Chinese Herbal Medicines 14 (2022) 459-463



Contents lists available at ScienceDirect

Chinese Herbal Medicines



journal homepage: www.elsevier.com/locate/chmed

Original Article Chemical constituents of *Lomatogonium carinthiacum* and *Halenia corniculata*

Aodungerile ^{a,b}, Xigurigan ^b, Tunumula ^b, Gang Bao ^b, Sudabilige ^b, Chaogebadalafu ^b, Chenlin He ^b, Qirigeer ^{a,b}, Laxinamujila Bai ^{a,b,*}, Shuzhen Bai ^{c,*}

^a NMPA Key Laboratory of Quality Control of Traditional Chinese Medicine (Mongolian Medicine), School of Mongolian Medicine, Inner Mongolia Minzu University, Tongliao 028000, China

^b College of Mongolian Medicine and Pharmacy, Inner Mongolia MinZu University, Tongliao 028000, China

^c College of College of Chemistry and Materials Science, Inner Mongolia MinZu University, Tongliao 028000, China

ARTICLE INFO

Article history: Received 13 February 2022 Revised 5 May 2022 Accepted 20 May 2022 Available online 1 July 2022

Keywords: bioactive compounds Halenia corniculate (L.) Corneaz. Lomatogonium carinthiacum (Wulf.) Reichb. Mongolian medicine

ABSTRACT

Objective: To study the chemical constituents from traditional Chinese (Mongolian) medicine, *Lomatogonium carinthiacum* and *Halenia corniculate*.

Methods: The chemical constituents were isolated and purified by silicagel column, Sephadex LH-20, ODS and high performance liquid chromategramphy. The structures were identified by NMR and MS analysis technics.

Results: Twelve compounds were isolated and identified as isovitexin (1), Luteolin-5-*O*- β -*D*-glucoside (2), Isosaponarin (3), Luteolin-7-*O*- β -*D*-glucoside (4,7), 1,4,8-Trimethoxy-xanthone-6-*O*- β -*D*-glucoronyl-(1 \rightarrow 6)*O*- β -*D*glucoside (5), friginoside*D* (6), 1-hydroxy-2,3,5-trimethoxyxanthone (8), 1-hydroxy-2,3,4,5-tet ramethoxyxanthone (9), 1-hydroxy-2,3,4,7-tetramethoxyxanthone(10), 1-hydroxy-2,3,4,5,7-pentame thoxyxanthone (11) and usnic acid (12).

Conclusion: Compounds 6 and 12 are obtained from *L. carinthiacum* and *H. corniculate* for the first time. © 2022 Tianjin Press of Chinese Herbal Medicines. Published by ELSEVIER B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Traditional Chinese (Mongolian) medicine, Lomatogonium carinthicum (Wulf.) Reichb. and Hallenia corniculata (L.) Corneaz. of Gentianaceae, are abbreviated as LZH and HM. They are bitter in taste and cold in nature, and have the functions of eliminating "Xieri", clearing away heat, healing wounds and invigorating stomach. L. carinthicum is a traditional Mongolian medicinal material with highly positive effect, especially for "Xieri associated" diseases, such as icteric hepatitis, cholecystitis, gastritis and other digestive tract diseases. Modern medical research has found that LZH and HM have the effects of lowering blood pressure, blood sugar and blood lipid, and have a certain inhibitory effect on HBV DNA (Hepatitis B virus) copy numberin cells, and can also be used in medical treatment or health food based on free radical scavenging test. The clinical medication of *H. corniculate* is consistent with that of L. carinthiacum. There are a lot of xanthones, terpenoids, flavonoids and phenols in two kinds of digda (Ba, 2007; Luo, 2006). Flavonoids and terpenoids of the secondary metabolism of Mongolian medicine L. carinthiacum. It's hasvarious effects, such as antioxidative, anti-inflammatory, hepatoprotective, antitumor, act as acholagogue, analgesic (Wu, Wang, Xin, Bai, & Sun, 2021). The main chemical constituents of Mongolian medicine H. corniculate are flavonoids, terpenoids and xanthones. It also has liverprotective effects (Tai et al., 2015; Gui et al., 2015). In order to provide theoretical basis for quality control and clinical application of LZH and HM, the chemical constituents of two kinds of Digda were systematically studied by using normal silica gel column, gel column chromatography and reversed phase preparative liquid chromatography, combined with MS and NMR spectroscopy. The present work describes the isolation and identification of compounds: asisoftexin (1), Lutelin-5-O- β -D-glucose (2), Isosapoanarin (**3**), Luteolin-7-O- β -D-glucoside (**4**,**7**), 1,4,8-Trimethoxyxanthone-6-*O*- β -*D*-glucoronyl-(1 \rightarrow 6) *O*- β -*D* glucoside (5), friginoside*D* (6), 1-hydroxy-2,3,5-trimethoxyxanthone (8), 1-hydroxy-2,3,4,5-tetra methoxyxanthone (9), 1-hydroxy-2,3,4,7-tetramethoxyxanthone (10), 1-hydroxy-2,3,4,5,7-pentamethoxyxanthone (11), usnic acid (12), compounds 6 and 12 were isolated from this two plant for the first time.

