Three New Labdane-Type Diterpenes from Wood, *Excoecaria agallocha*

Tenji KONISHI,*[,a] Masuji AZUMA,[a] Rie ITOGA,[a] Shiu KIYOSAWA,[a] Yasuhiro FUJIWARA,[a] and Yasuo SHIMADA[b]

Kyoto Pharmaceutical University,[a] 5 Nakauchi-cho, Misasagi, Yamashina-ku, Kyoto 607, Japan and Mitsuboshi Seiyakusho,[b] 153, Gose, Nara 639–22, Japan. Received July 5, 1995; accepted September 11, 1995

From the wood of *Excoecaria agallocha* LINN., three new labdane-type diterpenes, *ent*-11α-hydroxy-3-oxo-13-*epi*-manoyl oxide (4), *ent*-16-hydroxy-3-oxo-13-*epi*-manoyl oxide (5) and *ent*-15-hydroxy-labda-8(17),13*E*-diene-3-one (6) were isolated together with three known compounds, *ent*-3-oxo-13-*epi*-manoyl oxide (ribenone,1), *ent*-3β-hydroxy-13-*epi*-manoyl oxide (ribenol, 2) and *ent*-13-*epi*-manoyl oxide (3), and their structures were determined.

Key words *Excoecaria agallocha*; Euphorbiaceae; labdane diterpene; ribenone; ribenol; *ent*-13-*epi*-manoyl oxide

Excoecaria agallocha LINN. (Euphorbiaceae) is distributed on seashores and edge-mangroves, sometimes cultivated for wind- and sea-breaks in tropical Africa and East Asia. The leaves and milky fluid obtained from damaged branches have been used as a fish poison in New Caledonia and in Okinawa, the resinous wood including latex, the so-called "Okinawa-jinko," has also been used as a substitute for the incense of agalwood (Jinko).[1)]

From the latex of the plant, skin irritant substances, generally called irritant *Excoecaria* factors, have been obtained and characterized as Daphnane-type diterpene orthoesters.[1,2)]

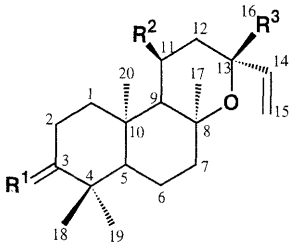
We have studied the isolation and structures of the constituents of resinous woods collected from the plant of *E. agallocha* grown on the island of Okinawa.

The ether extract obtained from the wood was separated by various types of chromatography (see Experimental) to give six constituents, tentatively named Compounds **1**, **2**, **3**, **4**, **5** and **6**. Compounds **1**, **2** and **3** were identified as ribenone, ribenol and *ent*-13-*epi*-manoyl oxide, respectively, by comparisons of their optical rotations and some spectral data with published data.[3–5)]

Compound **4** was obtained as colorless prisms of mp 114—116 °C, $[\alpha]_D$ −59.2°. In the electron impact mass (EI-MS) spectrum, compound **4** showed a molecular ion peak $[M]^+$ at *m/z* 320 and characteristic ion peaks at *m/z* 217, 206 and 151 due to fragmentation of the A, B ring skeleton, as exhibited in the spectrum of **1**.[6)] The infrared (IR) spectrum was also similar to that of **1** with absorption bands characteristic of carbonyl (1699 cm^{-1}), vinyl (1647, 960, 912 cm^{-1}), and ether (1130 cm^{-1}) groups. However, in **4**, the absorption band of a hydroxy group was very distinct at 3450 cm^{-1}. The ^{1}H-NMR spectrum of **4** was also similar to that of **1** except for the presence of an extra signal for a hydroxy methine proton, δ 4.17, and two singlet signals of the methyl group at δ 1.00 and 1.24 ppm, which exhibited shifts to a lower field, by 0.16 and 0.1 ppm, respectively, compared with the corresponding methyl proton signals of **1**.

