Studies on the Constituents of *Lonicera* Species. XIII.[1] New Fernane Type Triterpenoids from the Leaves of *Lonicera gracilipes* var. *glandulosa* Maxim.

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Five new fernane type triterpenoids, ferna-7,9(11)-diene-3α,16α-diol (1), 3α,16α-dihydroxyferna-7,9(11)-dien-12-one (2), ferna-7,9(11)-diene-3α,16α,19α-triol (3), 3α,16α-dihydroxyfern-8-en-11-one (4) and 3α,16α-dihydroxyfern-8-ene-7,11-dione (5), were isolated from the leaves of *Lonicera gracilipes* var. *glandulosa* Maxim. The structures of these compounds were elucidated on the basis of spectroscopic evidence.

Key words *Lonicera gracilipes* var. *glandulosa*; Caprifoliaceae; triterpenoid

Our previous studies on the constituents of the leaves of *Lonicera gracilipes* var. *glandulosa* Maxim. (Caprifoliaceae) have led to the isolation and structure elucidation of iridoid and secoiridoid glycosides,[2] flavone glycosides,[3] polyhydric alcohol glycosides,[4] coumarin glycoside,[5] methyl dicaffeoyl quinates,[6] neolignan glycosides,[7] megastigmane glycosides[8] and glycerol glycosides.[1] As a continuation of our investigation of this plant, we have isolated five new fernane type triterpenoids, ferna-7,9(11)-diene-3α,16α-diol (**1**), 3α,16α-dihydroxyferna-7,9(11)-dien-12-one (**2**), ferna-7,9(11)-diene-3α,16α,19α-triol (**3**), 3α,16α-dihydroxyfern-8-en-11-one (**4**) and 3α,16α-dihydroxyfern-8-ene-7,11-dione (**5**), whose structures are described in this paper. This is the first report of the isolation of fernane type triterpenoids from the plants of the *Lonicera* species. The isolation and purification were carried out as described in the Experimental section.

Compound **1** was isolated as colorless needles, mp 178—180 °C, $[\alpha]_D$ −110.8°. The molecular formula was determined to be $C_{30}H_{48}O_2$ by high-resolution (HR)-MS. The IR spectrum exhibited hydroxyl (3612, 3470 cm^{-1}) absorption. The UV absorption maxima at 231 (sh), 237 and 246 (sh) nm implied the presence of a $\Delta^{7,9(11)}$-diene system in a triterpene skeleton.[9] The electron ionization (EI)-MS gave fragment ion peaks at *m/z* 422 (M^+-H_2O) and 404 (M^+-2H_2O), indicating that **1** has two hydroxyl groups. Further, EI-MS of **1** showed significant fragment ion peaks at *m/z* 271 (a) and 253 (b) arising from D-ring fission, which are characteristic of the cleavage of pentacyclic triterpene-7,9(11)-dienes (Chart 2).[10a] The ^{1}H-NMR spectrum indicated the presence of six tertiary methyl groups, two secondary methyl groups, two hydroxy methine groups and two trisubstituted olefinic protons. The ^{13}C-NMR spectrum (Table 1) revealed 30 carbon signals, which were assigned by the distortionless enhancement by polarization transfer (DEPT) as eight methyl, seven methylene, eight methine and seven quaternary carbons. Detailed analyses of the ^{1}H- and ^{13}C-NMR spectra were undertaken with the aid of ^{1}H–^{1}H shift correlation spectroscopy (^{1}H–^{1}H COSY) and ^{13}C–^{1}H shift correlation spectroscopy (^{13}C–^{1}H COSY) spectra. The ^{1}H-detected heteronuclear multiple bond correlation (HMBC) spectrum showed correlations between H-3 and C-5 and C-23; H-7 and C-5; H_3-25 and C-1, C-5 and C-9; H_3-26 and C-8, C-13 and C-15; H_3-27 and C-12, C-14 and C-18; H_3-28 and C-16, C-18 and C-21; H_3-29 and C-21; and H_3-30 and C-21 (Fig. 1). The above