* Corresponding authors. E-mail addresses: namujila@126.com (L. Bai), aodun@imun.edu.cn (S. Bai).

https://doi.org/10.1016/j.chmed.2022.05.001

1674-6384/© 2022 Tianjin Press of Chinese Herbal Medicines. Published by ELSEVIER B.V.

This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

2. Materials and methods

2.1. Instruments and materials

NMR spectra were made on a Bruker AVAIVCE III-500 nuclear magnetic resonance spectrometer (Bruker, Germany) and EP4-004 ion trap mass spectrometer (Waters, USA) with TMS as internal standard. Shimadzu Preparative Liquid Chromatograph (LD-20AT), Venusil MP C₁₈ reverse phase chromatography column (100 A°, 21.2 mm × 250 mm, 10 μ m), Thin layer column chromatography silica gel (Qingdao Ocean Chemical Plant) and Sepade × LH-20 dextran gel (Swedish Pharmacia Company) were used for column chromatography, and precoated silica gel and GF₂₅₄ thin layer plates (Qingdao Ocean Chemical Plant) were used for the TLC. All solvents used were of analytical grade (Shandong Yuwang Industrial Company).

The medicinal materials were collected from Xiwuzhumuqin Banner, and were identified as *Lomatogonium carinthiacum* (Wulf.) Reichb (20190729). and *Halenia corniculata* (L.) Cornaz (20190804). By Professor BuHebateer, College of Mongolian Medicine, Inner Mongolia Minzu University.

2.2. Extraction and separation

Separate samples of *L. carinthiacum* (1.145 kg) and *H. corniculate* (1.142 kg) were dried and crushed in the shade, and extracted with 95% ethanol reflux for three times, each time for 3 h. The extract was concentrated under reduced pressure to obtain 0.5 kg of extract. Add 500 mL of deionized water and stir to form suspension, followed by adding petroleum ether (upper layer), dichloromethane (lower layer), *n*-butanol (upper layer) for extraction five times, combining the layers, and recovering to dryness under reduced pressure to obtain the LZH petroleum ether layer (120.5 g), dichloromethane layer (90.3 g), *n*-butanol layer (150.4 g), HM petroleum ether layer (115.3 g), dichloromethane (131.2 g), *n*-butanol layer (114.7 g).

The LZH *n*-butanol layer was separated using a gel chromatography column (100 g). Gradient elution was performed using methanol-dichloromethane (3:2) mixtures. The solvent was recovered to obtain the elution fractions F1 – F25. The eluate was detected by thin-layer chromatography, and the eluates of similar composition were combined to obtain compounds **4** (1.0 g) and **5** (0.5 g). Then the F11 and F13 – 14 fractions are combined, and the reversed-phase preparative liquid chromatograph (LD-20 AT) was used for preparative and separation. The mobile phase conditions were: methanol (B): water (A) gradient elution (B) (0.01–15 min-10%–20%, 15–30 min-20%–48%, 30–120 min-48%–60%, 120–180 min-60%–80% mobile phase B), detection wavelength: 284 nm, column temperature: 40 °C, compounds **1–3**, **6** (each compound weighs about 0.5 g) were obtained.

