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TRITERPENOIDS FROM *EUPHORBIA MACULATA*

SHUNYO MATSUNAGA, REIKO TANAKA and MASAO AKAGI

Osaka University of Pharmaceutical Sciences, 2-10-65 Kawai, Matsubara, Osaka 580, Japan

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Key Word Index—*Euphorbia maculata*; Euphorbiaceae; β-amyrin acetate; taraxeryl acetate; lupenyl acetate; 3β-acetoxy-30-norlupan-20-one; α-amyrenonol; gult-5-en-3β-yl acetate; ursa-9 (11):12-dien-3β-ol; sitosterol.

Abstract—Two new triterpenoids were isolated together with β-amyrin acetate, taraxeryl acetate, lupenyl acetate, 3β-acetoxy-30-norlupan-20-one, α-amyrenonol and sitosterol from the whole herb of *Euphorbia maculata*. The structures of the new compounds were characterized as gult-5-en-3β-yl acetate and ursa-9(11):12-dien-3β-ol on the basis of chemical and spectral evidence.

INTRODUCTION

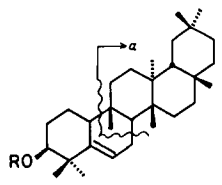
Euphorbia maculata L., an annual weed native to North America, is widely distributed in Japan. Its milky-white latex causes similar skin irritation to that of *E. supina*, belonging to the same genus [1]. Up to now, nothing has been reported about the biological activity or chemistry of *E. maculata*, though *E. supina* is used as a folk medicine for treatment of gastroenteric diseases such as diarrhoea and for healing purulent swellings [2, 3]. An examination of the less polar neutral extract of *E. maculata* led to the isolation of two new triterpene compounds along with five known triterpenoids and sitosterol. This paper describes the characterization of these compounds.

RESULTS AND DISCUSSION

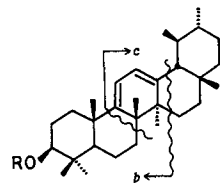
The neutral benzene extract of the dried whole herb afforded the known compounds, β-amyrin acetate (**1**), taraxeryl acetate (**2**), lupenyl acetate (**3**), 3β-acetoxy-30-norlupan-20-one (**4**), α-amyrenonol (**5**) and sitosterol (**6**), and two new triterpenoids **7a** and **8a**. Compounds **1**–**3** and **6** were identified by direct comparison with authentic samples, **4** and **5** were confirmed by syntheses of the corresponding compounds, respectively (see Experimental). Compound **4** had been isolated previously from *Claoxylon polot* (Euphorbiaceae) [4] while **5** had been obtained from *Ilex buergeri* [5], *I. goshiensis* (Aquifoliaceae) [6] and *Canarium zeylanicum* (Burceraceae) [7].

Compound **7a**, $C_{32}H_{52}O_2$ (M^+ at *m/z* 468), had eight Me groups (^{1}H NMR: δ0.85–1.16), an axial acetoxy group geminal to a methine proton (IR: 1723 and 1238 cm^{-1}; ^{1}H NMR: δ2.01 (3H, *s*) and 4.69 (1H, *t*, *J* = 2.9 Hz)) and a trisubstituted double bond (^{1}H NMR: δ5.56 (1H, *dt* like); ^{13}C NMR: δ120.01 (*d*) and 141.94 (*s*)). The EI-mass spectrum of **7a** contained strong peaks due to retro-Diels–Alder cleavage of the B-ring at *m/z* 274 (fragment a) and 259 [a – Me] characteristic of a triterpene-5-ene skeleton [8]. These data suggested that **7a** may be gult-5-en-3β-yl acetate. This was confirmed in the following way. Alkaline hydrolysis of **7a** furnished the alcohol **7b** identical in all respects with an authentic sample.

Although gult-5-en-3β-ol as well as gult-5-en-3-one have isolated from natural sources including *Euphorbia* species [9–12], there appears to be no prior report of the acetate in nature.



