Phytochemistry, 1980, Vol. 19, pp. 1989–1993. © Pergamon Press Ltd. Printed in England. 0031-9422/80/0901-1989 $02.00/0

THREE TRITERPENES AND OTHER TERPENOIDS FROM *CATHA CASSINOIDES*

C. BETANCOR, R. FREIRE, A. G. GONZALEZ, J. A. SALAZAR, C. PASCARD* and T. PRANGE*

Instituto de Productos Naturales Orgánicos, C.S.I.C., Departamento de Química Orgánica de la Universidad de La Laguna, Tenerife, Spain; *Institut de Chimie des Substances Naturelles, C.N.R.S., Gif-sur-Yvette, France

(*Received* 19 *November* 1979)

Key Word Index—*Catha cassinoides*; Celastraceae; peralillo; sitosterol; β-amyrin; ursolic acid; lup-20(29)-en-3β,30-diol; pentacyclic triterpenes; friedelin; 30-hydroxyfriedelan-3-one; 29-hydroxyfriedelan-3-one; 3-oxo-friedelan-29-oic acid; X-ray analysis.

Abstract—The investigation of stems and leaves of *Catha cassinoides* afforded, in addition to sitosterol, β-amyrin, ursolic acid, lup-20(29)-en-3β,30-diol and friedelin, three new pentacyclic triterpenes: 30-hydroxyfriedelan-3-one, 29-hydroxyfriedelan-3-one and 3-oxo-friedelan-29-oic acid. The structures of these were determined by spectral studies and correlations, and were confirmed by X-ray analysis of 29-hydroxyfriedelan-3-one acetate.

INTRODUCTION

In a previous paper [1] we reported the isolation of various nor-triterpene quinonoid compounds with antitumoural and antibacterial properties from the root bark of *Catha cassinoides*. This paper deals with the triterpene constituents of the stems and leaves of the same plant. In addition to β-amyrin, sitosterol, ursolic acid, lup-20(29)-en-3β,30-diol (**1a**) and friedelin (**3a**), three new triterpenes with the friedelane skeleton were obtained and identified as 30-hydroxyfriedelan-3-one (**3b**), 29-hydroxyfriedelan-3-one (**4a**) and 3-oxo-friedelan-29-oic acid (**4c**). The structures proposed are based on spectroscopic data, interconversion and comparison with friedelane (**5a**), epifriedelinol (**5b**) and polpunonic acid (**3d**). X-Ray analysis of the acetate of 29-hydroxyfriedelan-3-one determined the stereochemistry at C-20. In view of the results obtained it may be advisable to reconsider the structures proposed for the natural products octandrolal, octandrolol, octandrolic acid, octandronal, octandronol and octandronic acid, isolated from the bark of *Hydnocarpus octandra* [2].

RESULTS AND DISCUSSION

Compound **1a**, $C_{30}H_{50}O_2$, is a pentacyclic triterpene with an equatorial OH group at C-3 and a $CH_2{=}C{-}CH_2OH$ grouping as can be seen from the ^{1}H NMR signals at δ 3.25 (1 H, *dd*), 4.95 (2 H, broad *s*) and 4.15 (2 H, *s*) which changed to 4.45, 4.90 and 4.50 respectively in the spectrum of the diacetate **1b**. The off-resonance decoupled ^{13}C NMR spectrum of **1b** agreed with these assignations: two olefinic carbons observed at 149.29 (*s*) and 110.16 (*t*), a doublet at 80.86 and a triplet at 65.95 corresponding to the secondary and primary carbinols (ppm from TMS).

Lupenyl and lupanyl acetates **1c** and **2** were obtained from **1b** by hydrogenolysis in the presence of Pd/C. This confirmed the presence of the primary allylic alcohol and established the structure of **1a** as lup-20(29)-en-3β,30-diol (see Scheme 1). This substance had previously been isolated from the stems of *Quercus championi* [3] and the physical and spectral data of the compound from both sources agreed in all respects.