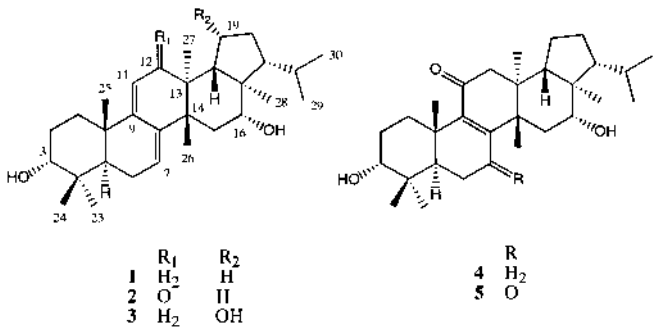

Chart 1

Table 1. ^{13}C-NMR Chemical Shifts of Compounds **1**—**5** (150 MHz)

Carbon	1	2	3	4	5
1	29.6	28.9	29.5	28.5	28.5
2	25.6	25.4	25.5	25.8	25.4
3	76.5	75.6	76.3	75.5	74.6
4	37.8	37.9	37.6	37.5	37.2
5	42.3	41.5	42.7	44.8	41.6
6	23.9	21.6	23.8	18.0	36.5
7	117.7	126.3	118.3	28.9	200.0
8	140.4	139.6	139.7	141.2	149.7
9	145.6	161.5	145.6	160.4	156.6
10	36.4	36.8	36.3	37.5	38.1
11	113.9	116.3	113.1	198.5	200.9
12	37.2	206.3	36.4	50.0	50.7
13	36.4	50.9	36.7	37.2	37.9
14	42.3	46.9	42.1	44.8	43.0
15	39.2	38.6	39.1	37.6	36.9
16	76.6	75.4	77.2	75.6	75.3
17	48.8	49.4	48.5	48.4	48.1
18	51.4	46.0	55.0	50.6	49.5
19	19.9	24.0	71.4	19.9	20.0
20	25.9	25.5	39.1	26.0	25.5
21	60.0	58.6	59.5	59.8	59.9
22	28.3	27.7	27.9	28.2[a]	28.1
23	27.8	27.5	27.7	28.2[a]	27.4
24	22.5	22.4	22.4	22.3	21.5
25	20.5	19.4	20.4	19.6	17.7
26	22.0	23.2	21.7	23.6	23.0
27	16.6	16.1	19.2	19.3	20.7
28	9.3	9.7	11.1	9.2	9.2
29	24.7	24.8	24.6	24.4	24.3
30	22.2	21.8	21.9	22.0	22.0

a) Signals were overlapped.

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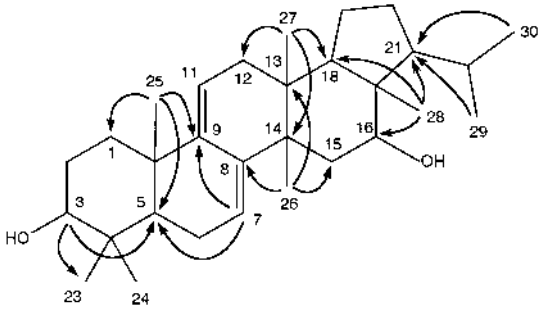