7a R=Ac
7b R=H



8a R=H
8b R=Ac

Compound **8a**, $C_{30}H_{48}O$ (M^+ at *m/z* 424), was a triterpene dienol which had a hydroxyl group (IR: 3360 and 1032 cm^{-1}) and a homoannular diene chromophore (UV: λ_{max} 281 nm; IR: 3030, 1638 and 830 cm^{-1}). Acetylation of **8a** gave a monoacetate (**8b**). The ^{1}H NMR spectrum of **8b** exhibited signals due to six tertiary methyl groups (δ0.86, 0.89, 0.91, 1.17 and 1.24), two secondary methyl groups (δ0.81 (*d*, *J* = 6.1 Hz) and 0.93 (*br s*)), one acetoxy methyl singlet (δ2.06) and a 3α-axial carbinolic methine proton [δ4.52 (1H, *dd*, *J* = 10.5 and 5.7 Hz)]. Furthermore, signals due to two vicinal protons arranged in the centre of a cisoid diene system were observed as a pair of symmetrical doublets at δ5.45 and 5.59 (each 1H, *J* = 5.8 Hz). In the EI-mass spectrum, two intense peaks arising from cleavage of both B-ring and D-ring were observed at *m/z* 255 (fragment c) and 271 (fragment b) for compound **8a** and *m/z* 255 (fragment c) and 313 (fragment b) for compound **8b**, respectively, indicating the presence of the cisoid diene at C-9 (11):12 of a pentacyclic triterpene carbon skeleton. All the above data suggested that **8a** was ursa-9 (11):12-dien-3β-ol. This was confirmed by

direct comparison of **8b** with authentic ursa-9 (11):12-dien-3β-yl acetate.

Ito and his colleague [13] reported both the isolation of marsformosanone [ursa-9(11):12-dien-3-one] along with marsformoxide (11α,12α-oxidotaraxer-3β-yl acetate) from *Marsdenia formosana* (Asclepiadaceae) and the synthesis of ursa-9(11):12 dien-3β-yl acetate by photochemical transformation of the latter compound [14]. To our knowledge, however, this is the first report of the isolation of compound **8a** in nature.

EXPERIMENTAL

Mps: uncorr; optical rotations: $CHCl_3$, 1 dm cell; UV: EtOH; IR: KBr discs; ^{1}H NMR: 90 or 300 MHz, $CDCl_3$ with TMS as int. standard. ^{13}C NMR: 75.4 MHz, $CDCl_3$ with TMS as int. standard. MS: double focussing mass spectrometer (accelerating voltage of 3–6.5 kV; ionizing potential 70 eV). TLC: Merck silica gel HF_{254}.

Plant material. E. maculata was collected in the field of Kitakatsuragi district, Nara Pref., Japan in September 1985. The material was identified by Mr M. Murata of the Department of Botany, Faculty of Science, Kyoto University, Kitashirakawa-oiwake-cho, Sakyo-ku, Kyoto, Japan. A voucher specimen of the plant is on file at the Institute of Medicinal Chemistry, Osaka University of Pharmaceutical Sciences.

Extraction and isolation of constituents. The air-dried whole herb of the plant (13.3 kg) was extracted with C_6H_6 (3 l × 5). The combined C_6H_6 soln was concd to *ca* 5 l, filtered, and then washed with 5% NaOH soln to remove acidic components. After evaporation of the solvent, the resulting dark-greenish residue (462 g) was subjected to silica gel CC (5 kg) using *n*-hexane, *n*-hexane–C_6H_6 in different proportions and C_6H_6 as eluants. Rechromatography of each residue collected from the fractions eluted with *n*-hexane–C_6H_6 (20:1, 10:1, 5:1 and 1:1) and C_6H_6 yielded the following compounds in order of their polarity; **1** (2.240 g), **2** (120 mg) and **7a** (58 mg) [from *n*-hexane–C_6H_6 (20:1)], **3** (123 mg) [from *n*-hexane–C_6H_6 (10:1)], **4** (72 mg) [from *n*-hexane–C_6H_6 (5:1)] **8a** (12 mg) and **5** (85 mg) [from *n*-hexane–C_6H_6 (1:1)] and **6** (9.235 g) [from C_6H_6].