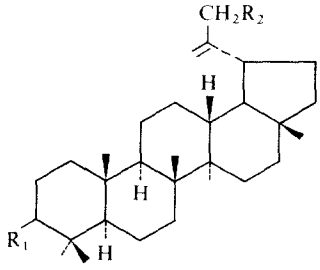
30-Hydroxyfriedelan-3-one (**3b**), $C_{30}H_{50}O_2$, had IR absorptions at 3450 and 1700 cm^{-1}. The ^{1}H NMR spectrum showed a two-proton singlet due to a $C\underline{H}_2{-}OH$ group at δ 3.25, (this moved to δ 3.75 in the spectrum of the acetate **3c**); six tertiary C-Me groups; a secondary methyl; no olefinic protons.

These data plus the MS fragmentation pattern (see Table 1 and Scheme 2) [4] and the negative Cotton effect seen in the CD spectrum (identical to that of friedelin) point to **3b** being a saturated keto-alcohol with a friedelane carbon skeleton.

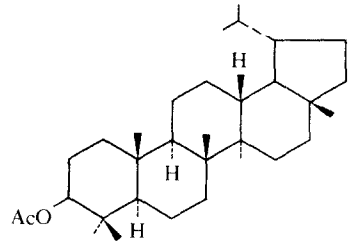
Taking into account the *m/e* of fragment **e** (141 in **3b** displaced to 183 in **3c**) and the low intensity of $[M^+ - R]$, the hydroxymethylene group should be located at C-20. Oxidation of **3b** with Jones' reagent followed by diazomethane treatment gave a methyl ester identical with methyl polpunonate (**3e**) [5] (direct comparison with authentic sample). **3b** is therefore 30-hydroxyfriedelan-3-one; this had been prepared from polpunonic acid but this is the first time that it has been isolated as a natural product.

29-Hydroxyfriedelan-3-one (**4a**), $C_{30}H_{50}O_2$, had two oxygen atoms corresponding to a carbonyl group (IR absorptions at 1705 cm^{-1}) and to a primary hydroxyl group (IR absorptions at 3500 cm^{-1}; ^{1}H NMR, two-proton singlet at δ 3.42). An acetate (**4b**) was formed, $C_{32}H_{52}O_3$, and a keto-aldehyde (**4d**), $C_{30}H_{48}O_2$, by means of mild oxidation with Jones' reagent. **4d** showed IR absorptions at 2700, 1725 and 1705 cm^{-1} and one proton singlet at δ 9.47 in ^{1}H NMR. Subsequent oxidation of **4d** yielded the natural keto-acid 3-oxofriedelan-29-oic acid (**4c**), $C_{30}H_{48}O_3$, the last product to be isolated from *Catha cassinoides*. The two substances could thus be correlated.

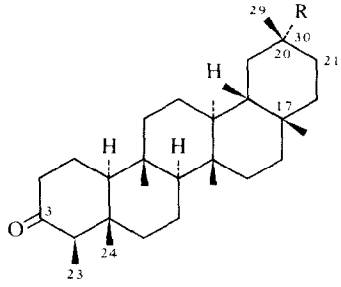
The presence of six tertiary methyl groups and a secondary methyl group in the ^{1}H NMR spectra of **4a** and **4c** and their MS fragmentation patterns (see Table 1 and Scheme 2) indicate that both substances have friedelane



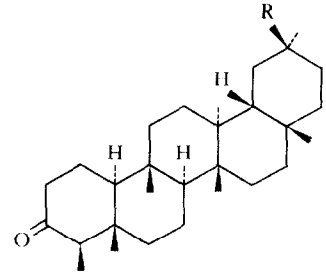
1a $R_1 = R_2 = OH$
1b $R_1 = R_2 = OAc$
1c $R_1 = OAc; R_2 = H$



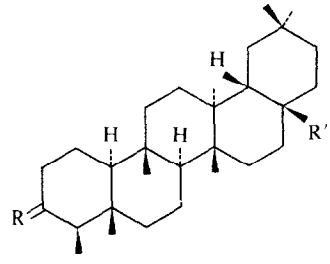
2



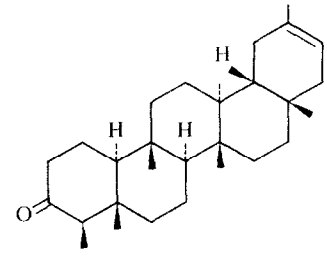
3a R = Me
3b R = CH_2OH
3c R = CH_2OAc
3d R = CO_2H
3e R = CO_2Me



