*Phytochemistry*, Vol 27, No 11, pp 3579–3584, 1988
Printed in Great Britain

0031-9422/88 $3.00 + 0.00


# TRITERPENE CONSTITUENTS FROM *EUPHORBIA SUPINA*

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(*Received* 26 *January* 1988)

**Key Word Index**—*Euphorbia supina*, Euphorbiaceae; whole herb, triterpenes; migrated hopanes; oleananes, migrated oleananes; taraxerane.

**Abstract**—In addition to four triterpenes previously found, 12 triterpenes were isolated from the whole herb of *Euphorbia supina* along with sitosterol. Nine of these were known triterpenes including fernane, simiarane and multiflorane skeletons. The remaining three were confirmed to be δ-amyrin formate, ferna-7:9(11)-dien-3β-ol and 11α,12α-oxidotaraxerol on the basis of chemical and spectroscopic evidence.

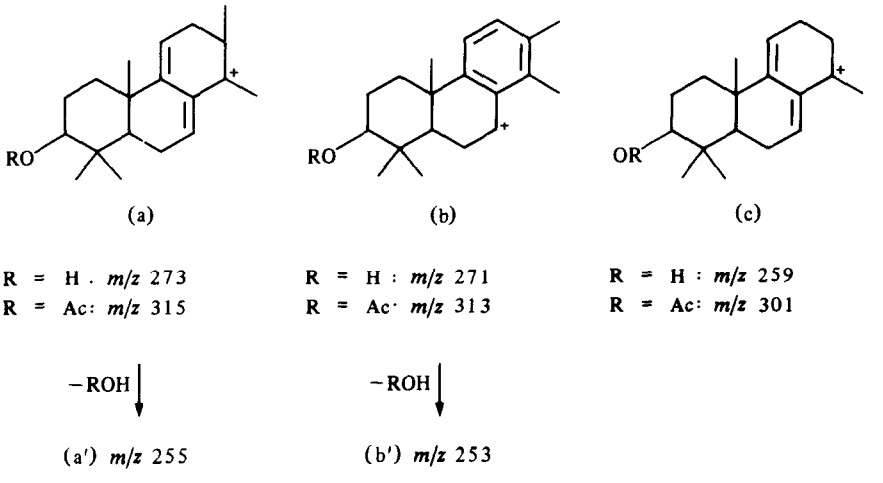
## INTRODUCTION

*Euphorbia supina*, an annual weed becoming naturalized from North America to Japan about one century ago [1], is documented for use as a folk medicine for the treatment of gastroenteric diseases and for healing suppurated swelling [2], although the latex produces a considerable skin irritation in some individuals This plant contained triterpenes, motiol (fern-7-en-3β-ol), hopenol-B (hop-22(29)-en-3β-ol) [3], 3β-hydroxyhexanordammaran-20-one [4] and spirosupinanonediol (**13**) [5] bearing a novel and biogenetically interesting migrated fernane skeleton, for which we proposed to call 'spirosupinane'. This paper reports the further characterization of 12 triterpenes isolated together with sitosterol from this plant

## RESULTS AND DISCUSSION

Less polar fractions of the neutral benzene extract of *E. supina* on repeated CC afforded 12 triterpenes. Nine of these were the known compounds, arundoin [3β-methoxyfern-9(11)-ene] (**1**), friedelin (**3**), simiarenol (**4**), isomultiflorenol (**5**), fern-8-en-3β-ol (**6**), δ-amyrin (**7**), taraxasterol (**8**), germanicol (**9**) and oleana-11 13(18)-dien-3β-ol (**11**). The known compounds were identified by direct comparison with authentic samples except for **7**, which was characterized on the basis of close agreement of its physical and spectral data with those already published Compound **6**, the most abundant triterpene constituent in this plant, has twice been found from the leaves of both *Evodia hortensis* (Rutaceae) [6] and *Strychnos potatorum* (Loganiaceae) [7], while **11** has recently been isolated from the stem bark of *Phyllanthus flexuosus* (Euphorbiaceae) [8]. The remaining three triterpenes **2**, **10** and **12**, were isolated as minor components. Compound **10** was purified by acetylation because it was poorly resolved from **11**.

That compound **2** was δ-amyrin formate was confirmed by HR mass spectrometry, in which four prominent peaks characteristic for fragmentation of olean-18-enes [9] were observed at *m/z* 235, 1704 $[C_{15}H_{23}O_2]^+$, 218.2014 $[C_{16}H_{26}]^+$, 205.1941 $[C_{15}H_{25}]^+$ and 191 1842 $[C_{14}H_{23}]^+$ besides peaks at *m/z* 454.3802 $[M]^+$, 409.3821 $[M-HCOO]^+$ and 408.3776 $[M-HCOOH]^+$. Alkaline hydrolysis of **2** gave δ-amyrin identical with **7**, while formylation of **7** furnished δ-amyrin formate identical in all respects with **2**. The $^1H$ and $^{13}C$ NMR spectra [see Experimental] supported the



structure. This is the first report of the isolation of **2** in nature, although α-amyrin formate [10] has been reported from *Marsdenia formosana* (Asclepiadaceae).

Compound **10**, $C_{30}H_{48}O$ ($[M]^+$ *m/z* 424), was purified as a monoacetate (**10a**); alkaline hydrolysis of **10a** gave **10**. The UV spectrum of **10a** showed the presence of a heteroannular diene system ($\lambda_{max}$ 233, 239 and 247 nm). In the $^1H$ and $^{13}C$ NMR spectra [see Experimental], **10a** displayed signals for six tertiary methyl groups, two secondary methyl groups, a C-3α actoxy-methine group and two vinylic protons [$\delta_H$ 5.17 (1H, *dif t*) and 5.41 (1H, *m*)] and four vinylic carbons [$\delta_C$ 114.23 (*d*), 117.09 (*d*), 141.09 (*s*), 145.39 (*s*)].

