).—Acetylation as just described gave in each case 3β,22α-acetoxystictane (8) (mixed m.p.).

Stictane-3,22-*dione* (11).—(*a*) Jones reagent was added dropwise to stictane-3β,22α-diol (180 mg) in acetone (5 ml) until an orange colour persisted. Work-up gave *stictane*-3,22-*dione* (11) (120 mg), m.p. 241—242° (from acetone); $[\alpha]_D^{20}$ +117·8° (*c* 0·32); $\nu_{max.}$ 1700 cm^{-1} (C=O) (Found: C, 81·6; H, 10·8. $C_{30}H_{48}O_2$ requires C, 81·7; H, 10·9%).

(*b*) Oxidation of (10) by Jones reagent as in (*a*) gave stictane-3,22-dione (11) (mixed m.p.).

2α-*Acetoxystictane*-3.22-*dione* (12).—Jones reagent was added dropwise to a stirred solution of the diol (4) (200 mg) in acetone (50 ml) until an orange colour persisted. Work-up in the usual way gave 2α-*acetoxystictane*-3,22-*dione* (175 mg), m.p. 212—213°; $\nu_{max.}$ 1750 (OAc), 1710, and 1700 cm^{-1} (C=O); δ 0·63 (3H), 0·91 (3H), 0·99 (3H), 1·10 (3H), and 1·16 (12H) (Me groups), 2·10 (3H, s, OAc), and 5·45 (1H, q, C*H*·OAc) (Found: C, 77·2; H, 9·9. $C_{32}H_{50}O_4$ requires C, 77·0; H, 10·1%).

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

Calcium–Liquid Ammonia Deacetoxylation of 2α-Acetoxystictane-3,22-dione (12).—A solution of the acetoxy-dione (12) (100 mg) in dry toluene (10 ml) was added during 5 min to a vigorously stirred solution of calcium (300 mg) in liquid ammonia (60 ml). After stirring for a further 15 minutes, solid ammonium chloride was added until the blue colour of the solution was discharged. The ammonia was allowed to evaporate at room temperature and the mixture was worked up in the usual way. P.l.c. on silica gel with E–H (1 : 3) gave stictane-3,22-dione (11) (60 mg), identical (m.p. and mixed m.p.) with an authentic specimen.

Stictane (13).—Stictane-3,22-dione (11) (40 mg) in hexane was added to freshly redistilled diethylene glycol (30 ml) which had been treated with sodium (300 mg). The hexane was distilled off as the temperature was increased to 180°. Completely anhydrous hydrazine (obtained by refluxing 98% hydrazine hydrate over potassium hydroxide for 3 h before distillation from the potassium hydroxide) was added until the solution was refluxing at 180° (solution temperature). After 24 h the temperature of the solution was raised to 210° by distilling off some of the hydrazine. After a further 24 h at 210° the mixture was cooled to room temperature, neutralized with 2N-hydrochloric acid, and worked up in the usual way. The product (30 mg) was filtered through neutral alumina (2 g; Woelm grade II) in hexane and gave *stictane* (13), m.p. 203—204° (from hexane–ethanol); $[\alpha]_D^{20}$ +12·2° (*c* 0·9); *m/e* 412 (M^+) and 191 (base peak) (Found: C, 87·6; H, 12·6. $C_{30}H_{52}$ requires C, 87·3; H, 12·7%).