4a R = CH_2OH
4b R = CH_2OAc
4c R = COOH
4d R = COH
4e R = CH_2OTs
4f R = CO_2Me
4g R = $CONH_2$



5a R = 2H; R′ = Me
5b R = β-OH α-H; R′ = Me
5c R = O; R′ = CH_2OH

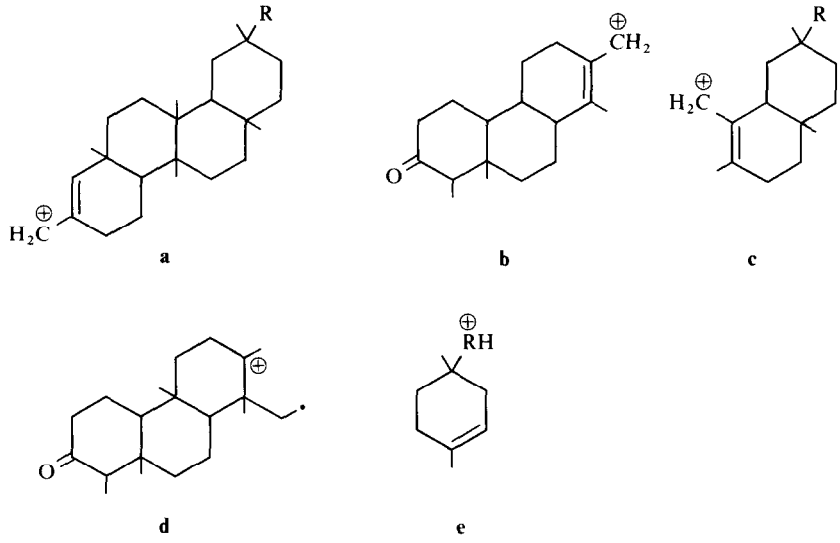


6

Scheme 1.

Table 1. MS data (% rel. int.)

	a	b	c	d	e	M^+	$M^+ - R$
3a	341 (22)	273 (100)	205 (237)	302 (43)	125 (200)	426 (28)	411 (13)
3b	357 (37)	273 (100)	221 (75)	302 (68)	141 (250)	442 (200)	411 (30)
3c	399 (15)	273 (100)	263 (18)	302 (23)	183 (113)	484 (80)	411 (10)
4a	357 (26)	273 (100)	221 (105)	302 (64)	141 (250)	442 (60)	411 (20)
4b	399 (14)	273 (100)	263 (57)	302 (53)	183 (170)	484 (25)	411 (10)
4c	371 (12)	273 (100)	235 (200)	302 (20)	155 (250)	456 (34)	411 (10)
4d	355 (79)	273 (100)	219 (21)	302 (8)	139 (270)	440 (80)	411 (16)
4f	385 (34)	273 (100)	249 (155)	302 (13)	169 (250)	470 (87)	411 (16)
6	325 (25)	273 (100)	189 (46)	302 (8)	109 (200)	410 (40)	



Scheme 2

skeletons, and in fact Huang–Minlon reduction of **4d** will give friedelane (**5a**). The position of the carbonyl group at C-3 was determined by its CD curve [identical to that of friedelin (**3a**), see Experimental] and by the fact that epifriedelinol (**5b**) could be obtained by $LiAlH_4$ reduction of the tosylate **4e**. In **4a** the hydroxymethylene group could only be sited at C-20 for the same reasons applied to 30-hydroxyfriedelan-3-one (**3b**). Comparison with a genuine sample of canophyllol (**5c**) [6] showed that this group was not located at C-17.

Oxidative decarboxylation of 3-oxofriedelan-29-oic acid (**4c**) and of polpunonic acid (**3d**) with lead tetraacetate in benzene containing cupric acetate gave in both cases the nor-triterpene **6**, $C_{29}H_{46}O$. In the ^1H NMR of **6**, the vinyl proton at C-21 appears as a multiplet at δ 5.30 ($W = 12$ Hz) and the methyl at C-20 as a broad singlet at δ 1.62. Thus the keto-alcohol **4a** and the keto-acid **4c** were shown to be 29-hydroxyfriedelan-3-one and 3-oxofriedelan-29-oic acid, respectively. These structures are the same as those assigned to the natural products octandronol and octandronic acid from *Hydnocarpus octandra* [2]. However, their physical and spectral data and direct comparison of 29-hydroxyfriedelan-3-one (**4a**) and octandronol suggest that they must be different substances.