Unambiguous skeletal information was obtained from the EI mass spectrum. Compounds **10** and **10a** showed significant peaks [a, a', b, b' and c] arising from D-ring fission, characteristic for cleavage of pentacyclic triterpene-7:9(11)-dienes [9, 11, 12]. The other important peak due to $[M-C_3H_7]^+$ was observed at *m/z* 381 and 423 in **10** and **10a**, respectively. These data indicated that **10** must be ferna-7:9(11)-dien-3β-ol. This was proved by synthesis of **10a**. Monoperphthalic acid oxidation of **6a** and subsequent CC of the resulting product afforded 8α,9α-oxidofernan-3β-yl acetate (**6b**) and ferna-7:9(11)-dien-3β-yl acetate identical in all respects with **10a**. Compound **10** is not reported in the literature, although ferna-7:9(11)-diene had been found in several ferns [13, 14] and 3β-methoxyferna-7:9(11)-diene [15] has been prepared by perbenzoic acid oxidation of arundoin (**1**), followed by acid hydrolysis.

Compound **12**, $C_{30}H_{48}O_2$ ($[M]^+$ *m/z* 440.3656), was an unsaturated epoxytriterpene alcohol which showed the presence of eight tertiary methyl groups, two vicinal methine protons on an epoxy ring [$\delta_H$ 2.81 (*d*) and 3.12 (*t*); $\delta_C$ 54.60 (*d*) and 58.27 (*d*)], one secondary carbinolic methine proton [$\delta_H$ 3.25 (*dd*); $\delta_C$ 78.99 (*d*)] and one trisubstituted double bond in the $^1H$ and $^{13}C$ NMR spectra [see Experimental]. On acetylation it gave an acetate (**12a**), which was identified by direct comparison with an authentic sample of 11α,12α-oxidotaraxeryl acetate (marsformoxide-B) [16] isolated from *Marsdenia formosana* (Asclepiadaceae). Thus, **12** was confirmed to be 11α,12α-oxidotaraxerol which appears to be a new natural product.

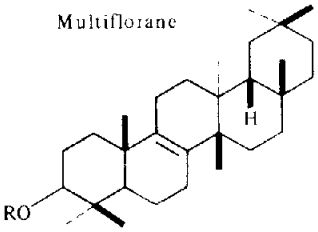
*Euphorbia supina* contained 16 triterpenes having 10 different skeletal systems. Seven of these belonged to hopane and its migrated analogues, including fernane and migrated fernane, rarely occurring in nature. Of interest also is the presence of 11α,12α-oxidotaraxerol which can be considered to be a biosynthetic intermediate for various triterpenes in plants [17].

## EXPERIMENTAL

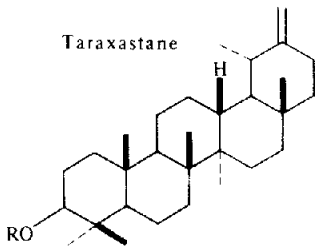
*General.* Mps: uncorr; optical rotations: $CHCl_3$; UV: EtOH; IR: KBr discs. $^1H$ NMR (90 or 300 MHz) and $^{13}C$ NMR (75.2 MHz): $CDCl_3$ with TMS int. std. EIMS (probe): 70 eV. CC: silica gel 60 (70–230 mesh, Merck) and alumina 90 (70–230 mesh, Merck). TLC: silica gel $HF_{254}$ and $PF_{254}$ (Merck).

*Extraction and separation of compounds.* Extn of the air-dried whole herb of *E. supina* (4 kg) with hot $C_6H_6$ and subsequent fractionation of the neutral ext (159.6 g) is described in ref. [3]. The extract was separated first by CC over silica gel (1.5 kg) into eight portions, [300 ml fractions, fraction Nos 1–15: *n*-hexane, Nos 16–24: *n*-hexane–$C_6H_6$ (10:1–5:1), Nos 25–42: *n*-hexane–$C_6H_6$ (3:1), Nos 43–55: *n*-hexane–$C_6H_6$ (3:1–2:1), Nos 56–86 and Nos 87–95: *n*-hexane–$C_6H_6$ (1:1), Nos 96–118: $C_6H_6$, Nos 119–130: $C_6H_6$–$CHCl_3$ (10:1)]. Evapn of solvents from the above gave residues A–H (A: 44.756 g; B: 2.462 g; C: 58.788 g; D: 2.093 g; E: 1.723 g; F: 0.206 g; G: 7.177 g; H: 1.302 g). Residues A and C were mixts of *n*-alkanes and *n*-alkanols, which were confirmed by IR and EIMS.

