Three New Polyyne (= Polyacetylene) Glucosides from the Edible Roots of *Codonopsis cordifolioidea*

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Three new linear C_{14} polyyne (= polyacetylene) glucosides, cordifolioidynes A – C (**1** – **3**), together with two known polyynes, lobetyol (**4**) and lobetyolin (**5**), and five known phenylpropanoids, *i.e.*, sinapinaldehyde (**6**), coniferaldehyde (**7**), coniferoside (**8**), sachaliside (**9**), and isoconiferin (**10**), were isolated from the roots of *Codonopsis cordifolioidea*. The structures of **1** – **3** were established from spectral evidences and by characterization of their hydrolysis products. Acid hydrolysis of **1** afforded the aglycone **1a**, while hydrolysis of **2** and **3** gave the cyclization products **2a** and **3a**, respectively. Compounds **4** – **10** were isolated from this plant for the first time. The antibacterial activity of compounds **1** – **5** were assessed against eight microbial strains by the agar dilution method, none of them exhibited antibacterial effects at concentrations up to 100 μg/ml.

Introduction. – The genus *Codonopsis* (Campanulaceae) is represented in China by 39 species. A number of *Codonopsis* species such as *C. pilosula* and *C. tangshen* are commonly used as herbal remedies due to their tonic effects [1]. In addition, the roots of some *Codonopsis* species including *C. cordifolioidea*, *C. bulleyana*, *C. micrantha*, and *C. subglobosa* are well-known vegetables in southwest China [2]. *C. cordifolioidea* Tsoong is a herbaceous plant spread in Yunnan, Tibet, and Sichuan Provinces [1]. Its roots, locally known as Choushen, have been used as a food in Yunnan Province since ancient times. Meanwhile, this species has become an important economic plant widely cultivated in several areas of Yunnan Province [3].

The tonic effects of *C. pilosula* have aroused broad interest in recent years, and some preliminary chemical, pharmacological, and clinical investigations have also been carried out on the other *Codonopsis* species with the general name of Choushen [4 – 9]. However, little is known about the constituents and the biological properties of *C. cordifolioidea*. During our investigation of the latter, the five polyynes (= polyacetylenes) **1** – **5**[1]), including the three new compounds **1** – **3**, and the five phenylpropanoids **6** – **10** were isolated (*Fig. 1*). In this paper, we describe the isolation and structure elucidation of these substances, and the assessment of the antibacterial properties of compounds **1** – **5**.

[1]) Arbitrary atom numbering; for systematic names, see *Exper. Part*.

