Tetranortriterpenoids and Related Compounds. Part 22.[1] New Apotirucallol Derivatives and Tetranortriterpenoids from the Wood and Seeds of *Chisocheton paniculatus* (Meliaceae)

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Five new compounds, the apo-tirucallol derivatives (1), (9), (13), and (16) and the tetranortriterpenoid vilasinin 1,3-diacetate (18), have been isolated from the wood of *Chisocheton paniculatus* (Meliaceae). From the seeds of the same tree four new tetranortriterpenoids have been obtained, including the γ-lactone (22), the hemiacetal (23), the γ-hydroxybutenolide (24), and 17β-hydroxy-6α-acetoxynimbinin (26). Compounds (22) and (23) are possible precursors of normal furanoid tetranortriterpenoids. ^{13}C and ^{1}H n.m.r. data for these nine compounds are reported.

COLUMN chromatography of the light petroleum extract of the wood of *Chisocheton paniculatus* (Meliaceae) afforded three new apo-tirucallol derivatives, compounds A (1), B (9), and C (13). Preparative t.l.c. of the mother-liquors yielded a further apotirucallol derivative, compound D (16), and the tetranortriterpenoid (18). We now present chemical and spectroscopic evidence for these structures.

Compound A (1), $C_{32}H_{48}O_6$, had hydroxy, acetate, and cyclohexanone absorptions in its i.r. spectrum [$\nu_{max.}(CCl_4)$ 3 570, 1 750, and 1 705 cm^{-1}]. The ^{1}H and ^{13}C n.m.r. spectra showed resonances (see Tables 1 and 2) for seven tertiary methyl groups, a trisubstituted double bond, a trisubstituted epoxide, a hemiacetal acetate, a secondary ether oxygen, and a secondary hydroxy group. Decoupling experiments indicated that the epoxide proton was coupled to the proton on the carbon bearing the ether oxygen and that this in turn was coupled to a methylene group at δ *ca.* 1.7. Comparison of these data with melianone acetate (2) [2] confirmed the structure of the side chain as in (1). The presence of the cyclohexanone, the secondary hydroxy, and the trisubstituted double bond in the residual tetracarbocyclic nucleus suggested an apo-tirucallol skeleton and led us to structure (1) for compound A. This was confirmed by the shift of the vinyl proton, H-15, from δ 5.48 in (1) to 5.26 in the ^{1}H n.m.r. spectrum of the corresponding diacetate (3). Similar acetylation shifts have been observed with the tetranortriterpenoid (4).[3]

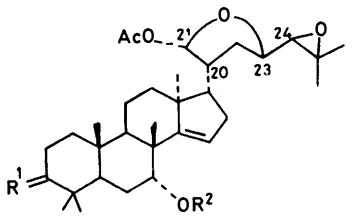
Final proof of structure (1) for compound A was obtained by converting it into the tetranortriterpenoid (4) using the conditions worked out by Buchanan and Halsall.[3] Thus treatment of (1) with sodium metaperiodate and aqueous perchloric acid followed by toluene-*p*-sulphonic acid in benzene afforded (4) whose physical and spectroscopic properties accorded with published data.[3] It was our intention to use this compound for a partial synthesis of meldenin (5), a tetranortriterpenoid from *Melia azadirachta*.[4] Reaction of (4) with thionyl chloride in pyridine gave the diene (6)

TABLE 1

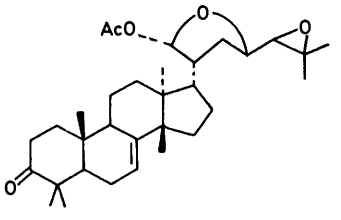
^{1}H N.m.r. spectra [a] of compounds from *C. paniculatus*

