Sesquiterpenes from the Roots of *Cichorium endivia*

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Twelve new sesquiterpene and sesquiterpene glycosides were obtained along with eleven known compounds from the roots of *Cichorium endivia* (Compositae). The compounds were identified as guaianolide, germacrene-d and elemanolide, based on spectroscopic methods and chemical evidence.

Key words  *Cichorium endivia*; Compositae; sesquiterpene glycoside; cichorioside; β-d-fructofuranoside

*Chicorium endivia* (Compositae) is indigenous to India and cultivated as a vegetable. Sesquiterpenes and their glycosides in this plant have already been reported. Recently, sesquiterpenes in chicory roots exhibited several biological activities. Lactucin, lactucopicrin, and 11β,13-dihydrolactucin showed anaglycosic and sedative activities in mice, and lactucin and lactucopicrin revealed antimalarial activity. Moreover, 8-deoxylactucin demonstrated the inhibitory effect to DNA binding of nuclear factor (NF)κB and cyclooxygenase (COX)-2 protein expression. Accordingly, we also started a detailed investigation of the constituents of the roots of *C. endivia*, seeking other sesquiterpenes and sesquiterpene glycosides, in the course of our research into terpenes and sesquiterpene glycosides of Compositous plants.

A methanol extract from the dried roots of *C. endivia* was suspended in water. The suspension was extracted with diethyl ether and partitioned into an ether-soluble fraction and a water-soluble fraction. The residue of each fraction was respectively chromatographed on a silica gel column and semi-preparative HPLC thereby affording compounds (1—23). The structural determination of known compounds was made based on comparisons of the NMR spectral data with data in the literature. Compounds 1—5, 8, 9, 14, 18, 19 and 20 were known sesquiterpenes and sesquiterpene glycosides, and identified as 8-deoxylactucin (1), lactucin (2), lactucopicrin (3), jacquinelin (4), crepidiaside B (5), 11β,13-dihydrolactucin (8), cichorioside B (9), cichorioside A (10), cichorioside C (19) and hypochoroside A (20).

Cichorioside D (6) was suggested to have the molecular formula C_{27}H_{38}O_{13} based on high resolution (HR)-FAB-MS [m/z: 593.2203 [M + Na]⁺]. In the 1H- and 13C-NMR spectra of 6, two anomic proton and carbon signals were observed at δ 4.89, 5.49 and δ 104.3, 102.6, in addition to signals due to the aglycone, and this aglycone was identified as 4, according to the similarity of the 13C-NMR spectral data. The acid hydrolysis of 6 and the J value and/or chemical shifts of each anomic proton signal showed that the sugar moiety consisted of β-d-glucopyranose and α-L-rhamnopyranose. Comparison of the 13C-NMR spectral data of 6 with those of 5 indicated that β-d-glucopyranose was linked at the C-15 position of the aglycone, which was confirmed by irradiation at the anomeric proton of β-d-glucopyranose (δ 4.89) in a nuclear Overhauser effect (NOE) difference experiment. Moreover, NOEs were observed between the anomeric proton of α-L-rhamnopyranose (δ 5.49) and H-6 of β-d-glucopyranose (δ 4.59, 4.17). On the basis of the above results, compound 6 was determined to be jacinjelin 15-O-α-L-rhamnopyranosyl-(1→6)-β-d-glucopyranoside.

HR-FAB-MS showed the molecular formula of cichorioside E (7) to be C_{27}H_{36}O_{14}. The 1H- and 13C-NMR spectra indicated that 7 was also jacinjelin 15-O-diglucoside. From the results of acid hydrolysis and the NMR spectral data, the sugar sequence of 7 was found to consist of β-d-glucopyranose and β-d-fructofuranose. In a 1H-detected heteronuclear multiple-bond connectivity (HMBC) experiment on 7, a long-range correlation was exhibited between the H-6 signal of β-d-glucopyranose (δ 4.27) and the C-2 signal of β-d-fructofuranosyl (δ 105.8). Thus, compound 7 was determined to be jacinjelin 15-O-β-d-fructofuranosyl-(2→6)-β-d-glucopyranoside.