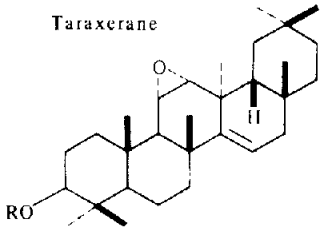
*Separation of residue B.* Repeated CC ($AgNO_3$–$Al_2O_3$ 1:4, 250 g) of residue B with a *n*-hexane–$C_6H_6$ gradient beginning



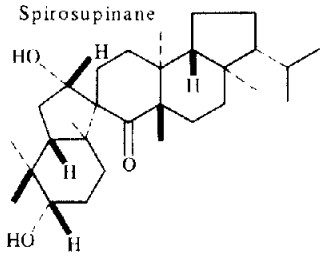

**5** R = H
**5a** R = Ac




**8** R = H
**8a** R = Ac




**12** R = H
**12a** R = Ac




**13**

with *n*-hexane afforded compounds **1** (10 mg), **2** (17 mg), **3** (29 mg) and the alkanol mixt (2.217 g)

*Arundoin* (**1**) [3β-*methoxyfern*-9(11)-ene]. Colourless needles, mp 242–243 5° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ −5 6° (*c* 0.58) (lit [15] mp 242–243°, $[\alpha]_D$ −5.3° (*c* 0 78), IR $\nu_{max}$ ($cm^{-1}$) 3030, 2970, 2860, 1630, 1450, 1380, 1260, 1182, 1113, 1013, 993, 972, 943, 872, 865, 815, 790, $^1H$ NMR (90 MHz) δ 0 73, 0 76, 0 80, 0 86, 0.95, 1 06 (each 3H, *s*, Me × 6), 0 83, 0 89 (each 3H, *d*, *J* = 6 1 Hz, *sec*-Me × 2), 2 67 (1H, *dd*, *J* = 12, 4 Hz, H-3α), 3.35 (3H, *s*, OMe), 5 34 (1H, *m*),EIMS *m/z* (rel int ) 440 $[M]^+$ (24), 425 (61), 393 (51), 367 (9), 355 (6), 350 (6), 326 (9), 323 (13), 287 (20), 273 (100), 261 (17), 255 (34), 241 (98), 229 (6), 205 (19) Compound **1** was identified by direct comparison (mmp, co-TLC, IR, $^1H$ NMR and EIMS) with an authentic sample [15]

*δ-Amyrin formate* (**2**) Colourless needles, $C_{31}H_{50}O_2$ ($[M]^+$ *m/z* 454 3802), mp 254–256°, $[\alpha]_D^{23}$ +15 2° (*c* 0 85), $R_f$ 0 61 ($C_6H_6$–$CHCl_3$–EtOAc, 10 10 1), IR $\nu_{max}$ ($cm^{-1}$): 2920, 2870, 1703, 1468, 1455, 1380, 1375, 1168, 1007, 962, $^1H$ NMR (300 MHz) δ 0 70 (3H, *s*), 0 86 (6H, *s*), 0 89 (6H, *s*), 0 94, 1.01, 1 16 (each 3H, *s*), 4 63 (1H, *dd*, *J* = 11, 6.5 Hz, H-3α), 8 12 (1H, *s*, –OCOH), $^{13}C$ NMR δ 16 41 (C-25), 16.60 (C-26), 17 71 (C-24), 18 35 (C-6), 21 30 (C-27), 21 74 (C-11), 23.80 (C-2, 30), 24 08 (C-28), 24 98 (C-15), 26 50 (C-12), 27 96 (C-23), 32 38 (C-29), 33 36 (C-20), 34 57 (C-17), 34 79 (C-7), 35.43 (C-21), 36 65 (C-16), 37 20 (C-10), 37 74 (C-4), 38.50 (C-22), 38 69 (C-1), 39 40 (C-19), 41 03 (C-8), 44.65 (C-14), 50 64 (C-9), 55 44 (C-5), 81.11 (C-3), 133 33 (C-17), 134 23 (C-13), 161 15 (HOCO–); EIMS *m/z* (rel. int ) 454 $[M]^+$ (52), 439 (34), 409 (2), 408 (2), 235 (5), 218 (38), 206 (53), 205 (100), 204 (72), 203 (28), 191 (14), 189 (37) Compound **2** was identified by direct comparison (mmp, co-TLC, IR, $^1H$ NMR, EIMS) with the synthetic sample described below

*Alkaline hydrolysis of* **2b**. Compound **2b** (33 mg) was refluxed with 0 05 M KOH in EtOH (20 ml) at 100° for 1 hr. After usual work-up, the resulting residue was purified by prep TLC (20 × 20 cm plate, 2 mm thick, $C_6H_6$–EtOAc, 10 1, UV detection) to give δ-amyrin mp 213 5–215° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ −51.0° (*c* 0 76), identical (mmp, TLC, IR, $^1H$ NMR, EIMS) with compound **7** described later

*Synthesis of* **2** A soln of 30% $COCl_2$ in $CCl_4$ (0 05 ml) was added to a soln of δ-amyrin (**7**) (15 mg) in pyridine (3 ml) containing 98% $HCO_2H$ (0.3 ml) under cooling and the mixt kept at 0° for 1 day Evapn *in vacuo* gave a residue, which was dissolved in $CHCl_3$ and washed with $H_2O$ Removal of solvent and prep TLC [$R_f$ 0 61 ($CHCl_3$)] of the resulting solid afforded δ-amyrin formate (12 mg), mp 252–253° (MeOH), identical in all respects with **2**

*Friedelin* (**3**) Colourless needles, mp 265–267° (EtOAc), $[\alpha]_D^{23}$ −24 8° (*c* 0 95) (lit [8] mp 261–264°, $[\alpha]_D$ −25°); IR $\nu_{max}$ ($cm^{-1}$) 2960, 2950, 2925, 2865, 1715, 1460, 1450, 1390, EIMS *m/z* (rel. int ) 426 $[M]^+$ (78), 411 (26), 341 (13), 302 (51), 273 (84), 205 (73), 95 (100) Compound **3** was identified by direct comparison with an authentic sample

*Separation of residue D* Residue D on CC over $AgNO_3$–$Al_2O_3$ (1 4, 210 g) afforded compounds **4** (87 mg) and **5** (276 mg) from *n*-hexane–$C_6H_6$ eluates