	(1)	(9)	(13)	(16)	(18)	(22)	(23)	(25)	(26)
1-H					4.92 (t, 3)	7.12 (d, 10)	7.12 (d, 10)	7.09 (d, 10)	7.13 (d, 10)
2-H					4.63 (t, 3)	5.93 (d, 10)	5.92 (d, 10)	5.92 (d, 10)	5.96 (d, 10)
3-H		4.64 (t, 3)	4.63 (t, 3)	3.40br (t, 3)					
5-H					2.65 (d, 10) *	2.45 (d, 13)	2.49 (d, 13)	2.50 (d, 13)	2.54 (d, 13) *
6-H					4.15 (3, 10) *	5.4 (m)	5.4 (m)	5.4 (m)	5.50 (3, 13) *
7-H	3.94br (s)	3.90br (s)	3.90br (s)	3.91br (s)	4.20 (3) *	5.4 (m)	5.4 (m)	5.4 (m)	5.58 (3) *
15-H	5.48 (t, 3)	5.49br (t)	5.47br (s)	5.47 (t, 3)	5.61br (t, 3)	5.4 (m)	5.4 (m)	5.4 (m)	5.80 (s)
21-H	6.23 (d, 4)	3.42, 3.95 (ABq, 12)	5.29br (m)	6.24 (d, 4)	7.35	3.94 (t, 9) 4.47 (dd, 8, 9)	3.44 (t, 9) 4.10 (m)	6.86br (s)	7.58
22-H					6.27			6.01br (s)	6.40
23-H	3.90 (m)	3.85 (m)	4.50 (m)	3.90 (m)	7.23				7.46
24-H	2.64 (d, 7)	2.87 (d, 9)	3.27 (m)	2.66 (d, 7)					
28-H					3.58 (2 H, s)				
OAc	2.04	2.05	2.05	2.03	1.98	1.99	1.96	1.99	1.98
					2.01	2.03	2.02	2.02	2.04
								2.17	
CMe	0.99	0.84	0.85	0.82	0.85	1.02	1.00	0.93	0.96
	1.03	0.88	0.90	0.87	0.97	1.16	1.15	1.16	1.19
	1.03	0.88	0.90	0.92	1.11	1.16	1.15	1.16	1.23
	1.09	1.00	1.06	1.01	1.19	1.25	1.24	1.23	1.27
	1.09	1.08	1.06	1.03		1.27	1.24	1.30	1.45
	1.26	1.25	1.24	1.26					
	1.31	1.28	1.28	1.30					

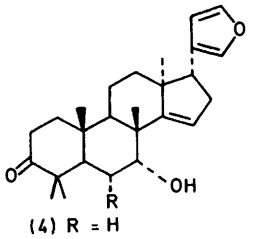
[a] Chemical shifts downfield from internal Me_4Si; solvent $CDCl_3$; multiplicities and coupling constants (Hz) in parentheses.
* ABX system, *J* values by first-order analysis.



(1) R^1 = O, R^2 = H
(3) R^1 = O, R^2 = Ac
(16) R^1 = H, α - OH, R^2 = H
(17) R^1 = H, α -OAc, R^2 = H



(2)



(4) R = H
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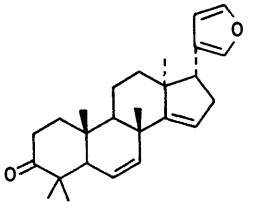

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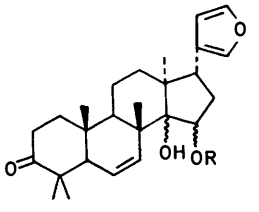
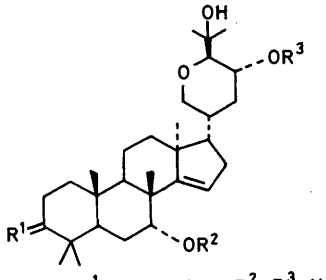
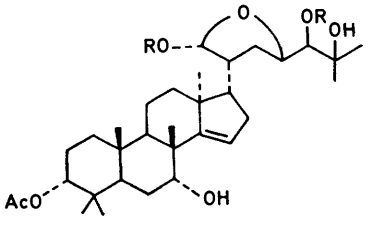


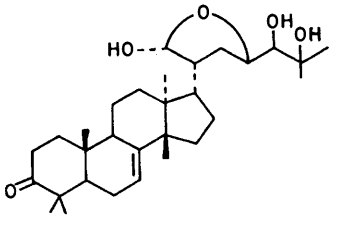
(7) R = H
(8) R = Ac



(9) R^1 = H, α -OAc, R^2 = R^3 = H
(10) R^1 = O, Δ^1, R^2 = Ac, R^3 = H
(11) R^1 = H, α -OAc, R^2 = H, R^3 = Ac
(12) R^1 = H, α -OAc; R^2 = R^3 = Ac



(13) R = H
(14) R = Ac



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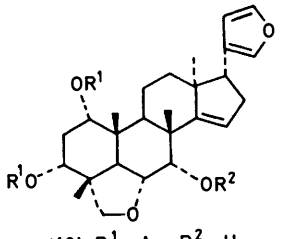
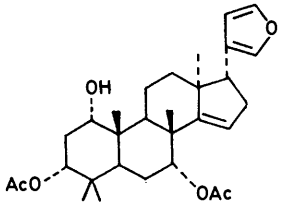