Comparison of the ^{13}C-NMR spectra (Table 1) of **1** and **4** suggested that the hydroxy group was located at the C-11, based on the substitution effects at the α and β positions. The configuration at C-11 in **4** could be assigned from the following data involving the ^{1}H–^{1}H coupling constant and ^{13}C chemical shifts revealed by the ^{1}H- and ^{13}C-NMR spectra.

The methine proton of H-11 at δ 4.17 indicated a double double doublet (ddd) coupling signal, suggesting a *trans-diaxial* relationship between the two protons of H-9 and 11, based on 9.5 or 10.0 Hz in the coupling constant



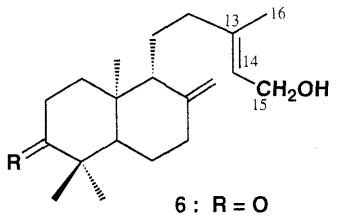
1 : R^1 = O, R^2 = H, R^3 = CH_3

2 : R^1 = α-OH, β-H, R^2 = H, R^3 = CH_3

3 : R^1 = H_2, R^2 = H, R^3 = CH_3

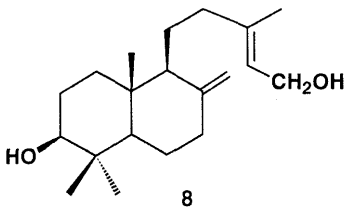
4 : R^1 = O, R^2 = OH, R^3 = CH_3

5 : R^1 = O, R^2 = H, R^3 = CH_2OH



6 : R = O

7 : R = α-OH, β-H



8

Chart 1

* To whom correspondence should be addressed.

Table 1. ^{13}C-NMR Spectral Data for Compounds **1**—**6** and **7** in $CDCl_3$[a]

Carbon	1	2	3	4	5	6	7
1	38.2	37.6	39.3	40.3	38.1	37.6	37.0
2	33.9	27.3	19.9	33.9	33.8	34.7	27.9
3	217.4	78.9	42.2	217.9	217.3	216.9	78.8
4	47.3	38.8	33.2	47.7	47.2	47.8	39.1[c]
5	54.6	55.2	56.4	54.8	54.5	55.2	54.6
6	20.8	19.5	18.6	20.8	20.7	25.1	24.0
7	42.2	43.0	43.1	42.2	42.0	38.2	38.3[b]
8	75.5	75.8	76.0	76.8	76.1	147.2	147.9
9	57.7	58.3	58.5	62.6	57.5	55.2	56.0
10	36.4	36.5	36.8	37.6	36.4	39.2	39.3[c]
11	16.4	15.9	15.9	65.6	15.7	22.3	21.9
12	34.8	34.7	34.8	45.3	28.3	37.8	38.2[b]
13	73.6	73.4	73.2	74.2	76.4	139.8	140.4
14	147.4	147.5	147.7	147.6	143.7	123.4	123.1
15	109.8	109.6	109.5	110.0	113.7	59.3	59.4
16	32.7	32.7	32.7	32.3	69.5	16.4	16.4
17	23.4	23.8	23.9	24.6	23.4	107.5	106.7
18	26.7	28.0	33.3	27.0	26.7	26.0	28.3
19	20.9	15.2	21.3	20.8	20.9	21.7	15.4
20	15.5	16.0	15.9	16.1	15.5	14.1	14.5

a) Signal assignments were based on DEPT and ^{13}C–^{1}H COSY spectra. *b*, *c*) Assignments may be interchanged.

for the two protons. Therefore, the orientation of the hydroxy group at C-11 was presumed to be equatorial in the general conformations of the A, B and C ring. In the ^{13}C-NMR spectrum, the lowfield shift of C-1, about 2.1 ppm compared with that of **1**, appeared also to be due to the deshielding effect of the equatorial hydroxy group at C-11. These observations were further supported by the nuclear Overhauser effect (NOE) between H-11 and the methyl protons of H-17 or 20 in the NOE difference spectrum of **4**.

The circular dichroism (CD) spectrum of **4** showed a negative Cotton effect at 290 nm similar to the spectrum of **1**.

Therefore, compound **4** was established as *ent*-11α-hydroxy-3-oxo-13-*epi*-manoyl oxide.