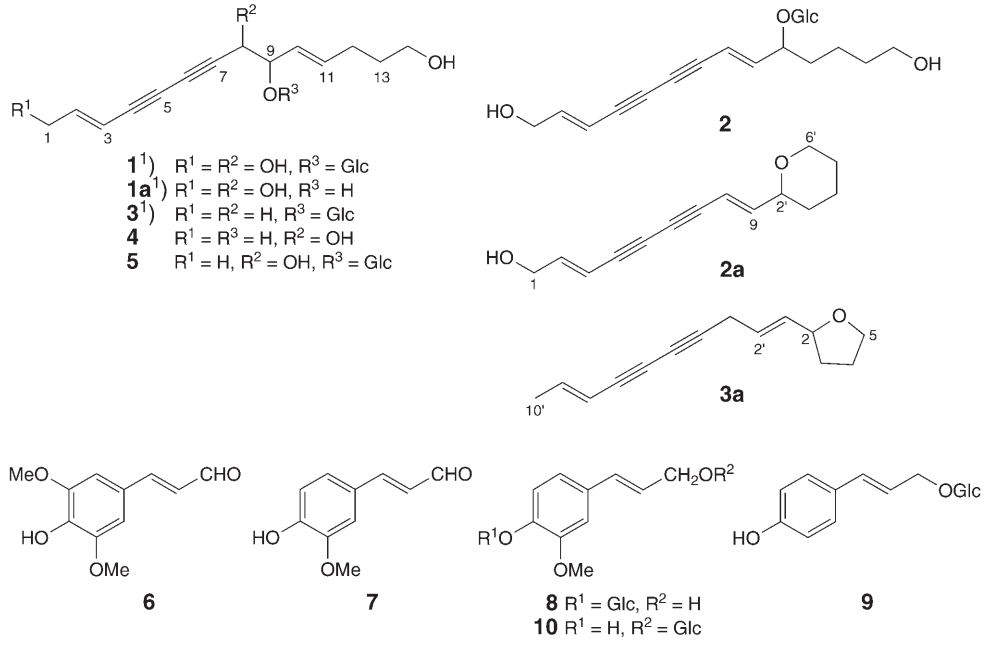

Fig. 1. *Structures of compounds* **1**–**10** *isolated from* C. cordifolioidea

Results and Discussion. – Compound **1** was obtained as a yellowish syrup from the BuOH extract. The molecular formula of **1** was determined to be $C_{20}H_{28}O_9$ on the basis of the HR-ESI-MS (*m/z* at 411.1675 ($[M-H]^-$)). The UV (284, 267, 254, and 241 nm) and IR absorptions (2234 and 1640 cm^{-1}) indicated the presence of two C≡C bonds and one C=C bond in conjugation [10]. Acid hydrolysis of **1** gave D-glucose and aglycone **1a**. The absolute configuration of glucose was assigned as D from the positive optical rotation. The vicinal diol group of **1a** was concluded to be in the *threo*-form by the coupling constants ($J = 6.2$ Hz) of H–C(8) and H–C(9)[1]) [11][12]. Further NMR data (*Table*) and the HMBC results (*Fig. 2*) allowed to assign the structure of **1a** as *threo*-tetradeca-2,10-diene-4,6-diyne-1,8,9,14-tetrol[1]), and **1** was assigned as *threo*-9-(*β*-D-glucopyranosyloxy)tetradeca-2,10-diene-4,6-diyne-1,8,14-triol[1]) and named cordifolioidyne A. Both compounds **1** and its aglycone **1a** are new compounds.

The ^{1}H-NMR spectrum of **1** exhibited a sugar moiety with an anomeric proton at δ(H) 4.31 (*d*, $J =$ 7.5 Hz), together with four CH_2 groups, two O-bearing CH groups at δ(H) 4.44 (*d*, $J = 6.2$ Hz) and 4.27 (br. *dd*, $J = 8.0$, 6.2 Hz), and two pairs of olefinic protons (δ(H) 6.41, 5.92, 5.80, and 5.46). The ^{13}C-NMR spectrum showed the presence of a sugar moiety corresponding to a glucopyranose, together with fourteen signals ascribable to four alkyne C-atoms at δ(C) 77.5, 74.2, 71.0, and 81.8, four oxygenated C-atoms at δ(C) 62.6, 66.5, 81.7, and 62.2, two high-field CH_2 groups at δ(C) 29.7 and 32.9, and four olefinic C-atoms at δ(C) 148.3, 108.4, 126.5, and 138.9. The above data suggested **1** to be a C_{14} polyynyl glucoside. The ^{1}H,^{1}H-COSY plot showed two spin systems in the backbone, which were CH_2(1) to H–C(3) and H–C(8) to CH_2(14). The connection of C(3) to C(8) *via* the conjugated diynes was deduced from the observed HMBC (*Fig. 2*) CH_2(1)/C(4) and C(5), and H–C(8)/C(5) and C(6). Note that HMBC over three bonds were detected, due to the existence of a conjugated system. A similar phenomenon was also