The HM *n*-butanol layer was separated using a gel chromatography column (100 g). Gradient elution was performed using methanol-dichloromethane (3:2) mixtures. The solvent was recovered and eluted and separated, and 39 fractions (F1–F14, F1'–12' and F1"–13") were obtained. The eluent was detected by thinlayer chromatography, and the eluents of similar composition were combined to obtain compounds **11** (1.0 g), **7** (1.0 g), and **12** (2.0 g). Then combine F7–12, F3'–12' and F3"–F13", and use a reversedphase preparative liquid chromatograph (LD-20AT) for preparative separation. The mobile phase conditions were: methanol (B): water (A) gradient elution (0.01–15 min 10%–20%, 15–30 min 20%–48%, 30–120 min 48%–60%, 120–180 min 60%–80% mobile phase B), detection wavelength: 284 nm, column temperature: 40 °C, compounds **8–10** (each compound weighs about 0.5 g) were obtained (Fig. 1).

3. Results

3.1. Chemical composition of L. carinthiacum

Compound 1: Yellowish brown powder, soluble in methanol, ESI-MS m/z 447.2 [M–H][–], C₂₁H₂₀O₁₁, ¹H NMR (500 MHz, DMSO d_6) δ 13.56 (s,1H, OH), 7.92 (d, *J* = 8.5 Hz, 2H, H-2',6'), 6.92 (d, *J* = 8.3 Hz, 2H, H-3',5'), 6.76 (s, 1H, H-3), 6.47 (s,1H, H-8), 4.58 (d, *J* = 9.8 Hz, 1H) for linked glycosodically terminal hydrogen atom. The above data are consistent with isovitexin data reported in literature (Li, Suo, Liao, & Ding, 2008).

Compound **2**: Yellow powder, soluble in methanol, ESI-MS m/z 455.3 [M + Na]⁺,C₂₁H₂₀O₁₀, ¹H NMR (500 MHz,DMSO d_6) δ 7.35 (br s, 1H, H-2'), 7.36 (br s, 1H, H-6'), 6.86(d, J = 8.0 Hz, 1H, H-5'), 6.76 (br s, 1H, H-8), 6.65 (br s, 1H, H-3), 6.53 (s, 1H, H-6), 4.69 (d, J = 7.3 Hz, 1H, H-1″), ¹³C NMR (125 MHz, DMSO d_6) δ 176.93 (C-4), 163.67 (C-7),161.28 (C-2), 158.72 (C-5), 158.41 (C-9), 149.50 (C-4'), 145.80 (C-3'), 121.37 (C-1'), 118.51 (C-6'), 116.00 (C-5'), 113.03 (C-2'), 107.78 (C-10), 105.53 (C-3), 104.85 (C-1″),104.71 (C-6), 98.29 (C-8), 77.57 (C-3″), 75.60 (C-5″), 73.68 (C-2″), 69.67 (C-4″), 60.83 (C-6″). The above data is consistent with the data reported in the literature for luteolin-5-*O*-β-*D*-glucose (Sun, Wang, Li, Zheng, & Shen, 1997).

Compound **3**: Yellow powder, ESI-MS m/z 595.1 [M + H]⁺, $C_{27}H_{30}O_{15}$, ¹H NMR (500 MHz, DMSO d_6) δ 13.59 (s, 1H, OH), 7.47–7.33 (m, 2H, H-2',6'), 6.86 (d, J = 7.9 Hz, 1H, H-3',5'), 6.63 (s, 1H, H-8), 6.43 (s, 1H, H-3), 4.57 (d, J = 9.8 Hz, 1H, H-1", H-1"). ¹³C NMR (125 MHz, DMSO d_6) δ 182.22 (C-4), 163.76 (C-7), 161.70 (C-4'), 161.15 (C-5), 156.77 (C-9), 128.88 (C-2'), 121.55 (C-1'), 116.46 (C-5'), 109.45 (C-6), 103.45 (C-3), 103.14 (C-10), 94.24 (C-8), 82.02 (C-5"), 80.82 (C-1"), 79.45 (C-3"), 76.83 (C-5"'), 76.22 (C-3"''), 73.76 (C-2"''), 73.60 (C-1"), 71.09 (C-4"'), 70.65 (C-2"), 69.63 (C-4"''), 64.59 (C-6"''), 61.95 (C-6"). The above data is consistent with the isosaponarin data reported in the literature (Takahiro, Young & Akira, 2005).