β-Amyrin acetate (**1**). Colourless needles, mp 241–242.5° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ + 68.9° (*c* 0.94) (lit. [15] mp 241–242°, $[\alpha]_D$ + 81°); IR ν_{max} 1722 and 1240 (OAc), 1635 and 812 cm^{-1} (–C=C–H); ^{1}H NMR (90 MHz): δ0.84 (3H, *s*, H-28), 0.88 (12H, *s*, H-23, 24, 29, 30), 0.98 (6H, *s*, H-25, 26), 1.14 (3H, *s*, H-27), 2.07 (3H, *s*, OAc), 4.54 (1H, *dd*, *J* = 11, 6 Hz, H-3α), 5.21 (1H, *t*, *J* = 3.5 Hz, H-12); EIMS *m/z* (rel. int.): 468 $[M]^+$ (3.5), 453 (2), 408 $[M - HOAc]^+$ (4), 218 (100), 203 (47). Compound **1** was identified by direct comparison with the sample prepared by acetylation (Ac_2O–C_5H_5N, room temp.) of authentic β-amyrin (mmp, TLC, MS and ^{1}H NMR).

Taraxeryl acetate (**2**). Colourless needles, mp 299–302° (EtOAc), $[\alpha]_D^{23}$ + 16.9° (*c* 0.52) (lit. [16] mp 304–305°, $[\alpha]_D^{20}$ + 9°); IR ν_{max} 1720 and 1243 (OAc), 1638 and 815 cm^{-1} (–C=C–H); ^{1}H NMR (300 MHz): δ0.82 (3H, *s*), 0.86 (3H, *s*), 0.88 (3H, *s*). 0.9 (3H, *s*), 0.91 (3H, *s*), 0.95 (6H, *s*), 1.07 (3H, *s*), 2.04 (3H, *s*, OAc), 4.46 (1H, *dd*, *J* = 11, 6.5 Hz, H-3α), 5.53 (1H, *dd*, *J* = 8.3, 3.7 Hz, H-15); EIMS *m/z* (rel. int.): 468 $[M]^+$ (12), 453 (6), 408 $[M - HOAc]^+$ (5), 344 (31), 329 (23), 284 (25), 269 (30), 204 (100). Compound **2** was identified by direct comparison with the sample prepared by acetylation (Ac_2O–C_5H_5N, room temp.) of taraxerol isolated from *Taraxacum officinale* [17] (mmp, TLC, IR, MS and ^{1}H NMR).

Lupenyl acetate (**3**). Colourless needles, mp 215–216° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ + 35.5° (*c* 0.35) (lit. [18] mp 221–222°. $[\alpha]_D$ + 39°); IR ν_{max} 1727 and 1239 (OAc), 3060, 1637 and 865 cm^{-1} (–C=CH_2); ^{1}H NMR (90 MHz): δ0.79 (3H, *s*, H-28), 0.85 (9H, *s*, H-23, 24, 25), 0.95 (3H, *s*, H-27), 1.04 (3H, *s*, H-26), 1.70 (3H, *s*, H-30), 2.04 (3H, *s*, OAc), 4.47 (1H, *dd*, *J* = 11, 6 Hz, H-3α), 4.56 and 4.67 (each 1H, *dd*, *J* = 2.5 Hz, H-29); EIMS *m/z* (rel. int.): 468 $[M]^+$ (92), 453 (21), 408 $[M - HOAc]^+$ (21), 249 (33), 218 (64), 204 (58), (100). Compound **3** was identified by direct comparison with an authentic sample of lupenyl acetate (mmp, TLC, IR, MS and ^{1}H NMR).