*Simiarenol* (**4**) Colourless leaflets, mp 213 5–215° $Me_2CO$), $[\alpha]_D^{23}$ +47 7° (*c* 0.46) (lit. [18, 19] mp 210°, $[\alpha]_D$ +50.3°), IR $\nu_{max}$ ($cm^{-1}$) 3510, 3040, 2950, 2930, 2860, 1640, 1468, 1450, 1382, 1365, 1178, 1058, 837, $^1H$ NMR (300 MHz) δ 0 78, 0 89, 0 93, 1 01, 1 05, 1 14 (each 3H, *s*, Me × 6), 0.83, 0 89 (each 3H, *d*, *J* = 6 5 Hz, *sec*-Me × 2), 3 47 (1H, *t*, *J* = 3 5 Hz, H-3α), 5 62 (1H, *td*, *J* = 2 Hz, H-6); EIMS *m/z* (rel int ) 426 $[M]^+$ (2), 411 (2), 408 (3), 274 (43), 259 (64), 245 (12), 231 (27), 205 (21), 95 (100) Acetylation of **4** (12 mg) with $Ac_2O$–pyridine (1 1, 4 ml) gave simiarenyl acetate (**4a**), mp 217–218° , $[\alpha]_D^{23}$ +82 7° (*c* 0 33) (lit. [18] mp 209°, $[\alpha]_D$ +73 9°), IR $\nu_{max}$ ($cm^{-1}$) 1728, 1642, 1260, 842, $^1H$ NMR (90 MHz) δ 0 79, 0 90, 0.94, 1.02, 1 06, 1 09 (each 3H, *s*), 0 83, 0.90 (each 3H, *d*, *J* = 6 Hz), 2.02 (3H, *s*, OAc), 4.76 (1H, *t*, *J* = 3.5 Hz, H-3α), 5 62 (1H, *m*, H-6), EIMS *m/z* (rel int.) 468 $[M]^+$ (2), 408 (21), 274 (100), 259 (90), 245 (10), 231 (27), 205 (16), 95 (71) Simiarenol was identified by direct comparison (mmp, co-TLC, IR, $^1H$ NMR, EIMS) with an authentic sample

*Isomultiflorenol* (**5**). Colourless needles, mp 185–187° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ +27.9° (*c* 0 97) (lit [20] mp 181–182°, $[\alpha]_D$ +24°), IR $\nu_{max}$ ($cm^{-1}$) 3630, 2940, 2860, 1480, 1460, 1380, 1362, 1105, 1030, 1003, 940, $^1H$ NMR (90 MHz). δ 0 81 (3H, *s*), 0 97 (9H, *s*), 0.99 (6H, *s*), 1 08 (6H, *s*), 3 23 (1H, *dd*, *J* = 11 5, 5.5 Hz, H-3α); EIMS *m/z* (rel int ) 426 $[M]^+$ (17), 411 (19), 408 (7), 259 (62), 247 (32), 241 (57), 229 (66), 218 (23), 205 (64), 191 (43), 95 (100) Acetylation of **5** (52 mg) with $Ac_2O$–pyridine (1 1, 6 ml) gave isomultiflorenyl acetate (**5a**), mp 227–228° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ +30 8° (*c* 0 74) (lit [20] mp 227–228°, $[\alpha]_D$ +30°), IR $\nu_{max}$ ($cm^{-1}$) 1735, 1250, $^1H$ NMR (300 MHz) δ 0 87, 0.88, 0.96 (each 3H, *s*), 0.98 (9H, *s*), 1 06, 1 07 (each 3H, *s*), 2 05 (3H, *s*, OAc), 4 50 (1H, *dd*, *J* = 11 5, 5.5 Hz, H-3α), EIMS *m/z* (rel int ) 468 $[M]^+$ (13), 453 (14), 408 (8), 255 (9), 241 (51), 229 (51), 218 (23), 203 (78), 95 (100). Compound **5** was identified by direct comparison (mmp, IR, $^1H$ NMR, EIMS) with an authentic sample [21]

*Separation of residue E* Residue E was further divided into five fractions (I–V) by CC ($AgNO_3$–$Al_2O_3$, 1 4, 170 g) employing *n*-hexane–$C_6H_6$ mixts (2:1–1·1). Repeated CC of each fractions furnished compounds **6** (1 426 g from I), **7** (183 mg from II), **8** (13 mg from III), **9** (15 mg from IV), and finally motiol and hopenol-B (from V) previously described [3]

*Fern-8-en-3β-ol* (**6**). Colourless needles, mp 200–202°, $[\alpha]_D^{23}$ +25 4° (lit [15] mp 199–200°, $[\alpha]_D$ +24 5°), IR $\nu_{max}$ ($cm^{-1}$) 3620, 2970, 2950, 2875, 1470, 1458, 1385, 1370, 1018; $^1H$ NMR (300 MHz) δ 0 76, 0 77, 0.80 (each 3H, *s*), 0 83, 0.89 (each 3H, *d*, *J* = 6.5 Hz, H-29, 30), 0 949, 0 953, 1.00 (each 3H, *s*), 3 24 (1H, *dd*, *J* = 11 5, 5 8 Hz, H-3α), EIMS: *m/z* (rel. int.) 426 $[M]^+$ (58), 411 (100), 408 (2), 259 (95), 241 (36), Acetylation of **6** (120 mg) with $Ac_2O$–pyridine (1 1, 4 ml) gave fern-8-en-3β-yl acetate (**6a**), mp 229–230° (*n*-hexane), $[\alpha]_D^{23}$ +26 3° (*c* 0 84) (lit [15] mp 226–227° $[\alpha]_D$ +20 3°), IR $\nu_{max}$ ($cm^{-1}$) 2975, 2950, 2850, 1740, 1470, 1454, 1440, 1380, 1370, 1240, 1035, 1015, 988; $^1H$ NMR (300 MHz): δ 0 75, 0 76, 0.87, 0 88, 0 95, 0 97 (each 3H, *s*, Me × 6), 0 83, 0 89, (each 3H, *d*, *J* = 6 5 Hz, H-29, H-30), 2.05 (3H, *s*, OAc), 4 50 (1H, *dd*, *J* = 11 5, 5 8 Hz, H-3α), EIMS *m/z* (rel. int.) 468 $[M]^+$ (5), 453 (12), 397 (17), 315 (8), 301 (45), 255 (17), 241 (67), 229 (14), 95 (100) It was identical in all respects with an authentic sample of **6a** [15]