Compound **4**: Yellow powder, a little soluble in methanol, ESI-MS *m*/*z* 447.2[M-H]⁻, C₂₁H₂₀O₁₁, ¹H NMR (500 MHz, DMSO *d*₆) δ 13.02 (s,1H,H-5), 7.45 (dd, *J* = 13.4, 4.9 Hz, 2H, H-2'), 6.90 (d, *J* = 8.3 Hz, 1H, H-5'), 6.79 (d, *J* = 1.3 Hz, 1H, H-8), 6.76 (s, 1H, H-3), 6.44 (d, *J* = 1.3 Hz, 1H, H-6), 5.09 (d, *J* = 7.4 Hz, 1H, C-1'). The above data is consistent with the data reported in the literature for luteolin-7-*O*-β-*D*-glucoside (ji et al., 1992).

Compound **5**: Yellow powder, soluble in methanol, ESI-MS m/z 611.2 [M + H]⁺, C₂₉H₃₈O₁₄, ¹H NMR (500 MHz, DMSO d_6) δ 7.37 (d, J = 9.1 Hz, 1H, H-2), 6.86(d, J = 9.1 Hz, 1H, H-3), 6.77(s, 2H, H-5), 5.40 (d, J = 2.5 Hz,1H) for linked glycosodically terminal hydrogen atom, 5.25–5.20 (m, 2H), 4.98 (t, J = 4.3 Hz, 2H, H-1'), 4.92 (dd, J = 9.3,6.4 Hz, 1H, H-1"), 3.89 (s, 6H, OCH₃), 3.82 (s, 3H, OCH₃). ¹³C NMR (125 MHz, DMSO d_6) δ 174.77 (C=O), 164.63 (C-8), 159.31 (C-6), 157.69 (C-4b), 152.92 (C-1), 146.28 (C-4a), 141.73 (C-4), 116.96 (C-2), 114.02 (C-8b), 108.44 (C-8a), 106.10 (C-3),104.62 (C-1"), 103.08 (C-1'), 100.92 (C-7), 95.45 (C-5), 77.03 (C-3'), 76.30 (C-5"), 73.84 (C-2"),70.17 (C-4'), 69.97 (C-4"), 69.12 (anomerio carbon), 66.12 (C-6"), 56.84 (C-8), 56.65 (C-5), 56.59 (C-1). The above data is consistent with the data reported in the literature for (Ba et al., 2014).

Compound **6**: Yellow powder, soluble in methanol, ESI-MS m/z 911.2 [M + H]⁺, C₄₂H₃₈O₂₃, ¹H NMR (500 MHz, DMSO- d_6), the hydrogen spectrum 12.40 (s, 2H) is hydroxyl group signal on the benzene ring, and its chemical shift value increases to 12.40 µg/ mL due to conjugation with the carbonyl group at the 4th position, which is 5,5^{*m*}-OH signal; 9.98 (s, 2H), 9.51 (s, 2H) is the hydroxyl signal on the benzene ring, which is 3,3^{*m*}-OH, 4',4^{*m*}-OH; 7.48 (d, J = 7.8 Hz, 2H) is the unsaturated olefin hydrogen signal, which is H-6',6^{*m*}; 6.91 (d, J = 8.4 Hz, 2H) is the unsaturated olefin hydrogen

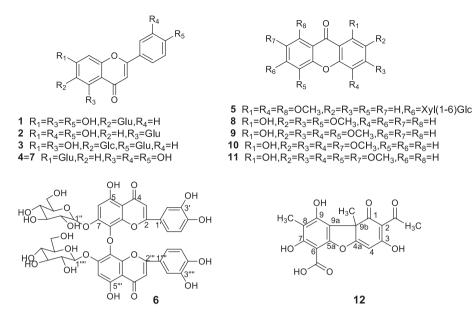


Fig. 1. Chemical structures of compounds 1-12.

