Two New Sesquiterpene Lactones and a Triterpene Glycoside from *Cichorium glandulosum*

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Two new sesquiterpene lactones, namely 8-*O*-methylsenecioylaustricin (**1**) and epi-8α-angeloyloxycichoralexin (**2**), as well as a new triterpene glycoside (taraxasterol-3-*O*-β-D-glucoside, **3**), together with the three known sesquiterpene lactones lactucin (**4**), lactucopicrin (**5**), and 11β,13-dihydrolactucin (**6**), were isolated from the stems of *Cichorium glandulosum* BOISS. ET HUET. The chemical structures were elucidated on the basis of spectroscopic methods.

Introduction. – The genus *Cichorium* L., belonging to the family Compositae, comprises over six species with major distribution areas in Europe and Asia. It is cultivated in countries such as the UK, Belgium, France, the Netherlands, Germany, South Africa, the USA, and India [1]. The extracts of these plant species possess diverse biological activities, such as cytotoxic, anaesthetic, anti-inflammatory, and antimicrobial effects, and have been used for a long time in the traditional medicines of China and India [2]. Other activities such as antihepatotoxic and antidiabetic were reported [3], and some sesquiterpene lactones from the genus *Cichorium* L. have been shown to possess cytotoxic or growth inhibitory activities on tumor cell lines and differentiation-inducing effect on human leukemia cells [4][5].

Cichorium glandulosum BOISS. ET HUET. (Compositae, Asteraceae) is well known in Uyghur folk medicine as a cholagogic and diuretic agent to improve the appetite, to increase digestion, and to cure liver diseases, *etc.* [1]. Previously, we reported on the chemical composition of the seeds of *C. glandulosum* [6–8], in which coumarins, flavonoids, and other phenolic compounds were dominant, and from the roots, three sesquiterpene lactones were separated by HSCCC [9]. Our previous hepatoprotective pharmacological studies of the herb [10] attracted further research interest. Several new promising bioactive compounds including two new sesquiterpenes **1** and **2**, and taraxasterol-3-*O*-β-D-glucoside (**3**), along with the three known compounds **4**–**6**, were isolated from the extracts of the stems of *C. glandulosum* (structures see *Fig. 1*).

Results and Discussion. – The 95% EtOH extract of *C. glandulosum* was partitioned with $CHCl_3$ and H_2O, the $CHCl_3$ layer was dried and further partitioned with petroleum ether and 90% MeOH, the aqueous MeOH fraction (*CGA4*) was used for chromatographic isolation of sesquiterpene lactones. From *CGA4*, two new