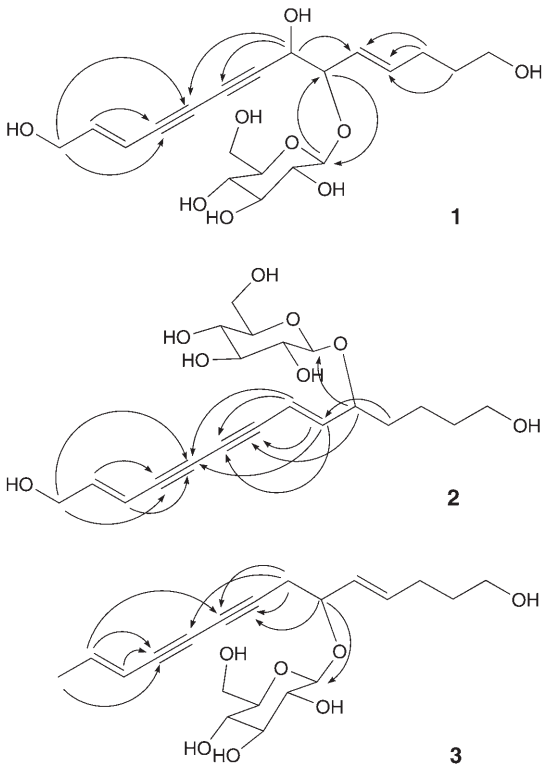

Fig. 2. *Selected HMBC data for compounds* **1**–**3**

observed in the structure of callyberyne A, a C_{21} polyyne from a marine sponge [13]. The attachment of the glucose moiety at C(9) was evident from the low-field chemical shift of C(9) at δ(C) 81.7. This was further confirmed by the HMBC H–C(9)/C(1′) and H–C(1′)/C(9). The anomeric configuration of the D-glucose was determined to be β-D from the coupling constant ($J = 7.5$ Hz) of anomeric proton. The two C=C bonds were both assigned as *trans* from the large vicinal coupling constants (^3J(H–C(2), H–C(3)) = 16.0 Hz, and ^3J(H–C(10), H–C(11)) = 15.5 Hz).

Compound **2** was obtained as yellowish crystals from the BuOH extract. Its molecular formula was assigned as $C_{20}H_{28}O_8$ by means of HR-ESI-MS (*m/z* at 461.0720 ([M + Cl]$^-$)). The ^{13}C-NMR spectrum of **2** (*Table*) showed twenty signals similar to those of compound **1**, suggesting **2** to be also a C_{14} polyynyl glucoside. The sugar moiety was a D-glucose as deduced from its typical chemical shifts and positive sign of optical rotation after acid hydrolysis. The latter did not yield the aglycone but the cyclization and dehydration product **2a**, which was previously isolated from the roots of *Campanula glomerata* L [14]. Therefore, the structure of **2** was elucidated as 10-(β-D-glucopyranosyloxy)tetradeca-2,8-diene-4,6-diyne-1,14-diol[1]) and named cordifolioidyne B.

The ^{1}H,^{1}H-COSY plot disclosed the presence of two spin systems, which were H–C(1) to H–C(3) and H–C(8) to H–C(14), resp. The HMBC (*Fig. 2*) H–C(1)/C(4) and C(5), H–C(2)/C(4), H–C(8)/

Table. *[1]H- and [13]C-NMR Data* (400 and 100 MHz, resp.; CD_3OD) *of Compounds* **1**–**3**. δ in ppm, J in Hz.

	1[1])		**2**[1])		**3**[1])	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
CH_2(1) or Me(1)	4.14 (*dd*, *J* = 4.4, 2.0)	62.6	4.14 (*dd*, *J* = 4.7, 2.5)	62.6	1.76 (*dd*, *J* = 6.9, 1.6)	18.8
H–C(2)	6.41 (*dt*, *J* = 16.0, 4.4)	148.3	6.40 (*dt*, *J* = 16.3, 4.7)	147.9	6.23 (*dq*, *J* = 16.0, 6.9)	144.4
H–C(3)	5.80 (br. *d*, *J* = 16.0)	108.4	5.85 (br. *d*, *J* = 16.3)	108.7	5.50 (*dd*, *J* = 16.0, 1.6)	110.6
C(4)		77.5		80.7		74.8
C(5)		74.2		78.1		73.3
C(6)		71.0		74.6		67.6
C(7)		81.8		80.1		80.3
H–C(8) or CH_2(8)	4.44 (*d*, *J* = 6.2)	66.5	5.97 (*d*, *J* = 16.0)	111.9	2.66 (*dd*, *J* = 16.8, 4.0), 2.55 (*dd*, *J* = 16.8, 7.6)	27.6
H–C(9)	4.27 (br. *dd*, *J* = 8.0, 6.2)	81.7	6.19 (*dd*, *J* = 16.0, 6.9)	148.0	4.42 (*ddd*, *J* = 8.4, 7.6, 4.0)	77.8
H–C(10)	5.46 (*dd*, *J* = 15.5, 8.0)	126.5	4.38 (*dt*, *J* = 13.0, 6.9)	78.1	5.38 (br. *dd*, *J* = 15.6, 8.4)	129.5
H–C(11) or CH_2(11)	5.92 (*dt*, *J* = 15.5, 6.8)	138.9	1.60–1.68 (*m*), 1.53–1.59 (*m*)	36.1	5.88 (*dt*, *J* = 15.6, 5.2)	137.3
CH_2(12)	2.16–2.22 (*m*)	29.7	1.40–1.47 (*m*)	22.5	2.21 (*dt*, *J* = 11.2, 5.2)	29.5
CH_2(13)	1.62–1.69 (*m*)	32.9	1.48–1.59 (*m*)	33.3	1.58–1.65 (*m*)	32.9
CH_2(14)	3.58 (*t*, *J* = 6.4)	62.2	3.54 (*t*, *J* = 6.3)	62.8	3.56 (*t*, *J* = 6.5)	62.1
H–C(1′)	4.31 (*d*, *J* = 7.5)	100.6	4.23 (*d*, *J* = 7.3)	101.4	4.30 (*d*, *J* = 7.8)	100.6
H–C(2′)	3.26–3.33 (*m*)	74.8	3.19–3.34 (*m*)	75.1	3.16–3.31 (*m*)	74.8
H–C(3′)	3.26–3.33 (*m*)	78.0	3.19–3.34 (*m*)	78.1	3.16–3.31 (*m*)	78.0
H–C(4′)	3.26–3.33 (*m*)	71.6	3.19–3.34 (*m*)	71.7	3.16–3.31 (*m*)	71.5
H–C(5′)	3.26–3.33 (*m*)	77.9	3.19–3.34 (*m*)	77.9	3.16–3.31 (*m*)	77.3
CH_2(6′)	3.85 (*dd*, *J* = 12.0, 6.1), 3.66 (*dd*, *J* = 12.0, 6.0)	62.6	3.85 (*dd*, *J* = 12.0, 2.0), 3.64 (*dd*, *J* = 12.0, 6.0)	62.7	3.84 (*dd*, *J* = 13.6, 1.8), 3.65 (*dd*, *J* = 13.6, 5.8)	62.6