signal, which is H-5', 5""; 6.73 (s, 2H) is the unsaturated olefin hydrogen signal, which is H-2',2""; 6.63 (s, 2H) is the unsaturated olefin hydrogen signal, which is H-6,6"", and 4.94 (d, J = 7.5 Hz, 1H) is the terminal hydrogen signal of glucose, which is H-1",1"". 5.42 (d, J = 4.0 Hz, 1H), 5.18 (d, J = 4.8 Hz, H), 5.12 (d, J = 5.3 Hz,1H), and 4.68(t, J = 5.6 Hz, 1H) are H2-H6 on the glucose group. ¹³CNMR (125 MHz, DMSO d_6), the carbon spectrum of 182.75 µg/mL is carbonyl carbon signal, which is C-4, 4"" signal, 146.17, 144.75, 127.39, 122.06, 119.66, 116.47, 114.00, 105.61, 103.11 µg/mL are 13 unsaturated ethylenic carbon signals. It is the carbon signal of flavone mother nucleus. 101.73 µg/mL is the terminal carbon signal of sugar, 77.74, 76.15, 73.67, 70.14, and 61.10 µg/mL is the C2-C6 signal of sugar. The above data is consistent with the friginoside *D* data reported in the literature (Wang et al., 2015).

The structure information of corresponding compounds was shown in (Table 1).

3.2. Chemical	composition of	of H.	corniculate

Compound **7**: Yellow powder, a little soluble in methanol, ESI-MS *m*/*z* 447 [M–H]⁻, C₂₁H₂₀O₁₁, ¹H NMR (500 MHz, DMSO *d*₆) δ 13.00 (s, 1H, H-5), 9.72 (br s, Hz, 2H, H-4',5'), 7.45(d, *J* = 8.4 Hz, 1H, H-2'), 7.42(d, *J* = 2.2 Hz, 1H, H-6'), 6.91(d, *J* = 8.3 Hz, 1H, H-5'), 6.79 (d, *J* = 2.1 Hz, 1H, H-8), 6.76 (s, 1H, H-3), 6.54 (d, *J* = 2.1 Hz, 1H, H-6), 5.09 (d, *J* = 7.4 Hz, 1H). ¹³C NMR (125 MHz, DMSO *d*₆) δ 182.37 (C-4), 164.93 (C-2), 163.41 (C-7), 161.60 (C-5), 157.41 (C-9), 50.39 (C-4'), 146.25 (C-3'), 121.84 (C-6'), 119.64 (C-1'), 116.44 (C-5'), 114.03 (C-2'), 105.80 (C-10), 103.64 (C-3), 100.4 (C-1"),100.32 (C-6), 95.17 (C-8), 77.62 (C-5"), 76.85 (C-3"), 73.57 (C-2"), 69.99 (C-4"), 61.06 (C-6"). The above data is consistent with the luteolin-7-*O*-*β*-*D*-glucoside da-ta reported in the literature (Ji, Ding, Fan, & Sun, 1992).

Compound **8**: Yellow powder, soluble in methanol, ESI-MS m/z325 [M + Na]⁺, C₁₆H₁₄O₆, ¹H NMR (500 MHz, DMSO d_6) δ 12.71 (s,

Table 1

¹ H and	¹³ C NMR	data	for	compounds	6	and	12
n anu	CINIMI	udid	101	compounds	υ	anu	12.

Pos.	Friginoside D		Pos.	Usnic acid		
	$\delta_{\rm H}$ (J in Hz)	δ_{C}		$\delta_{\rm H} (J \text{ in Hz})$	δ_{C}	
2, 2‴		164.68	1		198.25	
3, 3‴		103.11	2		109.53	
4, 4‴		182.75	2-COCH ₃	2.70 (s, 3H)	202.02, 28.17	
5,5‴-OH	12.40 (s, 2H)	152.77	3		191.93	
6,6‴	6.63 (s, 2H)		4	6.01 (s, 1H)	98.56	
7, 7‴		151.57	4a		179.60	
8, 8‴		127.39	5a		155.41	
9, 9‴		144.75	6		101.73	
10, 10‴		105.61	6-OCH ₃		32.35	
1', 1''''		122.06	6-COCH ₃	2.70 (s, 3H)	200.57	
2', 2''''	6.73 (s, 2H)	114.00	7-OH	13.35 (s, 1H)	164.08	
3', 3''''-OH	9.98 (s, 2H)	146.17	8		105.43	
4′, 4‴′-OH	9.51 (s, 2H)	150.32	8-CH3	2.13 (s, 3H)	7.78	
5',5''''	6.91 (d, J = 8.4 Hz, 2H)	116.47	9-OH	11.07 (s, 1H)	157.71	
6', 6''''	7.48 (d, J = 7.8 Hz, 2H)	119.66	9a		104.16	
1",1"""	4.94 (d, J = 7.5 Hz, 2H)	101.73	9b		59.28	
2", 2"""	5.42 (d, J = 4.0 Hz, 2H)	73.67	9b-CH ₃	1.79 (s, 3H)	31.55	
3", 3"""	5.18 (d, J = 4.8 Hz, 2H)	76.15				
4", 4"""	5.12 (d, J = 5.3 Hz, 2H)	70.14				
5", 5"""	4.68 (t, J = 5.6 Hz, 2H)	77.74				
6", 6"""		61.10				