Fig. 1. HMBC Correlations for **1**

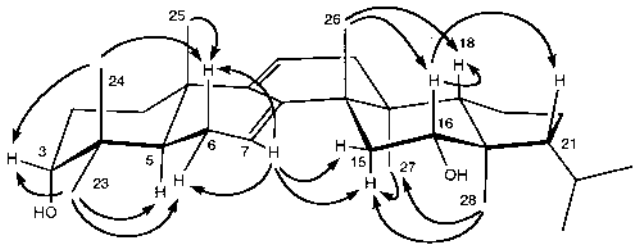

Fig. 2. NOEs Detected for **1**

spectral data indicated that **1** was a fernane or an arborane type triterpenoid with a $\Delta^{7,9(11)}$-diene system and hydroxyl groups at C-3 and C-16.[10] Nishimoto *et al.*[11] reported that the value of the optical rotation of a fernane type triterpenoid with a $\Delta^{7,9(11)}$-diene system, which had 13α,14β-methyl groups, was negative, and an arborane type triterpenoid with a $\Delta^{7,9(11)}$-diene system, which had 13β and 14α-methyl groups, was positive. The value of the optical rotation of **1** was negative. Thus, compound **1** was a fernane type triterpenoid, and the same conclusion was derived from difference nuclear Overhauser effect (NOE) spectra (Fig. 2) . The configuration of the hydroxyl groups at C-3 and C-16 were determined by the ^{1}H-NMR spectrum, in which the coupling patterns and constants for H-3 [δ 3.46 (dd, J=2.8, 2.6 Hz)] and H-16 [δ 3.76 (dd, J=11.4, 4.4 Hz)] suggested that the hydroxyl groups at C-3 and C-16 had α configurations, respectively. Accordingly, the structure of **1** was determined to be ferna-7,9(11)-diene-3α,16α-diol.

Compound **2** was isolated as colorless needles, mp 110—112 °C, $[\alpha]_D$ −157.8°. The molecular formula was determined to be $C_{30}H_{46}O_3$ by HR-MS. The IR spectrum exhibited hydroxyl (3618, 3446 cm^{-1}) and enone (1667 cm^{-1}) absorptions. The EI-MS gave fragment ion peaks at *m/z* 436 (M^+-H_2O) and 418 (M^+-2H_2O), indicating that **2** has two hydroxyl groups. The ^{1}H- and ^{13}C-NMR spectra of **2**, obtained with the aid of ^{1}H–^{1}H COSY and ^{1}H-detected heteronuclear multiple quantum coherence (HMQC) spectra, were similar to those of **1**, except that **2** contained one carbonyl group. The position of this carbonyl group was determined by HMBC spectrum, in which a cross peak was observed between H_3-27 at δ 1.08 and C-12 at δ 206.3, so that the carbonyl group is attached at C-12. In comparison with the ^{13}C-NMR data of **1**, the carbons at C-11 and C-13 of **2** were deshielded (Table 1), which supported the assignment of the carbonyl group at C-12. Therefore, the structure of **2** was determined to be 3α,16α-dihydroxyferna-7,9(11)-dien-12-one.

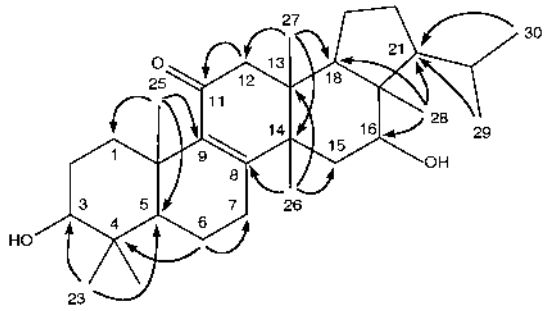

Fig. 3. HMBC Correlations for **4**

Compound **3** was isolated as colorless needles, mp 125—127 °C, $[\alpha]_D$ −125.0°. The molecular formula was determined to be $C_{30}H_{48}O_3$ by HR-MS. The IR spectrum showed hydroxyl (3619 cm^{-1}) absorption. The EI-MS gave fragment ion peaks at *m/z* 438 (M^+-H_2O), 420 (M^+-2H_2O) and 402 (M^+-3H_2O), indicating that **3** has three hydroxyl groups. The ^{1}H- and ^{13}C-NMR spectra of **3**, obtained with the aid of ^{1}H–^{1}H COSY and HMQC spectra, were similar to those of **1**, except for the presence of one more hydroxyl group. The position of this group was determined by the HMBC spectrum, in which a cross peak was observed between H-19 at δ 4.38 and C-13 at δ 36.7, so that the hydroxyl group is attached at C-19. In comparison with the ^{13}C-NMR data of **1**, the carbon signals for C-27 and C-28 appeared to shift downfield [2.6 ppm (C-27), 1.8 ppm (C-28)]. This is due to the δ_1-hydroxy substituent effect,[12] so that the configuration of the hydroxyl group was determined to be α. The same conclusion was derived from the nuclear Overhauser enhancement spectroscopy (NOESY) spectrum, in which a cross peak was observed between H-18 and H-19β. Based on this evidence, the structure of **3** was determined to be ferna-7,9(11)-diene-3α,16α,19α-triol.