(18) R^1 = Ac, R^2 = H
(19) R^1 = R^2 = H
(20) R^1 = R^2 = Ac



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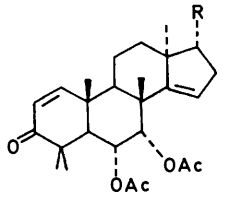
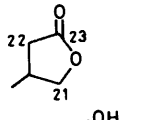
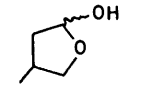




(22) R =



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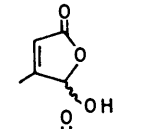
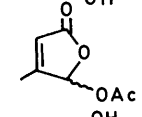
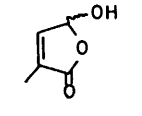


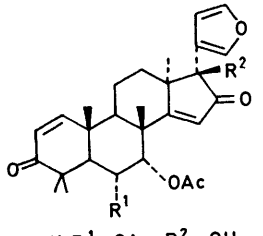
(24) R =



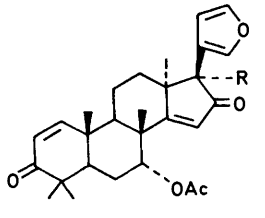
(25) R =



(31) R =



(26) R^1 = OAc, R^2 = OH
(28) R^1 = H, R^2 = OH
(30) R^1 = R^2 = H



(27) R = H
(29) R = OH

TABLE 2

^{13}C N.m.r. spectra * of compounds from *C. paniculatus*

Carbon atom	(1)	(9)	(13)	(16)	(18)	(22)	(23)	(25)	(26)
1	38.5	33.2	33.2	32.5	71.8	156.9	157.2	156.6	156.3
2	33.9	22.8	22.7	25.0	27.7	126.3	126.2	126.4	126.6
3	217.2	78.1	78.1	76.1	72.3	204.4	204.6	204.3	204.1
4	46.9	36.2	36.1	37.0	39.2 [a]	40.8	40.8	40.7	40.8
5	46.5	41.9 [a]	41.8 [a]	40.5 [a]	39.6	48.0	48.0	48.0	48.0
6	24.9	23.6	23.6	23.7	74.0	69.8	69.9	69.7	69.4
7	71.9	72.5	72.2	72.3	72.9	74.4	74.5	74.3	73.7
8	44.0	44.5	44.3	44.4	45.8 [a]	42.9	42.9	43.2	45.0
9	40.8	41.7 [a]	41.5 [a]	41.5 [a]	33.7	37.0	37.0	37.0	37.5
10	37.1	37.5	37.6	37.7	42.3 [a]	44.9	44.9	44.9	45.0
11	16.3	16.4	16.3	16.3	15.2	16.3	16.4	16.4	15.8
12	32.3 [a,b]	34.1 [b]	33.2 [b]	32.5 [b,c]	33.0 [b]	33.4 [a]	33.2	33.4 [a]	22.1
13	46.5	46.7	46.6	46.7	47.4	46.5	46.6	47.5	50.2
14	161.5	162.4	162.1	162.2	159.9	158.1	158.1	157.7	191.9
15	119.6	119.8	119.6	119.2	120.7	119.5	119.7	119.4	120.5
16	35.1 [b]	34.8 [b]	35.0 [b]	35.0 [c]	34.4 [b]	33.9 [a]	35.3	33.0 [a]	205.5
17	52.6	52.2	52.6	52.5	51.6	58.1	58.9	52.8	80.8
							58.2		
20	44.2	35.9	44.7	44.3	124.5	37.4	37.4	166.5	122.4
21	96.6	70.1	96.5	96.7	139.7	72.4	72.0	93.3	142.9
							70.4		
22	31.3 [a]	36.4	30.3	31.4 [b]	111.1	34.8	39.8	120.3	109.5
23	79.7	86.5	78.4	79.7	142.6	176.4	97.7	169.7	141.6
							98.3		
24	66.7	64.5	75.2	66.7					
25	57.1	74.1	73.7	57.1					
28					77.9				
Me	27.2	28.5	27.8	28.0		31.6	31.6	31.6	31.6
	26.2	27.9	27.6	27.9		26.8	26.8	26.9	31.1
	24.9	27.6	26.6	24.9		20.7	20.7	21.3	24.6
	21.1	24.0	26.6	22.1	26.2	20.4	20.4	20.7	20.8
	19.7	21.8	21.8	19.5	21.2	20.1	19.9	20.4	20.4
	19.3	19.2	19.8	19.3	19.5				
	14.9	15.2	15.1	15.2	15.4				
*Me*CO	21.5	21.4	21.4	21.5	21.2	21.3	21.3	21.3	21.2
					21.2	20.9	20.9	20.9	20.8
								20.7	
MeCO	170.0	171.0	171.0	169.9	170.3	170.2	170.2	170.2	170.2
					170.0	170.0	170.1	170.0	169.7
								169.0	

* Chemical shifts in p.p.m. downfield, from internal Me_4Si; solvent $CDCl_3$. [a-c] These assignments may be interchanged.