Compound **5** was obtained as colorless needles, mp 131—132 °C, $[\alpha]_D$ −72.1°. Its IR spectrum was similar to that of **4**, showing that both compounds had the same skeleton. **5** showed an ion peak $[M+H]^+$ at *m/z* 321 in the positive FAB-MS and a characteristic base peak $[M-CH_2OH]^+$ at *m/z* 289, which resulted in the elimination of the hydroxymethyl group, and characteristic fragment ion peaks at *m/z* 271, 219, 151 in the EI-MS of the manoyl skeleton.[6] In the ^{1}H-NMR spectrum, nonequivalent proton signals of the hydroxymethyl group appeared in the double doublet (dd) splittings at δ 2.99 and 3.33, following addition of D_2O this changed to a doublet (d), and the 16-methyl proton signal detected in **1** and others were not observed. The hydroxymethyl carbon signal was confirmed at δ 69.5 in the ^{13}C-NMR spectrum with the C-12, -13 and -14 signals, shifted due to β and γ effects presumed to result from hydroxylation at C-16.

The configuration of C-13 was determined by the NOE method. When the signals at δ 1.29 (H-17), δ 2.99 and 3.33 (H-16) were irradiated, NOEs were observed at a signal due to H-14, but NOEs were not observed following irradiation of H-17 and H-16. From these findings, and CD spectrum data, the structure of **5** was determined to be *ent*-16-hydroxy-3-oxo-13-*epi*-manoyl oxide.

Compound **6** was obtained as colorless needles, mp 110—112 °C, $[\alpha]_D$ −20.1°, and exhibited a molecular ion peak $[M]^+$ at *m/z* 304 in the EI-MS. The IR spectrum showed a hydroxy group at 3462 cm^{-1}, double-bonds at 1670, 1643, 891 and 783 cm^{-1} and a carbonyl group, while there were no ether absorption bands. The ^{1}H- and ^{13}C-NMR spectra showed the presence of a vinyl methyl group at δ_H 1.67, and δ_C 26.0 instead of the angular methyl of C-13 in **5**. In addition, an *exo*-methylene group and a trisubstituted olefin moiety were also observed. One carbonyl carbon appeared in the low field at δ_C 216.9 without any characteristic coupling system in the proton signals. These findings suggested that compound **6** is a labdadiene derivative corresponding to labda-8(17),13*E*-diene-3,15-diol (**8**).[7]

Compound **6** was treated with $NaBH_4$ in MeOH to give the diol (**7**) in high yield (90%). The IR, MS and ^{1}H-NMR spectral data for **7** resembled those of **8** except for the specific rotation sign. Comparison of the ^{1}H-NMR spectra of **7** with **2** showed that the hydroxy group of C-3 had the same orientation. The optical rotation of **7** exhibited a negative value, −24.6°, as did the enantiomer of **8**.[8]

In the NOE experiments on **6**, irradiation with H-16 at δ 1.67 showed enhancement of the H-15 supporting the assigned *E*-configuration at C-13.

Therefore, **6** was determined to be *ent*-15-hydroxy-labda-8(17),13*E*-diene-3-one.

To our knowledge, this is the first example of the isolation of manoyl oxide derivatives from the Euphorbiaceae.

Experimental

Melting points were measured with a Yanagimoto micro melting-point apparatus and are uncorrected. CD and optical rotations were recorded using a JASCO J-500C and Horiba digital polarimeter. IR spectra were measuerd with a Shimadzu FTIR-8100 spectrometer. NMR spectra were recorded on a Varian XL-300 spectrometer in $CDCl_3$ solution using tetramethylsilane (TMS) as an internal standard. Chemical shifts are expressed in ppm downfield from TMS and the coupling constants (*J*) in Hertz (Hz). The EI-MS, FAB-MS and High Resolution Positive FAB-MS (HRFAB-MS) (70 eV, glycerol and 3-nitrobenzyl alcohol as the matrix) were measured on a JEOL JSM-SX 102AQQ mass spectrometer.