C(5) and C(6), H–C(9)/C(5) and C(7), and H–C(10)/C(7) suggested that C(3) was connected with C(8) *via* a diyne group. The structure of aglycone of **2** was a known compound, which has been isolated from *Campamula medium* L [15]. The HMBC H–C(10)/C(1′) placed the glucose at C(10), this was further supported by the down-field shift of C(10) at δ(C) 78.1. The anomeric configuration was deduced to be β-D by the large coupling constant (J = 7.3 Hz) of H–C(1′). The two *trans* C=C bonds were deduced by large vicinal coupling constants (J(H–C(2),H–C(3)) = 16.3 Hz; J(H–C(8),H–C(9)) = 16.0 Hz).

Compound **3** was also obtained as a yellowish syrup from the BuOH extract. The molecular formula of **3** was assigned as $C_{20}H_{28}O_7$ by HR-ESI-MS (*m*/*z* at 415.1524 $[M + Cl]^-$). Acid hydrolysis of **3** gave D-glucose and **3a**. The resemblance of ^{13}C-NMR spectra (*Table*) of **1** and **3** suggested they are analogues. The structure of **3** was elucidated as 9-(β-D-glucopyranosyloxy)tetradeca-2,10-diene-4,6-diyn-14-diol[1]) and named cordifolioidyne C.

The main difference of **1** and **3** was that a Me group at δ(C) 18.8 and a CH_2 group at δ(C) 27.6 in the structure of **3** were oxygenated in **1**. The low-field chemical shift of δ(C) 77.8 of **3** indicated that the glucose moiety was positioned at C(9), which was also evidenced by the HMBC H–C(9)/C(1′). The anomeric configuration was β-D due to the large coupling constant (J = 7.8 Hz) of H–C(1′).

The absolute configuration of the aglycones of **1**–**3** was not established.

The seven known compounds were identified as lobetyol (**4**) [16], lobetyolin (**5**) [16], sinapinaldehyde (**6**) [17], coniferaldehyde (**7**) [17], coniferoside (**8**) [18], sachaliside (**9**) [18], and isoconiferin (**10**) [19] by comparison of their spectroscopic data (^{1}H- and ^{13}C-NMR and EI-MS) with those reported in the literature.

The antimicrobial properties of compounds **1**–**5** were tested against eight microbial strains. None of them showed inhibitory effects against the tested bacteria at concentrations up to 100 μg/ml (data not shown).