2α,3β-*Diacetoxyflavic*-22(29)-*ene* (16).—Phosphoryl chloride (60 ml) was added dropwise to 2α,3β-diacetoxystictan-22α-ol (3) (200 mg) in anhydrous pyridine (30 ml) and the mixture was kept for 24 h at room temperature. Work-up in the usual way gave a product (150 mg) which was filtered through alumina (6 g) with E–H (1 : 1). P.l.c. on silver nitrate-impregnated silica gel with E–H (1 : 4) gave 2α,3β-*diacetoxyflavic*-22(29)-*ene* (16), m.p. 199—200° (from hexane); $\nu_{max.}$ 3090, 884 (C=CH_2) 1640 (C=C), and 1740 cm^{-1} (OAc); δ 0·71 (3H), 0·91 (9H), 1·04 (3H), 1·18 (3H), and 1·67 (3H) (Me groups), 1·99 (3H, s, OAc), 2·05 (3H, s, OAc), 4·67 (2H, C=CH_2), 4·74 (1H, d, CH·OAc), and 5·16 (1H, sextet, CH·OAc) (Found: C, 77·8; H, 10·3. $C_{34}H_{54}O_4$ requires C, 77·5; H, 10·3%).

3β-*Acetoxyflavic*-22(29)-*ene* (17).—Phosphoryl chloride (1·5 ml) was added dropwise during 30 min to a stirred solution of 3β-acetoxystictan-22α-ol (9) (80 mg) in pyridine. After stirring for a further 3 h at room temperature the mixture was worked up in the usual way and the product purified by p.l.c. on silver nitrate-impregnated silica gel with E–H (1 : 9) to give 3β-*acetoxyflavic*-22(29)-*ene* (17) (50 mg), m.p. 238—239° (sublimed sample); $\nu_{max.}$ 3085, 882 (=CH_2), 1738, 1250 (OAc), and 1640 cm^{-1} (C=C); δ 0·67 (3H), 0·85 (6H), 0·89 (3H), 0·93 (3H), and 1·14 (3H) (Me groups), 1·66 (3H, s, C=CMe), 2·03 (3H, s, OAc), 4·51 (1H, m, C*H*·OAc), and 4·67br (2H, s, $W_{\frac{1}{2}}$ 5 Hz, C=CH_2) (Found: C, 81·9; H, 11·0. $C_{32}O_{52}O_2$ requires C, 82·0; H, 11·2%).

Flavic-22(29)-*en*-3-*one* (18).—22α-Hydroxystictan-3-one (10) (50 mg) in dry pyridine (7·5 ml) was heated under reflux with phosphoryl chloride (1·5 ml) for 1 h. Water was added cautiously to the cooled solution and the mixture worked up in the usual way. The product was purified by p.l.c. on silver nitrate-impregnated silica gel with H–E (9 : 1). *Flavic*-22(29)-*en*-3-*one* (18) (9 mg) had m.p. 202—203° (from hexane–ethanol); $\nu_{max.}$ 3070 (C=CH_2) 1708 (C=O), 1640 (C=C), and 899 cm^{-1} (=CH_2) (Found: C, 84·4; H, 11·5. $C_{30}H_{48}O$ requires C, 84·8; H, 11·3%).

22α-*Acetoxystictane*-2α,3β-*diol* (23).—2α,3β,22α-Triacetoxystictane (2) (300 mg) was stirred at room temperature with ethanolic potassium hydroxide (0·5%; 20 ml) for 24 h. Work-up in the usual way gave, after p.l.c. on silica gel with E–H (2 : 1), unchanged (2) (50 mg) and 22α-*acetoxystictane*-2α,3β-*diol* (23) (170 mg), m.p. 280—282° (from acetone); $\nu_{max.}$ (Nujol) 3350, 3250 (OH), 1740, and 1240 cm^{-1} (OAc); $\nu_{max.}$ (0·005M in CCl_4) 3628 (free OH) and 3594 cm^{-1} (bonded OH); δ 0·82 (6H), 0·85 (3H), 0·90 (3H), 0·93 (3H), 0·96 (3H), 1·02 (3H), and 1·16 (3H) (Me groups), 2·03 (3H, s, OAc), 2·98 (1H, d, CH·OH), 3·73 (1H, m, $W_{\frac{1}{2}}$ 26 Hz, CH·OH), and 4·68 (1H, d, CH·OAc) (Found: C, 76·5; H, 10·7. $C_{32}H_{54}O_4$ requires C, 76·4; H, 10·8%).