*δ-Amyrin* (**7**) Colourless needles, mp 213 5–216° ($Me_2CO$), $[\alpha]_D^{23}$ −54.8° (*c* 0 95) (lit [22] mp 213–216 5°, $[\alpha]_D$ −52°), IR $\nu_{max}$ ($cm^{-1}$) 3450, 2940, 2860, 1460, 1450, 1383, 1362, 1040, $^1H$ NMR (90 MHz) δ 0 71, 0.76 (each 3H, *s*), 0 86 (6H, *s*), 0 94, 1 00, 1.02, 1 17 (each 3H, *s*), 3.27 (1H, *dd*, *J* = 11.5, 6 Hz, H-3α), EIMS *m/z* (rel int.) 426 $[M]^+$ (19), 411 (12), 408 (5), 218 (56), 207 (36), 206 (38), 205 (100), 204 (33), 203 (38), 189 (49), 109 (88) Acetylation of **7** (25 mg) with $Ac_2O$–pyridine (1 2, 2 ml) gave δ-amyrin acetate (**7a**), mp 207–209° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ −36 5° (*c* 0.87) (lit. [22] mp 208 5–209 5°, $[\alpha]_D$ −35°), IR $\nu_{max}$ ($cm^{-1}$) 1732, 1245, $^1H$ NMR (300 MHz) δ 0 70, 0 84, 0.85, 0 87, 0.88, 0.93, 1.01, 1 15 (each 3H, *s*, Me × 8), 2 05 (3H, *s*, OAc), 4 50 (1H, *dd*, *J* = 11.5, 5 8 Hz, H-3α), EIMS· *m/z* (rel int ) 468 $[M]^+$ (15), 453 (8), 218 (38), 207 (8), 206 (33), 205 (100), 204 (47), 203 (43), 189 (68), 109 (95). The above data were in good agreement with those published for δ-amyrin and its acetate [19]

*Taraxasterol* (**8**) Colourless needles, mp 225–227° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ +94 2° (*c* 0 35) (lit [23] mp 226–227°, $[\alpha]_D$ +97°), IR $\nu_{max}$ ($cm^{-1}$) 3450, 3070, 2970, 2948, 2865, 1640, 1480, 1460, 1450, 1385, 1372, 1042, 880, $^1H$ NMR (90 MHz): δ 0 76 (3H, *s*), 0 86 (6H, *s*), 0 93, 0 97, 1 03 (each 3H, *s*), 1 03 (3H, *d*, *J* = 6 5 Hz, H-29), 3 20 (1H, *dd*, *J* = 10 5, 6 5 Hz, H-3α), 4 62 (2H,

*d*, $J = 2.5$ Hz, H-30); EIMS: *m/z* (rel. int.) 426 $[M]^+$ (22), 411 (8), 408 (10), 229 (11), 218 (24), 207 (73), 189 (100). Compound **8** was acetylated as usual to give an acetate (**8a**) mp 257–259° (MeOH–$CHCl_3$) $[\alpha]_D^{23}$ +97.6° (*c* 1.02) (lit [23] mp 256–257°), $[\alpha]_D$ +100°); IR $\nu_{max}$ ($cm^{-1}$) 3070, 1723, 1640, 1242, 885; $^1H$ NMR (300 MHz): $\delta$ 0.843, 0.849, 0.854, 0.88, 0.93, 1.02 (each 3H, *s*, Me × 6), 1.02 (3H, *d*, $J = 6.5$ Hz, H-29), 2.05 (3H, *s*, OAc), 4.49 (1H, *dd*, $J = 10.5$, 6 Hz, H-3α), 4.61 (2H, *t* like, $J = 2.5$ Hz, H-30); EIMS: *m/z* (rel. int.) 468 $[M]^+$ (11), 453 (3), 408 (10), 249 (15), 229 (14), 205 (27), 189 (100). Compound **8a** was identified by direct comparison (mmp, co-TLC, IR, $^1H$ NMR, EIMS) with authentic material isolated from *Taraxacum officinale* [24].

