acyl groups, forming the observed product 11. Such a rearrangement is a somewhat more elaborate example of that seen for 8. The second intermediate carbonium ion, 16, stabilizes itself through loss of a benzyl cation[9] to form the second naphthalenic product, 12, and ultimately benzyl acetate, 10. The nearest precedent for this unusual fragmentation appears to be the previously mentioned decomposition of 1-(α-hydroxybenzyl)-2-naphthol.[6]

Experimental Section[10]

Preparation of 2-*endo*-Acetoxy-1-benzyl-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (5). The alcohol 4 (51 mg, 2.5 mmol) was added to 1 mL of acetic anhydride containing 5 mg of *p*-toluenesulfonic acid, and the solution was heated under nitrogen at 55–60 °C for 4 h. The solution was poured onto ice, the product was extracted with ether, and the ether extract was washed with dilute sodium bicarbonate and water, dried ($MgSO_4$), and evaporated. The crude acetate, 5 (50 mg, mp 73–77 °C), was recrystallized from chloroform/60–80 °C petroleum ether: mp 76–78 °C; IR (Nujol) 1740, 1250, 1230, 1055, 755, 700 cm^{-1}; NMR ($CDCl_3$) 1.19 (dd, J_1 = 3 Hz, J_2 = 12 Hz, 1 H), 1.83 (s, 3 H), 2.4–3.0 (m, 1 H), 3.50 (s, 2 H), 5.10 (dd, J_1 = 3 Hz, J_2 = 9 Hz, 1 H), 5.31 (d, J = 5 Hz), 7.2–7.5 (m, 9 H). Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.59; H, 6.06.

Aromatization and Rearrangement of 4. The preceding reaction was repeated with 0.65 g (3.18 mmol) of 4, and the solution was heated at 120–125 °C for 4 h. The crude reaction product (0.61 g) on analysis by NMR showed a 2:1 ratio of **7a** to **6**. This was chromatographed on silica gel, using 10:3 mixture of 30–60 °C petroleum ether/benzene. 1-(α-Acetoxybenzyl)naphthalene (**7a**; 0.25 g, 29%) eluted first followed by 0.17 g of a mixture of **7a** and **6**, and finally 0.15 g (17%) of 2-acetoxy-1-benzylnaphthalene, 6, was collected, mp (from benzene) 49–52 °C. This latter compound was identical in its spectroscopic properties with an authentic sample:[2] mp 52–53 °C; IR (neat) 1750, 1360, 1200, 1170, 800, 750, 740, 730, 700, 690 cm^{-1}; NMR ($CDCl_3$) 2.26 (s, 3 H), 4.38 (s, 2 H), 7.1–8.2 (m, 11 H). The spectral properties of **7a** were as follows: IR (neat) 1740, 1365, 1230, 1020, 790, 770, 690 cm^{-1}; NMR ($CDCl_3$) 2.13 (s, 3 H), 7.2–8.2 (m, 13 H).

Conversion of 7a to 1-(α-Hydroxybenzyl)naphthalene (7b). Hydrolysis of **7a** (100 mg, 0.36 mmol) was effected by refluxing an ether solution (15 mL) of the compound under nitrogen with 0.05 g (1.3 mmol) of lithium aluminum hydride for 6 h. After destruction of the excess hydride with ethyl acetate, water was added and the ether layer was decanted, washed with water, dried ($MgSO_4$), and evaporated. The residual oil crystallized on treatment with 30–60 °C petroleum ether: 76 mg (90%); mp 75–79 °C; IR (Nujol) 3300, 1040, 970, 775, 755, 670 cm^{-1}; NMR ($CDCl_3$) 2.45 (br s, 1 H, exchanges with D_2O), 6.40 (s, 1 H), 7.0–8.2 (m, 12 H). These spectra were identical with those of an authentic sample[3] of **7b**, mp 89–91 °C.