22α-*Acetoxystictan*-3β-*ol* (24).—A stirred solution of 3β,22α-diacetoxystictane (8) (150 mg) in ethanolic 2% potassium hydroxide (35 ml) was slowly warmed to 60° and the reaction was followed by t.l.c. When an optimum yield of the compound of intermediate R_F value was detected (about 10 min) the mixture was worked up in the usual way and the products were separated by p.l.c. on silica gel with E–H (1 : 4). The intermediate R_F compound, 22α-*acetoxystictan*-3β-*ol* (24) (95 mg), had m.p. 272—274° (sublimed sample); $\nu_{max.}$ 3450 (OH), 1730, and 1245 cm^{-1} (OAc); δ 2·04 (3H, s, OAc), 3·24 (1H, t, C*H*·OH), and 4·69 (1H, d, C*H*·OAc) (Found: C, 79·2; H, 11·0. $C_{32}H_{54}O_3$ requires C, 79·0; H, 11·2%). The lowest R_F compound was stictane-3β,22α-diol (7) (m.p. and mixed m.p.) and the highest R_F compound was unchanged starting material (8).

22α-*Acetoxy*-5(4 ⟶ 3)abeo-*stict*-3-*ene* (25).—A solution of 22α-acetoxystictan-3β-ol (24) (35 mg) in benzene–hexane (1 : 9) (10 ml) was stirred with an excess of freshly sublimed phosphorus pentachloride (50 mg). After 30 min at room temperature, the mixture was worked-up in the usual way. P.l.c. on silica gel with E–H (1 : 9) gave 22α-*acetoxy*-5(4 ⟶ 3)abeo-*stict*-3-*ene* (25) (30 mg), m.p. 250—251° (sublimed sample); $\nu_{max.}$ 1735 and 1240 cm^{-1} (OAc); δ 0·75 (3H), 0·85 (3H), 0·89 (3H), 0·93 (3H), 0·96 (3H), and 1·07 (3H) (Me groups), 1·56 and 1·72 (3H each, s, C=CMe_2), 2·04 (3H, s, OAc), and 4·71 (1H, d, C*H*·OAc) (Found: C, 82·2; H, 11·4. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%).

5(4 ⟶ 3)abeo-*Stict*-3-*en*-22α-*ol* (26).—A solution of 22α-acetoxy-5(4 ⟶ 3)*abeo*-stict-3-ene (25) (15 mg) in ether (50 ml) was stirred with a slight excess of LAH for 1 h at 20°. The excess of reagent was destroyed with wet ether and the mixture was worked up in the usual way. P.l.c. on silica gel with E–H (1 : 3) gave 5(4 ⟶ 3)abeo-*stict*-3-*en*-22α-*ol* (26) (12 mg), m.p. 265—266° (sublimed sample), $\nu_{max.}$ 3500 cm^{-1} (OH); δ 0·76 (6H), 0·89 (3H), 0·98 (6H), and 1·06 (3H) (Me groups), 1·56 and 1·70 (3H each, s, C=CMe), and 3·15 (1H, d, C*H*·OH) (Found: C, 84·7; H, 11·9. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8%).

22α-*Acetoxystict*-2-*ene* (27).—Phosphoryl chloride (1 ml) was added dropwise during 30 min to a stirred solution of 22α-acetoxystictan-3β-ol (24) (30 mg) in pyridine (15 ml). After stirring for a further 3 h at room temperature the mixture was worked up in the usual way and the product purified by p.l.c. on silver nitrate-impregnated silica gel with E–H (1 : 9) to give 22α-*acetoxystict*-2-*ene* (27) (18 mg), m.p. 246—248° (sublimed sample); $\nu_{max.}$ 3065, 1632,

721 (CH=CH), 1735, and 1240 cm^{-1} (OAc); δ 0·82 (3H), 0·85 (3H), 0·88 (6H), 0·91 (3H), 0·92 (6H), and 1·13 (3H) (Me groups), 2·03 (3H, s, OAc), 4·70 (1H, d, CH·OAc), and 5·41 (2H, m, $W_{\frac{1}{2}}$ 3 Hz, CH=CH) (Found: C, 82·1; H, 10·9. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%).