Proof for the stereochemistry of C-20 other than the inter-relation with polpunonic acid was sought by abstracting the βH atom at C-18. However, lead tetraacetate and I_2 reaction of 29-hydroxyfriedelan-3-one (**4a**), 3-oxofriedelan-29-oic acid amide (**4g**) and 30-hydroxyfriedelan-3-one (**3b**) always produces the same nor-triterpene, **6**, and nowhere is there evidence that compounds are formed as a result of 18-H abstraction.

Furthermore, the stereochemistry at C-20 was unambiguously elucidated by X-ray analysis* of the acetate **4b**. The compound crystallized as small needles. The cell parameters, determined on a four-circle automatic diffractometer were: $a = 13.982$; $b = 6.486$; $c = 16.688$ Å; $\beta = 113.7°$ and $Z = 2$ (monoclinic $P2_1$). Because of the paucity of the diffraction data, the structure was solved

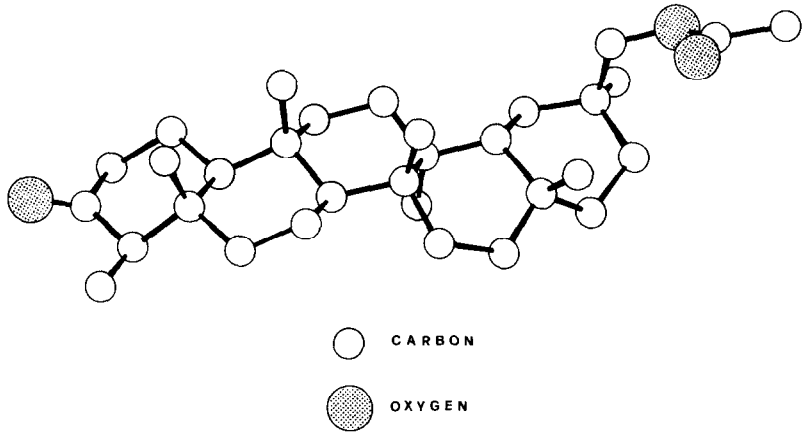


Fig. 1

* The X-ray analysis data are deposited at the Crystallography Department at the University of Cambridge.

with some difficulty by multisolution techniques (direct methods). Refinements were carried out by block diagonal least-squares procedures with isotropic thermal factors to a conventional R value of 9.8%. No attempt was made to refine the structure anisotropically. The final view of the molecule is shown in Fig. 1 with the C-20 substituent in a β-position, rings A, B and C adopting a chair conformation, ring D a twist-boat conformation and ring E an almost perfect boat conformation with the C-17 methyl and the C-20 acetoxy methyl groups in axial positions. This unusual disposition was also noted in the X-ray analysis of epifriedelinol [7].

From the foregoing it would seem that the structures assigned to the series of triterpenes isolated earlier from *Hydnocarpus octandra* should be revised. The IR and ^{1}H NMR spectra of octandronol are identical to those of canophyllol (**5c**). It may be that the *H. octandra* triterpenes possess an oxidized methyl at C-17.

EXPERIMENTAL

Mps were determined on a Kofler block and are uncorr. Optical rotations were measured in $CHCl_3$ and ^{1}H NMR spectra in $CDCl_3$ with TMS as int. ref. Dry column chromatography was carried out on Si gel (0.063–0.02 mm). The spray reagent for TLC was H_2SO_4–HOAc–H_2O (1:20:4).

Isolation of the terpenoids. The stems and leaves of the plant, collected near Igueste de Candelaria, Tenerife, were finely cut and extracted with hot EtOH and concd *in vacuo*. The residue was chromatographed on Si gel and eluted with C_6H_6, C_6H_6–EtOAc, EtOAc giving: friedelin (**1a**; 0.02%), β-amyrin (0.02%), sitosterol (0.01%), 29-hydroxyfriedelan-3-one (**4a**; 0.01%), 3-oxofriedelan-29-oic acid (**4c**; 0.02%), 30-hydroxyfriedelan-3-one (0.01%), lup-20(29)-en-3,30-diol (0.03%), ursolic acid (0.01%), separated by repeated dry column chromatography.