Polyynes are reported for the first time from *C. cordifolioidea*. However, this type of compounds has been previously found in *C. pilosula* and *C. tangshen* [20]. Polyynes have also been evidenced in several other genera of the family Campanulaceae, including *Campanula*, *Lobelia*, *Platycodon*, *Trachelium*, and *Wahlenbergia* [16]. As to the known phenylpropanoids **6**–**10**, they are also isolated for the first time from the genus *Codonopsis*.

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Experimental Part

General. Column chromatography (CC) and vacuum liquid chromatography (VLC): silica gel (200–300 mesh and 10–40 μm; *Qingdao Marine Chemical Factory*, China); C_{18} reversed-phase silica gel (40–63 μm; *Daiso Co.*, Japan); *Sephadex LH-20* (*Amersham Pharmacia Biotech*, Sweden); *MCI* gel *CHP 20P* (75–150 μm; *Mitsubishikasei*, Tokyo, Japan). TLC: silica gel GF_{254} (10–40 μm; *Qingdao Marine Chemical Factory*, China). All solvents were distilled before use. Melting point: *XRC-1* micro-melting-point apparatus; uncorrected. Optical rotations: *Jasco 20C* digital polarimeter. UV Spectra: *Shimadzu UV-2401PC* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Bruker Tensor-27-FT-IR* spectrometer; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker AM-400* spectrometer; chemical shifts δ in ppm rel. to Me_4Si as an internal reference, coupling constant J in Hz. ^{1}H,^{1}H-COSY, HMQC, and HMBC: *DRX-500* spectrometer. EI-MS and FAB-MS: *VG Auto-Spec-3000* spectrometer; for FAB-MS, glycerol or 3-nitrobenzyl alcohol (NBA) was used as matrix; in *m*/*z*. HR-ESI-MS: *API QSTAR-Pulsar-1* spectrometer.

Plant Material. The roots of *C. cordifolioidea* were collected from the Yiliang area of Yunnan Province, P. R. China, in November 2006, and identified by Prof. *Xi-Wen Li*, Kunming Institute of Botany, Chinese Academy of Sciences, P. R. China. A voucher specimen (No. CHYX0390) was deposited at the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany.

Extraction and Isolation. Dried and powdered roots of *C. cordifolioidea* (13 kg) were extracted with 95% EtOH (3 × 40 l, 2 h each) under reflux. The combined extracts were concentrated and partitioned sequentially with petroleum ether (3 × 1500 ml), AcOEt (3 × 1500 ml), and BuOH (3 × 1000 ml). The AcOEt extract (100 g) was subjected to CC (SiO_2, $CHCl_3$/MeOH 99:1 → 50:50): *Fractions 1–7. Fr. 2* (10 g) was subjected to CC (*Sephadex LH-20*, $CHCl_3$/MeOH 6:4): *Fr. 2.1–2.5. Fr. 2.3* (2.3 g) was further separated by VLC (petroleum ether/AcOEt 30:1 → 2:1): **7** (50 mg). *Fr. 2.4* (1.9 g) was purified by VLC (petroleum ether/AcOEt 20:1 → 5:1): **6** (50 mg). *Fr. 5* (12 g) was fractionated by CC (SiO_2, $CHCl_3$/Me_2CO 9:1 → 1:1): *Fr. 5.1–5.4.* Repeated CC of *Fr. 5.3* (4.7 g) with *Sephadex LH-20* ($CHCl_3$/MeOH 6:4), SiO_2, and C_{18} (MeOH/H_2O 50:50 → 100:0) gave **4** (20 mg). The BuOH-soluble extract (60 g) was fractionated by CC (SiO_2, $CHCl_3$/MeOH 95:5 → 30:70): *Fractions A–D. Fr. A* (12 g) was subjected to CC (*MCI gel CHP 20P*, MeOH/H_2O 50:50 → 100:0): *Fr. A.1–A.4. Fr. A.1* (4.5 g) was subjected to CC (*Sephadex LH-20*, MeOH): *Fr. A.1.1. Fr. A.1.1* (2.8 g) was purified by VLC (SiO_2) and CC (C_{18}): **1** (160 mg), **2** (80 mg), and **10** (30 mg). *Fr. A.2* (2.3 g) was subjected to CC (*Sephadex LH-20*, MeOH): *Fr. A.2.1–A.2.3. Fr. A.2.2* (1.2 g) was subjected to VLC (SiO_2) and CC (C_{18}), MeOH/H_2O 50:50 → 90:10): **9**