22α-*Acetoxystictane* (28).—A solution of 22α-acetoxystict-2-ene (27) (15 mg) in ethyl acetate (15 ml) was hydrogenated over Adams catalyst for 18 h (uptake 1·1 mol. equiv.). Removal of the catalyst and evaporation gave 22α-*acetoxystictane* (28) (15 mg), m.p. 248—249° (sublimed sample); $\nu_{max.}$ 1735 and 1240 cm^{-1} (OAc); δ 2·04 (3H, s, OAc) and 4·70 (1H, d, C*H*·OAc) (Found: C, 81·8; H, 11·5. $C_{32}H_{54}O_2$ requires C, 81·6; H, 11·6%).

Flavica-2,21-*diene* (29) *and Flavica*-2,22(29)-*diene* (30).—Phosphoryl chloride (2 ml) was added dropwise during 30 min to a stirred solution of stictane-3β,22α-diol (7) (250 mg) in pyridine (30 ml). After stirring for a further 3 h at room temperature the mixture was worked up in the usual way and the products separated by p.l.c. on silver nitrate-impregnated silica gel with E–H (1 : 9) to give the dienes (29) (31 mg) and (30) (94 mg). *Flavica*-2,21-*diene* (29), the higher R_F component, had m.p. 172° (sublimed sample); $\nu_{max.}$ 3065, 1632, and 721 cm^{-1} (CH=CH); δ 0·58 (3H), 0·89 (9H), 0·92 (3H), and 1·12 (3H) (Me groups), 1·56 and 1·72 (3H each, s, C=CMe_2), and 5·39—5·47 (major peak at 5·41) (2H, m, CH=CH) (Found: C, 88·4; H, 11·7. $C_{30}H_{48}$ requires C, 88·1; H, 11·8%). *Flavica*-2,22(29)-*diene* (30), the lower R_F component, had m.p. 165° (sublimed sample); $\nu_{max.}$ 3080, 1640, 882 (C=CH_2), 3065, 1632, and 721 cm^{-1} (CH=CH); δ 0·68 (3H), 0·90 (9H), 0·93 (3H), and 1·13 (3H) (Me groups), 1·67 (3H, s, C=CMe), 4·67br (2H, s, $W_{\frac{1}{2}}$ 4 Hz, C=CH_2), and 5·39—5·47 (major peak at 5·42) (2H, m, CH=CH) (Found: C, 88·0; H, 11·8%).

Flavic-2-*ene* (31).—A solution of flavica-2,22(29)-diene (30) (20 mg) in hexane (20 ml) was hydrogenated over Adams catalyst. After 10 min the rapid uptake of hydrogen ceased. Removal of the catalyst and evaporation gave *flavic*-2-*ene* (32) (20 mg), m.p. 158° (sublimed sample); $\nu_{max.}$ 3065, 1632, and 721 cm^{-1} (CH=CH); δ 0·65 (3H), 0·76 (1·5H), 0·82 (1·5H), 0·86 (1·5H), 0·89 (9H), 0·92 (4·5H), and 1·13 (3H) (Me groups), and 5·39—5·47 (major peak at 5·42) (2H, m, CH=CH) (Found: C, 87·6; H, 12·4. $C_{30}H_{50}$ requires C, 87·8; H, 12·2%).

Stictan-22α-*ol* (32).—(*a*) A mixture of 22α-hydroxystictan-3-one (70 mg), hydrazine hydrate (99%; 1·5 ml), concentrated hydrochloric acid (2 drops), and redistilled diethylene glycol (20 ml) was heated at 130° for 3 h. After addition of potassium hydroxide (50 mg) the solution was kept for 1 h at 130°. The temperature was raised to 220° by distilling off some of the hydrazine. The solution was refluxed at this temperature for 10 h and worked up in the usual way. P.l.c. on silica gel with E–H (2 : 3) gave *stictan*-22α-*ol* (32) (50 mg), m.p. 212—213°.