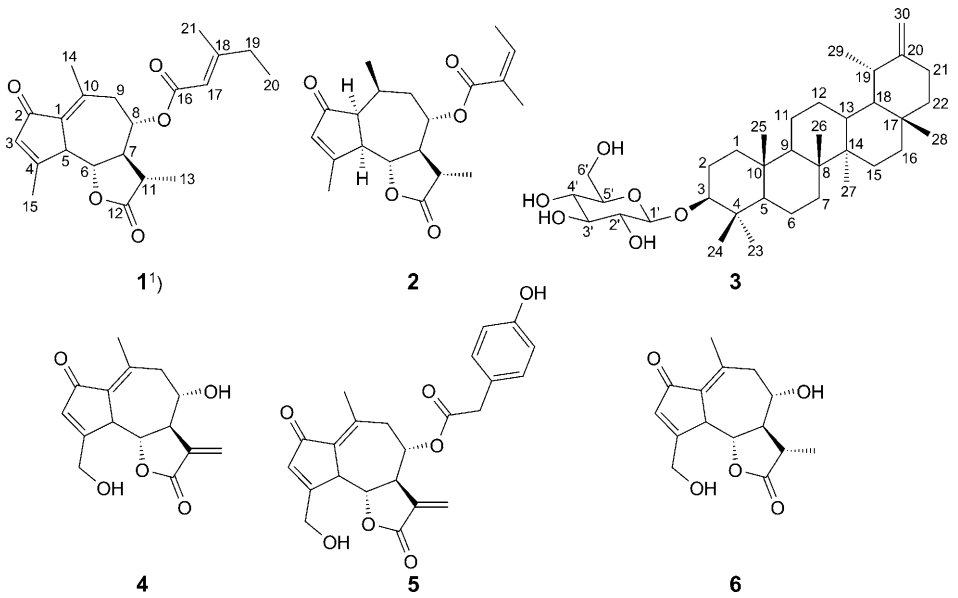

Fig. 1. *Structures of isolated compounds from* C. glandulosum

compounds 8-*O*-methylsenecioylaustricin, epi-8α-(angeloyl)oxycichoralexin and a new triterpene glycoside, together with three known sesquiterpene lactones, lactucin, lactucopicrin, and 11β,13-dihydrolactucin, were isolated and identified.

8-*O*-Methylsenecioylaustricin (**1**) was isolated as white needles. The HR-FAB-MS showed a *pseudo*-molecular ion peak at *m*/*z* 359.1893 ($[M+H]^+$, calc. 359.1858) corresponding to the molecular formula $C_{21}H_{26}O_5$, with nine degrees of unsaturation. The IR spectrum of **1** showed an α,β-unsaturated ester (1712 cm^{-1}) in addition to a γ-lactone CO group (1787 cm^{-1}), and an α,β-unsaturated ketone (1641, 1618 cm^{-1}) group. The UV spectrum in MeOH showed maxima at 225 nm (α,β-unsaturated ester) and 253 nm (α,β-unsaturated ketone).

The ^{1}H- and ^{13}C-NMR spectra (*Table 1*) of **1** showed signals typical of a lactucin-like skeleton [11][12]. The ^{13}C-NMR spectrum resolved 21 C-atom signals, which were determined by chemical shifts, DEPT, and the HSQC spectrum as five Me groups, two sp^3 CH_2, four sp^3 CH groups (two oxygenated ones at δ(C) 69.1 and 81.2), three C=O groups (δ(C) 195.2, 176.9, and 165.3), and three C=C bonds (*Table 1*).

The ^{1}H-NMR spectrum showed the presence of three Me *singlet*s (δ(H) 2.21, 2.31, and 2.46), one Me *doublet* (δ(H) 1.32, *d*, $J=6.6$), one Me *triplet* (δ(H) 1.08, *t*, $J=6.5$), and two olefinic H-atoms (δ(H) 6.19 (*s*) and 5.65 (*s*)). The HSQC and HMBC spectra led to the identification of two partial structures: CH(5)–CH(6)–CH(7)–CH(8)–CH_2(9)–C(10)–Me(14)[1]) and CH(7)–CH(11)–Me(13); moreover, the C(1)–C(2)(=O)–CH(3)–C(4)–Me(15) and Me(15)–C(4)–CH(5) partial structures were readily deduced by HMBC. Connection of these fragments finished the

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

Table 1. *^{1}H- and ^{13}C-NMR Data of* **1** *and* **2**[1]). At 600 and 150 MHz, resp.; δ in ppm, J in Hz, in $CDCl_3$.

	1		**2**	
	δ(C)	δ(H)	δ(C)	δ(H)
C(1) or H–C(1)	133.1		53.1	2.75 (*dd*, *J* = 7.2, 3.5)
C(2)	195.2		208.4	
H–C(3)	135.8	6.19 (*s*)	132.4	6.07 (*s*)
C(4)	169.5		178.8	
H–C(5)	51.6	3.41 (*d*, *J* = 10.2)	52.6	3.12 (*dd*, *J* = 7.2, 10.2)
H–C(6)	81.2	3.73 (*dd*, *J* = 10.2, 10.2)	77.7	4.45 (*dd*, *J* = 10.2, 10.2)
H–C(7)	59.3	2.48–2.52 (*m*)	54.9	2.28–2.33 (*m*)
H–C(8)	69.1	4.87 (*t*, *J* = 9.1)	71.6	5.27 (*td*, *J* = 11.4, 4.2)
H_α–C(9)	44.9	2.72 (*dd*, *J* = 13.8, 10.2)	41.2	2.20–2.22 (*m*)
H_β–C(9)		2.40 (*dd*, *J* = 13.8, 5.4)		1.64–1.70 (*m*)
C(10) or H–C(10)	145.4		31.5	2.59–2.60 (*m*)
H–C(11)	40.8	2.51–2.53 (*m*)	40.0	2.60–2.62 (*m*)
C(12)	176.9		177.6	
Me(13)	15.0	1.32 (*d*, *J* = 6.6)	15.9	1.32 (*d*, *J* = 7.8)
Me(14)	21.4	2.46 (*s*)	15.8	0.87 (*d*, *J* = 7.8)
Me(15)	19.9	2.31 (*s*)	20.5	2.23 (*s*)
C(16)	165.3		166.7	
H–C(17) or C(17)	113.3	5.65 (br. *s*)	126.9	
C(18) or H–C(18)	164.9		140.0	6.14–6.17 (*m*)
CH_2(19) or Me(19)	33.9	2.22 (br. *q*, *J* = 7.2)	15.8	2.01 (*dq*, *J* = 6.6, 0.6)
Me(20)	11.9	1.08 (*t*, *J* = 6.5)	19.4	1.91 (*s*)
Me(21)	19.0	2.21 (br. *s*)		