Rearrangement and Decomposition of 1-Benzyl-1,4-epoxy-3,4-dihydro-2(1*H*)-naphthalenone (9). The ketone, 9 (2.78 g, 11.1 mmol), was dissolved in 30 mL of acetic anhydride containing 0.5 g of *p*-toluenesulfonic acid and heated under nitrogen for 24 h at 120 °C. The reaction products (3.5 g) were isolated as described above and chromatographed on silica gel, eluting with benzene. The first material collected (0.96 g, fraction A) was dissolved in hot ethanol. On cooling, the starting material, 9, crystallized (NMR, IR, mixture melting point). The filtrate, on evaporation, provided an oil with spectroscopic properties identical with those of benzyl acetate. Analysis (NMR) of this fraction gave a 36% yield of benzyl acetate and a 13% recovery of 9.

Following fraction A, two subsequent fractions were collected, fraction B (0.45 g) and C (1.92 g). The last fraction was sublimed under vacuum (0.05 mm) at 130 °C, and the sublimate was recrystallized from benzene/60–80 °C petroleum ether to provide 1,2-diacetoxynaphthalene, 12: mp 108–110 °C; IR (Nujol) 1760, 1240, 1210, 1190, 1160 cm^{-1}; NMR ($CDCl_3$) 2.30 (s, 3 H), 2.40 (s, 3 H), 7.1–7.9 (m, 6 H). These properties were identical with those of an authentic sample,[5] mp 108–110 °C.

The residue from this sublimation was chromatographed on silica gel as described above to provide 2-acetoxy-1-(α-acetoxybenzyl)naphthalene, 11, mp 95–100 °C, identified by comparison of its spectral properties with those of an authentic sample.

Fractions B and C were analyzed by NMR, and a yield of 21% for 11 and 58% for 12 was determined.

Preparation of 2-Acetoxy-1-(α-acetoxybenzyl)naphthalene (11). 2-Hydroxy-1-(α-hydroxybenzyl)naphthalene was prepared in 80% yield by a literature procedure.[6] Treatment of the diol with hot acetic anhydride containing *p*-toluenesulfonic acid catalyst provided the diacetate, 11: mp 104–6 °C; IR (Nujol) 1755, 1740, 1230, 1200, 1010, 970, 750, 690 cm^{-1}; NMR ($CDCl_3$) 2.13 (s, 3 H), 2.32 (s, 3 H), 7.1–8.2 (m, 11 H). Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43. Found: C, 75.22; H, 5.52.

A sample of 11 was heated for 24 h at 120 °C under nitrogen in acetic anhdyride containing a catalytic amount of *p*-toluenesulfonic acid. The compound was recovered unchanged.

Registry No. 4, 73194-77-1; 5, 78199-47-0; 6, 78199-48-1; 7a, 78199-49-2; 7b, 642-28-4; 9, 73194-62-4; 10, 140-11-4; 11, 78199-50-5; 12, 6336-79-4; 2-hydroxy-1-(α-hydroxybenzyl)naphthalene, 40473-53-8.

(9) We thank a referee for suggesting this possibility.

(10) Melting points are uncorrected. NMR spectra were determined with the use of a Varian T-60 instrument and IR spectra were recorded on a Beckman IR-10 spectrometer.

Constituents of *Trichilia hispida* (Meliaceae). 4. Hispidols A and B, Two New Tirucallane Triterpenoids

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We reported earlier the isolation and identification of four tirucallane triterpenoids (3–6)[1,2] and three limonoids[2,3] from the leaves of *Trichilia hispida* Penning. (ined.) (Meliaceae). We now report the isolation from the same source and characterization of two new crystalline triterpenoids, which we term hispidols A (1) and B (2) (Chart I).

Column chromatography of the lowest R_f constituents (below sapelin B (4)) of the ethanol extract of these leaves followed by recrystallization gave hispidol A (1), mp 118 °C, and hispidol B (2), mp 253–254 °C. Both gave molecular ion peaks at m/e 476 in their electron-impact mass spectra, which, with their elemental analyses, indicated molecular formula $C_{30}H_{52}O_4$, confirmed by high-resolution mass spectroscopy. Comparison of this molecular formula with that of sapelins A (3) and B (4) suggested that 1 and 2 could be dihydro derivatives of 3 and 4 in which either the double bond was reduced or the ether linkage had not been formed.