[δ 6.05 (dd, *J* 10, 3 Hz, H-6), 5.45 (d, *J* 10 Hz, H-7)]. The formation of a 6,7-double bond provided further evidence for the apo-tirucallol nature of (1). Unfortunately osmium tetraoxide reacted preferentially with the trisubstituted double bond of (6) to give the diol (7) which was converted into the monoacetate (8) [δ 5.32 (t, *J* 8 Hz, H-15), 5.70br (2 H, s, H-6 and -7)]. Lack of material prevented full characterisation of (7) and (8) and further work on the synthesis of meldenin.

The spectroscopic properties of compound B (9), $C_{32}H_{52}O_6$ [$\nu_{max.}$(CCl_4) 3 610, 3 560, 3 515, and 1 727 cm^{-1}], revealed the presence of seven tertiary methyl groups, a trisubstituted double bond, one tertiary and two secondary hydroxy groups, a secondary acetate, and a primary–secondary cyclic ether. The nature of the side-chain as in (9) was readily deduced from the similarity of the appropriate data, especially the H-24 doublet (*J* 9 Hz) at δ 2.87, with those recorded for grandifoliolenone (10) and the closely related sapelins C and D.[5] The remaining information suggested an apo-tirucallol skeleton with a 3α-acetate and 7α-hydroxy group and led to structure (9) for compound B. This was confirmed by the ^1H n.m.r. spectra of the corresponding diacetate (11) and triacetate (12) (sapelin D triacetate [5]). The side-chain resonances of the diacetate (11) parallelled those of grandifoliolenone acetate [5] with H-15 remaining unchanged. In the triacetate (12) H-15 shifted upfield from δ 5.49 to 5.29 as expected on formation of a 7α-acetate.[3]

Compound C (13), $C_{32}H_{52}O_7$ [$\nu_{max.}$(CCl_4) 3 610—3 300 and 1 725 cm^{-1}] lacked the epoxide of (1) and the cyclic ether of (9). However the presence of a hemiacetal [δ_C 96.5 (d)] indicated a side-chain related to that of compound A. From the spectroscopic properties we were able to detect, in addition to the hemiacetal, seven tertiary methyl groups, a trisubstituted double bond, one tertiary and two secondary hydroxy groups, and a secondary acetate. This information could be satisfactorily assembled to give structure (13) for compound C.

Acetylation of (13) afforded a mixture from which the triacetate (14) was isolated by preparative t.l.c. In its ^1H n.m.r. spectrum it had *inter alia* signals arising from a hemiacetal acetate and a secondary acetate proton [δ 4.79 (d, *J* 4 Hz)]. Decoupling experiments clearly demonstrated that the latter was H-24 and confirmed the side-chain sequence. Melianodiol (15) has the same side chain and there is good agreement between the above and published data.[6]

The fourth apo-tirucallol derivative, compound D (16), $C_{32}H_{50}O_6$, was very similar to compound A (1). It

differed in the lack of a ketonic carbonyl group and in the appearance of a new secondary hydroxy group. This suggested that D was dihydro-A (16). The ^{1}H n.m.r. spectrum of the corresponding monoacetate (17) was in accord with this proposal and had a >C*H*OAc resonance at δ 4.65 (H-3). As in the other three compounds the 7α-hydroxy group was more resistant to acetylation under normal conditions and the signal for H-15 did not exhibit an upfield shift.

The fifth new compound was the tetranortriterpenoid (18), $C_{30}H_{40}O_7$. It had a tetracarbocyclic skeleton with the characteristic β-substituted furan, four tertiary methyls, a trisubstituted double bond, a secondary hydroxy, two secondary acetates, and a primary–secondary cyclic ether. Irradiation at δ 2.11 caused the collapse of the two C*H*OAc triplets to singlets, indicating that they were attached to C-1 and -3. The H-5, -6, -7 spin system and the cyclic ether were readily identified by spin decoupling and by comparison with vilasinin (19).[7] Confirmation of structure (18) was obtained by acetylation which afforded the known compound vilasinin triacetate (20).[7]

The extract yielded another tetranortriterpenoid whose spectroscopic properties identified it as 14,15-deoxyhavanensin 3,7-diacetate (21).[8]

We also examined the light petroleum extract of the seeds of *C. paniculatus*. This proved to be a rich source of tetranortriterpenoids but many were present in small amount. Careful preparative t.l.c. resulted in the isolation of four new compounds, E (22), F (23), G (24), and H (25), whose structures were deduced on the evidence presented below. The known compounds 6α-acetoxynimbinin (6α-acetoxy-14,15-epoxyazadiradione),[9] gedunin,[10] and 6α-acetoxygedunin [9] were also obtained.