3β-Acetoxy-30-norlupan-20-one (**4**). Colourless needles, mp 276–278° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ + 3.5° (*c* 0.33) (lit. [4] mp 262–263°, $[\alpha]_D^{20}$ + 9.0°); IR ν_{max}: 1722 and 1248 (OAc), 1706 cm^{-1} (C=O); ^{1}H NMR (90 MHz): δ0.77 (3H, *s*, H-28), 0.86 (9H, *s*, H-23, 24, 25), 0.97 (3H, *s*, H-27), 1.03 (3H, *s*, H-26), 2.06 (3H, *s*, OAc), 2.16 (3H, *s*, H-29), 4.48 (1H, *dd*, *J* = 11, 6 Hz, H-3α); EIMS *m/z* (rel. int.): 470 $[M]^+$ (2), 410 $[M - HOAc]^+$ (23), 395 (11), 367 $[M - HOAc - MeCO]^+$ (19), 231 (11), 203 (36), 189 (100). Compound **4** (20 mg) was hydrolysed with 0.05 M KOH–EtOH to give 3β-hydroxy-30-norlupan-20-one (18 mg), mp 238–240°, $[\alpha]_D^{23}$ – 13.8° (*c* 0.42) (lit. [19] mp 237–239°, $[\alpha]_D$ – 10°); IR ν_{max}: 3458 and 1037 (OH), 1687 cm^{-1} (C=O); ^{1}H NMR (90 MHz): 0.77 (6H, *s*, H-23, 28), 0.84 (3H, *s*, H-24), 0.97 (6H, *s*, H-25, 27), 1.02 (3H, *s*, H-26), 2.15 (3H, *s*, H-29), 3.20 (1H, *dd*, *J* = 11, 6.5 Hz, H-3α); EIMS *m/z* (rel. int.): 428 $[M]^+$ (9), 413 (3), 410 (33), 395 (14), 367 $[M - H_2O - MeCO]^+$ (15), 207 (51), 189 (100).

Compound **4** was identified by direct comparison with synthetic 3β-acetoxy-30-norlupan-20-one (mmp, TLC, IR, MS and ^{1}H NMR).

Synthesis of 3β-acetoxy-30-norlupan-20-one. To a soln of lupenyl acetate (27 mg) and OsO_4 (1 mg) in dioxane (7 ml) containing H_2O (1.5 ml) $NaIO_4$ (36 mg) was gradually added under stirring and the mixture was allowed to stand at room temp. for 72 hr. The reaction mixture was treated with H_2S and the precipitate of OsS was filtered off. Dilution of the filtrate with H_2O (30 ml) gave a ppt. which was extracted with $CHCl_3$. The usual work-up, followed by purification with prep. TLC (Merck silica gel PF_{254}, C_6H_6–$CHCl_3$–EtOAc 2:2:1) afforded 3β-acetoxy-30-norlupan-20-one (25 mg), mp 276–278° (MeOH–$CHCl_3$), identical in all respects with compound **4**.

α-Amyrenonol (**5**). Colourless needles, mp 204–205.5° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ + 114.9° (*c* 0.21) (lit. [6] mp 206–208°, $[\alpha]_D$ + 96°); UV λ_{max} 250.5 nm (ε 7,600) [–C=C–C=O]; IR ν_{max} 3430 and 1038 (OH), 1658 (–C=C–C=O), 1620 and 838 cm^{-1} (–C=C–H); ^{1}H NMR (300 MHz): δ0.81 (3H, *d*, *J* = 6 Hz), 0.81 (3H, *s*), 0.95 (3H, *br s*), 1.00 (3H, *s*), 1.14 (3H, *s*), 1.17 (6H, *s*), 1.30 (3H, *s*), 3.23 (1H, *dd*, *J* = 11.5, 5.5 Hz, H-3α), 5.54 (1H, *s*, H-12); EIMS *m/z* (rel. int.): 440 $[M]^+$ (16), 425 (6), 422 (4), 273 (100), 232 (84). Acetylation of **5** (22 mg) with Ac_2O and C_5H_5N (1:1, 2 ml) gave an acetate (21 mg), mp 286–288° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ + 116° (*c* 0.21) (lit. [20] mp 286–288°, $[\alpha]_D$ + 101°); UV λ_{max} 251 nm (ε 10000); IR ν_{max}: 1715 and 1245 (OAc), 1642 cm^{-1} (–C=C–C=O); ^{1}H NMR (300 MHz): δ0.81 (3H, *d*, *J* = 6.1 Hz), 0.82 (3H, *s*), 0.88 (3H, *s*), 0.88 (3H, *s*), 0.94 (3H, *br s*), 1.17 (3H, *s*), 1.19 (3H, *s*), 1.29 (3H, *s*), 2.05 (3H, *s*, OAc), 4.55 (1H, *dd*, *J* = 11.5, 5.5 Hz, H-3α), 5.54 (1H, *s*, H-12); EIMS *m/z* (rel. int.): 482 $[M]^+$ (12), 422 $[M - HOAc]^+$ (11), 407 $[M - HOAc - Me]^+$ (10), 273 (100), 232 (58). This acetate was identified by direct comparison with a synthetic sample of α-amyrenonyl acetate (3β-acetoxyurs-12-en-11-one) (mmp, TLC, IR, MS and ^{1}H NMR).