The 250-MHz ^1H NMR spectra of 1 and 2 (Table I) showed the latter to be the case. NMR spectral comparisons were complicated by the very low solubility of 2 in $CDCl_3$; its spectrum was run in pyridine-d_5 along with those of 1 and 3 for comparison. The pyridine-d_5 spectra of 1 and 2 differ significantly from one another only in the

(1) Jolad, S. D.; Wiedhopf, R. M.; Cole, J. R. *J. Pharm. Sci.* **1977**, *66*, 889.

(2) Jolad, S. D.; Hoffmann, J. J.; Cole, J. R.; Tempesta, M. S.; Bates, R. B. *J. Org. Chem.* **1980**, *45*, 3132. Partial formula R_1 in this reference depicts the wrong configuration at C24.

(3) Jolad, S. D.; Hoffmann, J. J.; Schram, K. H.; Cole, J. R.; Tempesta, M. S.; Bates, R. B. *J. Org. Chem.* **1981**, *46*, 641.

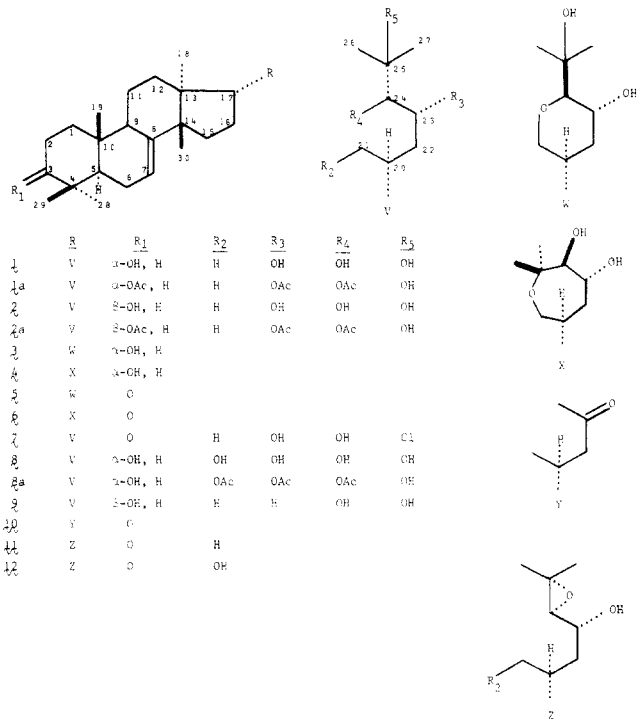
0022-3263/81/1946-4085$01.25/0

Table I. ^{1}H NMR Shifts (δ) and Coupling Constants (Hz, in parentheses) for Compounds 1–3, 1a, and 2a