HR-FAB-MS revealed the molecular formula of cichorioside F (10) to be C_{23}H_{26}O_{10}. Comparison of the 1H- and 13C-NMR spectral data of 10 with those of 7, 8 and 9 and acid hydrolysis of 10 suggested that 10 was 11β,13-dihydrolactucin 15-O-β-d-fructofuranoside. The attached position of the β-d-fructofuranosyl group was identified by observation of a long-range correlation between the C-2 signal of β-d-fructofuranose (δ 106.1) and the H-15 signal of the aglycone (δ 5.45).

The molecular formulae of cichorioside G (11) and H (12) were suggested to be C_{23}H_{26}O_{10}, respectively, by HR-FAB-MS. Acid hydrolysis of 11 and 12 afforded β-d-glucose as each sugar moiety. Compound 11 was determined to be 11β,13-dihydrolactucin 8-O-β-d-glucopyranoside, on the basis of 1H- and 13C-NMR spectral data of 8 and deacymitracarin 8-O-β-d-glucopyranoside. The 13C-NMR spectral data of compound 12 were similar to those of 11, but the oxygenated methine signal was observed at δ 80.6. Because this methine carbon was correlated with H-8 (δ 2.40) and H-14 (δ 2.67) in the HMBC experiment, this signal was assignable to C-9 of the aglycone. Additionally, the anomeric proton signal of β-d-glucopyranoside (δ 4.86) showed a long-range correlation with this C-9 signal. In the NOE difference experiment, observation of an NOE between H-6 [δ 3.61 (1H, t, J = 10.0 Hz)] and H-8β [δ 1.46 (1H, t, J = 13.0 Hz)] suggested that H-8β and H-8α were pseudoaxial and pseudoequatorial, respectively. And the coupling constant of H-9 [δ 4.55 (1H, d, J = 5.5 Hz)] revealed that the orientation of H-9 was pseudoequatorial, namely, β. Thus, the β-d-glucopyranosyl group was attached at the α-side of C-9, and cichorioside H (12) was determined to be 9α-hydroxyjacquinel 9-O-β-d-glucopyranoside.

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were observed as follows: H-5 (experimental). Comparison of the 1H-NMR spectroscopic data for C 28H31NO9 by HR-FAB-MS [M+H] a. Based on the above evidence, the structure of the compound was elucidated to be C 21H28O10. From measurements of two dimensional (2D)-NMR (1H–1H shift correlation spectroscopy (COSY), 13C-detected heteronuclear multiple quantum coherency (HMQC) and HMBC), assignments of the proton and carbon signals were accomplished (see Table 1 and Experimental). Comparison of the 1H-NMR spectroscopic data of 13 with those of parthoxetine 17 indicated the presence of a β,α-unsaturated-γ-lactone in 16. The 13C-NMR spectrum of 16 showed two more olefin carbon signals (δ 152.0, 120.8), one acetyl carbon signal (δ 106.9), one oxygenated quaternary carbon signal (δ 73.9) and two oxygenated methylene carbon signals (δ 73.7, 60.2). On the other hand, in the 1H-NMR spectrum, two olefin proton signals [δ 6.82 (1H, brd, J=11.0 Hz) and 7.29 (1H, d J=11.0 Hz)] and two sets of oxygenated methylene proton signals [δ 4.10 (1H, d, J=8.5 Hz), 4.21 (1H, d J=8.5 Hz) and δ 4.77 (1H, d J=13.5 Hz), 4.94 (1H, d J=13.5 Hz)] were present. Regarding the above signals, the J CH8 were confirmed as follows in the HMBC experiment: δ 152.0 and 6.82, δ 120.8 and 7.29, δ 73.7 and 4.10, 4.21, and δ 60.2 and 4.77, 4.99. These signals were assignable (see Table 1 and Experimental).