The carbon skeletons of the new compounds were readily identified by their spectroscopic data and by comparison with known compounds. Thus compound E (22), $C_{30}H_{40}O_7$, [$\nu_{max.}$(CCl_4) 1 792 (γ-lactone), 1 750 (acetate), and 1 682 (enone) cm^{-1}] with five tertiary methyl groups, two mutually coupled secondary acetates, a trisubstituted double bond, and a Δ^1-3-ketone had a 6α-acetoxyazadirone skeleton as in (22). The typical furan resonances were absent and were replaced by those of a γ-lactone ring. The position of the lactone carbonyl group (C-23) was established by the ^{1}H n.m.r. spectrum which showed the H_2-21 protons as a triplet (*J* 9 Hz) at δ 3.94 and a doublet of doublets (*J* 9, 8 Hz) at δ 4.47, respectively. These collapsed to an AB quartet (*J* 9 Hz) on irradiation at δ 2.75 (H-20). During the course of our work the *X*-ray structure of a tetranortriterpenoid, with the same γ-lactone side-chain, from *Cneorum tricoccum*, appeared.[11]

It was apparent from their spectroscopic properties that compounds F (23) and G (24) had the same carbon skeleton as E (22) and differed only in the nature of the degraded side-chain. Compound F was unstable and difficult to characterise. The ^{13}C n.m.r. spectrum indicated that it was a mixture. The presence of a carbon resonance at δ_C 97.7 (d) suggested a cyclic hemiacetal as in (23). The equilibration at C-23 in such a system could account for the multiple nature of the ^{13}C n.m.r. spectrum. The presence of the hemiacetal function was established by Jones oxidation of (23) to give, in good yield, the γ-lactone (22) described above.

Compound G (24) was insoluble in chloroform and was converted into the corresponding acetate (25) whose spectroscopic properties revealed a β-substituted γ-acetoxybutenolide [δ_C 169.7 (s, C-23), 230.3 (d, C-22), 93.3 (d, C-21), and 166.5 (s, C-20); δ_H 6.86 (s, H-21) and 6.01 (s, H-22)]. Several examples of this type have been reported recently.[1,12,13] The γ-hydroxybutenolide presumably arises by oxidation of the furan ring and the possibility that it is an artefact has not been excluded. On the other hand, the γ-lactone, at the same oxidation level as the furan, and the hemiacetal, at a lower oxidation level, may represent intermediate stages in the formation of the furan from the intact side chain *e.g.* of (1).

Compound H, $C_{30}H_{36}O_8$ was readily assigned the structure 17β-hydroxy-6α-acetoxyazadiradione (26). It lacked the typical H-17 resonances in its ^{1}H and ^{13}C n.m.r. spectra and had instead a tertiary hydroxy group [$\nu_{max.}$(CCl_4) 3 590 cm^{-1}; δ_H *ca.* 2.5 (exchangeable with D_2O); δ_C 80.8 (s)]. We had no direct evidence for the configuration at C-17. However during the course of our work Kraus and Cramer reported [14] the isolation of 17-epiazadiradione (27) and 17β-hydroxyazadiradione (28). Previously Voelter and his colleagues had published [15] a different 17-hydroxy compound without evidence for the configuration at C-17. Therefore this must be 17α-hydroxyazadiradione (29). An examination of the ^{13}C n.m.r. spectra of these compounds [14,15] revealed that the signal for C-20 shifted from δ 118.4 in azadiradione (30) to 123.6 in 17-epiazadiradione (27) (Δδ 5.2) and similarly from δ 122.6 in 17β-hydroxyazadiradione (28) to 129.0 in Voelter's compound (Δδ 6.4). The corresponding C-20 resonance in our compound appeared at δ 122.4, suggesting that it was 17β-hydroxy-6α-acetoxyazadiradione (26).