(*b*) Hydrazine hydrate (99%; 2 ml) and concentrated hydrochloric acid (6 drops) were added to a solution of 22α-acetoxystictan-2-one (43) (300 mg) in redistilled diethylene glycol (80 ml) and the mixture was heated at 130° for 3 h. After addition of solid potassium hydroxide (300 mg) the solution was kept at 130° for a further 1 h before the low boiling compounds were distilled off as the solution temperature was raised to 215°. The solution was refluxed for 10 h at this temperature, cooled, and worked up in the usual way. Filtration of the product in ether through alumina (15 g) gave stictan-22α-ol (32) (200 mg), m.p. 212—213°; $\nu_{max.}$ 3510 cm^{-1} (OH); δ 3·14 (1H, d, C*H*·OH) (Found: C, 84·3, H, 12·0. $C_{30}H_{52}O$ requires C, 34·0; H, 12·2%).

Reduction of 22α-acetoxystictan-3-one (40) (100 mg) as just described gave stictan-22α-ol (32) (80 mg). Acetylation of (32) gave 22α-acetoxystictane (28), identical (m.p. and mixed m.p.) with the acetate prepared by hydrogenation of 22α-acetoxystict-2-ene (27).

Flavic-22(29)-*ene* (33).—Stictan-22α-ol (32) (30 mg) in anhydrous pyridine (4·5 ml) was treated with freshly distilled phosphoryl chloride (0·9 ml) and kept at room temperature for 36 h. The mixture was worked up in the usual way, and the product, dissolved in hexane, was filtered through neutral alumina (2 g; Woelm grade II). P.l.c. on silver nitrate-impregnated silica gel with H gave *flavic*-22(29)-*ene* (33) (16 mg), m.p. 178° (from ethanol–hexane); $\nu_{max.}$ 3080, 875 (=CH_2), and 1640 cm^{-1} (C=C); δ 0·68 (3H), 0·81 (3H), 0·85 (3H), 0·88 (3H), 0·93 (3H), and 1·14 (3H) (Me groups), 1·67 (3H, s, C=CMe), and 4·67 (2H, s, C=CH_2) (Found: C, 88·0; H, 12·3. $C_{30}H_{50}$ requires C, 87·7; H, 12·3%).

Flavicane (19).—Flavic-22(29)-ene (33) (13 mg) in ethyl acetate (10 ml) was hydrogenated over Adams catalyst for 2 h (uptake 1·1 mol. equiv.). Removal of the catalyst and evaporation gave *flavicane* (19) (13 mg), m.p. 147—148° (from hexane–ethanol); δ 0·64 (3H), 0·75 (1·5H), 0·81 (4·5H), 0·85 (4·5H), 0·88 (3H), 0·91 (4·5 H), and 1·13 (3H); *m/e* 412 (M^+) and 191 (base peak) (Found: C, 87·6; H, 12·7. $C_{30}H_{52}$ requires C, 87·3; H, 12·7%).