framework of an austricin-like lactone. The ^{1}H-NMR signals δ(H) 5.65 (br. *s*, 1 H), 2.22 (br. *q*, *J* = 7.2, 2 H), 2.21 (br. *s*, 3 H), and 1.08 (*t*, *J* = 6.5, 3 H), as well as the C-atom signals at δ(C) 165.3 (C(16)), 113.3 (C(17)), 164.9 (C(18)), 33.9 (C(19)), 11.9 (C(20)), and 19.0 (C(21)), were undoubtedly assigned to a methyl senecioate moiety (MeSen) [13][14], and further evidence was provided by the FAB-MS fragmentation of **1**, which gave fragment ions at *m*/*z* 245 ($[M - \text{MeSen}]^+$) and 97 ($[\text{MeSen}]^+$, base peak), as shown in *Fig. 2*. The relative configuration of **1** was established by a ROESY experiment (*Fig. 3*), in which the correlations of H–C(5)/H–C(7) and H–C(6)/H–C(8)/H–C(11) indicated that H–C(5) and H–C(7) were α-oriented, and H–C(6), H–C(8), and H–C(11) were β-oriented. According to the literature [15], the coupling constant of J(5,6) of H–C(5) in β-oriented form would be *ca.* 4.2 Hz, but, in our experiment, J(5,6) was 10.2 Hz, which was in agreement with a α-orientation of H–C(5). Therefore, the structure of **1** was assigned to be 8-*O*-methylsenecioylaustricin (*Fig. 1*).

Epi-8α-angeloyloxycichoralexin (**2**) was isolated as colorless needles. The HR-FAB-MS showed a *pseudo*-molecular ion peak at *m*/*z* 347.1888 ($[M + H]^+$, calc. 347.1858) corresponding to the molecular formula $C_{20}H_{26}O_5$. The IR showed ν_{max} 1766 cm^{-1} (γ-lactone), 1695 cm^{-1} (α,β-unsaturated ketone), 1616 cm^{-1} (C=C bond), and 1157 cm^{-1} (ν(C–O) in ester). The UV spectrum in MeOH showed a maximum at 225 nm (α,β-unsaturated ester).