Several other compounds with 6α-acetoxyazadiradione skeletons and modified C_4 side-chains, including the alternative γ-hydroxybutenolide (31), were present in the seed extract. The most interesting had an aldehyde resonance at δ 9.99 (1 H, s) and an AB quartet (*J* 5.5 Hz) at δ 6.12 and 6.52. Unfortunately lack of material prevented full characterisation of these minor constituents.

EXPERIMENTAL

For general experimental details see Part 20.[16]

*Extraction.—Wood.** Powdered wood (5.4 kg) of *C. paniculatus* was continuously extracted with light petroleum in a Soxhlet apparatus. The oily extract (41 g) was chromatographed over Grade IV alumina (1 kg) in light petroleum. The initial fractions eluted with increasing proportions of chloroform in light petroleum yielded β-sitosterol (4 g). The fractions eluted with increasing

* We thank Mr. J. A. Akinniyi for examining the extract of the root wood, which gave similar results.

proportions of ethyl acetate in chloroform crystallised on addition of ether–light petroleum and afforded, in increasing order of polarity, compounds A—C. *Compound A* (1) (700 mg) had m.p. 209—211° (from ether–methanol), *m/e* 510 (*P* − 18) (Found: C, 72.6; H, 9.25. $C_{32}H_{48}O_6$ requires C, 72.7; H, 9.1%). *Compound B* (9) (300 mg) was crystallised from ether–light petroleum and had m.p. 204—206°, *m/e* 514 (*P* − 18) (Found: C, 72.0; H, 10.0. $C_{32}H_{52}O_6$ requires C, 72.15; H, 9.85%). *Compound C* (13) (600 mg) had m.p. 145—150° (from chloroform–ether), *m/e* 530 (*P* − 18) (Found: C, 70.0; H, 9.2. $C_{32}H_{52}O_7$ requires C, 70.0; H, 9.5%). Preparative t.l.c. of the mother-liquors using ethyl acetate–carbon tetrachloride (6 : 4) gave compound D and the tetranortriterpenoid, vilasinin diacetate. Compound D (16) (50 mg) was obtained as a gum, *m/e* 470 (*P* − AcOH). *Vilasinin* 1,3-*diacetate* (18) (200 mg) was crystallised from methanol and had m.p. 128—131°, *m/e* 512, $\nu_{max.}$(CCl_4) 3 560 and 1 735 cm^{-1} (Found: C, 70.3; H, 8.1. $C_{30}H_{40}O_7$ requires C, 70.3; H, 7.9%). Extraction of a minor band on the plate gave the known compound 14,15-deoxyhavanensin 3,7-diacetate (21) (8 mg), whose ^1H n.m.r. spectrum accorded with reported data.[8]

Seeds. Ground seeds (500 g) of *C. paniculatus* were extracted with light petroleum in a Soxhlet apparatus. The oily extract (180 g), obtained on removal of the solvent, deposited a solid (5.5 g) on treatment with light petroleum. This solid was chromatographed on Grade IV alumina eluting with increasing amounts of ethyl acetate in chloroform. The early fractions contained mainly fat (2 g). The later fractions showed many spots on analytical t.l.c. Multiple preparative t.l.c. using 30% ethyl acetate–carbon tetrachloride and 1% methanol–chloroform afforded the following compounds. (a) *Compound E* (22) (42 mg) had m.p. 236—240° (from chloroform–ether), *m/e* 512 (Found: C, 70.45; H, 7.8. $C_{30}H_{40}O_7$ requires C, 70.3; H, 7.8%). (b) Compound F (23) (40 mg) was a gum which was difficult to purify. Oxidation with Jones reagent gave a product identical with compound E (22). (c) Compound G (24) (120 mg) was a chloroform-insoluble powder, *m/e* 508 (*P* − 18). Acetylation under the usual conditions yielded a mixture (epimers ?) from which the major acetate (25) (60 mg) was obtained as a gum by preparative t.l.c. (Found: *m/e*, 568. $C_{32}H_{40}O_9$ requires *M*, 568). (d) *Compound H*, 17β-*hydroxy*-6α-*acetoxyazadiradione* (26) (18 mg), m.p. 288—292° (from methanol–ether–light petroleum), $\nu_{max.}$ (CCl_4) 3 590, 1 752, 1 720, and 1 682 cm^{-1} (Found: *m/e*, 524.240 71. $C_{30}H_{36}O_8$ requires *M*, 524.240 99). The known compounds, 6α-acetoxynimbinin (6α-acetoxy-14,15-epoxyazadiradione) (15 mg),[9] m.p. 167—169°, gedunin (20 mg),[10] m.p. 216—220°, and 6α-acetoxygedunin (40 mg),[9] m.p. 270—274°, were also isolated and readily identified spectroscopically.