	3 [a]	1 [a]	1a [a]	2a [a]	3 [b]	1 [b]	2 [b]
H-2		1.91 (m)				1.73 (m), 1.99 (m)	
H-3	3.46 (bs)	3.46 (bs)	4.68 (bs)	4.52 (dd, 10.5, 5.3)	3.67 (bs)	3.67 (bs)	3.48 (dd, 11.0, 5.1)
H-5	1.78 (dd, 11.4, 5.9)	1.78 (dd, 11.6, 5.9)	1.76 (dd, 11.7, 5.9)			2.20 (dd, 12.0, 5.2)	
H-6	2.00 (m)	2.02 (m)				2.01 (m), 2.07 (m)	1.86 (m), 2.07 (m)
H-7	5.26 (m)	5.26 (m)	5.24 (m)	5.24 (m)	5.33 (m)	5.33 (m)	5.33 (m)
H-9	2.33 (m)	2.33 (m)			2.41 (m)	2.49 (m)	
H-11					1.55 (m), 2.20 (m)		
H-18	0.79 (s)	0.83 (s)	0.84 (s)	0.80 (s)	0.72 (s)	0.82 (s)	0.83 (s)
H-19	0.77 (s)	0.77 (s)	0.77 (s)	0.76 (s)	0.84 (s)	0.86 (s)	0.90 (s)
H-20						1.71 (m)	
H-21	3.38 (dd, 11.5, 2.5), 3.95 (d, 11.5)	0.93 (d, 5.5)	0.96 (d, 5.5)	0.95 (d, 5.5)	3.47 (~d, 11.6), 4.06 (~d, 11.6)	1.12 (d, 5.9)	1.14 (d, 5.9)
H-22		1.91 (m)			1.82 (m), 2.30 (m)	2.33 (dd, 11.0, 9.2)	2.33 (dd, 11.0, 9.2)
H-23	3.91 (m)	4.13 (dd, 9.0, 5.4)	5.42 (ddd, 8.6, 5.5, 1.6)	5.42 (ddd, 8.8, 5.5, 1.5	4.34 (m)	4.58 (m)	4.57 (m)
H-24	2.90 (d, 9.0)	3.18 (s)	4.90 (d, 1.6)	4.89 (d, 1.5)	3.33 (d, 9.0)	3.67 (s)	3.66 (s)
H-26, H-27	1.28 (s), 1.31 (s)	1.31 (s), 1.32 (s)	1.20 (s), 1.25 (s)	1.19 (s), 1.24 (s)	1.60 (s), 1.61 (s)	1.61 (s), 1.63 (s)	1.61 (s), 1.63 (s)
H-28	100 (s)	0.98 (s)	0.97 (s)	0.93 (s)	1.15 (s)	1.14 (s)	1.17 (s)
H-29	0.92 (s)	0.92 (s)	0.84 (s)	0.85 (s)	0.96 (s)	0.96 (s)	1.12 (s)
H-30	0.94 (s)	0.94 (s)	0.95 (s)	0.94 (s)	1.04 (s)	1.03 (s)	1.02 (s)
3-OH					5.72	5.65	5.77
23-OH					6.20 or 6.51	5.44	5.42
24-OH						5.65	5.63
25-OH					6.20 or 6.51	5.99	5.97
H_2O					5.00	4.90	4.90
3-OAc			2.08	2.05			
23-OAc, 24-OAc			2.07, 2.20	2.07, 2.20			

[a] In $CDCl_3$. [b] In pyridine-d_5.