Lup-20(29)-en-3β,30-diol (**1a**). Mp 237–239° (MeOH–$CHCl_3$), $[\alpha]_D$ − 12° (*c* 0.160); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1650, 915 (CH_2=C); ^{1}H NMR: δ 0.75, 0.78, 0.82, 0.93, 0.96, 1.03 (18 H, *s* each, six Me groups), 3.25 (1 H, *dd*, $J_{ax,ax}$ = 9, $J_{ax,eq}$ = 7 Hz, C-3), 4.15 (2 H, *s*, C-30), 4.95 (2 H, *br s*, $W_{1/2}$ = 6 Hz, C-29); MS (probe) 70 eV *m/e* (rel. int.): 220 (100), 442 M$^+$ (88), 424 (M$^+$ − H_2O; 50), 411 (M$^+$ − CH_2OH; 28), 385 (M$^+$ − CH_2=C−CH_2OH; 14).

Acetate (**1b**). Mp 170–172° ($CHCl_3$–MeOH), $[\alpha]_D$ + 9° (*c* 0.260); IR ν_{max}^{KBr} cm^{-1}: 1730, 1245 (OAc), 1650, 915, 3030 (CH_2=C); ^{1}H NMR: δ 0.78, 0.85 × 3, 0.92, 1.02 (18 H, *s* each, six Me groups), 2.00 (3 H, *s*, OAc), 2.08 (3H, *s*, OAc), 4.45 (1 H, C-3), 4.50 (2 H, *br s*, $W_{1/2}$ = 4 Hz, C-30), 4.90 (2 H, *br s*, $W_{1/2}$ = 6 Hz, C-29); ^{13}C NMR, ppm (TMS = 0) (multiplicity): 170.71 (*s*), 149.29 (*s*), 110.16 (*t*), 80.86 (*d*), 65.95 (*t*), 55.42 (*d*), 50.35 (*d*), 49.00 (*d*), 44.37 (*d*), 43.02 (*s*), 42.84 (*s*), 40.95 (*s*), 39.85 (*t*), 38.45 (*t*), 38.12 (*d*), 37.84 (*s*), 37.10 (*s*), 35.47 (*t*), 34.30 (*t*), 31.36 (*t*), 27.96 (*q*), 27.46 (*t*), 26.50 (*t*), 23.73 (*t*), 21.11 (*q*), 20.95 (*q*), 18.24 (*t*), 17.76 (*q*), 16.53 (*q*), 16.17 (*q*), 16.05 (*q*), 14.58 (*q*); MS (probe) 70 eV *m/e* (rel. int.): 202 (100), 526 M$^+$ (6), 466 (M$^+$ − HOAc; 18). (Found: C, 77.41; H, 10.52. Calc for $C_{34}H_{54}O_4$: C, 77.56; H, 10.26%).

Friedelin (**3a**). Mp 258–259° (C_6H_6–EtOAc), $[\alpha]_D$ − 25° (*c* 0.225); IR ν_{max}^{KBr} cm^{-1}: 1710 (C=O); ^{1}H NMR: δ 0.72, 0.87, 0.94, 1.00 × 2, 1.05, 1.18 (21 H, *s* each, seven Me groups), 0.86 (3 H, *d*, J = 7 Hz, C-23), 2.20–2.40 (3 H, *m*, C-2 and C-4); CD, (*c* 1.24 dioxan), 22°, $[\theta]_{330}$0, $[\theta]_{302}$ − 9730, $[\theta]_{294}$ − 10 390, $[\theta]_{240}$0.

30-Hydroxyfriedelan-3-one (**3b**). Mp 270–272° (MeOH–$CHCl_3$), $[\alpha]_D$ − 24° (*c* 0.088); IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 1700 (C=O); ^{1}H NMR: δ 0.72, 0.86, 0.92, 1.03 × 2, 1.21 (18 H, *s* each, six Me groups), 0.86 (3 H, *d*, J = 7 Hz, C-23), 2.20–2.40 (3 H, *m*, C-2 and C-4), 3.25 (2 H, *s*, C-30); MS, see Table 1. (Found: C, 81.35; H, 11.39. Calc. for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38%).