2α,22α-*Diacetoxystictan*-3β-*ol* (37) *and* 3β,22α-*Diacetoxystictan*-2α-*ol* (38).—A solution of 22α-acetoxystictane-2α,3β-diol (23) (1·0 g) in pyridine (60 ml) was stirred with acetic anhydride (2·5 ml) at 20° until t.l.c. indicated that optimum monoacetylation had occurred (about 60 min). The mixture was worked up in the usual way and the products were chromatographed on alumina (60 g). Elution with E–B (1 : 1; 200 ml) gave 2α,3β,22α-triacetoxystictane (2) (100 mg); E–H (9 : 1) (300 ml) eluted 2α,22α-*diacetoxystictan*-3β-*ol* (37) (400 mg) and ether (300 ml) eluted 3β,22α-*diacetoxystictan*-2α-*ol* (38) (390 mg). Elution with ether–ethanol (19 : 1) gave unchanged 22α-acetoxystictane-2α,3β-diol (23) (45 mg). 2α,22α-Diacetoxystictan-3β-ol (37) (70 mg) had m.p. 242—244° (from acetone); δ 0·81 (3H), 0·85 (6H), 0·90 (3H), 0·92 (3H), 1·01 (3H), 1·04 (3H), and 1·14 (3H) (Me groups), 2·04 (3H, s, OAc), 2·05 (3H, s, OAc) 3·19 (1H, d, CH·OH), 4·70 (1H, d, CH·OAc), and 5·02 (1H, sextet, CH·OAc) (Found: C, 75·0; H, 10·4. $C_{34}H_{56}O_5$ requires C, 74·9; H, 10·4%). 3β,22α-Diacetoxystictan-2α-ol (38) (50 mg) had m.p. 232—234° (from acetone); δ 0·81 (3H), 0·86 (6H), 0·89 (3H), 0·90 (3H), 0·93 (3H), 0·96 (3H), and 1·14 (3H) (Me groups), 2·03 (3H, s, OAc), 2·12 (3H, s, OAc), 3·84 (1H, m, $W_{\frac{1}{2}}$ 18 Hz, C*H*·OH), 4·51 (1H, d, C*H*·OAc), and 4·69 (1H, d, C*H*·OAc) (Found: C, 74·9; H, 10·1. $C_{34}H_{56}O_5$ requires C, 74·9; H, 10·4%).

2α,22α-*Diacetoxystictan*-3-*one* (39).—2α,22α-Diacetoxystictan-3β-ol (37) (60 mg) in acetone (10 ml) was oxidised with an excess of Jones reagent at 0°. The mixture was quenched with aqueous 5% potassium carbonate after 30 min and worked up in the usual way to give 2α,22α-*diacetoxystictan*-3-*one* (39) (40 mg), m.p. 229—231°; δ 0·82 (3H), 0·85 (3H), 0·92 (6H), 1·10 (3H), 1·13 (3H), and 1·14 (6H) (Me groups), 2·04 (3H, s, OAc), 2·11 (3H, s, OAc), 4·70 (1H, d, CH·OAc), and 5·45 (1H, q, CH·OAc) (Found: C, 75·4; H, 10·2. $C_{34}H_{54}O_5$ requires C, 75·2; H, 10·0%).

22α-*Acetoxystictan*-3-*one* (40) *and Stictan*-3-*one* (41).—A solution of 2α,22α-diacetoxystictan-3-one (39) (800 mg) toluene (30 ml) was added dropwise during 10 min to a vigorously stirred solution of calcium (2 g) in liquid ammonia (300 ml). After stirring for a further 30 min bromobenzene was added until the blue colour of the solution was discharged. The ammonia was then allowed to evaporate at room temperature and the mixture was worked up in the usual way. Chromatography on silica gel with E–H (1 : 9) gave the ketones (41) (40 mg) and (40) (680 mg). *Stictan*-3-*one* (41), the higher R_F component, had m.p. 214—215° (sublimed sample); $\nu_{max.}$ 1702 cm^{-1} (C=O) (Found: C, 84·6; H, 11·9. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8%). 22α-*Acetoxystictan*-3-*one* (40), the lower R_F component, had m.p. 285—286° (sublimed sample); $\nu_{max.}$ 1730, 1245 (OAc), and 1702 cm^{-1} (C=O); δ 2·05 (3H, s, OAc) and 4·73 (1H, d, C*H*·OAc) (Found: C, 79·2; H, 10·7. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%).