Preparative high performance liquid chromatography (HPLC) was carried out on an LC-09 instrument (Nihon Bunseki Kogyo). Column chromatography was carried out on Kiesel gel 60 (230—400 mesh, Merck), Sephadex LH-20 (Pharmacia) and Jai-Gel GS-310 (Nihon Bunseki Kogyo).

Extraction and Isolation The wood of *Excoecaria agallocha* LINN. (665 g), was crushed into small pieces and extracted with ether (3 l × 3). The combined extracts were evaporated under reduced pressure to give a brown syrup (103 g) which was subsequently purified by repeated silica-gel chromatography using a binary solvent system (hexane + AcOEt gradient and $CHCl_3$ + MeOH gradient) and preparative recycling HPLC (Jai-Gel GS-310, 20 × 500 mm × 2, MeOH) to afford ribenone (**1**, 1.3 g), ribenol (**2**, 136 mg), **3** (32 mg), **4** (60.6 mg), **5** (64.0 mg) and **6** (128.3 mg).

Ribenone (1) Colorless needles from MeOH, mp 117.5—118.0 °C, $[\alpha]_D^{20}$ −76.0° (*c* = 0.73, $CHCl_3$). CD (*c* = 2.6 × 10^{-5}, $CHCl_3$) $\Delta\varepsilon^{26}$ (nm): 0 (320), −1.35 (290), 0 (250). IR (KBr) cm^{-1}: 1705 (C=O), 1637, 1414, 960, 904 (vinyl), 1082 (ether). EI-MS *m/z*: 304 $[M]^+$, 289 $[M-CH_3]^+$, 271 $[M-CH_3-H_2O]^+$, 234 $[M-C_4H_6O]^+$, 206 $[C_{14}H_{22}O]^+$, 191 $[C_{13}H_{19}O]^+$, 151 $[C_{10}H_{15}O]^+$. *Anal.* Calcd for $C_{20}H_{32}O_2$: C, 78.89; H, 10.59. Found: C, 78.74; H, 10.80. ^{1}H-NMR ($CDCl_3$) δ: 0.84 (3H, s,

H-20), 1.01 (3H, s, H-19), 1.09 (3H, s, H-18), 1.14 (3H, s, H-16), 1.26 (3H, s, H-17), 1.81 (1H, dd, J=3.1, 9.0 Hz, H-7α), 1.90 (1H, ddd, J=4.5, 7.5, 13.0 Hz, H-1α), 2.24 (1H, dd, J=3.1, 10.0 Hz, H-12), 2.45 (1H, ddd, J=4.5, 8.0, 15.5 Hz, H-2β), 2.53 (1H, ddd, J=7.5, 10.0, 15.5 Hz, H-2α), 4.93 (1H, dd, J=1.0, 11.0 Hz, H-15a), 4.98 (1H, dd, J=1.0, 18.0 Hz, H-15b), 6.15 (1H, dd, J=11.0, 18.0 Hz, H-14). ^{13}C-NMR ($CDCl_3$): Table 1.

Ribenol (2) Colorless needles from MeOH, mp 75.0—75.5 °C, $[\alpha]_D^{26}$ −36.1° (c=0.5, $CHCl_3$). IR (KBr) cm^{-1}: 3350 (OH), 1635, 1410, 962, 908 (vinyl), 1091 (ether). EI-MS m/z: 291 $[M-CH_3]^+$, 273 $[M-CH_3-H_2O]^+$, 255 $[273-H_2O]^+$, 236 $[M-C_4H_6O]^+$, 208 $[C_{14}H_{24}O]^+$, 190 $[C_{14}H_{22}]^+$. Positive FAB-MS m/z: 307 $[M+H]^+$. HRFAB-MS m/z: Calcd for $C_{20}H_{35}O_2$ $(M+H)^+$: 307.2637. Found: 307.2661. ^{1}H-NMR ($CDCl_3$) δ: 0.73 (3H, s, H-20), 0.75 (3H, s, H-19), 0.98 (3H, s, H-18), 1.13 (3H, s, H-16), 1.22 (3H, s, H-17), 1.78 (1H, dd, J=3.1, 9.0 Hz, H-7α), 2.22 (1H, dd, J=3.1, 10.0 Hz, H-12), 3.22 (1H, ddd, J=5.5, 5.5, 11.0 Hz, changed to dd by the addition of D_2O, H-3α), 4.92(1H, dd, J=1.0, 11.0 Hz, H-15a), 4.97 (1H, dd, J=1.0, 18.0 Hz, H-15b), 6.10 (1H, dd, J=11.0, 18.0 Hz, H-14). ^{13}C-NMR ($CDCl_3$): Table 1.