Compound **4** was isolated as colorless needles, mp 130—132 °C, $[\alpha]_D$ −10.7°. The molecular formula was determined to be $C_{30}H_{48}O_3$ by HR-MS. The IR spectrum exhibited hydroxyl (3617, 3451 cm^{-1}) and enone (1651 cm^{-1}) absorptions. The EI-MS gave fragment ion peaks at *m/z* 438 (M^+-H_2O) and 420 (M^+-2H_2O), indicating that **4** has two hydroxyl groups. The ^{1}H- and ^{13}C-NMR spectra of **4**, obtained with the aid of ^{1}H–^{1}H COSY and HMQC spectra, showed signals attributable to a fernane type triterpenoid derivative.[10a] The HMBC spectrum showed correlations between H_2-6 and C-4 and C-7; H_2-12 and C-11; H_3-23 and C-3 and C-5; H_3-25 and C-1, C-5 and C-9; H_3-26 and C-8, C-13 and C-15; H_3-27 and C-12, C-14 and C-18; H_3-28 and C-16, C-18 and C-21; H_3-29 and C-21; and H_3-30 and C-21 (Fig. 3). From the above spectral data, **4** was determined to be 3,16-dihydroxyfern-8-en-11-one. The stereochemistry of the hydroxyl groups at C-3 and C-16 was determined by the ^{1}H-NMR spectrum, in which the coupling patterns and constants for H-3 [δ 3.45 (br s)] and H-16 [δ 3.76 (dd, J=11.1, 4.3 Hz)] suggested that the hydroxyl groups at C-3 and C-16 had α configurations, respectively. Accordingly, the structure of **4** was determined to be 3α,16α-dihydroxyfern-8-en-11-one.

Compound **5** was isolated as colorless needles, mp 103—105 °C, $[\alpha]_D$ −8.3°. The molecular formula was determined to be $C_{30}H_{46}O_4$ by HR-MS. The IR spectrum showed hydroxyl (3620 cm^{-1}) and enone (1651 cm^{-1}) absorptions. The

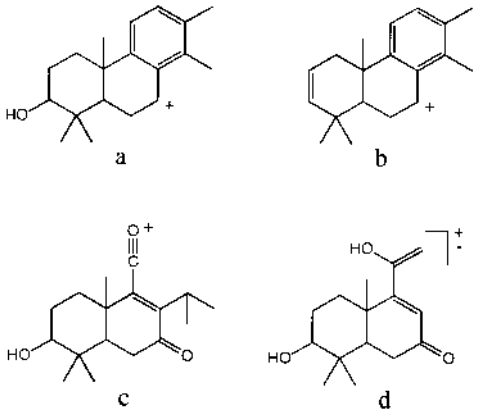

Chart 2

UV absorption maximum at 270 nm implied the presence of a transoid ene-dione chromophore.[13] The EI-MS gave fragment ion peaks at *m/z* 452 (M^+-H_2O) and 434 (M^+-2H_2O), indicating that **5** has two hydroxyl groups. Furthermore, the EI-MS of **5** showed significant fragment ion peaks at *m/z* 277 (c) and 250 (d), diagnostic of triterpenoids having an 8-ene-7,11-dione moiety (Chart 2).[13] The ^{1}H- and ^{13}C-NMR spectra of **5**, obtained with the aid of ^{1}H–^{1}H COSY and HMQC spectra, were similar to those of **4**, except for the presence of one more carbonyl group. The position of this carbonyl group was determined by an HMBC spectrum, in which cross peaks were observed between H_2-6 at δ 2.41 and 2.48 and C-7 at δ 200.0, so that the carbonyl group is attached at the C-7. Therefore, the structure of **5** was determined to be 3α,16α-dihydroxyfern-8-ene-7,11-dione.