Chart I

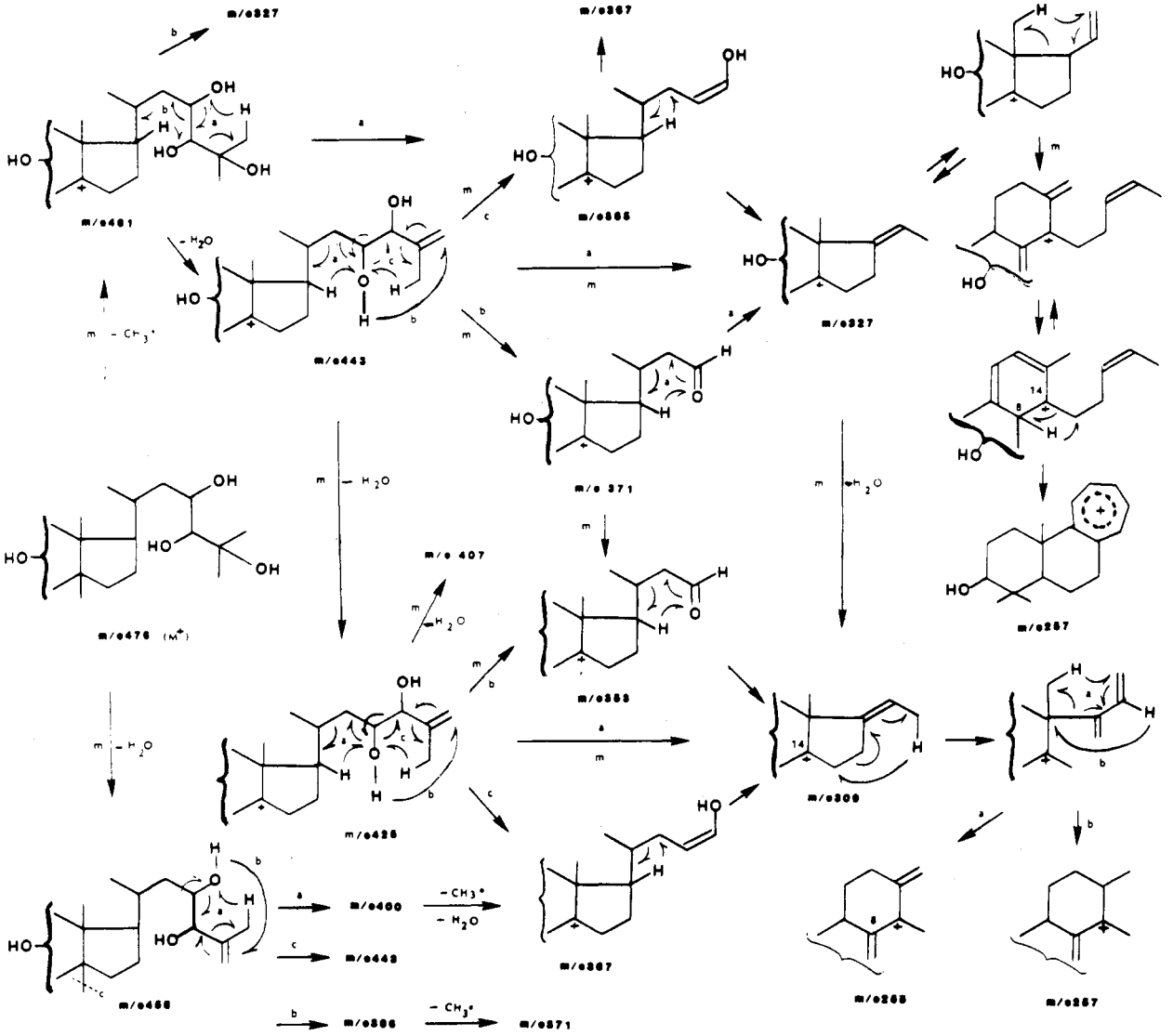


absorptions of protons in the vicinity of C3. **2**, with its HC3–HC2 coupling constants of 11.0 and 5.1 Hz and thus equatorial 3-OH, is clearly the C3 epimer of **1**, whose HC3 absorption closely matches that of sapelin A (**3**) in both solvents. The only differences in the spectra of hispidol A (**1**) and sapelin A (**3**) come in the side-chain absorptions; most striking is the replacement of the C21 methylene pattern of **3** at δ 3.3–4.1 by a methyl doublet at δ 0.9–1.1, showing the ring in the side chain of **3** to be absent in **1**. The locations of the three hydroxyl groups in the side chains of **1** and **2**, suspected by analogy with **3** and **4** to be at C23, C24, and C25, were readily verified from the shifts and coupling constants of the protons in the side chain.

On biogenetic groupds, the configruations at all centers except C24 in hispidol A (**1**) might be expected to be the same as in compounds **3–6** which occur in the same plant.[1,2] Supporting evidence for all centers except C20, C23, and C24 is the close correspondence in shifts between **1** and sapelin A (**3**) except for the side-chain protons. Confirmatory evidence for the side-chain configurations shown for **1** and **2** comes from ^{1}H NMR spectral comparisons with related tirucallanes: bourjotinolone C (**7**)[4] and sapelin F (**8**) and its tetraacetate (**8a**).[5,6] Especially striking is the zero coupling constant observed between HC23 and HC24 in the alcohols **1**, **2**, and **7**, which increases to 1.5–1.6 Hz in the acetates **1a**, **2a**, and **8a**. All of the chemical shifts reported for sapelin F tetraacetate (**8a**)[5] are virtually the same as those in Table I for hispidol A triacetate (**1a**) except for C21 protons and acetate. A further close model is 3*S*,24*S*,25-trihydroxytirucall-7-ene (**9**),[7] like hispidol B