Table 1. 13C-NMR Data of Compounds 6, 7, 10—13, 16, 17, and 21—23

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Measured in pyridine-d5 solution at 35°C. a, b) Signal assignments may be exchanged in each column. G1c: β-d-glucopyranose, Rha: α-L-ribofuranose, Fru: β-L-fructofuranos, Apio: β-d-apiofuranose.

copyranoside.

HR-FAB-MS showed the molecular formula of cichiorosiabei I (13) to be C21H22O10. From measurements of two dimensional (2D)-NMR (1H–1H shift correlation spectroscopy (COSY), 13C-detected heteronuclear multiple quantum coherency (HMQC) and HMBC), assignments of the proton and carbon signals were accomplished (see Table 1 and Experimental). Comparison of the 1H-NMR spectroscopic data of 13 with those of parthoxetine 17 indicated the presence of a β,α-unsaturated-γ-lactone in 16. The 13C-NMR spectrum of the aglycone moiety of 16, two methylene, two methine and one olefin carbon signal, 1H-11 (δ 3.47, 3.32) and C-11 (δ 68.3), C-4 (δ 55.8), H-4 (δ 2.81) and C-13 (δ 54.1); H-1 (δ 3.80) and C-13. Thus, the prolyl group was linked at the C-13 position, and 15 was elucidated to be 11β,13-dihydro-13-prolyl-lactocipirin.

HR-FAB-MS indicated the molecular formula of both cichiorosiabei J (16) and K (17) to be C21H22O10. In the 13C-NMR spectrum of the aglycone moiety, two methylene, two methine and one olefin carbon signal, were observed at δ 33.6, 27.6, 49.2, 48.3 and 149.6 together with an exomethylene carbon signal at δ 110.8. The 2D-NMR experiment suggested that these carbons composed a cyclopentane ring system with an exomethylene. Comparison of the 13C-NMR spectral data of 16 with those of parthoxetine 17 indicated the presence of a β,α-unsaturated-γ-lactone in 16. The 13C-NMR spectrum of 16 showed two more olefin carbon signals (δ 152.0, 120.8), one acetyl carbon signal (δ 106.9), one oxygenated quaternary carbon signal (δ 73.9) and two oxygenated methylene carbon signals (δ 73.7, 60.2). On the other hand, in the 1H-NMR spectrum, two olefin proton signals [δ 6.82 (1H, brd, J=11.0 Hz) and 7.29 (1H, d J=11.0 Hz)] and two sets of oxygenated methylene proton signals [δ 4.10 (1H, d, J=8.5 Hz), 4.21 (1H, d J=8.5 Hz) and δ 4.77 (1H, d J=13.5 Hz), 4.94 (1H, d J=13.5 Hz)] were present. Regarding the above signals, the J CH8 were confirmed as follows in the HMBC experiment: δ 152.0 and 6.82, δ 120.8 and 7.29, δ 73.7 and 4.10, 4.21, and δ 60.2 and 4.77, 4.99. These signals were assignable (see Table 1 and Experimental).
Experimental) based on the appearance of long-range correlations in the HMBC experiment. The $^{3}J_{HCOC}$ between H-14 ($\delta$ 4.21, 4.10) and C-6 ($\delta$ 106.9) suggested an ether linkage. Moreover, in the NOE difference experiment, NOEs were observed between H-1 ($\delta$ 3.01) and H-14 ($\delta$ 4.21); H-14 ($\delta$ 4.21) and H-5 ($\delta$ 3.78); H-14 ($\delta$ 4.10) and H-9 ($\delta$ 6.82); H-8 ($\delta$ 7.29) and H-13 ($\delta$ 4.77, 4.94); and H-13 and the anomeric proton of $\beta$-D-glucopyranose ($\delta$ 4.87). Thus, C-14 was present on the $\beta$-side of C-10, H-1 and H-5 retained $\beta$-orientations, and the sugar was linked at the C-13 position. On the basis of these results, the relative structure of 16 was determined as shown in Chart 1. The NMR spectral data of 17 were similar to those of 16. On comparison of the $^{13}$C-NMR spectral data of 17 with those of 16, one acetal carbon signal and one oxygenated quaternary carbon signal were also found at $\delta$ 110.5 and 88.3, and a hydroxymethyl carbon signal was present at $\delta$ 65.2, instead of the oxygenated methylene carbon signal. These carbon signals were assigned to C-6, C-10 and C-14, respectively, based on the result of the HMBC experiment. In consideration of the molecular formula and existence of the acetal carbon at C-6 and oxygenated quaternary carbon at C-10, 17 possessed an ether linkage between the C-6 and C-10 positions. Moreover, the presence of NOEs between H-9 ($\delta$ 6.82) and H-14 ($\delta$ 4.05, 4.11), H-14 and H-1 ($\delta$ 3.30), H-1 and H-5 ($\delta$ 3.88), and H-9 and H-2 ($\delta$ 1.59) suggested that C-14 was present on the $\alpha$-side of C-10, and H-1 and H-5 also retained $\beta$-orientations. Hence, the relative structure of 17 was identified as shown in Chart 1.