The more polar fractions (2.8 g) of the column could not be separated and were acetylated with acetic anhydride in pyridine on a steam-bath for 0.5 h. Analytical t.l.c. indicated the presence of at least ten compounds. Lack of material prevented full characterisation.

Acetylation Reactions.—Acetates were prepared by treatment of the alcohols with acetic anhydride in pyridine on a steam-bath for 0.5 h. Compound A acetate (3) was not obtained crystalline, δ_H 1.02 (6 H), 1.04 (6 H), 1.14, 1.29, and 1.33 (Me), 1.95 and 2.06 (OAc), 2.68 (1 H, d, *J* 7 Hz, 24-H), 3.95 (1 H, m, 23-H), 5.26 (2 H, m, 7- and 15-H), and 6.27 (1 H, d, *J* 3 Hz, 21-H) (Found: *m/e*, 510.3345. $C_{34}H_{50}O_7$ − CH_3CO_2H requires *M*, 510.3345). Compound B (9) afforded a mixture which was separated by preparative t.l.c. (30% ethyl acetate–carbon tetrachloride) to give the *diacetate* (11), m.p. 213—215° (from chloroform–ether), $\nu_{max.}$(CCl_4) 3 575 and 1 737 cm^{-1}; δ_H 0.83, 0.86 (6 H), 0.98, 1.06, 1.14, and 1.17 (Me), 2.01 and 2.06 (OAc), 3.16 (1 H, d, *J* 9 Hz, 24-H), 3.58 and 4.04 (ABq, *J* 12 Hz, 21-H_2), 3.93 (1 H, t, *J* 3 Hz, 7-H), 4.67 (1 H, t, *J* 3 Hz, 3-H), 4.98 (1 H, m, 23-H), and 5.49br (1 H, d, *J* 3 Hz, 15-H)] (Found: *m/e*, 556.376 13. $C_{34}H_{54}O_7$ − H_2O requires *M*, 556.376 35), and the triacetate (12) (sapelin D triacetate [5]), m.p. 160—162° (from chloroform–ether), *m/e* 598 (*P* − 18), $\nu_{max.}$(CCl_4) 3 575, 1 732, and 1 737 cm^{-1}, δ_H 0.73, 0.86, 0.88, 1.10, 1.14, and 1.17 (Me), 1.94, 2.00, and 2.07 (OAc), 3.16 (1 H, d, *J* 9 Hz, 24-H), 3.56 and 4.04 (ABq, *J* 12 Hz, 21-H_2), 4.66 (1 H, t, *J* 3 Hz, 3-H), 4.97 (1 H, m, 23-H), 5.16 (1 H, t, *J* 3 Hz, 7-H), 5.29br (1 H, d, *J* 3 Hz, 15-H). Compound C (13) yielded, after preparative t.l.c., the *triacetate* (14) as a gum, δ_H 0.81, 0.86 (6 H), 1.03 (6 H), 1.25, 1.29 (Me), and 2.05 (6 H), 2.13 (OAc), 3.91 (1 H, *t*, *J* 3 Hz, 7-H), 4.51 (1 H, m, H-23), 4.65 (1 H, t, *J* 3 Hz, 3-H), 4.79 (1 H, d, *J* 4 Hz, 24-H), 5.48br (1 H, t, *J* 3 Hz, 15-H), and 6.08 (1 H, d, *J* 3 Hz, 21-H) (Found: *m/e*, 572.371 15. $C_{36}H_{56}O_9$ − CH_3CO_2H requires *M*, 572.371 24). Compound D (16) gave the non-crystalline *acetate* (17), δ_H 0.81, 0.86 (6 H), 1.03 (6 H), 1.25, and 1.29 (Me), 2.03 and 2.05 (OAc), 2.65 (1 H, d, *J* 7 Hz, 24-H), 3.91 (2 H, m, 7- and 23-H), 4.65 (1 H, t, *J* 3 Hz, 3-H), 5.48br (1 H, t, 15-H), 6.25 (1 H, d, *J* 3 Hz, 21-H) (Found: *m/e*, 512.350 06. $C_{34}H_{52}O_7$ − CH_3CO_2H requires *M*, 512.350 15). Vilasinin-1,3-diacetate (18) afforded the known triacetate (20), m.p. 220°, identified by its spectroscopic data.[7]

Tetranortriterpenoid (4).[3]—Compound A (1) (870 mg) in tetrahydrofuran (150 ml) was treated with sodium metaperiodate (2 g) in water acidified with 70% perchloric acid (3 drops). The solution was stirred at room temperature for 24 h. The precipitated sodium iodate was filtered off and washed with tetrahydrofuran. Sodium hydrogencarbonate (100 mg) was added, the solvent removed *in vacuo*, and and excess of water added. Extraction with chloroform yielded a yellow gum which was dissolved in benzene (100 ml) and refluxed for 2 h with toluene-*p*-sulphonic acid (1 mg). The product was chromatographed on Grade IV alumina in ether–light petroleum. The fractions eluted with ether afforded the known furanoid tetranortriterpenoid (4) [3] (400 mg) which was crystallised from methanol–ether and had m.p. 157—177°.