(4) Breen, G. J. W.; Ritchie, E.; Sidwell, W. T. L.; Taylor, W. C. *Aust. J. Chem.* **1966**, *19*, 455.
(5) Chan, W. R.; Taylor, D. R.; Yee, T. H. *J. Chem. Soc. C* **1971**, 2662.
(6) Lyons, C. W.; Taylor, D. R. *J. Chem. Soc., Chem. Commun.* **1975**, 517.
(7) Shermann, M. M.; Borris, R. P.; Ogura, M.; Cordell, G. A.; Farnsworth, N. R. *Phytochemistry* **1980**, *19*, 1499.

Scheme I. Major Fragment Ions (above *m/e* 250) in the Mass Spectra of Hispidols A (1) and B (2)



(2) except lacking the 23-hydroxyl group; the ^1H NMR spectra of the acetate of **9** and hispidol B acetate (**2a**) are very similar. That the C20 configurations in **1** and **2** are as shown (i.e., that they belong to the tirucallane rather than the euphane series) is supported by the downfield positions of their C21 methyl doublets as well as their negative optical rotations.[8]

The ^{13}C NMR shifts of the hispidols, **1** and **2**, in pyridine-d_5 are given in Table II along with those of hispidol B acetate (**2a**) and sapelin A (**3**) in $CDCl_3$. The solvent effects on the shifts are less here than for the proton spectra as the carbon atoms are more protected from the solvent, making comparisons easier. Assignments for **1**, **2**, and **2a** were made with the aid of off-resonance spectra and, in many cases, by analogy with **3**.[2] Selective ^1H–^{13}C decoupling on hispidol A (**1**) also helped in assigning the methyl carbon shifts and indicated that the C28, C29, and C30 shifts were interchanged in ref 2 for compounds **3**–**6**; the correct assignments for **3** are given in Table II. This assumes that the HC28, HC29, and HC30 shifts (Table I) have been assigned correctly, as seems very likely in view of many previous ^1H NMR studies of closely related compounds.[4-8] That C29 (axial) should absorb upfield from C28 (equatorial) in such a triterpenoid due to steric compression has much precedent.[9]

The differences in ^{13}C shifts between hispidols A (**1**) and B (**2**), all in the vicinity of C3, strongly support their being C3 epimers with the former possessing the axial hydroxyl. The changes in parts per million in going from equatorial hydroxyl in **2** to axial hydroxyl in **1** are as follows: C3, −3.0; C2, −2.0; C4, −1.5; C1, −5.7; C5, −6.3; C29, 6.7; and C28, 0.4. The magnitudes and signs of the C1, C5, and C29 changes are typical for gauche vs. anti arrangements in such systems.[9]

The virtually identical mass spectra of hispidols A (**1**) and B (**2**) strongly support their proposed constitution. The lower mass region (below *m/e* 300) is very similar to those of sapelins A (**3**) and B (**4**), but in the upper mass region (above *m/e* 300), all the major fragment ion peaks (base peak at *m/e* 371) are shifted to higher mass numbers by two. The proposed breakdown pattern (Scheme I) was substantiated by high-resolution exact measurements and metastable peaks (m). High-resolution measurement showed the *m/e* 257 (18%) to consist of $C_{18}H_{25}O$ and $C_{19}H_{29}$ in a 3:1 ratio. The loss of 44 and 58 mass units, equivalent to the elements of acetaldehyde and acetone, respectively, is reminiscent of the fragmentation pattern of bourjotone (**10**),[4] which exhibited strong M − 58 and M

(8) Itoh, T.; Tamura, T.; Matsumoto, T. *Lipids* **1976**, *11*, 434.