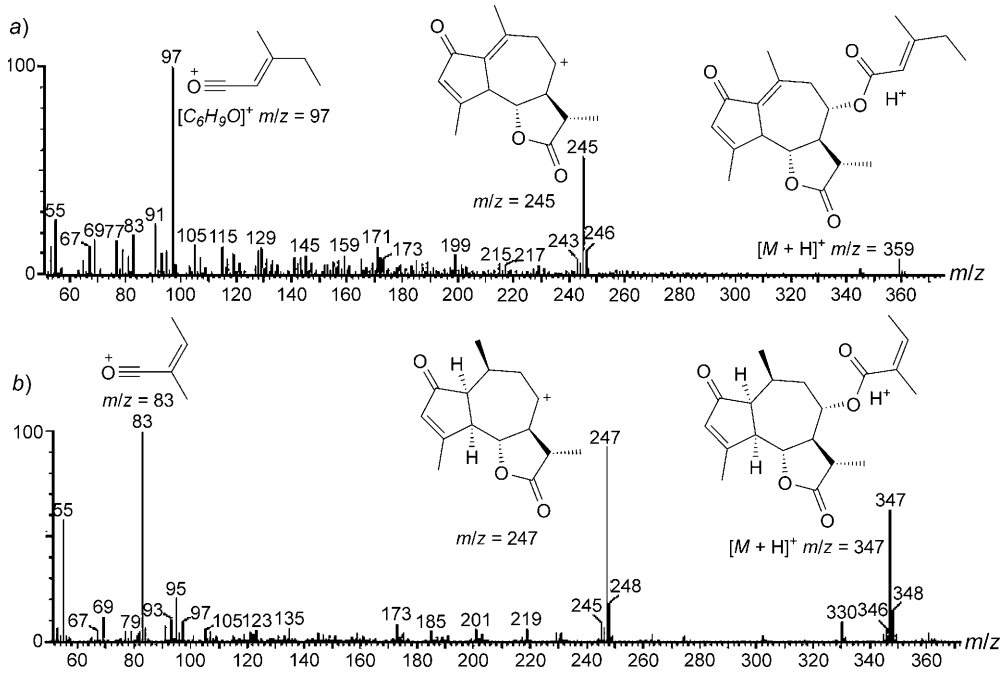

Fig. 2. *FAB-MS of a*) **1** *and b*) **2**: *analysis of main fragment ions*

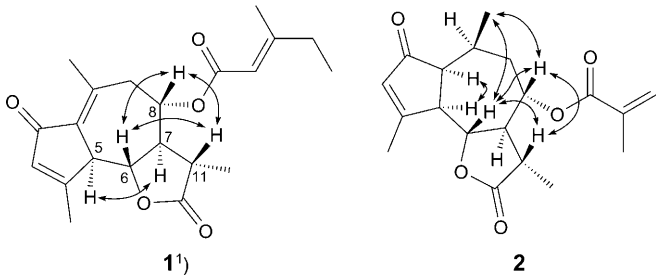

Fig. 3. *Selected key NOE correlations of* **1** *and* **2**

From the interpretation of the ^{13}C-NMR (DEPT) spectrum, compound **2** was found to have five Me groups, one CH_2 and nine CH groups, one α,β-unsaturated ketone (δ(C) 208.4 ppm), one C=O (δ(C) 177.6 ppm) in a lactone ring, one in an α,β unsaturated ester (δ(C) 166.7 ppm), and two quaternary sp^2 C-atoms (δ(C) 126.9 and 178.8 ppm). Moreover, by careful study of the HSQC and HMBC spectra, three partial structures were deduced: Me(14)–CH(10)–CH(1)–CH(5)–CH(6)–CH(7)–CH(8)–CH_2(9)–CH(10)[1]), –CH(7)–CH(11)–Me(13), and CH(1)–C(2)(=O)–CH(3)=C(4)–CH(5). These data agreed with the skeleton of a cichoralexin-like sesquiterpene lactone [16]. In addition, the presence of an angeloyloxy moiety was on

the basis of C-atom signals at δ(C) 166.7 (C(16)), 126.9 (C(17)), 140.0 (C(18)), 15.8 (C(19)), and 19.4 (C(20)) and H-atom signals at δ(H) 6.14–6.17 (*m*, 1 H), 2.01 (*dq*, *J* = 6.6, 0.6, 3 H), and 1.91 (br. *s*, 3 H) [17]. The FAB-MS of **2** exhibited fragment ion peaks at *m*/*z* 247 ([*M* – acyl – H_2O]$^+$) and 83 ([angeloyloxy]$^+$, base peak) supporting the above deduction (*Fig. 2*).