Acetate (**3c**). Mp 170–171° (MeOH); IR ν_{max}^{KBr} cm^{-1}: 1700 (C=O), 1730, 1250 (OAc); ^{1}H NMR: δ 0.72, 0.87, 1.04 × 2, 1.05, 1.22 (18 H, *s* each, six Me groups), 0.86 (3 H, *d*, J = 7 Hz, C-23), 2.07 (3 H, *s*, OAc), 3.75 (2 H, *s*, C-30); MS, see Table 1. (Found: C, 79.25; H, 10.78. Calc. for $C_{32}H_{52}O_3$: C, 79.29; H, 10.81%).

29-Hydroxyfriedelan-3-one (**4a**). Mp 268–269° (MeOH–$CHCl_3$), $[\alpha]_D$ − 15° (*c* 0.260); IR $\nu_{max}^{CHCl_3}$cm^{-1}: 3610 (OH), 1710 (C=O); ^{1}H NMR: δ 0.72, 0.87, 1.00 × 2, 1.08, 1.17 (18 H, *s* each, six Me groups), 0.87 (3 H, *d*, J = 7 Hz, C-23), 2.20–2.50 (3 H, *m*, C-2 and C-4), 3.42 (2 H, *s*, C-29); CD (*c* 1.22 dioxan), 22°, $[\theta]_{330}$0, $[\theta]_{302}$ − 9075, $[\theta]_{294}$ − 9702, $[\theta]_{240}$0; MS, see Table 1. (Found: C, 81.30; H, 11.40. $C_{30}H_{50}O_2$ requires: C, 81.39; H, 11.38%).

Acetate (**4b**). Mp 188–190° (MeOH), $[\alpha]_D$ − 10° (*c* 0.270); IR ν_{max}^{KBr} cm^{-1}: 1700 (C=O), 1730, 1250 (OAc); ^{1}H NMR: δ 0.72, 0.87, 1.00 × 2, 1.07, 1.18 (18 H, *s* each, six Me groups), 0.87 (3 H, *d*, J = 7 Hz, C-23), 2.08 (3 H, *s*, OAc), 3.90 (2 H, *s*, C-29); ^{13}C NMR, ppm (TMS = 0) (multiplicity) 212.62 (*s*), 171.20 (*s*), 72.73 (*t*), 59.56 (*d*), 58.22 (*d*), 53.14 (*d*), 42.60 (*d*), 42.10 (*s*), 41.48 (*t*), 41.37 (*t*), 39.84 (*s*), 38.32 (*s*), 38.08 (*t*), 37.46 (*s*), 35.89 (*t*), 35.59 (*t*), 32.27 (*t*), 32.10 (*q*), 31.97 (*s*), 30.39 (*t*), 30.21 (*t*), 29.96 (*s*), 29.52 (*q*), 28.24 (*t*), 22.26 (*t*), 20.92 (*q*), 20.12 (*q*), 18.54 (*q*), 18.25 (*t*), 18.00 (*q*), 14.65 (*q*), 6.78 (*q*); MS, see Table 1. (Found: C, 79.28; H, 10.76. $C_{32}H_{52}O_3$ requires: C, 79.29; H, 10.81%).

3-Oxofriedelan-29-oic acid (**4c**). Mp 260–262° (MeOH), $[\alpha]_D$ 0° (*c* 0.260); IR $\nu_{max}^{CHCl_3}$cm^{-1}: 3500, 3200–2500 (COOH), 1700 (C=O); ^{1}H NMR: δ 0.72, 0.87, 1.00, 1.05 × 2, 1.25 (18 H, *s* each, six Me groups), 0.87 (3 H, *d*, J = 7 Hz, C-23), 2.20–2.40 (3 H, *m*, C-2 and C-4); MS, see Table 1. (Found: C, 78.88; H, 10.62. $C_{30}H_{48}O_3$ requires: C, 78.90; H, 10.59).