*Germanicol* (**9**). Colourless needles, mp 173–175° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ +6.2° (*c* 0.44) (lit. [25] mp 176–177°, $[\alpha]_D$ +5.8°); IR $\nu_{max}$ ($cm^{-1}$) 3600, 3030, 2940, 2860, 1630, 1467, 1450, 1387, 1378, 1360, 1040, 1030, 855, 845; $^1H$ NMR (90 MHz) $\delta$ 0.74, 0.77, 0.88 (each 3H, *s*, Me × 3), 0.95 (6H, *s*, Me × 2), 0.98, 1.03, 1.08 (each 3H, *s*, Me × 3), 3.24 (1H, *dd*, $J = 11$, 6 Hz, H-3α) 4.88 (1H, *s*, H-19); EIMS: *m/z* (rel. int.) 426 $[M]^+$ (17), 411 (23), 408 (6), 231 (18), 218 (38), 189 (100), 177 (87). Compound **9** (25 mg) was acetylated in the usual manner to give an acetate (**9a**) mp 279–281° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ +19.0° (*c* 0.57) (lit. [25] mp 279–280°, $[\alpha]_D$ +18.8°; [26] mp 275–276°); IR $\nu_{max}$ ($cm^{-1}$) 3030, 1735, 1640, 1258, 868, 855; $^1H$ NMR (300 MHz): $\delta$ 0.73, 0.84, 0.85, 0.91, 0.937, 0.944, 1.02, 1.08 (each 3H, *s*, Me × 8), 2.05 (3H, *s*, OAc), 4.49 (1H, *dd*, $J = 11.5$, 6.2 Hz, H-3α), 4.86 (1H, *s*, H-19); EIMS: *m/z* (rel. int.) 468 $[M]^+$ (11), 453 (16), 408 (6), 231 (12), 218 (16), 204 (95), 189 (100), 177 (69). Germanicol was identified by direct comparison (mmp, co-TLC, IR, $^1H$ NMR, EIMS) with authentic material.

*Separation of residue F.* Residue F was a complex triterpene alcohol mixt (IR: 3450 $cm^{-1}$) on TLC and CC. Acetylation of F ($Ac_2O$–pyridine, 1:1, 10 ml), followed by CC of the resulting product (198 mg) over $AgNO_3$–$Al_2O_3$ (1:4) afforded **10a** (12 mg) and **11a** (53 mg), respectively.

*Ferna-7:9(11)-dien-3β-yl acetate* (**10a**). Colourless needles, mp 256–257° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ −135.1° (*c* 0.29); UV $\lambda_{max}$ nm (ε) 233, 239, 247 (14000, 15800, 10000) [heteroannular diene]; IR $\nu_{max}$ ($cm^{-1}$) 3020, 2950, 2860, 1727, 1620, 1470, 1460, 1380, 1370, 1250, 1032, 980, 942, 910, 875; $^1H$ NMR (300 MHz): $\delta$ 0.68, 0.76, 0.86, 0.90, 0.94, 0.96 (each 3H, *s*, Me × 6), 0.84, 0.91 (each 3H, *d*, $J = 6.5$ Hz, H-29, 30), 2.06 (3H, *s*, OAc), 4.51 (1H, *dd*, $J = 10.5$, 5.5 Hz, H-3α), 5.17 (1H, *dif t*, $J = 4$ Hz, H-11), 5.41 (1H, *m*, $W_{1/2} = 11$ Hz, H-7); $^{13}C$ NMR (75.2 MHz): $\delta$ 14.02, 16.35, 16.58, 20.57, 20.88, 22.14, 22.99, 27.51 (Me × 8), 21.33 (OAc), 20.15, 23.60, 24.22, 28.30, 28.58, 35.21, 36.16, 37.46 ($CH_2$ × 8), 30.74, 48.14, 52.29, 59.68 (CH × 4), 80.96 (C-3), 114.23, 117.09 (—CH= × 2), 36.25, 36.90, 37.91, 40.16, 43.08 (>C< × 5), 141.09, 145.39 (>C= × 2), 170.96 (OAc); EIMS: *m/z* (rel. int.) 466 $[M]^+$ (100), 451 (12), 423 (4), 406 (6), 391 (22), 381 (4), 315 (13), 313 (14), 301 (20), 273 (8), 255 (37), 253 (19), 239 (16), 171 (26). Compound **10a** was identified by direct comparison (mmp, co-TLC, IR, $^1H$ NMR, EIMS) with the synthetic sample described below.

*Ferna-7:9(11)-dien-3β-ol* (**10**). Compound **10a** (5 mg) was saponified with 0.05 M KOH–EtOH (10 ml) at 100° for 1 hr to give **10**, mp 193–196.5° (MeOH–$CHCl_3$), IR $\nu_{max}$ ($cm^{-1}$) 3450, 3020, 2930, 2860, 1470, 1440, 1380, 1376, 1363, 1040, 1010, 980; $^1H$ NMR (300 MHz): $\delta$ 0.69 (3H, *s*, H-27), 0.76 (3H, *s*, H-28), 0.84 (3H, *d*, $J = 6.5$ Hz, H-29), 0.89 (3H, *s*, H-23), 0.90 (3H, *s*, H-26), 0.91 (3H, *d*, $J = 6.5$ Hz, H-30), 0.92 (3H, *s*, H-25), 0.98 (3H, *s*, H-24), 3.24 (1H, *dd*, $J = 10.5$, 5.5 Hz, H-3α), 5.16 (1H, *t*, $J = 4$ Hz, H-11), 5.42 (1H, *m*, $W_{1/2} = 10$ Hz, H-7); EIMS: *m/z* (rel. int.) 424 $[M]^+$ (100), 409 (10), 391 (10), 381 (3), 273 (15), 271 (25), 259 (47), 255 (22), 253 (10), 241 (20), 173 (11).