3β,22α-*Diacetoxystictan*-2-*one* (42).—(*a*) 3β,22α-Diacetoxystictan-2α-ol (38) (50 mg) in acetone (10 ml) was oxidised with a slight excess of Jones reagent at room temperature. The mixture was worked up in the usual way to give a product which, after p.l.c. on silica gel with E–H (2 : 3), gave 3β,22α-*diacetoxystictan*-2-*one* (42) (40 mg), m.p. 237°; δ 0·81 (3H), 0·86 (9H), 0·92 (3H), 0·93 (3H), 1·17 (3H), and 1·23 (3H) (Me groups), 2·04 (3H, s, OAc), 2·16 (3H, s, OAc), 4·71 (1H, d, CH·OAc), and 4·88 (1H, s, C*H*·OAc) (Found: C, 75·3; H, 9·9. $C_{34}H_{54}O_5$ requires C, 75·2; H, 10·0%).

22α-*Acetoxystictan*-2-*one* (43) *and Stictan*-2-*one* (44).—A solution of 3β,22α-diacetoxystictan-2-one (42) (500 mg) in toluene (15 ml) was added dropwise during 10 min to a vigorously stirred solution of calcium (1·4 g) in liquid ammonia (225 ml). After stirring for a further 20 min bromobenzene was added until the blue colour of the solution was discharged. The ammonia was then allowed to evaporate at room temperature and the mixture worked up in the usual way. Chromatography on silica gel with E–H (1 : 9) gave the ketones (44) (15 mg) and (43) (390 mg). *Stictan*-2-*one* (44), the higher R_F component, had m.p. 208—210° (sublimed sample); $\nu_{max.}$ 1700 cm^{-1} (C=O) (Found: C, 84·1; H, 11·6. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8%). 22α-*Acetoxystictan*-2-*one* (43), the lower R_F component, had m.p. 269—270° (sublimed sample); $\nu_{max.}$ 1730, 1245 (OAc), and 1702 cm^{-1} (C=O); δ 2·04 (3H, s, OAc) and 4·71 (1H, d, C*H*·OAc) (Found: C, 79·4; H, 11·1. $C_{32}H_{52}O_3$ requires C, 79·2; H, 10·9%).

Repetitions of the deacetoxylation experiments in which ammonium chloride was substituted for bromobenzene (in the work-up procedure) gave stictane-3β,22α-diol (7) and stictane-2β,22α-diol (46) as the major products from reactions with 2α,22α-diacetoxystictan-3-one (39) and 3β,22α-diacetoxystictan-2-one (42), respectively.

Stictane-2β,22α-*diol* (46).—A solution of 22α-acetoxystictan-2-one (43) (80 mg) in ether was stirred with a slight excess of LAH for 1 h at 20°. Excess of reagent was destroyed with wet ether and the mixture was worked up in the usual way. P.l.c. on silica gel with E–H gave *stictane*-2β,22α-*diol* (46) (75 mg), m.p. 254—256° (sublimed sample); $\nu_{max.}$ 3510 cm^{-1} (OH); δ 3·15 (1H, d, C*H*·OH) and 3·16 (1H, m, $W_{\frac{1}{2}}$ 5 Hz, C*H*·OH) (Found: C, 80·8; H, 11·6. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%).

Stictane-2,22-*dione* (45).—A solution of stictane-2β,22α-diol (46) (60 mg) in acetone (30 ml) was stirred with a slight excess of Jones reagent for 5 min at 20°. The mixture was poured into saturated sodium hydrogen carbonate solution and worked up in the usual way to give *stictane*-2,22-*dione* (45), m.p. 233—235° (sublimed sample); $\nu_{max.}$ 1700 cm^{-1} (C=O) (Found: C, 81·5; H, 11·1. $C_{30}H_{48}O_2$ requires C, 81·7; H, 11·0%).

Stictane-2β,22β-*diol* (47).—A solution of stictane-2,22-dione (46) (50 mg) in ether (20 ml) was stirred with a slight excess of LAH for 1 h at 20°. Excess of reagent was destroyed with wet ether and the mixture was worked up in the usual way. P.l.c. on silica gel with E–H (1 : 1) gave *stictane*-2β,22β-*diol* (47) (42 mg), m.p. 243—244° (sublimed sample); $\nu_{max.}$ 3520 cm^{-1} (OH); δ 3·16br (2H, s, $W_{\frac{1}{2}}$ 6 Hz, C*H*·OH) (Found: C, 80·8; H, 11·6. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%).