(60 mg). *Fr. B* (22 g) was submitted to CC (SiO_2, $CHCl_3$/MeOH 15:1 → 3:1): *Fr. B.1–B.3. Fr. B.2.* (7 g) was subjected to CC (*MCI gel CHP 20P*, MeOH/H_2O 50:50 → 90:10): *Fr. B.2.1–B.2.3. Frs. B.2.1* and *B.2.2* were subjected to repeated VLC (SiO_2) and CC (C_{18}): **3** (50 mg), **5** (1.5 g), and **8** (60 mg).

Acid Hydrolysis. A soln. of **1** (29 mg) in 1N HCl/MeOH 2:1 (2 ml) was heated at 90° for 6 h. The mixture was neutralized with 1N NaOH and extracted with AcOEt. The aq. layer was evaporated and subjected to CC (*Sephadex LH-20*, MeOH) followed by VLC (SiO_2, 10–40 μm), $CHCl_3$/MeOH/H_2O 3:1:0.1): D-glucose (2 mg). The AcOEt extract was subjected to CC (SiO_2, 10–40 μm), $CHCl_3$/Me_2CO 30:1 → 10:1): **1a** (4 mg).

As described for **1**, **2**, or **3** (13 mg each) was subjected to acid hydrolysis, to afford D-glucose, and **2a** (2 mg), or **3a** (1 mg), resp.

Antibacterial Assay. The antibacterial properties of polyynes **1**–**5** were tested by the agar dilution method [21]. The bacterial strains employed were *Staphylococcus aureus* CMCC26001 (CMCC, National Center for Medical Culture Collections, Beijing, P. R. China), *Escherichia coli* CMCC44103, *Salmonella typhimurium* CMCC80087, and *Shigella flexneri* CMCC51335, besides the clinical isolates *Staphylococcus epidermidis*, *Bacillus subtilis*, *Salmonella paratyphi*-A, and *Salmonella paratyphi*-B. For agar dilution tests, the compounds (2 mg each) were first dissolved in 0.2 ml of DMSO; serial dilutions of test compounds were prepared in *Müller–Hinton* agar (MHA) medium as described by the CLSI (Clinical and Laboratory Standards Institute, Wayne, PA, USA) [22]. Cefradine and gentamycin were used as reference standards to control the sensitivity of the test strains. Plates containing only MHA medium and 1% DMSO in MHA medium served as negative and solvent controls. Tests were performed in triplicate and repeated once.

threo-*9-(β-*D*-Glucopyranosyloxy)tetradeca-2,10-diene-4,6-diyne-1,8,14-triol* (= rel-*(1*R*,2*R*,7*E*)-2,9-Dihydroxy-1-[(1*E*)-5-hydroxypent-1-en-1-yl)non-7-ene-3,5-diyn-1-yl β-*D*-Glucopyranoside*; **1**): Yellowish syrup. $[\alpha]_D^{24.4} = -43.33$ ($c = 0.10$, MeOH). UV ($CHCl_3$): 284 (4.07), 267 (4.19), 254 (4.04), 241 (3.79). IR (KBr): 3442, 2925, 2234, 1640, 1160, 1078, 1044. ^{1}H- and ^{13}C-NMR: *Table.* FAB-MS (neg.): 503 ($[M +$ glycerol $- H]^-$), 411 ($[M - H]^-$). HR-ESI-MS: 411.1675 ($[M - H]^-$, $C_{20}H_{27}O_9^-$; calc. 411.1655).

threo-*Tetradeca-2,10-diene-4,6-diyne-1,8,9,14-tetrol* (= rel-*(4*E*,6*R*,7*R*,12*E*)-Tetradeca-4,12-diene-8,10-diyne-1,6,7,14-tetrol*; **1a**): Yellowish syrup. ^{1}H-NMR (CD_3OD, 500 MHz): 6.40 (*dt*, $J = 16.0$, 4.7, H–C(2)); 5.92–5.75 (*m*, H–C(11)); 5.82 (br. *d*, $J = 16.0$, H–C(3)), 5.58 (*dd*, $J = 15.4$, 6.9, H–C(10)); 4.22 (*d*, $J = 6.7$, H–C(8)); 4.14–4.13 (*m*, CH_2(1)); 3.98 (*dd*, $J = 15.4$, 6.7, H–C(9)); 3.57 (*t*, $J = 6.5$, CH_2(14)); 2.17–2.12 (*m*, CH_2(12)); 1.66–1.61 (*m*, CH_2(13)). FAB-MS (pos.): 435 ($[M + 2$ glycerol $+ H]^+$), 343 ($[M +$ glycerol $+ H]^+$).