Compounds **1**, **4** and **5** are presumably biosynthesized from the postulated intermediate, fern-8-ene-3α,16α-diol, in the presence of an effective and specific oxidase enzyme in the plant. The co-occurence of compound **1** with compounds **2** and **3** in this plant indicate that the former compound plays a role as a precursor for the formation of the latter compounds.

Experimental

General Procedures Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were determined with a JASCO DIP-360 digital polarimeter. IR spectra were recorded with a Perkin–Elmer FT-IR 1725X infrared spectrophotometer and UV spectra with a Beckman DU-64 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded with JEOL LA 600 (600 and 150 MHz) spectrometer. Chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard (s, singlet; br s, broad singlet; d, doublet; br d, broad doublet; dd, double doublet; br dd, broad double doublet; ddd, double double doublet; m, multiplet). The EI- and HR-MS were recorded on a JEOL JMS-DX 303 mass spectrometer. Column chromatography was carried out on Kieselgel 60 (Merck; 230—400 mesh) or Cosmosil 75C_{18}-OPN (Nacalai Tesque). Preparative HPLC was carried out on a Tosoh HPLC system (pump, CCPD; detector, UV-8011) using a Cosmosil 5C18-AR (10 mm i.d.×25 cm) column (Nacalai Tesque).

Plant Material The leaves of *L. gracilipes* var. *glandulosa* were collected in October 1990, in Sendai, Japan.

Extraction and Isolation Fresh leaves of *L. gracilipes* var. *glandulosa* (0.2 kg) were extracted with MeOH. The MeOH extract was concentrated under reduced pressure and the residue was suspended in a small excess of H_2O. This suspension was successively extracted with $CHCl_3$, Et_2O, AcOEt and *n*-BuOH. The $CHCl_3$ soluble fraction was concentrated under reduced pressure to produce a residue (23.6 g). This residue was chromatographed on a silica gel column using *n*-hexane–acetone (3 : 1), and the eluate was separated into seven fractions (frs. 1—7). Fraction 3 was rechromatographed on a 75C_{18} open column using MeOH–H_2O (3 : 1), and the eluate was separated into eight fractions (frs. 3-1—3-8). Fraction 3-1 was subjected to a silica gel column using benzene–AcOEt (9 : 1) to give **1** (14.6 mg). Fraction 4 was rechromatographed on a 75C_{18} open column using MeOH–H_2O (3 : 1), and the eluate was separated into 15 fractions (frs. 4-1—4-15). Fraction 4-7 was subjected to preparative HPLC [MeOH–H_2O (3 : 1); flow rate, 1.5 ml/min; detection, 230 nm] to give **2** (0.7 mg). Fraction 4-9 was subjected to preparative HPLC [MeOH–H_2O (3 : 1); flow rate, 1.5 ml/min; detection, 254 nm] to give **4** (5.6 mg) and **5** (1.2 mg). Fraction 4-10 was subjected to preparative HPLC [MeOH–H_2O (3 : 1); flow rate, 1.5 ml/min; detection, 234 nm] to give **3** (1.5 mg).