HR-FAB-MS showed the molecular formula of cichorioside L (21) to be C$_{26}$H$_{40}$O$_{13}$. The $^{13}$C-NMR spectrum of 21 was similar to that of 20, but signals due to one more sugar unit were observed, which was identified as apiose by acid hydrolysis. Acid hydrolysis of 21 also afforded 20 together with apiose, and comparison of the $^{13}$C-NMR spectral data of the sugar moiety in 21 with those of icariside D$_{18}$ and F$_{2}^{19}$.
suggested β-D-apiofuranose was linked at the C-6 position of β-D-glucopyranose of 20. This sugar sequence was supported by results of the NOE difference experiment. Namely, irradiation of the anomeric protons of 20 revealed NOEs to H-8, H-6, H-13 (δ 1.67), H-14 (δ 1.45); H-14 and H-15 (δ 1.86); and H-15 and H-6, suggesting a β-orientation for H-8, the existence of a C-13 methyl group on the β-side of C-11, and the C-14 and C-15 methyl groups being oriented above the plane of the medium ring. Hence, the structure of 22 was identified as shown in Chart 1.

Cichorioside N (23) possessed the molecular formula, C_{21}H_{32}O_{9}, according to HR-FAB-MS. The 13C-NMR spectrum of 23 showed four olefin carbon signals (δ 110.9, 111.6, 144.6, 148.2), three methyl carbon signals (δ 13.2, 15.0, 20.5), and one hydroxymethine carbon signal (δ 68.6) together with the signals due to the γ-lactone and β-D-glucopyranosyl groups. In the 1H-NMR spectrum, characteristic signals due to a vinyl group and one olefin proton were observed at δ 4.92 (1H, dd, J=17.5, 1.0 Hz), 4.98 (1H, dd, J=11.0, 1.0 Hz), 5.87 (1H, dd, J=17.5, 11.0 Hz) and 6.63 (1H, d, J=1.0 Hz), respectively, along with the methyl proton signals [δ 1.07 (3H, s), 1.63 (3H, d, J=7.0 Hz) and 1.86 (3H, d, J=1.0 Hz)]. Thus, this compound was suggested to be an elemenotype of sesquiterpene glucoside. The proton and carbon signals of 23 were assignable (see Table 1 and Experimental) based on the 2D-NMR measurements. The HMBC experiment indicated a long-range correlation between the anomeric proton signal of β-D-glucopyranosyl (δ 5.13) and the C-3 signal (δ 144.6). Furthermore, an aldehyde proton signal was observed at δ 9.92 in the 1H-NMR spectrum of 23a obtained by enzymatic hydrolysis of 23. These results indicated that 23 was an enol glucoside at C-3. The J value of H-5 signals showed that H-5 oriented to α. The observed NOE between H-3 (δ 6.63) and H-5α (δ 2.31) indicated an E-configuration of the double bond between the C-3 and C-4 positions. Additionally, NOEs between H-14 (δ 1.07) and H-6 (δ 4.42), H-8 (δ 4.19); H-5α and H-7 (δ 1.95); H-7 and H-13 (δ 1.63) suggested that H-6, H-7, and H-8 had β, α, and β-orientations, respectively, and the C-13 methyl group was present on the α-side of C-11. Thus, these results led us to conclude the structure of 23 shown in Chart 1.