Synthesis of α-amyrenonyl acetate. α-Amyrin (25 mg) was acetylated (Ac_2O–C_5H_5N 1:1, 4 ml) as usual to give α-amyrin acetate (25 mg), mp 225–227°, M^+ at *m/z* 468 ($C_{32}H_{52}O_2$). A mixture of α-amyrin acetate (20 mg) in HOAc (15 ml) and CrO_3

(20 mg) in 90% HOAc (3.5 ml) was heated on a steam bath for 2 hr. The reaction mixture was worked up as usual yielding a residue, which on purification by prep. TLC (C_6H_6–EtOAc 5:1) afforded α-amyrenonyl acetate, mp 286–288°, $[\alpha]_D^{23}$ + 117° (*c* 0.35), identical in all respects with the acetate of compound **5**.

Sitosterol (**6**). Colourless needles, mp 137–139° (MeOH–$CHCl_3$) (lit. [21] mp 138–139°). Compound **6** was identified by direct comparison with an authentic sitosterol (TLC, IR and MS).

Gult-5-en-3β-yl acetate (**7a**). Colourless needles, mp 190–191.5° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ + 76.8° (*c* 0.50) (lit. [5] mp 192–194°, $[\alpha]_D$ + 79°); IR ν_{max}: 1723 and 1238 (Ac), 1639 and 814 (–C(H)=C–H), 1380 and 1360 cm^{-1} (*gem* dimethyl); ^1H NMR (300 MHz): δ0.85, 0.95, 0.99, 1.00, 1.05, 1.07, 1.10, 1.16 (each 3H, *s*, 8 × tert, Me), 2.01 (3H, *s*, OAc), 4.69 (1H, *t*, *J* = 2.9 Hz, H-3α), 5.56 (1H, *dt* like, *J* = 5.5, 1.8 Hz, H-6); ^{13}C NMR: δ16.41 (*q*), 18.41 (*q*), 18.91 (*t*), 19.58 (*q*), 21.22 (*q*), 23.49 (*t*), 25.04 (*q*), 25.49 (*t*), 28.28 (*s*), 29.11 (*q*), 30.14 (*s*), 30.40 (*t*), 32.03 (C × 2, *q* and *t*), 32.36 (*q*), 33.09 (*t*), 34.48 (*q*), 34.62 (*t*), 34.78 (*s*), 35.10 (*t*), 36.02 (*t*), 37.88 (*s*), 38.98 (*t*), 39.09 (*s*), 39.31 (*s*), 43.11 (*d*), 47.38 (*d*), 49.58 (*d*), 78.60 (*d*), 120.01 (*d*), 141.94 (*s*), 170.85 (*s*); EIMS *m/z* (rel. int.): 468 $[M]^+$ (15), 408 $[M - HOAc]^+$ (9), 393 $[M - Me - HOAc]^+$ (8), 274 [fragment a] (88), 259 [a – Me] (100), 245 (8), 205 (6).

Alkaline hydrolysis of **7a**. Compound **7a** (22 mg) was hydrolysed with 0.05 M KOH in EtOH (13 ml) on a steam bath for 2 hr. After usual work-up, the crude product was chromatographed on silica gel to give the alcohol **7b** (20 mg) as colourless needles, mp 210–213° (MeOH–$CHCl_3$), $[\alpha]_D^{23}$ + 63.3° (*c* 0.71) (lit. [5] mp 210–211.5°, $[\alpha]_D$ + 64°); IR ν_{max}: 3428 and 1037 cm^{-1} (OH); ^1H NMR (90 MHz): δ0.85, 0.96, 0.99, 1.01, 1.05, 1.10, 1.14, 1.17 (each 3H, *s*, 8 × tert Me), 3.47 (1H, *t*, *J* = 3Hz, H-3α), 5.63 (1H, *m*, *w*/2 = 4 Hz, H-6); EIMS *m/z* (rel. int.): 426 $[M]^+$ (4), 408 $[M - H_2O]^+$ (22), 274 [fragment a] (97), 259 [a – Me] (100), 245 (17), 205 (51). **7b** was identified by direct comparison with an authentic sample of gult-5-en-3β-ol (mmp, TLC, IR, MS and ^1H NMR).