1H, H-1), 7.70 (dd, *J* = 8.0,1.3 Hz, 1H, H-6), 7.56–7.53 (m, 1H, H-8), 7.43 (d, *J* = 8.0 Hz, 1H, H-7), 6.89 (s, 1H, H-4), 3.98 (d, *J* = 8.8 Hz, 6H, OCH₃), 3.75 (s, 3H, OCH₃). The above data is consistent with the1-hydroxy-2,3,5-trimethoxyxanthone data reported in the literature (Wang, Zhou, Cui, Zhao, & Yang, 2009).

Compound **9**: Yellow needle-like crystals, soluble in methanol, ESI-MS m/z 335.3 [M + Na]⁺, C₁₇H₁₆O₇, ¹H NMR (500 MHz, DMSO *d*₆) δ 12.55 (s, 1H, H-1), 7.71 (d, *J* = 8.0 Hz, 1H, H-5), 7.56 (d, *J* = 8.0 Hz, 1H, H-6), 7.43 (t, *J* = 8.0 Hz, 1H, H-8), 4.07 (s, 3H, OCH₃), 4.01 (s, 3H, OCH₃), 3.93 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃). The above data is consistent with the 1-hydroxy-2,3,4,5,tetramethoxy Xanthone data reported in the literature (Jin et al., 2008).

Compound **10**: Yellow needle-like crystals, soluble in methanol, ESI-MS m/z 355.4 [M + Na]⁺, C₁₇H₁₆O₇, ¹H NMR (500 MHz, DMSO d_6) δ 7.70 (d, J = 9.1 Hz, 1H, H-5), 7.55–7.50 (m, 2H, H-6,8), 4.07 (s, 1H, OCH₃), 3.89 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃). The above data is consistent with the 1-hydroxy-2,3,4,7-tetrame thoxyxanthone data reported in the literature (Ru et al., 2010).

Compound **11**: Yellow powder, soluble in methanol, ESI-MS m/z 385.4 [M + Na]⁺, C₁₈H₁₈O₈, ¹H NMR (500 MHz,DMSO d_6) δ 12.58 (s, 1H, H-1), 7.15 (d, J = 2.5 Hz, 1H, H-6), 7.07(d, J = 2.7 Hz, 1H, H-8), 4.06 (s, 3H, OCH₃), 3.99 (s, 3H, OCH₃), 3.91 (s, 3H, OCH₃), 3.88 (s, 3H, OCH₃), 3.82 (s, 3H, OCH₃). The above data is consistent with the 1-hydroxy-2,3,4,5,7-PentamethOxyXan-thone data reported in the literature (Liu, Liu, & Shi, 2009).

Compound 12: Yellow needle-like crystals, soluble in dichloromethane, ESI-MS *m*/*z* 345.0[M-H]⁻, C₁₇H₁₄O₈, ¹H NMR (500 MHz, CDCl₃), The hydrogen spectrum 13.35 (s, 1H) is a hydroxyl hydrogen signal, and the chemical shift value increases to 13.35 μ g/mL because it is conjugated with the carbonyl group at the 6th position, which is 7-OH; 11.07 (s, 1H) is a hydroxyl signal on the benzene ring, which is 9-OH; 6.01 (s, 1H) is an alkene hydrogen signal, which is H-4; 2.70 (s, 3H) is a methyl signal, adjacent to carbonyl, and the chemical shift value increases to 2.70 µg/mL, which means that 2-COCH₃; 2.70 (s, 3H) is a methyl signal, 2.70 μ g/mL is 6-COCH₃; 2.13 (s, 3H) is a methyl signal because it is adjacent to benzene ring and chemical shift value increases to 2.13 ug/mL, which is 8-CH₃; and 1.79 (s, 3H) is a methyl signal, which is 9b-CH₃. ^{13}C NMR (125 MHz, CDCl₃), the carbon spectra of 202.02, 200.57, 98.56 µg/mL are three ketocarbonyl carbon signals, 191.93 µg/ mL is unsaturated olefin carbon signal, 179.60, 164.08, 157.71, 155.41, 109.53, 105.43, 104.16, 101.73, and 98.56 µg/mL is C-9b signal, 32.35, 31.55, 28.17, 7.78 µg/mL is 4 methyl signals. The above data is consistent with the data of usnic acid reported in the literature (La, Tang, Bao, & Bao, 2013).