Diene (6).—Tetranortriterpenoid (4) (140 mg) in pyridine was treated with thionyl chloride (10 drops) at ice temperature for 0.5 h. The mixture was poured into ice–water and extracted with chloroform. The product was chromatographed over Grade IV alumina in light petroleum–ether to give the crystalline *diene* (6) (28 mg), m.p. 180—192° (from methanol), δ_H 0.80, 0.93, 1.04, 1.08, and 1.18 (Me), 5.45br (1 H, d, *J* 10 Hz, 7-H), 5.50br (1 H, t, 15-H), 6.05 (1 H, dd, *J* 3, 10 Hz, 6-H), 6.25, 7.22, and 7.32 (furan H) (Found: *m/e*, 378.255 78. $C_{26}H_{34}O_2$ requires *M*, 378.255 866).

Diol Monoacetate (8).—Diene (6) in ether–pyridine was treated with an excess of osmium tetraoxide and the reaction left in the dark for 24 h. Preparative t.l.c. of the crude product yielded the non-crystalline *diol* (7), δ_H 0.7, 0.97, 1.03, 1.1, and 1.21 (Me), 4.27 (1 H, dd, *J* 8, 6 Hz, 15-H), 5.77br (1 H, s, 6- and 7-H), 6.22, 7.15, and 7.32 (furan H), which was acetylated on a steam-bath for 1 h to give the non-crystalline *monoacetate* (8), δ_H 0.72, 0.93, 1.02, 1.08, and 1.20 (Me), 2.08 (OAc), 5.32 (1 H, t, *J* 8 Hz, 15-H), 5.70br (2 H, s, 6- and 7-H), 6.23, 7.15, and 7.32 (furan H).

Assignment of ^{13}C *N.M.R. Resonances.*—Assignments are based on chemical shift rules, multiplicities in off-resonance-decoupled spectra, correlation with ^{1}H chemical shifts using two off-resonance-decoupled spectra, and comparison with published data for similar compounds. Signals at lower field than 60 p.p.m. are easily assigned by these means. Of the quaternary carbons C-13 shows a small residual long-range coupling with 15-H in the off-resonance-decoupled spectra (irradiating at 0 p.p.m.). In compounds (1), (9), (13), and (16) C-8 and -10 are essentially unchanged, C-10 being assigned by comparison.[17] C-4 shows a 10 p.p.m. upfield shift from (1) to (16) and a further small high-field acetylation shift in (9) and (13). In (22), (23), (25), and (26) the assignments of C-4 and -10 are reversed with respect to azadiradione derivatives [14] because of the *γ-gauche-* and *anti*-effects of the 6α-OAc substituent. C-8 varies slightly as the C-17 substituent is changed.

Of the methine carbons C-17 is assigned by its absence in (26). C-5 moves upfield from (1) to (16) on the introduction of a *γ-gauche*-hydroxy group and C-9 remains unchanged.[18] Because of 6α-OAc, C-5 is expected to be at lower field in (22), (23), (25), and (26) than in (1) (*cf.* ref. 14). The remaining methine is C-20 in the various C-17 substituents.

Of the methylene carbons C-11 is at highest field. The resonances at *ca.* 33 p.p.m. in (25) must be C-12 and -16; the other assignments for (22), (23), and (26) then follow. For (1) and (16) C-12, -16, and -22 are invariant. C-1 and C-2 in (1) are assigned by comparison [17] and both move appreciably to higher field in (16). The assignment of C-6 then follows and does not change in (9) and (13). C-1 and C-2 show acetylation shifts from (16) to (9) and (13).

The methyl carbons are not assigned with the exception of the acetates, which are recognised by larger residual coupling in the off-resonance-decoupled spectra.

The assignments for (18) are made by comparison as far as possible, but suitable model systems are not available. The spectrum for (23) shows doubling and reduction in intensity of some resonances associated with the substituent at C-17 and it is possible that not all relevant peaks are resolved.

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