The relative configuration of **2** was established by a ROESY experiment (*Fig. 3*), in which the correlations H–C(1)/H–C(5)/H–C(7) and H–C(6)/H–C(8)/H–C(11)/Me(14) indicated that H–C(1), H–C(5), and H–C(7) were α-oriented, and H–C(6), H–C(8), H–C(11), and Me(14) were β-oriented. Further evidence was found in the literature [16]; the chemical shifts of α-oriented H–C(1) and β-oriented H–C(5) would be at *ca.* 1.94 (*dd*, *J* = 10, 5.5) and 2.82 ppm (*dd*, *J* = 10, 5.5), respectively. And if both H–C(1) and H–C(5) were α-oriented, the chemical shift of H–C(1) is expected at *ca.* 2.69 ppm (*dd*, *J* = 3.5, 7.0) and H–C(5) at 3.09 ppm (*dd*, *J* = 8.5, 8.5). In our experiment, the signal for H–C(1) was observed at 2.75 ppm (*dd*, *J* = 3.5, 7.2) and the signal for H–C(5) at 3.12 ppm (*dd*, *J* = 7.2, 10.2). Therefore, H–C(1) and H–C(5) in compound **2** were both assigned to be α-oriented. Thus, compound **2** was identified as epi-8α-angeloyloxycichoralexin, an unreported structure, which is the *C(1)*-epimer of 8α-(angeloyloxy)cichoralexin [17].

The structure of taraxasterol-3-*O*-β-D-glucoside (**3**, 100 mg), a white powder with a melting point of 216–218° was elucidated based on the following evidence: The ^{1}H-NMR spectrum ((D$_5$)pyridine, 400 MHz) of compound **3** exhibited six 3 H *singlet*s at δ(H) 0.81, 0.91, 0.91, 0.95, 1.01, and 1.32, which were assigned to the tertiary Me(25), Me(27), Me(28), Me(26), Me(24), and Me(23) groups, respectively. A 3 H *doublet* at δ(H) 1.04 (*J* = 6.8) was assigned to the secondary Me(29) group. A characteristic downfield *doublet* of *doublet*s at δ(H) 3.42 (*dd*, *J* = 11.6, 3.2) was due to a H-atom geminal to an O-bearing substituent. The downfield *singlet*s at δ(H) 4.73 and 4.78 were assigned to the exocyclic CH_2(30) olefinic H-atoms. The most downfield *doublet* at δ(H) 4.96 (*d*, *J* = 8.0, 1 H) was assigned to the anomeric H-atom of β-glucose. In addition, six H-atoms belonging to a glucopyranosyl moiety could be found between δ(H) 4.0 and 4.6.

The ^{13}C-NMR and DEPT spectrum of **3** ((D$_5$)pyridine, 100 MHz) showed resonances for 36 C-atoms. The downfield resonances at δ(H) 154.8 and 107.6 were assigned to the C(20) and C(30) olefinic C-atoms, respectively. One CH group at δ(C) 88.9 was assigned to RO–C(3). The resonances at δ(C) 106.9, 78.8, 78.3, 75.8, 71.9, and 63.1 were assigned to the C-atoms of the glucopyranosyl moiety. The resonances at δ(C) 14.9, 16.1, 16.5, 16.9, 19.8, 25.6, and 28.2 were ascribed to the Me groups (Me(27), Me(24), Me(26), Me(25), Me(28), Me(29), and Me(23), resp.). The overall NMR data were in good agreement with a taraxastane-type skeleton [18] and one glucopyranosyl moiety (*Table 2*). Unambiguous assignments of the ^{1}H- and ^{13}C-NMR signals were achieved by combination of DEPT, HSQC, and HMBC. The HMBCs of compound **3** are listed in *Table 2*. In addition, the ESI-MS of compound **3** showed *m*/*z* 666 ([*M* + 2 K]$^+$), 635 ([*M* + 2 Na + 1]$^+$), 634 ([*M* + 2 Na]$^+$), 590 ([*M* + 2 H]$^+$), and 577 ([*M* – CH_2OH]$^+$). In this mode, the expected molecular ion peak (*m*/*z* 588) could not be detected. From the above mentioned analysis, the molecular formula of compound **3** was deduced as $C_{36}H_{60}O_6$, and its chemical structure was identified as taraxasterol-3-*O*-β-D-glucoside (*Fig. 1*).

Table 2. *^{1}H- and ^{13}C-NMR Data of* **3**. At 400 and 100 MHz, resp.; δ in ppm, J in Hz, in (D_5)pyridine.