Ferna-7,9(11)-diene-3α,16α-diol (1) Colorless needles, mp 178—180 °C. $[\alpha]_D^{20}$ −110.8° (c=1.46, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3612, 3470. UV λ_{max}^{MeOH} nm (log ε): 231 (sh) (3.88), 237 (3.91), 246 (sh) (3.70). HR-MS *m/z*: 440.3658 (M^+, Calcd for $C_{30}H_{48}O_2$; 440.3654). EI-MS *m/z*: 440 (M^+), 422 (M^+-H_2O), 407 ($M^+-H_2O-CH_3$), 404 (M^+-2H_2O), 389 ($M^+-2H_2O-CH_3$), 361 ($M^+-2H_2O-C_3H_7$), 271 (a), 253 (b). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 0.69 (3H, s, H_3-27), 0.76 (3H, s, H_3-28), 0.88 (3H, d, J=7.0 Hz, H_3-30), 0.935 (3H, s, H_3-25), 0.941 (3H, s, H_3-26), 0.943 (3H, s, H_3-24), 0.95 (3H, s, H_3-23), 1.07 (3H, d, J=6.6 Hz, H_3-29), 1.26 (1H, m, H-21), 1.48 (1H, br d, J=11.5 Hz, H-15α), 1.53 (1H, m, H-18), 1.67 (1H, m, H-15β), 1.68 (1H, m, H-5), 2.07 (1H, br d, J=18.0 Hz, H-6β), 2.13 (1H, ddd, J=18.0, 5.1, 4.8 Hz, H-6α), 3.46 (1H, dd, J=2.8, 2.6 Hz, H-3), 3.76 (1H, dd, J=11.4, 4.4 Hz, H-16), 5.21 (1H, br dd, J=2.6, 1.8 Hz, H-11), 5.43 (1H, br d, J=2.2 Hz, H-7). ^{13}C-NMR (150 MHz, $CDCl_3$): see Table 1.

3α,16α-Dihydroxyferna-7,9(11)-dien-12-one (2) Colorless needles, mp 110—112 °C. $[\alpha]_D^{20}$ −157.8° (c=0.07, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3618, 3446, 1667. UV λ_{max}^{MeOH} nm (log ε): 284 (3.95). HR-MS *m/z*: 454.3480 (M^+, Calcd for $C_{30}H_{46}O_3$; 454.3447). EI-MS *m/z*: 454 (M^+), 439 (M^+-CH_3), 436 (M^+-H_2O), 421 ($M^+-H_2O-CH_3$), 418 (M^+-2H_2O), 403 ($M^+-2H_2O-CH_3$), 393 ($M^+-H_2O-C_3H_7$), 375 ($M^+-2H_2O-C_3H_7$). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 0.81 (3H, s, H_3-28), 0.88 (3H, d, J=6.6 Hz, H_3-30), 0.98 (3H, s, H_3-24), 0.99 (3H, s, H_3-23), 1.01 (3H, s, H_3-25), 1.06 (3H, d, J=6.6 Hz, H_3-29), 1.07 (3H, s, H_3-26), 1.08 (3H, s, H_3-27), 3.49 (1H, br s, H-3), 3.82 (1H, dd, J=11.4, 4.4 Hz, H-16), 5.49 (1H, s, H-11), 5.89 (1H, br d, J=2.2 Hz, H-7). ^{13}C-NMR (150 MHz, $CDCl_3$): see Table 1.