*Synthesis of* **10a** *and* **6b**. A soln of 0.00028 M monoperphthalic acid in $Et_2O$ (10 ml) was added into a soln of **6a** (50 mg) in $Et_2O$ (15 ml) and the mixt. refluxed for 6 hr. Treatment of the soln with 5% $Na_2CO_3$ and evapn of solvent afforded a residue, which was subjected to silica gel CC. Elution with *n*-hexane $C_6H_6$ (10:1) furnished ferna-7:9(11)-dien-3β-yl acetate (17 mg), mp 255–257°, $[\alpha]_D^{23}$ −133.8° (*c* 0.62), identical in all respects with **10a**. Further elution with *n*-hexane–$C_6H_6$ (3:1) afforded 8α,9α-oxidofernan-3β-yl acetate (**6b**) (24 mg), mp 311–312° (MeOH–$CHCl_3$); IR $\nu_{max}$ ($cm^{-1}$) 2950, 2870, 1730, 1470, 1450, 1390, 1375, 1256, 1013, 987, 960, 913, 880; $^1H$ NMR (90 MHz): $\delta$ 0.77 (3H, *s*), 0.85 (6H, *s*), 0.83, 0.88 (each 3H, *d*, $J = 6$ Hz), 1.03 (3H, *s*), 1.06 (6H, *s*), 2.02 (3H, *s*, OAc), 4.41 (1H, *br m*); EIMS: *m/z* (rel. int.) 484 $[M]^+$ (4), 466 (17), 451 (7), 441 (3), 424 (8), 406 (11), 391 (25), 289 (44), 255 (16), 253 (12), 229 (25), 208 (36), 205 (15), 203 (21), 189 (32), 136 (100).

*Oleana-11:13(18)-dien-3β-yl acetate* (**11a**). Colourless needles, $[M]^+$ *m/z* 466.3819 (calc. for $C_{32}H_{50}O_2$: 466.3811), mp 229 231°, $[\alpha]_D^{23}$ −61.5° (*c* 0.73) (lit. [8] mp 230–233°, $[\alpha]_D$ −61.5°); IR $\nu_{max}$ ($cm^{-1}$) 3020, 1725, 1620, 1240, 1140, 1020, 980, 900; $^1H$ NMR (300 MHz): $\delta$ 0.71, 0.75, 0.86, 0.87, 0.92, 0.95, 0.96, 1.06 (each 3H, *s*, Me × 8), 2.04 (3H, *s*, OAc), 4.52 (1H, *dd*, $J = 11.5$, 6 Hz H-3α), 5.51 (1H, *dd*, $J = 11.8$, 1.6 Hz, H-12), 6.38 (1H, *dd*, $J = 11.8$, 3.3 Hz, H-11); EIMS: *m/z* (rel. int.) 466 $[M]^+$ (100). Compound **11a** (10 mg) was hydrolysed with 0.05 M KOH–EtOH (15 ml) at 100° for 1 hr to give oleana-11:13(18)-dien-3β-ol (**11**) (6 mg), mp 233–235°, $[\alpha]_D^{23}$ −63.4° (*c* 0.41) (lit. [8] mp 232–234.5°, $[\alpha]_D^{23}$ −61.3°); IR $\nu_{max}$ ($cm^{-1}$) 3470, 3022, 1637, 1600, 1075, 1020, 975, 960, 935, 758; $^1H$ NMR (300 MHz): $\delta$ 0.71, 0.75, 0.78, 0.89 (each 3H, *s*, Me × 4), 0.96 (6H, *s*, Me × 2), 0.99, 1.06 (each 3H, *s*, Me × 2), 3.25 (1H, *dd*, $J = 11.5$, 6 Hz, H-3α), 5.52 (1H, *dd*, $J = 11.8$, 1.6 Hz, H-12), 6.38 (1H, *dd*, $J = 11.8$, 3.3 Hz, H-11); EIMS: *m/z* (rel. int.) 424 $[M]^+$ (100). Compounds **11** and **11a** were identified by direct comparison (mmp, TLC, UV, IR, $^1H$ NMR and $^{13}C$ NMR) with authentic materials.

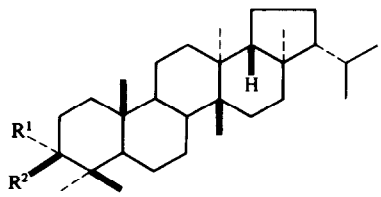
*Sitosterol.* Recrystallization of residue G from MeOH–$CHCl_3$ afforded sitosterol (4.894 g), mp 137.5 139° (lit. [8] mp 138–139°), which was identified by direct comparison with an authentic sample.

*Separation of residue H.* Repeated CC of residue H over $AgNO_3$–silica gel (1:4, 150 g) afforded **12** (108 mg) from $C_6H_n$ $CHCl_3$ (10:1) eluates.

11α,12α-*Oxidotaraxerol* (**12**). Colourless needles, mp 286–288° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ −38.9° (*c* 0.98) (lit. [16] mp 285–288°); IR $\nu_{max}$ ($cm^{-1}$) 3500, 3030, 2940, 2910, 2850, 1630, 1458, 1440, 1390, 1380, 1365, 1180, 1140, 1095, 1055, 1042, 1020, 1006, 918, 888, 873, 860, 832, 805; $^1H$ NMR (300 MHz): $\delta$ 0.83 (6H, *s*, Me × 2) 0.86, 0.97, 0.99, 1.01 (each 3H, *s*, Me × 4), 1.08 (6H, *s*, Me × 2), 2.81 (1H, *d*, $J = 4.4$ Hz, H-12), 3.12 (1H, *t*, $J = 4.4$ Hz, H-11), 3.25 (1H, *dd*, $J = 10.5$, 5.8 Hz, H-3α), 5.55 (1H, *dd*, $J = 8.3$, 3.5 Hz, H-15); $^{13}C$ NMR: $\delta$ 15.45 (C-25), 16.97 (C-24), 18.91 (C-6), 19.56 (C-30), 26.86 (C-2), 27.07 (C-26), 27.90 (C-23), 28.72 (C-20), 29.93 (C-28), 30.24 (C-27), 33.16 (C-7), 33.66 (C-29), 35.24 (C-16), 35.41 (C-17), 36.56 (C-21, C-13), 37.49 (C-10), 38.21 (C-1, 22), 38.66 (C-4), 38.86 (C-8), 40.35 (C-19), 48.08 (C-18), 51.99 (C-9), 53.65 (C-11), 54.60 (C-5), 58.27 (C-12), 78.99 (C-3), 118.89 (C-15), 157.13 (C-14); EIMS *m/z* (rel. int.) 440.3656 [M$^+$, calc. for $C_{30}H_{48}O_2$ 440.3652] (39), 425 (28), 422 (30), 407 (32), 389 $[M - 2H_2O - Me]^+$ (33), 316.2407 $[C_{21}H_{32}O_2]^+$ (26), 301.2165 $[C_{20}H_{29}O_2]^+$ (66), 259 (27), 220.1825 $[C_{15}H_{24}O]^+$ (47), 135 (88), 108 (100).