In this investigation, twelve new sesquiterpene and sesquiterpene glycosides were obtained along with eleven known compounds. From the previous literatures, the major and bioactive sesquiterpene constituents in the roots of this plant were considered to be guaianolides such as lactucin, 8-deoxylactucine and lactucopicrin. However, because many kinds and a large amount of guaiane-type sesquiterpene glycosides were contained in the roots, we are interested in the biological activities of these glycosides as well as guaianolides. And this is the first report on the occurrence of an elemenotype sesquiterpene glucoside in Cichorium spp.

**Experimental**

**General Procedure** Optical rotation measurements were obtained using a JASCO DIP-1000 digital polarimeter. FAB-MS spectra were collected on a JEOL JMS-700 spectrometer in m-nitrobenzyl alcohol or glycerol, whereas both 1H- and 13C-NMR spectra were recorded in pyridine-d$_5$, solution at 35 °C on a JEOL JNM A-400 (400, 100.40 MHz, respectively) spectrometer. Chemical shifts are given in the δ (ppm) with tetramethylsilane (TMS) as an internal standard. UV spectra were measured with a JASCO V-630 spectrophotometer. A Hitachi G-3000 gas chromatograph was utilized for GC and JASCO 800 and 900 system instruments were employed for...
HPLC analyses.

**Plant Material** The roots of *C. endivia* (No. 3254M) were provided by Saladocos Co., Ltd. These dried materials were stored in a herbarium of the University of Shizuoka.

**Extraction and Isolation** The dried roots of *C. endivia* (3.1 kg) were extracted three times with MeOH under reflux. The extract was concentrated under reduced pressure and the residue was suspended in H$_2$O. This suspension was extracted with Et$_2$O. The Et$_2$O extract was evaporated to dryness, and the residue (58.5 g) was then chromatographed on a silica gel column with a CHCl$_3$-MeOH-H$_2$O (98:2:1) system to get four fractions (A (26.4 g), B (4.2 g), C (0.7 g)) and D (2.1 g). Using semi-preparative HPLC (Inertsil ODS-3 30 mm i.d.$	imes$50 mm and Capcellpak ODS-UC 150 3 mm i.d.$	imes$50 mm) YMC-ODS 20 mm i.d.$	imes$25 mm: 20—25% MeOH in water and 25—50% MeOH in water), fraction B (1.4 g) afforded compounds 1 (6 mg), 2 (20 mg), 3 (42 mg), 4 (22 mg), 5 (55 mg) and 14 (14 mg).

The H$_2$O layer of the MeOH extract was passed through a porous polymer gel (Mitsuishi Diaion HP-20) column with absorbed material being eluted with MeOH-H$_2$O (1:1), MeOH-H$_2$O (7:3) and MeOH, respectively. The MeOH-H$_2$O (1:1) fraction from the Diaion HP-20 column was dried in vacuo, and the residue (19.7 g) was subjected to silica gel column chromatography with a CHCl$_3$-MeOH-H$_2$O (90:10:1—90:10:16) system to obtain three fractions (A (1.8 g), B (1.6 g) and C (4.3 g)). Using semi-preparative HPLC (Inertsil ODS-3 30 mm i.d.$	imes$50 mm and Capcellpak ODS-UC 150 3 mm i.d.$	imes$50 mm) YMC-ODS 20 mm i.d.$	imes$25 mm: 7.5—20% MeOH in water and 25—40% MeOH in water), fractions B (0.5 g) and C (3.9 g) yielded compounds 1 (20 mg), 2 (6 mg), 5 (937 mg), 6 (8 mg), 7 (13 mg), 8 (60 mg), 10 (8 mg), 11 (25 mg), 12 (4 mg), 13 (41 mg), 15 (21 mg), 16 (3 mg), 17 (4 mg), 18 (72 mg), 19 (128 mg), 20 (64 mg), 21 (3 mg), 22 (9 mg) and 23 (25 mg).