Ferna-7,9(11)-diene-3α,16α,19α-triol (3) Colorless needles, mp 125—127 °C. $[\alpha]_D^{20}$ −125.0° (c=0.15, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3619. UV λ_{max}^{MeOH} nm (log ε): 231 (sh) (3.97), 237 (3.99), 246 (sh) (3.79). HR-MS *m/z*: 456.3587 (M^+, Calcd for $C_{30}H_{48}O_3$; 456.3604). EI-MS *m/z*: 456 (M^+), 438 (M^+-H_2O), 420 (M^+-2H_2O), 405 ($M^+-2H_2O-CH_3$), 402 (M^+-3H_2O), 387 ($M^+-3H_2O-CH_3$), 359 ($M^+-3H_2O-C_3H_7$), 253 (b). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 0.91 (3H, d, J=7.0 Hz, H_3-30), 0.93 (3H, s, H_3-26), 0.95 (3H, s, H_3-24), 0.94 (3H, s, H_3-25), 0.96 (3H, s, H_3-23), 1.06 (3H, s, H_3-27), 1.07 (3H, d, J=6.6 Hz, H_3-29), 1.11 (3H, s, H_3-28), 1.17 (1H, d, J=5.9 Hz, H-18), 3.47 (1H, br s, H-3), 3.68 (1H, dd, J=11.0, 4.0 Hz, H-16), 4.38 (1H, ddd, J=8.3, 5.5, 2.8 Hz, H-19), 5.26 (1H, br d, J=5.5 Hz, H-11), 5.45 (1H, br s, H-7). ^{13}C-NMR (150 MHz, $CDCl_3$): see Table 1.

3α,16α-Dihydroxyfern-8-en-11-one (4) Colorless needles, mp 130—132 °C. $[\alpha]_D^{20}$ −10.7° (c=0.56, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3617, 3451, 1651. UV λ_{max}^{MeOH} nm (log ε): 257 (3.69). HR-MS *m/z*: 456.3560 (M^+, Calcd for $C_{30}H_{48}O_3$; 456.3604). EI-MS *m/z*: 456 (M^+), 441 (M^+-CH_3), 438 (M^+-H_2O), 420 (M^+-2H_2O). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.70 (3H, s, H_3-28), 0.88 (1H, d, J=5.6 Hz, H_3-30), 0.89 (3H, s, H_3-24), 0.96 (3H, s, H_3-27), 0.99 (3H, s, H_3-23), 1.06 (1H, d, J=6.6 Hz, H_3-29), 1.10 (3H, m, H-6β), 1.14 (3H, s, H_3-26), 1.22 (3H, s, H_3-25), 1.24 (1H, m, H-6α), 2.05 (1H, d, J=18.5 Hz, H-12β), 2.14 (1H, d, J=18.5 Hz, H-12α), 3.45 (1H, br s, H-3), 3.76 (1H, dd, J=11.1, 4.3 Hz, H-16). ^{13}C-NMR (150 MHz, $CDCl_3$): see Table 1.

3α,16α-Dihydroxyfern-8-ene-7,11-dione (5) Colorless needles, mp 103—105 °C. $[\alpha]_D^{20}$ −8.3° (c=0.12, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620, 1666. UV λ_{max}^{MeOH} nm (log ε): 270 (3.81). HR-MS *m/z*: 470.3435 (M^+, Calcd for $C_{30}H_{46}O_4$; 470.3396). EI-MS *m/z*: 470 (M^+), 452 (M^+-H_2O), 437 ($M^+-H_2O-CH_3$), 434 (M^+-2H_2O), 419 ($M^+-2H_2O-CH_3$), 409 ($M^+-H_2O-C_3H_7$), 391 ($M^+-2H_2O-C_3H_7$), 277 (c), 250 (d). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 0.77 (3H, s, H_3-28), 0.87 (1H, d, J=6.6 Hz, H_3-30), 0.95 (3H, s, H_3-24), 0.98 (3H, s, H_3-23), 1.06 (3H, s, H_3-27), 1.07 (1H, d, J=6.3 Hz, H_3-29), 1.27 (3H, s, H_3-25), 1.30 (3H, s, H_3-26), 2.16 (1H, d, J=18.8 Hz, H-12β), 2.27 (1H, d, J=18.8 Hz, H-12α), 2.41 (1H, dd, J=18.5, 4.5 Hz, H-6α), 2.48 (1H, dd, J=18.5, 13.5 Hz, H-6β), 2.75 (1H, dd, J=13.5, 4.5 Hz, H-15β), 3.49 (1H, br s, H-3), 3.74 (1H, dd, J=10.7, 4.4 Hz, H-16). ^{13}C-NMR (150 MHz, $CDCl_3$): see Table 1.

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