Ursa-9(11):12-dien-3β-ol (**8a**). Colourless needles, mp 150–151.5° (MeOH – $CHCl_3$), $[\alpha]_D^{23}$ + 362.6° (*c* 0.31) (lit. [20] mp 157–158°, $[\alpha]_D^{20.5}$ + 360°); UV λ_{max} 281 nm (ε 9900) [homoannular diene]; IR ν_{max}: 3360 and 1032 (OH), 3030, 1638 and 830 cm^{-1} (diene); ^1H NMR (300 MHz): δ0.82, 0.86, 0.89, 1.03, 1.18, 1.21 (each 3H, *s*, 6 × tert Me), 0.81 (3H, *d*, *J* = 6 Hz) and 0.93 (3H, *br s*) [2 × sec Me], 3.24 (1H, *dd*, *J* = 11, 5.5 Hz, H-3α), 5.45 and 5.60 (each 1H, *d*, *J* = 5.8 Hz, H-11, 12); EIMS *m/z* (rel. int.): 424 $[M]^+$ (100), 406 $[M - H_2O]^+$ (5), 271 [fragment *b*] (34), 255 [fragment c] (94).

Acetylation of compound **8a**. A soln of **8a** (7 mg) in C_5H_5N (0.5 ml) was acetylated with Ac_2O (0.5 ml) at room temp. overnight. After usual work-up, the crude product was chromatographed over silica gel to give an acetate (**8b**) as colourless prisms, mp 165–166° (MeOH–$CHCl_3$, $[\alpha]_D^{23}$ + 341.2° (*c* 0.18) (lit. [13] mp 165–167°, $[\alpha]_D^{25}$ + 336°); UV λ_{max} 281 nm (ε 10 000) (homoannular diene); IR ν_{max}: 1736 and 1243 (OAc), 3030, 1638 and 830 cm^{-1} (diene); ^1H NMR (300 MHz): δ0.86 (3H, *s*), 0.89 (6H, *s*), 0.91 (3H, *s*), 1.17 (3H, *s*), 1.24 (3H, *s*), [6 × tert Me], 0.81 (3H, *d*, *J* = 6.1 Hz) and 0.93 (3H, *br s*) [2 × sec Me], 2.06 (3H, *s*, OAc), 4.52 (1H, *dd*, *J* = 10.5, 5.7 Hz, H-3α), 5.45 and 5.59 (each 1H, *d*, *J* = 5.8 Hz, H-11, 12); ^{13}C NMR: δ16.75 (*q*, C-29), 17.42* (*q*, C-24), 17.55* (*q*, C-25), 18.20 (*t*, C-6), 21.33 (*q*, Me–COO–), 21.52 (*q*, C-30), 22.16 (*q*, C-26), 24.28 (*t*, C-2), 25.46 (*q*, C-27), 26.10 (*t*, C-16), 28.16 (*q*, C-23), 28.23 (*t*, C-15), 28.72 (*q*, C-28), 31.22† (*t*, C-21), 31.97† (*t*, C-7), 33.69 (*s*, C-17), 37.00 (*t*, C-1), 37.88 (*s*, C-10), 38.55 (*s*, C-4), 39.00‡ (*d*, C-19), 39.47‡ (*d*, C-20), 40.69 (*s*, C-8), 41.36 (*t*, C-22), 43.10 (*s*, C-14), 51.23 (*d*, C-5), 57.33 (*d*, C-18), 80.62 (*d*, C-3), 115.51 (*d*, C-11), 123.00 (*d*, C-12), 141.37 (*s*, C-13), 154.18 (*s*, C-9), 171.02 (*s*, MeCOO) [*†‡ values may be interchangeable]; EIMS *m/z* (rel. int.): 466 $[M]^+$ (100), 406 $[M - HOAc]^+$ (5), 313 [fragment b] (9), 255 [fragment c] (56). Compound **8b** was identified by direct comparison with the authentic sample of ursa-9(11):12-dien-3β-yl acetate (mmp, TLC, IR, MS and ^1H NMR).

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