	δ(C)	δ(H)	Key HMBC (H → C)
CH_2(1)	38.6	0.90–0.92 (*m*), 1.61–1.62 (*m*)	2, 3, 9, 10, 25
CH_2(2)	26.5	1.84–1.85 (*m*), 1.67–1.69 (*m*)	1, 10, 3, 4
H–C(3)	88.9	3.42 (*dd*, *J* = 11.6, 3.2)	1′, 4, 23, 24
C(4)	41.1		
H–C(5)	55.9	0.74–0.75 (*m*)	1, 6, 10, 23, 24, 25
CH_2(6)	18.5	1.42–1.43 (*m*), 1.31–1.33 (*m*)	5, 7, 8, 10
CH_2(7)	34.7	1.41–1.42 (*m*)	5, 6, 8, 9, 14, 26
C(8)	41.1		
H–C(9)	50.6	1.26–1.27 (*m*)	5, 8, 11, 25, 26
C(10)	37.0		
CH_2(11)	21.6	1.50–1.51 (*m*)	8, 9, 10, 12
CH_2(12)	26.8	1.10–1.11 (*m*), 1.63–1.64 (*m*)	9, 13, 11, 18
H–C(13)	39.4	1.58 (*t*, *J* = 12.8)	18, 27, 14
C(14)	42.2		
CH_2(15)	26.9	1.61–1.62 (*m*), 0.90–0.91 (*m*)	14, 16, 17, 27
CH_2(16)	39.1	1.26–1.28 (*m*), 1.13–1.14 (*m*)	15, 17, 18, 28
C(17)	34.4		
H–C(18)	48.8	0.91–0.93 (*m*)	13, 17, 19
H–C(19)	39.7	2.13 (*t*, *J* = 6.4)	18, 20, 29, 30
C(20)	154.8		
CH_2(21)	25.9	2.45–2.47 (*m*), 2.22–2.24 (*m*)	19, 20, 22, 30
CH_2(22)	39.0	1.40–1.41 (*m*)	17, 18, 20, 21
Me(23)	28.2	1.32 (*s*)	3, 4, 5, 24
Me(24)	16.1	1.01 (*s*)	3, 4, 5, 23
Me(25)	16.9	0.81 (*s*)	1, 5, 9, 10
Me(26)	16.5	0.95 (*s*)	7, 8, 9, 14
Me(27)	14.9	0.91 (*s*)	8, 13, 14, 15
Me(28)	19.8	0.91 (*s*)	16, 17, 18, 22
Me(29)	25.6	1.04 (*d*, *J* = 6.8)	18, 19, 20
CH_2(30)	107.6	4.78 (*s*), 4.73 (*s*)	19, 20, 21, 29
H–C(1′)	106.9	4.96 (*d*, *J* = 8.0)	3, 2′, 3′, 5′
H–C(2′)	75.8	4.04 (*dd*, *J* = 7.6, 7.6)	1′, 3′, 5′
H–C(3′)	78.3	4.23 (*dd*, *J* = 8.8, 8.4)	2′, 4′
H–C(4′)	71.9	4.26 (*dd*, *J* = 8.8, 8.8)	3′, 5′, 6′
H–C(5′)	78.8	4.25–4.27 (*m*)	3′, 4′, 6′
CH_2(6′)	63.1	4.60 (*d*, *J* = 12.0), 4.42 (*dd*, *J* = 12.0, 5.2)	4′, 5′

Compounds **4**–**6** were identified as lactucin, lactucopicrin, and 11β,13-dihydrolactucin, respectively, on the basis of their spectra and comparison with published values.

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Experimental Part

General. TLC: pre-coated silica gel *60 F254* (*Qingdao Haiyang Chemical Co. Ltd.*), visualization under UV light (254 and 365 nm) and by spraying with anisaldehyde/H_2SO_4 reagent, or visualized in I_2 vapor. Column chromatography (CC): silica gel *H* (SiO_2; *Qingdao Haiyang Chemical Co. Ltd.*), or

Sephadex LH-20 (*Pharmacia*). IR Spectra: *BIO-RAD FTS 165* spectrometer; in cm^{-1}; in KBr pellets. ^1H-, ^{13}C-, and 2D-NMR spectra: *Varian unity Inova-600* NMR and *Bruker DRX-400* instruments, at 295 K; δ in ppm rel. to Me_4Si, *J* in Hz. ESI-MS: *Accu TOF CS* (*Jeol*, Japan). HR-FAB-MS: *AutoSpec Ultima-TOF* mass spectrometer (*Micromass*, UK); in *m/z*; recorded at the Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, P. R. China.