(9) Majumder, P. L.; Maiti, R. N.; Panda, S. K.; Mal, D.; Raju, M. S.; Wenkert, E. *J. Org. Chem.* **1979**, *44*, 2811 and references therein.

(10) Lyons, C. W.; Taylor, D. R. *J. Chem. Soc., Chem. Commun.* **1976**, 647.

Table II. ^{13}C NMR Chemical Shifts (δ) for Hispidols A (1) and B (2), Sapelin A (3), and Hispidol B Acetate (2a)

atom	3 [a]	1 [b]	2 [b]	2a [a]
C-1	31.3 (t)	31.9	37.6	36.8
C-2	25.4 (t)	26.6	28.6	24.2
C-3	76.3 (d)	75.3	78.3	81.2
C-4	37.6 (s)	38.0	39.5	37.9
C-5	44.6 (d)	44.9	51.2	50.8
C-6	23.9 (t)	24.4	24.4	23.8
C-7	118.2 (d)	118.6	118.5	117.8
C-8	145.9 (s)	146.4	146.1	145.7
C-9	48.6 (d)	49.2	49.3	48.8
C-10	34.8 (s)	35.2	35.2	34.8
C-11	17.9 (t)	18.4	18.4	18.1
C-12	33.1 (t)	34.4	34.3	33.2
C-13	43.3 (s)	43.8	43.8	43.6
C-14	51.4 (s)	51.6	51.4	51.1
C-15	33.9 (t)	34.4	34.3	33.9
C-16	27.3 (t)	28.7	28.6	27.9
C-17	44.8 (d)	54.4	54.4	53.6
C-18	13.0 (q)	13.5	13.5	13.2
C-19	21.9 (q)	22.0	22.1	21.9
C-20	37.6 (d)	34.4	34.3	33.9
C-21	70.2 (t)	19.5 (q)	19.6 (q)	21.4 (q)
C-22	36.5 (t)	42.4	42.3	38.0
C-23	64.7 (d)	69.5	69.5	70.4
C-24	86.5 (d)	76.8	76.8	76.8
C-25	74.2 (s)	73.8	73.8	72.5
C-26, C-27	23.9, 28.5 (q)	27.3, 27.8	27.2, 27.8	26.3, 27.2 [c]
C-28	27.8 (q)	28.7	28.3	27.2 [c]
C-29	22.2 (q)	22.2	15.5	15.9
C-30	27.4 (q)	27.6	27.4	27.6 [c]
C=O				170.5, 170.7, 171.0 (s)
MeC=O				18.4, 20.9, 21.4 (q)

[a] In $CDCl_3$. [b] In pyridine-d_5. [c] May be reversed.

– (15 + 58) peaks. That the losses of 72 mass units gave isobutyraldehyde was supported by strong peaks at m/e 72 (87%) and 71 (71%); these compositions were verified by exact measurements.

Hispidols **A** (1) and **B** (2) are probably derived in nature by acid-catalyzed addition of water to the epoxide group in a side chain like that of **11**, synthesized from bourjotinolone C (**7**) with base; though **11** has not been found in nature, it was suggested that **7** is an artifact formed from natural **11** during workup with HCl.[4] Epoxide **11** can serve as a precursor to epoxide **12**,[4] which can give the other tirucallane derivatives **3**–**6** found in the same plant as well as many other tirucallanes found in different plants.[4,6,10]

Experimental Section

The high-resolution mass spectral data were obtained at a resolution of 7000 by scanning the mass range from m/e 100 to 500 repetitively at 25 s/dec, using PFK as the internal standard. Metastable ion spectra were recorded by either scanning the magnetic (B) and electrostatic (E) fields at constant accelerating voltage with the B/E ratio constant to obtain the daughters of parents or by scanning the accelerating voltage at constant B and E for determining parents of daughters. Samples were introduced by using a direct probe. The normal ionizing voltage was 70 eV with a source temperature of 250 °C. All other experimental conditions specified in ref 2 and 3 apply.