***ent*-13-*epi*-Manoyl Oxide (3)** Colorless prisms from MeOH, mp 99.5—101.5 °C, $[\alpha]_D^{26}$ −45.5° (c=4.0, $CHCl_3$). IR (KBr) cm^{-1}: 1415, 959, 912 (vinyl), 1075 (ether). EI-MS m/z: 290 $[M]^+$, 275 $[M-CH_3]^+$, 257 $[M-CH_3-H_2O]^+$, 220 $[M-C_4H_6O]^+$, 192 $[C_{14}H_{24}]^+$, 177 $[C_{13}H_{21}]^+$, 137 $[C_{10}H_{17}]^+$. Positive FAB-MS m/z: 291 $[M+H]^+$, 275 $[M-CH_3]^+$, 273 $[M+H-H_2O]^+$. ^{1}H-NMR ($CDCl_3$) δ: 0.72 (3H, s, H-20), 0.78 (3H, s, H-19), 0.85 (3H, s, H-18), 1.13 (3H, s, H-16), 1.22 (3H, s, H-17), 1.77 (1H, dt, J=3.0, 12 Hz, H-7α), 2.21 (1H, m, H-12), 4.91 (1H, dd, J=1.0, 11.0 Hz, H-15a), 4.96 (1H, dd, J=1.0, 18.0 Hz, H-15b), 6.02 (1H, dd, J=11.0, 18.0 Hz, H-14). ^{13}C-NMR ($CDCl_3$): Table 1.

***ent*-11α-Hydroxy-3-oxo-13-*epi*-manoyl Oxide (4)** Colorless prisms from aqueous MeOH, mp 114—116 °C, $[\alpha]_D^{22}$ −59.2° (c=0.96, $CHCl_3$). CD ($c=1.4\times10^{-5}$, $CHCl_3$) $\Delta\varepsilon^{26}$ (nm): 0 (320), −1.87 (290), 0 (250). IR (KBr) cm^{-1}: 3450 (OH), 1699 (C=O), 1647, 1412, 960, 912 (vinyl), 1130 (ether). EI-MS m/z: 320 $[M]^+$, 305 $[M-CH_3]^+$, 287 $[M-CH_3-H_2O]^+$, 269 $[287-H_2O]^+$, 217 $[C_{15}H_{21}O]^+$, 206 $[C_{14}H_{22}O]^+$, 151 $[C_{10}H_{15}O]^+$. Positive FAB-MS m/z: 321 $[M+H]^+$. HRFAB-MS m/z: Calcd for $C_{20}H_{33}O_3$ $(M+H)^+$: 321.2430. Found: 321.2430. ^{1}H-NMR ($CDCl_3$) δ: 1.00 (3H, s, H-20), 1.04 (3H, s, H-19), 1.11 (3H, s, H-18), 1.24 (3H, s, H-16), 1.27 (3H, s, H-17), 1.80 (2H, m, H-1, 7), 2.50 (3H, m, H-2, 9), 4.17 (1H, ddd, J=4.5, 9.5, 10.0 Hz, H-11β), 4.95 (1H, dd, J=1.0, 11.0 Hz, H-15a), 5.08 (1H, dd, J=1.0, 18.0 Hz, H-15b), 6.00 (1H, dd, J=11.0, 18.0 Hz, H-14). ^{13}C-NMR ($CDCl_3$): Table 1.