Plant Material. The aerial parts of *C. glandulosum* were bought at Jimsar County, Xinjiang of China, in October 2007. The plant was authenticated by Prof. *L. Y. Zhang* and *G. M. Shen* as *Cichorium glandulosum* BOISS. ET HUET. and a voucher specimen was deposited at the Herbarium of Xinjiang Institute of Physics & Chemistry, Chinese Academy of Sciences.

Extraction and Isolation. The air-dried aerial parts of *C. glandulosum* (6 kg) were cut into pieces and extracted at r.t. with 95% EtOH. The extract was concentrated under reduced pressure to give 720 g of crude residue. The residue was partitioned between H_2O and $CHCl_3$, the $CHCl_3$ layer afforded 280 g residue which was further partitioned between petroleum ether (PE) and 90% MeOH (aq.) 228 g. Of extract was obtained from 90% MeOH layer after evaporation (*CGA4*). 200 g of *CGA4* was first fractionated by CC (2 kg of SiO_2; PE/AcOEt: 50 : 1, 30 : 1, 15 : 1, 10 : 1, 7 : 1, 5 : 1, 3 : 1, 1 : 1, 1 : 3) to give eight main fractions: *Frs. A–I*. Compounds **1** (42 mg) and **2** (23 mg) were obtained from *Fr. E* (PE/AcOEt 7 : 1) after repeated chromatography on CC (SiO_2; PE/AcOEt 7 : 1, 5 : 1, 3 : 1) and (*Sephadex LH-20*; $CHCl_3$/MeOH 1 : 1). *Fr. G* (PE/AcOEt 3 : 1) afforded compound **4** (lactucin, 56 mg), and *Fr. H* afforded compounds **5** (lactucopicrin, 109 mg) and **6** (11β,13-dihydrolactucin, 17 mg) after separation on CC (PE/AcOEt, 5 : 1, 3 : 1, 1 : 1). Compound **3** (100 mg) was obtained from *Fr. I* after filtration of the precipitate in MeOH.

8-O-*Methylsenecioylaustricin* (= rel-*(3a*R,*4*S,*9b*R*)-2,3,3a,4,5,7,9a,9b-Octahydro-3,6,9-trimethyl-2,7-dioxoazuleno[4,5-*b*]furan-4-yl (2*E*)-3-Methylpent-2-enoate*; **1**). White needles. M.p. 150–151°. UV (MeOH): 252.8 (3.2), 224.6 (3.2), 196.6 (2.4). IR: 2936, 1787, 1712, 1698, 1641, 1618, 1452, 1377, 1220, 1147. ^1H- and ^{13}C-NMR: *Table 1*. FAB-MS: *Fig. 2*. HR-FAB-MS: 359.1893 ($[M+H]^+$; calc. 359.1858).

Epi-8α-angeloyloxycichoralexin (= rel-*(3a*R,*4*S,*6*S,*6a*S,*9a*R,*9b*R*)-2,3,3a,4,5,6,6a,7,9a,9b-Decahydro-3,6,9-trimethyl-2,7-dioxoazuleno[4,5-*b*]furan-4-yl (2*Z*)-2-Methylbut-2-enoate*; **2**). Colorless needles. M.p. 166–167°. UV (MeOH): 225.0 (7.4). IR (KBr): 2956, 1766, 1695, 1616, 1157, 1006. ^1H- and ^{13}C-NMR: *Table 1*. FAB-MS: *Fig. 2*. HR-FAB-MS: 347.1888 ($[M+H]^+$; calc. 347.1858).

Taraxasterol-3-O-*β*-D-*glucoside* (= *(3β,18α,19α)-Urs-20(30)-en-3-yl β*-D-*Glucopyranoside*; **3**). White powder. M.p. 216–218°. ^1H- and ^{13}C-NMR: *Table 2*. ESI-MS: 666 ($[M+2\,K]^+$), 635 ($[M+2\,Na+1]^+$), 634 ($[M+2\,Na]^+$), 590 ($[M+2\,H]^+$), 577 ($[M-CH_2OH]^+$).

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