*10-(β-*D*-Glucopyranosyloxy)tetradeca-2,8-diene-4,6-diyne-1,14-diol* (= *(2*E*,8*E*)-10-Hydroxy-1-(4-hydroxybutyl)deca-2,8-diene-4,6-diyn-1-yl β-*D*-Glucopyranoside*; **2**): Yellowish crystals. M.p. 127–128°. $[\alpha]_D^{24.6} = -151.67$ ($c = 0.10$, MeOH). UV (MeOH): 313 (8.44), 294 (4.52), 277 (4.35), 262 (4.08), 247 (4.52), 237 (4.64), 230 (4.64). IR (KBr): 3419, 2932, 2874, 2850, 2207, 2130, 1657, 1628, 1463, 1366, 1162, 1076, 1032, 988, 960. ^{1}H- and ^{13}C-NMR: *Table.* FAB-MS (neg.): 791 ($[2M - H]^-$), 487 ($[M +$ glycerol $- H]^-$), 395 ($[M - H]^-$), 233 ($[M - H -$ Glc$]^-$). HR-ESI-MS: 431.1466 ($[M + Cl]^-$, $C_{20}H_{28}ClO_8^-$; calc. 431.1472).

*(2*E*,8*E*)-9-(Tetrahydro-2*H*-pyran-2-yl)nona-2,8-diene-4,6-diyn-1-ol* (**2a**): Yellowish solid. ^{1}H-NMR ($CDCl_3$, 500 MHz): 6.40 (*dt*, $J = 16.0$, 5.0, H–C(2)); 6.26 (*dd*, $J = 16.0$, 4.8, H–C(9)); 5.85 (br. *d*, $J = 16.0$, H–C(3)); 5.78 (br. *d*, $J = 16.0$, H–C(8)); 4.26 (br. *d*-like, CH_2(1)); 4.01 (br. *d*, $J = 11.4$, H_a–C(6′)); 3.86 (*m*, H–C(2′)); 3.46 (*t*, $J = 9.2$, H_b–C(6′)); 1.67–1.64 (*m*, CH_2(4′)); 1.56–1.47 (*m*, CH_2(5′)); 1.37–1.29 (*m*, C(3′)). FAB-MS (pos.): 510 ($[2M + 2K]^+$), 471 ($[2M + K]^+$), 255 ($[M + K]^+$).

*9-(β-*D*-Glucopyranosyloxy)tetradeca-2,10-diene-4,6-diyn-14-ol* (= *(7*E*)-1-[(1*E*)-5-Hydroxypent-1-en-1-yl]non-7-ene-3,5-diyn-1-yl β-*D*-Glucopyranoside*; **3**): Yellowish syrup. $[\alpha]_D^{24.9} = -16.67$ ($c = 0.10$, MeOH). UV (MeOH): 282 (4.10), 266 (4.21), 252 (4.07), 239 (3.83). IR (KBr): 3418, 2932, 2882, 2234, 2140, 1640, 1630, 1158, 1077, 1045, 1024. ^{1}H- and ^{13}C-NMR: *Table.* FAB-MS (neg.): 759 ($[2M - H]^-$), 471 ($[M +$ glycerol $- H]^-$). HR-ESI-MS: 415.1524 ($[M + Cl]^-$, $C_{20}H_{28}ClO_7^-$; calc. 415.1523).