***ent*-16-Hydroxy-3-oxo-13-*epi*-manoyl Oxide (5)** Colorless needles from MeOH, mp 131—132 °C, $[\alpha]_D^{21}$ −72.1° (c=0.40, $CHCl_3$). CD ($c=1.1\times10^{-4}$, $CHCl_3$) $\Delta\varepsilon^{26}$ (nm): 0 (320), −1.08 (290), 0 (250). IR (KBr) cm^{-1}: 3516 (OH), 1699 (C=O), 1423, 953, 908 (vinyl), 1078 (ether). EI-MS m/z: 289 $[M-CH_2OH]^+$, 271 $[289-H_2O]^+$, 253 $[271-H_2O]^+$, 219 $[C_{15}H_{23}O]^+$, 151 $[C_{10}H_{15}O]^+$. Positive FAB-MS m/z: 321 $[M+H]^+$. HRFAB-MS m/z: Calcd for $C_{20}H_{33}O_3$ $(M+H)^+$: 321.2429. Found: 321.2432. ^{1}H-NMR ($CDCl_3$) δ: 0.85 (3H, s, H-20), 1.02 (3H, s, H-19), 1.10 (3H, s, H-18), 1.29 (3H, s, H-17), 1.82 (1H, dd, J=3.0, 9.0 Hz, H-7), 1.91 (1H, ddd, J=4.5, 7.5, 13.0 Hz, H-1α), 2.03 (1H, ddd, J=3.5, 3.5, 13.5 Hz, H-12), 2.16 (1H, dd, J=3.3, 9.8 Hz, OH, disappeared by additon of D_2O), 2.46 (1H, ddd, J=4.5, 7.5, 15.5 Hz, H-2), 2.54 (1H, ddd, J=7.5, 10.0, 15.5 Hz, H-2), 2.99 (1H, dd, J=9.8, 10.8 Hz, H-16), 3.33 (1H, dd, J=3.3, 10.8 Hz, H-16), 5.12 (1H, d, J=18.0 Hz, H-15), 5.13 (1H, dd, J=10.0, 11.0 Hz, H-15), 5.91 (1H, ddd, J=1.0, 11.0, 18.0 Hz, H-14). ^{13}C-NMR ($CDCl_3$): Table 1.

***ent*-15-Hydroxy-labda-8(17),13*E*-diene-3-one (6)** Colorless needles from MeOH, mp 110—112 °C, $[\alpha]_D^{19}$ −20.1° (c=1.61, $CHCl_3$). IR (KBr) cm^{-1} : 3462 (OH), 1686 (C=O), 3080, 1643, 891, 783 (exocyclic double bond, vinyl). EI-MS m/z: 304 $[M]^+$, 289 $[M-CH_3]^+$, 286 $[M-H_2O]^+$, 271 $[M-CH_3-H_2O]^+$, 218 $[C_{15}H_{22}O]^+$, 123 $[C_8H_{11}O]^+$. Positive FAB-MS m/z: 304 $[M]^+$, 287 $[M+H-H_2O]^+$. HRFAB-MS m/z: Calcd for $C_{20}H_{32}O_2$ $(M)^+$: 304.2402. Found: 304.2414. ^{1}H-NMR ($CDCl_3$) δ: 0.87 (3H, s, H-20), 1.02 (3H, s, H-19), 1.09 (3H, s, H-18), 1.67 (3H, s, H-16), 1.85 (1H, ddd, J=7.0, 9.0, 14.0 Hz, H-7), 2.05 (1H, ddd, J=4.0, 6.5, 13.0 Hz, H-1α), 2.39 (1H, ddd, J=4.0, 6.0, 15.3 Hz, H-2), 2.44 (1H, ddd, J=2.5, 4.0, 13.5 Hz, H-12), 2.63 (1H, ddd, J=6.5, 12.5, 15.3 Hz, H-2), 4.15 (2H, d, J=7.0 Hz, H-15), 4.65 (1H, br d, J=1.3, 3.0 Hz, H-17), 4.92 (1H, dd, J=1.3, 3.0 Hz, H-17), 5.39 (1H, t, J=7.0 Hz, H-14). ^{13}C-NMR ($CDCl_3$): Table 1.