Methyl ester (**4f**). Obtained from **4c** by treatment with CH_2N_2 in Et_2O: mp 203–204° ($CHCl_3$–MeOH), $[\alpha]_D$ 0° (*c* 0.271); IR, $\nu_{max}^{CHCl_3}$ cm^{-1}: 1700 (C=O), 1720 COOMe); ^{1}H NMR δ 0.72, 0.87, 1.00, 1.02, 1.04, 1.24 (18 H, *s* each, six Me groups), 0.86 (3 H, *d*, J = 7 Hz, C-23), 2.20–2.60 (3 H, *m*, C-2 and C-4), 3.7 (3 H, *s*, OMe); ^{13}C NMR ppm (TMS = 0) (multiplicity): 212.58 (*s*), 179.43 (*s*), 59.50 (*d*), 58.22 (*d*), 53.15 (*d*), 51.77 (*q*), 42.49 (*d*), 42.05 (*s*), 44.49 (*t*), 41.31 (*t*), 40.47 (*s*), 39.67 (*s*), 38.32 (*t*), 38.08 (*s*), 37.53 (*s*), 35.53 × 2(*t*), 32.83 (*t*), 31.91 (*q*), 31.79 (*q*), 31.43 (*t*), 30.27 (*t*), 29.53 (*s*), 28.55 (*t*), 22.27 (*t*), 20.87 (*q*), 18.21 (*t*), 17.64 × 2(*q*), 14.64 (*q*), 6.78 (*q*); CD, (*c* 1.24 dioxan), 22°, $[\theta]_{330}$0, $[\theta]_{302}$ − 9240, $[\theta]_{294}$ − 10 260, $[\theta]_{240}$0; MS, see Table 1. (Found: C, 79.00; H, 10.20. $C_{31}H_{50}O_3$ requires: C, 79.10; H, 10.71%).

Lupenyl and lupanyl acetates (**1c** and **2**). **1b** (0.034 g) in dry EtOAc was shaken with Pd/C 10% catalyst (0.023 g) in H_2 at room temp. for 3 hr. Standard work-up followed by dry column chromatography (C_6H_6) gave **1c** (0.015 g)—mp 221–222°, $[\alpha]_D$ + 39° (*c* 0.024), identical with an authentic sample of lupenyl acetate (mmp, IR, ^{1}H NMR)—and **2** (0.012 g)—mp 265–267°; ^{1}H NMR: δ 0.75, 0.85, 0.92, 1.05 (24 H, *s* each, eight Me groups), 2.05 (3 H, *s*, OAc), 4.4 (1 H, C-3); MS (probe) 70 eV *m/e* (rel. int.): 470 M$^+$ (23), 427 (M$^+$−Me−CH−Me; 8), 410 (M$^+$−HOAc 27), 191 (100).

Methyl polpunonate (**3e**). **3b** (0.04 g) dissolved in Me_2CO was treated with Jones' reagent at room temp. to give the acid **3d** (0.032 g)—mp 272–273° (MeOH–$CHCl_3$)—which was then methylated with CH_2N_2 in Et_2O and purified by dry column chromatography to give **3e** (0.027 g) identical with an authentic sample of methyl polpunonate (mmp, TLC, IR, ^{1}H NMR).

Aldehyde (**4d**). This was obtained by the controlled oxidation of **4a** with Jones' reagent at 0°: mp 215–216° ($CHCl_3$–MeOH), $[\alpha]_D$ − 13° (*c* 0.300); IR ν_{max}^{KBr} cm^{-1}: 2700, 1725 (CHO), 1705 (C=O); ^{1}H NMR: δ 0.72, 0.86, 0.95, 1.01, 1.06 × 2, (18 H, *s* each six Me groups), 0.86 (3 H, *d*, J = 7 Hz, C-23), 9.47 (1 H, *s*, C-29);

MS, see Table 1. Oxidation of **4d** with Jones' reagent at room temp. yielded an acid identical with the natural compound, **4c**.

Friedelane (**5a**). Compound **4d** (0.04 g) in 10 ml diethylene glycol and 0.6 ml hydrazine hydrate was refluxed for 2 hr. After cooling, NaOH (0.08 g) was added and the soln was heated for 3 hr to 190°. The usual work-up gave **5a** (0.012 g), mp 248–249°, $[\alpha]_D$ + 20° (*c* 0.200): MS, see Table 1, identical to the product obtained by the Huang–Minlon reduction of friedelin (**3a**).