The structure information of corresponding compounds was shown in (Table 1).

4. Discussion

"Digda" which belongs to Mongolian medicine LZH (called Habiligan-Digda in Mongolian medicine), as a characteristic medicinal material of traditional Mongolian medicine was included in the Pharmaceutical Standards of the Ministry of Health (Mongolian Medicine) in 1998. LZH is mainly used as the main component of Digda-4 and Digda-8 decoction, which has the functions of invigorating the stomach, retreating yellow and protecting the liver (Wu, Wang, Xin, Bai, & Sun, 2021). The Mongolian medicine HM (the Mongolian medicine is called Xiyiri-Digda), has the functions of removing "Xieri" and clearing away fever. Decocted and boiled single use or with the compatibility of medicines *Chrysosplenium nudicaule* Bunge in Ledeb., *Dryopteris crassirhizoma* Nakai, *Thlaspi* arvense L., *Dianthus superbus* L., *Rosa rugosa* Thunb., etc., It is made into Digda-25, used for a bitter mouth, thirst, jaundice, high fever,

headache and other "xieri" diseases; It was made into Meng Huamao Ganning tablet, which was used for liver and gallbladder fever and yellow stain caused by Xieri fever. It is used for yellow eyes, bitter mouth, high fever, headache, yellow urine, Xeri fever, wound fever, pulse fever and other diseases (Ao & Bu, 2013). By reviewing the literature, we found compounds isovitexin and usnic acid has anti-cancer effects, such as isovitexin inhibits cell viability and self-renewal and promotes apoptosis in non-small cell lung cancer (NSCLC) cells by inhibiting Wnt/β-catenin signaling pathway (Zhao, Ding, & Li, 2022). Usnic acid is characteristic to lichens, possessing pharmacological activities such as anti-virus, anti-bacteria, anti-humor, anti-inflammatory, analgesic, and anaesthetic effects (Wuken et al, 2018). Present study can be further improved. There are few studies on the two types of Digda. In recent years, with the rapid rise of traditional medicine and the acceleration of the modernization of Mongolian medicine, modern research on "Digda type" Mongolian medicine is also increasing. The study of chemical composition provides a scientific basis for the development and utilization of "Digda" unique medicinal materials, making fundamental contributions for the study of chemical constituents of Mongolian medicinal materials LZH and HM.

5. Conclusion

Twelve monomer compounds were isolated and identified from "Digda" Mongolian medicinal materials LZH and HM. Among them, six compounds were isolated from LZH, and HM identified six compounds. Compounds **6** and **12** were isolated from this plant for the first time. The monomeric compound usnic acid was isolated from HM for the first time through experimental study, which provided a strong basis for future research.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was supported by the Inner Mongolia Autonomous Region undergraduate colleges and universities directly undergraduates in 2019 "Double First class" construction special fund Mongolian Medicine Research and Innovation Team Construction Project (No.190302), 2021 Grassland Talents (No. CYYC21003), Open Project of NMPA Key Laboratory f Quality Control of Traditional Chinese Medicine (Mongolian Medicine) (No. MDK2021073).