Hispidols A (1) and B (2). The fraction containing these alcohols, which had R_f values slightly lower than sapelin B (**4**), was isolated following the procedure outlined earlier for the isolation of **5** and **6**.[2] Rechromatography of this fraction (EM SiO_2-60; CH_2Cl_2 with increasing concentration of EtOAc) yielded two sets of fractions, A and B. Fraction A, when rechromatographed (EM SiO_2-60; CH_2Cl_2 with increasing concentrations of MeCN), yielded hispidol A (**1**), which crystallized from MeOH–CH_2Cl_2 as colorless needles: mp 118 °C, $[\alpha]^{25}_D$ –80° (pyridine); NMR and mass spectral parameters are given in Tables I and II and Scheme I; IR (KBr) 3340, 1370, 820 cm^{-1}.

Anal. Calcd for $C_{30}H_{52}O_4$: C, 75.6; H, 10.9. Found: C, 75.3; H, 11.1.

Fraction B (foam), after being washed with CH_2Cl_2–EtOAc (1:1) and after addition of MeOH–CH_2Cl_2, gave hispidol B (**2**) as lustrous rectangular prisims: mp 252–253 °C, $[\alpha]^{25}_D$ –57° (pyridine; NMR and mass spectral parameters are given in Tables I and II and Scheme I; IR (KBr) superimposable with hispidol A (**1**).

Anal. Calcd for $C_{30}H_{52}O_4$: C, 75.6; H, 10.9. Found: C, 75.4; H, 11.2.

Hispidol A Triacetate (1a). Acetylation of hispidol A (**1**) overnight at room temperature with excess Ac_2O–pyridine gave **1a** as colorless foam, homogeneous on TLC. The IR [($CHCl_3$) 3600, 1735, 1380, 1240, 820 cm^{-1}] and ^1H NMR (Table I) spectra were in accord with structure **1a**.

Hispidol B Triacetate (2a). Similar treatment of hispidol B (**2**) with Ac_2O–pyridine followed by crystallization from ether–hexane gave **2a**, mp 146–148 °C, identical R_f value with that of **1a**. The IR [($CHCl_3$) superimposable with **1a**], NMR (Tables I and II), and mass [m/e 602 (M^+, 19.6), 587 (14.4), 569 (62.7), 542 (4.7), 528 (34.4), 527 (91.7), 510 (12), 509 (31.6), 484 (6.8), 467 (32.6), 449 (29.7), 425 (7.3), 409 (16.8), 407 (16.9), 389 (33.3), 369 (39.2), 367 (10.6), 353 (25.6), 335 (15.4), 309 (48.4)] spectra were in accord with structure **2a**.

Anal. Calcd for $C_{36}H_{58}O_7$: C, 71.76; H, 9.63. Found: C, 71.73; H, 9.85.

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Registry No. 1, 78739-37-4; **1a**, 78739-38-5; **2**, 78739-39-6; **2a**, 78739-40-9; **3**, 26790-93-2.

Convenient Laboratory Preparation of Glyoxal-d_2 and 2,4,6,8-Tetrakis(methoxycarbonyl)bicyclo[3.3.0]octane-3,7-dione-1,5-d_2

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Glyoxal-d_2 has been prepared in low yield by the oxidation of ethylene-d_4 with a mixture of selenium dioxide and phosphorus pentoxide at 200 °C[1,2] and by the ozonization of acetylene-d_2 in a special apparatus.[3,4] While these may serve to make small amounts of glyoxal-d_2 for spectroscopic studies, they do not constitute bench-scale preparations suitable for organic synthesis. The strategy conceived to guide the development of such a procedure was to use a derivative of glyoxal which would contain C–H bonds sufficiently acidic to exchange with D_2O. Because it is an established source of glyoxal for further reactions,[5] glyoxal bis(sodium bisulfite) was chosen for study.

Results

Although both heat and base (sodium carbonate) were found to facilitate the exchange, heat was found to give better results than base catalysis, as the latter caused more decomposition. The best procedure proved to be the gentle refluxing of a saturated D_2O solution of glyoxal bis(sodium

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