Epifriedelinol (**5b**). **4a** (0.072 g) in dry Py was stirred with *p*-toluene–sulfonic chloride (0.160 g) at 0° for 3 days. The usual work-up yielded the tosylate (**4e**) (0.09 g). To 0.08 g of this tosylate in 10 ml dry THF, a suspension of $LiAlH_4$ (0.09 g) in THF (4 ml) was added while stirring and the mixture was refluxed for 2 hr. After excess $LiAlH_4$ was eliminated, first with MeOH and then with H_2O, the reaction product was extracted with Et_2O and purified by dry column chromatography (C_6H_6–EtOAc) to give the alcohol (**5b**) (0.022 g): mp 280–282°, $[\alpha]_D$ + 19° (*c* 0.120); IR ν_{max}^{KBr} cm^{-1}: 3500 (OH); ^1H NMR δ 0.88, 0.97, 1.00 × 4, 1.18 (21 H, each, seven Me groups), 3.7 (1 H, *m*, C-3); MS, see Table 1. Its mp was undepressed by admixture with a sample of epifriedelinol prepared by $LiAlH_4$ reduction of friedelin (**3a**). The IR and ^1H NMR of the two samples were also superimposable.

29-*Nor-friedel*-20-*en*-3-*one* (**6**). The acid (**4c**) (0.20 g) was dissolved in dry C_6H_6 (150 ml) and cupric acetate (0.24 g) and lead tetraacetate (0.42 g) were added. The mixture was refluxed under N_2 for 5 hr. The usual work-up was applied and the nor-triterpene **6** (0.12 g) was recovered. Acid **3d** when treated the same way gave the same substance in similar yield.

6 was also obtained from **3b**, **4a** and **4g**. **4a** (0.04 g) was dissolved in dry cyclohexene, lead tetraacetate (0.11 g) and I_2 (0.02 g) were added, the mixture was stirred at room temp and irradiated with a Wolfram 100 W lamp for 1 hr. Work-up gave **6** (0.02 g): mp 220–221°; $[\alpha]_D$ − 77° (*c* 0.280) IR ν_{max}^{KBr} cm^{-1}: 1700 (C=O); ^1H NMR, δ 0.72, 0.90 × 4 (15 H, *s* each, five Me groups), 0.86 (3 H, *d*, *J* = 7 Hz, C-23), 1.62 (3 H, *br s*, $W_{1/2}$ = 6 Hz, C-30), 5.30 (1 H, *m*, $W_{1/2}$ = 12 Hz, C-21); MS, see Table 1. (Found: C, 84.70; H, 11.22. $C_{29}H_{46}O$ requires: C, 84.81; H, 11.29%). The same reaction applied to **3b** and **4g** gave in both cases the same product in about the same yield. **4g** was obtained from **4c** by treatment first with oxalyl chloride and then with conc. NH_3.

Acknowledgements—Part of this work has been subsidized by a Spanish Government grant towards the technical and cultural development of the Canary Islands. Dr. F. delle Monache let us have a sample and the spectra of polpunonic acid, Dr. M. V. S. Sultanbawa provided us with the spectra and a sample of octandronol, and Dr. B. R. Pai forwarded us a sample of canophyllol.

REFERENCES

1. González, A. G., Francisco, C. G., Freire, R., Hernández, R., Salazar, J. A. and Suárez, E. (1975) *Phytochemistry* **14**, 1067.
2. Gunasekera, S. P. and Sultanbawa, S. (1977) *J. Chem. Soc. Perkin Trans.* **1**, 418.
3. Wai-Haan Hui and Man-Moon Li (1977) *J. Chem. Soc. Perkin Trans.* **1**, 897.
4. Shannon, J. S., Macdonald, C. G. and Courtney, J. L. (1963) *Tetrahedron Letters* 173.
5. Delle Monache, F., de Mellò, J. F., Marini-Bettòlo, G. B., Gonçalves de Lima, O. and D'Albuquerque, I. L. (1972) *Gazz. Chim. Ital.* **102**, 636.
6. Govindachari, T. R., Viswanathan, N., Pai, B. R., Ramadas Rao, U. and Srinivasan, M. (1967) *Tetrahedron* **23**, 1901.
7. Laing, M., Burke-Laing, M. E., Bartho, R. and Weeks, C. M. (1977) *Tetrahedron Letters* 3839.