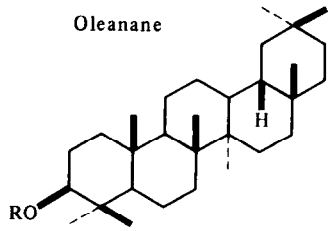
*Acetylation of compound* **12**. A soln of **12** (21 mg) in pyridine (2 ml) was acetylated with $Ac_2O$ (2 ml) at room temp overnight. After usual work-up, the resulting product was recrystallized from MeOH–$CHCl_3$ to give an acetate **12a** (16 mg) as colourless needles, mp 302–305°, $[\alpha]_D^{23}$ −42.8° (*c* 0.51) (lit. [16] mp 305–308°, $[\alpha]_D$ −31°); IR $\nu_{max}$ ($cm^{-1}$) 3050, 2940, 2930, 2875, 1732, 1638, 1460, 1440, 1397, 1383, 1376, 1260, 1100, 1030, 993, 920, 904, 878, 862, 840, 820, 808; $^1H$ NMR (300 MHz): $\delta$ 0.82,

Fernane



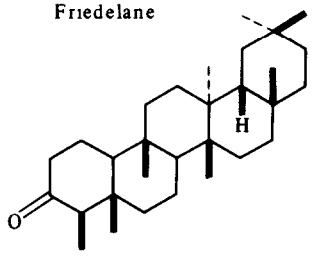
**1** $R^1$ = H, $R^2$ = OMe 9(11)-ene
**6** $R^1$ = H, $R^2$ = OH } 8-ene
**6a** $R^1$ = H, $R^2$ = OAc }
**6b** $R^1$ = H, $R^2$ = OAc 8,9-epoxide
**10** $R^1$ = H, $R^2$ = OH } 7,9(11)-diene
**10a** $R^1$ = H, $R^2$ = OAc }

Oleanane



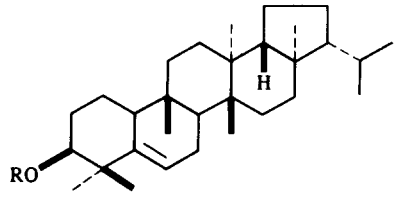
**2** R = CHO } 13(18)-ene
**7** R = H }
**7a** R = Ac }
**9** R = H } 18-ene
**9a** R = Ac }
**11** R = H } 11,13(18)-diene
**11a** R = Ac }

Friedelane



**3**

Simiarane



**4** R = H
**4a** R = Ac

0.86, 0.87, 0.90, 0.97, 1.00, 1.08, 1.10 (each 3H, *s*, Me × 8), 2.05 (3H, *s*, OAc) 2.80 (1H, *d*, $J$ = 4.4 Hz, H-12), 3.11 (1H, *t*, $J$ = 4.4 Hz, H-11), 4.52 (1H, *dd*, $J$ = 10.5, 5.8 Hz, H-3α), 5.55 (1H, *dd*, $J$ = 8.3, 3.5 Hz, H-15); $^{13}$C NMR· δ 16.58 (C-25), 17.00 (C-24), 18.80 (C-6), 19.50 (C-30), 21.27 (OAc), 23.24 (C-2), 27.03 (C-26), 27.88 (C-23), 28.72 (C-20), 29.83 (C-28), 30.24 (C-27), 33.16 (C-7), 33.66 (C-29), 35.24 (C-16), 35.38 (C-17), 36.56 (C-13, C-21), 37.49 (C-10), 37.63 (C-4), 37.91 (C-1), 38.22 (C-22), 38.92 (C-8), 40.27 (C-19), 48.11 (C-18), 51.84 (C-9), 53.47 (C-11), 54.65 (C-5), 58.17 (C-12), 80.67 (C-3), 118.92 (C-15), 157.08 (C-14), 170.79 (OAc); EIMS: *m/z* (rel. int.) 482 $[M]^+$ (36), 467 (12), 464 (11), 422 (3), 404 (13), 389 (14), 358 (6), 343 (11), 259 (38), 220 (20), 135 (88), 108 (100). Compound **12a** was identified by direct comparison (mmp, co-TLC, IR, $^1$H NMR, $^{13}$C NMR, EIMS) with authentic material.

*Acknowledgements*—The authors thank Professor T. Ohmoto (Faculty of Pharmaceutical Sciences, Toh-hoh University for arundoin) Dr W. H Hui (Department of Chemistry, University of Hong Kong) for simiarenol, Dr J Vaquett (Laboratoire de Materieremedicale, U. E. R. des Sciences pharmaceutiques et biologiques, France) for isomultiflorenol, Professor Y. Hirata (Faculty of Pharmaceutical Sciences, Meijyo University) for germanicol, Professor S. Natori (Meiji College of Pharmacy) for fern-8-en-3β-yl acetate and Dr J. Lai (Applied Chemistry Institute, Scigi Women's College, Taiwan) for marsformoxide B. We also thank Miss M. Nabae of this University for NMR measurements

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