References

- Ao, W. L. J., & Bu, H. B. T. E. (2013). Traditional Mongolian medicine and prescriptions. Inner Mongolia Science and Technology Press, 46–47.
- Ba, G. N., Chen, Y. L., Ba, D. R. H., Tong, Y. F., Ye, R. G., & Wang, Q. H. (2014). Two new xanthones from Lomatogonium carinthiacum. Chinese Journal of Natural Medicines, 12(9), 693–696.
- Ba, G. N. (2007). Mongolian medicine prescription. Neimenggu People's Publishing House, 7, 95.
- Gui, R., Bai, M. R., Liu, X., La, X. N. M. J. L., Bao, M. L., & Ba, G. N. (2015). Protective effect and mechanism analysis of alcohol extract of Mongolian medicine *Halenia corniculate* on chemically acute liver injury in rats. *Journal of Chinese Medicinal Materials*, 38(12), 2583–2585.
- Ji, L. J., Ding, J. Y., Fan, S. F., & Sun, H. F. (1992). Study on chemical constituents of Gentianopsis barbata var. stennocalyx H.W.LI EX T.N.HO. Journal of Integrative Plant Biology, 3(3), 203–207.
- Jin, Z., Mi, J. A., Qi, S. S., Ki, Y. K., Yun, H. H., Jei, M. R., & Jin, W. K. (2008). Inhibitors of bone resorption from *Halenia corniculata*. Archives of Pharmacal Research, 31(7), 850–855.
- La, X. N. M. J. L., Tang, Y. X., Bao, H. Y., & Bau, T. (2013). Chemical constituents from Usnea longgisima, a traditional Mongolian medicine. *China Journal of Chinese Materia Medica*, 38(13), 2125–2128.

Aodungerile, Xigurigan, Tunumula et al.

- Li, Y. L., Suo, Y. R., Liao, Z. X., & Ding, L. S. (2008). The glycosides from Lomatogonium rotatum. Natural Product Research, 22(3), 1989–11202.
- Liu, X., Liu, Y., & Shi, Y. P. (2009). Xanthom glycosides from Tibetan herb Halenia elliptica. China Journal of Chinese Materia Medica, 34(5), 580–582.
- Luo, B. S. (2006). Mongolian pharmacy. Neimenggu. People's Publishing House, 94–97.
 Ru, F., Jian, G. S., Xiao, W. L., Chun, T. C., John, H. K. Y., & Yan, W. (2010).
 Identification of the metabolites of biologically active xanthones isolated from
 Halenia elliptica D. Don by high performance liquid chromatography coupled to
 ion trap time-of-flight mass spectrometry. Chinese Chemical Letters, 22(7),
 839–842.
- Sun, L. P., Wang, J. R., Li, X. R., Zheng, S. Z., & Shen, X. W. (1997). Studies on the chemical constituents of Eriostachys Elsholtzia (Elshltzia eriostachys) II. Isolation and identification of flavonoids constituents. *Chinese Herbal Medicine*, 11, 646–648.
- Takahiro, H., Young, S. Y., & Akira, K. (2005). Five novel flavonoids from Wasabia japonica. *Tetrahedron*, 61(29), 7037–7044.
- Tai, B. D. L. H., La, X. N. M. J. L., Gui, R., Bai, M. R., Bao, M. L., & Ba, G. N. (2015). Chemical constituents in petroleum ether extract of Mongolian

medicine Halenia corniculate. Journal of Chinese Medicinal Materials, 38(11), 1001-4454.

- Wang, G. S., Zhou, X. P., Cui, J., Zhao, X. M., & Yang, X. H. (2009). Iridoid compounds in the buds of *Lonicera ruprechtiana* Regel. *Chinese Journal of Medicinal Chemistry*, 19(3), 206–208.
- Wang, Q. H., Wu, J. S., Wu, X. L., Han, N. R. C. K. T., Tai, W. Q., Dai, N. Y. T., ... Ao, W. L. J. (2015). Anti-inflammatory effects and structure elucidation of flavonoid and biflavonoid glycosides from Artemisia frigida Willd. Monatshefte für Chemie -Chemical Monthly, 146(2), 383–387.
- Wu, R. T. Y., Wang, M. L., Xin, Y., Bai, C. L., & Sun, B. E. (2021). Modern Research Progress of Mongolian Medicine Lomatogonium carinthiacum (Wulf) Reichb. Journal of Inner Mongolia University for Nationalities, 36(2), 144–147.
- Wuken, S. N., Jiao, S. G., Yang, X. Y., Gao, X. L., Qu, C. H., Zhang, Q., ... Chai, X. Y. (2018). Chemical and pharmacological progress on usnic acid and its derivatives. *China Journal of Chinese Materia Medica*, 43(19), 3811–3821.
- Zhao, F. Z., Ding, C. Z., & Li, X. M. (2022). Effect of isovitexin on self renewal and apoptosis in non-small cell lung cancer cells. *The Chinese Journal of Clinical Pharmacology*, 38(3), 219–223.