Stictan-22-*one* (48).—A solution of stictan-22α-ol (32) (135 mg) in acetone (35 ml) was stirred at 20° with a slight excess of Jones reagent for 5 min. Work-up in the usual way and filtration of the product in benzene through alumina (5 g) gave *stictan*-22-*one* (48) (125 mg), m.p. 265—266° (sublimed sample); $\nu_{max.}$ 1700 cm^{-1} (C=O) (Found: C, 84·2; H, 11·6. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8%).

Stictan-22β-*ol* (49).—A solution of stictan-22-one (48) (40 mg) was stirred with a slight excess of LAH for 1 h at 20°. Excess of reagent was destroyed with wet ether and the mixture was worked up in the usual way. P.l.c. on silica gel with E–H (1 : 3) gave *stictan*-22β-*ol* (49) (38 mg), m.p. 268—270° (sublimed sample); $\nu_{max.}$ 3540 cm^{-1} (OH); δ 3·15 (2H, m, $W_{\frac{1}{2}}$ 6 Hz, C*H*·OH) (Found: C, 84·1; H, 11·9. $C_{30}H_{52}O$ requires C, 84·0; H, 12·2%).

22β-*Acetoxystictane* (50).—A solution of stictan-22β-ol (49) (20 mg) in pyridine (5 ml) and acetic anhydride (5 ml) was kept at room temperature. After 3 days t.l.c. indicated only a trace of acetylated product. The solution temperature was then raised to 60° for 2 days and the mixture was worked up in the usual way. P.l.c. on silica gel with E–H (1 : 3) gave 22β-*acetoxystictane* (50) (17 mg), m.p. 268—269° (sublimed sample); $\nu_{max.}$ 1735 and 1250 cm^{-1} (OAc); δ 2·03 (3H, s, OAc) and 4·66 (1H, m, $W_{\frac{1}{2}}$ 5 Hz) (Found: C, 81·4; H, 11·4. $C_{32}H_{54}O_2$ requires C, 81·6; H, 11·6%).

Stictane-3β,22β-*diol* (51).—Stictane-3,22-dione (11) (100 mg) in anhydrous ether (25 ml) was heated under reflux with a slight excess of LAH for 5 h. Work-up in the usual way gave a product (90 mg) which t.l.c. showed to be a mixture of three compounds. P.l.c. on silica gel with E–H (3 : 2) gave (at lower R_F) stictane-3β,22α-diol (7) (10 mg). Crystallization of the higher R_F compound (70 mg) from acetone gave *stictane*-3β,22β-*diol* (51), m.p. 270—271°; $[\alpha]_D^{20}$ +10·6° (*c* 0·66), $\nu_{max.}$ 3490 cm^{-1} (OH); δ 3·14 (2H, m, C*H*·OH) (Found: C, 81·1; H, 11·5. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%).

3β-*Acetoxystictan*-22β-*ol* (52).—A solution of stictane-3β,22β-diol (51) (300 mg) in pyridine (20 ml) was stirred with acetic anhydride (5 ml) for 2 h at 20°. The mixture was then worked up in the usual way and the product chromatographed on silica gel with E–H (1 : 3) to give, as the major product, 3β-*acetoxystictan*-22β-*ol* (52) (210 mg), m.p. 296—297°; $\nu_{max.}$ 3560 (OH), 1730, and 1245 cm^{-1} (OAc); δ 2·04 (3H, s, OAc), 3·16br (1H, s, $W_{\frac{1}{2}}$ 5 Hz, C*H*·OH), and 4·41 (1H, m, C*H*·OAc) (Found: C, 79·1; H, 11·0. $C_{32}H_{52}O_3$ requires C, 79·0; H, 11·1%).

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