*2-[(1*E*,8*E*)-Deca-1,8-diene-4,6-diyn-1-yl]tetrahydrofuran* (**3a**): Yellowish solid. ^{1}H-NMR ($CDCl_3$, 500 MHz): 6.29 (*dq*, $J = 15.6$, 6.8, H–C(9′)); 5.75 (br. *d*, $J = 15.0$, 7.0, H–C(1′)); 5.62 (*dt*, $J = 15.0$, 5.1, H–C(2′)); 5.50 (br. *d*, $J = 15.6$, H–C(8′)); 4.29 (*dt*, $J = 7.0$, 6.5, H–C(2)); 3.89 (*dt*, $J = 7.5$, 7.0, H_a–C(5)); 3.76 (*dt*, $J = 7.5$, 6.5, H_b–C(5)); 3.07 (*d*, $J = 5.1$, CH_2(3′)); 2.06–2.00 (*m*, H_a–C(3)); 1.96–1.85 (*m*,

CH_2(4)); 1.79 (d, J = 6.8, Me(10′)); 1.65–1.56 (m, H_b–C(3)). FAB-MS (pos.): 423 ($[2M + Na]^+$). FAB-MS (neg.): 353 ($[M + NBA]^-$).

REFERENCES

[1] D. Y. Hong, Y. S. Lian, L. D. Shen, 'Flora of China', Science Publishing House, Beijing, 1983, Vol. 73, p. 32.
[2] Yunnan Corporation of Materia Medica, 'Yunnan Zhongyao Ziyuan Minglu', Science Publishing House, Beijing, 1993, p. 544.
[3] Z. J. Chen, Q. H. Wei, J. Y. Zhou, *Yunnan J. Tradit. Chin. Med. Mater*. **2006**, *27*, 49.
[4] S. Z. Li, G. Z. Ye, *J. Yunnan College Tradit. Chin. Med.* **1994**, *17*, 17.
[5] Q. F. Duan, H. Zhao, Y. Q. Wang, *J. Yunnan Univ. Nationalities (Nat. Sci. Ed.)* **2003**, *12*, 39.
[6] Q. F. Duan, J. S. Zhao, *J. Yunnan Univ. Nationalities (Nat. Sci. Ed.)* **2002**, *11*, 159.
[7] Y. Q. Shang, *J. Yunnan Tradit. Chin. Med*. **2001**, *24*, 15.
[8] Y. L. Li, J. J. Fu, L. Shi, *Acad. J. Kunming Med. College* **1996**, *17*, 57.
[9] Y. G. Chen, Y. Zhu, J. X. Wei, N. J. Liang, *Acad. J. Kunming Med. College* **1994**, *15*, 70.
[10] D. G. Crosby, N. Aharonson, *Tetrahedron* **1967**, *23*, 465.
[11] M. S. Lehner, A. Steigel, R. Bauer, *Phytochemistry* **1997**, *46*, 1023.
[12] H.-J. Jung, B.-S. Min, J.-Y. Park, Y.-H. Kim, H.-K. Lee, K.-H. Bae, *J. Nat. Prod.* **2002**, *65*, 897.
[13] A. Umeyama, C. Nagano, S. Arihara, *J. Nat. Prod.* **1997**, *60*, 131.
[14] R. K. Bentley, J. K. Jenkins, E. R. H. Jones, V. Thaller, *J. Chem. Soc. C* **1969**, 830.
[15] S. O. Badanyan, R. K. Bentley, J. K. Jenkins, E. R. H. Jones, V. Thaller, *J. Chem. Soc., Perkin Trans. 1* **1973**, 145.
[16] K. Ishimaru, M. Osabe, L. Yan, T. Fujioka, K. Mihashi, N. Tanaka, *Phytochemistry* **2003**, *62*, 643.
[17] Y. X. Cheng, J. Zhou, Z. T. Ding, *Acta Bot. Yunn.* **2000**, *22*, 365.
[18] A. Tolonen, M. Pakonen, A. Hohtola, J. Jalonen, *Chem. Pharm. Bull*. **2003**, *51*, 467.
[19] T. Nakanishi, N. Iida, Y. Inatomi, H. Murata, A. Inada, J. Murata, F. A. Lang, M. Iinuma, T. Tanaka, *Heterocycles* **2004**, *63*, 2573.
[20] G. Han, X. He, J. Yang, M. Yuda, R. Kasai, K. Otani, O. Tanaka, *Zhongguo Zhongyao Zazhi* **1990**, *15*, 105.
[21] C. N. Baker, S. N. Banerjee, F. C. Tenover, *J. Clin. Microbiol.* **1994**, *32*, 1261.
[22] Clinical and Laboratory Standards Institute, 'Methods for Dilution Antimicrobial Susceptibility Tests for Bacteria That Grow Aerobically, Approved Standards', 7th edn. (M7-A7), Wayne, 2006.

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