Reduction of 6 by $NaBH_4$ A solution of **6** (30 mg) and $NaBH_4$ (50 mg) in MeOH (2 ml) was allowed to stand for 30 min at room temperature. The reaction mixture was diluted with 2% $NaHCO_3$ and then extracted with chroloform. The organic layer was washed with water, dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by column chromatography to give **7** as colorless needles (28 mg).

7: mp 162—163 °C (lit.[8] 160.5—162 °C), $[\alpha]_D^{25}$ −24.6° (c=0.5, $CHCl_3$) (lit.[8] −27°). IR (KBr) cm^{-1}: 3200—3400 (OH), 3080, 1645, 891, 860 (*exo*-cyclic double bond, vinyl). EI-MS m/z: 306 $[M]^+$, 291 $[M-CH_3]^+$, 288 $[M-H_2O]^+$, 273 $[M-CH_3-H_2O]^+$, 255 $[273-H_2O]^+$, 187 $[C_{14}H_{19}]^+$, 175 $[C_{13}H_{19}]^+$, 135 $[C_{10}H_{15}]^+$, 107 $[C_8H_{11}]^+$. Positive FAB-MS m/z: 307 $[M+H]^+$, 289 $[M+H-H_2O]^+$. HRFAB-MS m/z: Calcd for $C_{20}H_{34}O_2$ $(M)^+$: 306.2404. Found: 306.2415. ^{1}H-NMR ($CDCl_3$) δ: 0.69 (3H, s, H-20), 0.77 (3H, s, H-19), 0.99 (3H, s, H-18), 1.67 (3H, s, H-16), 2.41 (1H, ddd, J=2.5, 4.0, 13.0 Hz, H-12), 3.25 (1H, dd, J=4.5, 11.5 Hz, H-3), 4.15 (2H, d, J=7.0 Hz, H-15), 4.53 (1H, dd, J=1.3, 3.0 Hz, H-17), 4.85 (1H, dd, J=1.3, 3.0 Hz, H-17), 5.38 (1H, tq, J=1.0, 7.0 Hz, H-14). ^{13}C-NMR ($CDCl_3$): Table 1.

Acknowledgment The authors are grateful to Miss K. Oda of this university for mass spectral measurements.

References

1) Ohigashi H., Katsumata H., Kawazu K., Koshimizu K., Mitsui T., *Agr. Biol. Chem.*, **38**, 1093 (1974).
2) Karalai C., Wiriyachita P., Opfekuch H. J., Hecker E., *Planta Medica*, **60**, 351 (1994); Wiriyachita P., Hajiwangoh H., Boonton P., Adolf W., Opfekuch H. J. O., Hecker E., *ibid.*, **51**, 368 (1985).
3) Granados A. G., Jiménez M. B., Matínez A., Parra A., Rivas F., Arias J. M., *Phytochemistry*, **37**, 741 (1994); Granados A. G., Martines A., Onorato M. E., *ibid.*, **24**, 517 (1985).
4) González A. G., Fraga B. M., Hernández M. G., Luis J. G., *Phytochemistry*, **12**, 1113 (1973).
5) Anthonsen T., Bergland G., *Acta Chem. Scand.*, **24**, 1860 (1970); Almovist S. O., Enzell C. R., Wehrli F. W., *ibid.*, **B29**, 695 (1975); Cheng Y. S., von Rudluff E., *Tetahedron Lett.*, **14**, 1131 (1970).
6) Enzell C. R., Ryhage R., *Arkiv för Kemi*, **23**, 367 (1964).
7) Forster P. G., Ghisaberti E. L., Jefferries P. R., *Phytochemistry*, **24**, 2991 (1985); Braun S., Breitenbach H., *Tetrahedron*, **33**, 145 (1977).
8) Mahazan J. R., Ferreia L. A. L., *An. Acad. Brasil Cienc.*, **43**, 611 (1971).