**Cichorioside D (6): Amorphous powder.** $[\alpha]_{D}^{23} = -42^\circ$ (c=0.78, MeOH).

UV $\lambda_{max}^{nm}$ (MeOH) nm (log e): 256 (4.19), 261 (4.15), 353 (4.59) [M + Na]$^+$). HR-FAB-MS $m/z$: 593.2203 (Calcd for C$_{34}$H$_{43}$O$_{6}$Na$_{2}$: 593.2210).

**Cichorioside E (7): Amorphous powder.** $[\alpha]_{D}^{20} = -56.9^\circ$ (c=1.09, MeOH).

UV $\lambda_{max}^{nm}$ (MeOH) nm (log e): 256 (4.11). FAB-MS: m/z 609 [M + Na]$^+$.

**Cichorioside F (10): Amorphous powder.** $[\alpha]_{D}^{23} = 33^\circ$ (c=0.76, MeOH).

UV $\lambda_{max}^{nm}$ (MeOH) nm (log e): 256 (4.14). FAB-MS: m/z 463 [M + Na]$^+$.

**Cichorioside G (11): Amorphous powder.** $[\alpha]_{D}^{20} = -30^\circ$ (c=0.85, pyridine).

UV $\lambda_{max}^{nm}$ (log e): 257 (4.08). FAB-MS: m/z 441 [M + H]$^+$.

**Cichorioside H (12): Amorphous powder.** $[\alpha]_{D}^{23} = +62^\circ$ (c=0.39, MeOH).

UV $\lambda_{max}^{nm}$ (log e): 256 (4.20). FAB-MS: m/z 441 [M + H]$^+$.

**Cichorioside I (13): Amorphous powder.** $[\alpha]_{D}^{23} = -73^\circ$ (c=1.14, MeOH).

UV $\lambda_{max}^{nm}$ (log e): 258 (4.20). FAB-MS: m/z 463 [M + Na]$^+$.

**Cichorioside J (16): Amorphous powder.** $[\alpha]_{D}^{23} = -11^\circ$ (c=0.32, MeOH).

UV $\lambda_{max}^{nm}$ (log e): 277 (4.00). FAB-MS: m/z 461 [M + Na]$^+$.

**Cichorioside K (17): Amorphous powder.** $[\alpha]_{D}^{23} = +110^\circ$ (c=0.45, MeOH).

UV $\lambda_{max}^{nm}$ (log e): 263 (3.91). FAB-MS: m/z 461 [M + Na]$^+$.

**Cichorioside L (21): Amorphous powder.** $[\alpha]_{D}^{23} = +12^\circ$ (c=0.27, MeOH).

UV $\lambda_{max}^{nm}$ (log e): 583 [M + Na]$^+$. FAB-MS: m/z 583.2380 (Calcd for C$_{39}$H$_{48}$O$_{18}$Na$_{2}$: 583.2367).

**Cichorioside M (22): Amorphous powder.** $[\alpha]_{D}^{23} = -10^\circ$ (c=0.35, pyridine).

UV $\lambda_{max}^{nm}$ (log e): 257 (4.08). FAB-MS: m/z 441 [M + H]$^+$.

**Cichorioside N (23): Amorphous powder.** $[\alpha]_{D}^{23} = +40^\circ$ (c=0.35, pyridine).

UV $\lambda_{max}^{nm}$ (log e): 257 (4.08). FAB-MS: m/z 441 [M + H]$^+$.

**Cichorioside O (24): Amorphous powder.** $[\alpha]_{D}^{23} = -15^\circ$ (c=0.35, pyridine).

UV $\lambda_{max}^{nm}$ (log e): 257 (4.08). FAB-MS: m/z 441 [M + H]$^+$.

**Cichorioside P (25): Amorphous powder.** $[\alpha]_{D}^{23} = +78^\circ$ (c=0.35, pyridine).

UV $\lambda_{max}^{nm}$ (log e): 257 (4.08). FAB-MS: m/z 441 [M + H]$^+$.
3.99 (1H, brt, 8.0, H-2), 3.94 (1H, brt, 9.0, H-4), 3.54 (1H, dd, 11.0, 7.0, H-11), 3.42 (1H, brd, 11.0, 9.0, H-10), 2.49 (overlapping, H-2×2, 2H-9), 2.32 (1H, brt, 11.0, 9.5, H-7), 1.91 (3H, brs, H-15), 1.85 (3H, brs, H-14), 1.82 (overlapping, H-3).  

Chichoriosis M (22a): Amorphous powder. [α]D +23° (c = 0.23 MeOH). FAB-MS m/z: 267 [M+H] +. HR-FAB-MS m/z: 289.1416 (Calcd for [C11H10O8Na] +, 289.1409). 13C-NMR (pyridine-d5 at 35 °C) δ: 179.2 (C-12), 136.4 (C-4), 132.4 (C-10), 130.7 (C-5), 129.6 (C-1), 79.6 (C-8), 78.1 (C-3), 65.0 (C-6), 55.8 (C-7), 47.5 (C-9), 41.0 (C-11), 36.1 (C-2), 16.9 (C-14), 11.8, 11.6 (C-13, C-15). 1H-NMR (pyridine-d5 at 35 °C) δ: 6.62 (1H, brs, C-3-OH), 6.38 (1H, brd, 3.0, C-6-OH), 5.05 (overlapping, H-5), 5.04 (overlapping, H-1), 4.72 (1H, td, 10.0, 3.0, H-6), 4.69 (1H, td, 10.5, 2.0, H-8), 4.49 (1H, brd, 10.0, 6.0, H-3), 3.27 (1H, quin, 7.5, H-11), 2.93 (1H, brd, 12.5, 4.0, H-2), 2.51 (1H, td, 10.5, 2.5, H-5), 2.50 (1H, td, 10.5, 0.0, H-2), 2.43 (1H, dd, 12.5, 10.5, H-9), 1.83 (3H, d, 1.5, H-15), 1.45 (3H, d, 1.5, H-14).  

Chichoriosis N (23a): Amorphous powder. [α]D +37° (c = 0.23 MeOH). FAB-MS m/z: 289 [M+Na]+. HR-FAB-MS m/z: 298.1416 (Calcd for [C11H10O8Na] +, 298.1409). 13C-NMR (pyridine-d5 at 35 °C) δ: 178.9 (C-12), 147.6 (C-1), 113.3 (C-3), 78.6 (C-6), 68.3 (C-5), 59.5 (C-7), 51.8 (C-5), 50.8 (C-9), 45.3 (C-4), 43.0 (C-10), 41.2 (C-11), 19.0 (C-14), 16.7 (C-15), 14.9 (C-13). 1H-NMR (pyridine-d5 at 35 °C) δ: 9.92 (1H, d, 2.5, H-5), 9.42 (1H, d, 5.5, C-5-OH), 5.76 (1H, dd, 17.0, 11.0, H-1), 5.07 (1H, dd, 11.0, 1.0, H-2), 5.05 (1H, dd, 17.0, 1.0, H-2), 4.51 (1H, 1Hd, 1.1, H-6), 4.15 (1H, m, H-7), 2.86 (1H, dq, 12.0, 7.0, H-11), 2.58 (1H, q, 7.5, 2.5, H-4), 1.94 (overlapping, H-9), 1.92 (overlapping, H-5, H-7), 1.79 (1H, dd, 13.0, 1.0, H-9), 1.60 (3H, dq, 7.0, 1.0, H-11), 1.24 (3H, d, 7.5, 1.5, 1.15 (3H, s, H-14)).  

The residue of each H2O layer was reacted with n-cysteine methyl ester hydrochloride, hexamethyldisilazane and trimethylsilyl chloride in pyridine using the above procedures. n-Glucose was detected in all preparations.  

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References  


