

Two New Components from *Serratula strangulata* Iljin

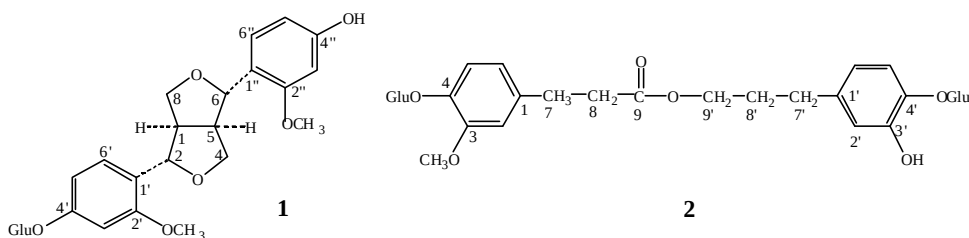
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Abstract: From the alcoholic extract of the whole plants of *Serratula strangulata*, two new compounds, named strangusin-A (**1**) and strangusin-B (**2**) have been isolated and their structures were established by spectroscopic method.

Keywords: *Serratula strangulata*, lignan, phenolic compound, Compositae, strangusin-A, strangusin-B.

The genus *Serratula* (Compositae) consists of about 70 species distributed throughout the world. Among them, *S. chinensis* has been used as a folk medicine to treat chickenpox, toxicosis, high cholesterol¹. In order to find active principles, the chemical constituents of *Serratula strangulata* were studied and a new lignan **1** and a new phenolic compound **2** were isolated from the alcoholic extract of the rhizome. In this paper, we report the structural elucidation of the compound **1** and **2**.



Compound **1**, obtained as a colourless gum, was assigned the molecular formula $C_{26}H_{32}O_{11}$ by HR-FABMS (m/z 520.1957; Calc.: 520.1945). Its UV spectrum showed bands at 242 (log ϵ 4.23) and 280 nm (4.12), characteristic of a biphenyl chromophore. The IR spectrum (KBr) indicated the presence of hydroxyl (3383cm^{-1}) and phenyl groups and double bonds (2929 , 1602 , 1514 , 1462cm^{-1}). The mass spectrum exhibited a base peak at m/z 325 $[M-C_6H_{11}O_5-OMe-H]^+$ and fragment ions at m/z 357 $[M-C_6H_{11}O_5]^+$ and 340 $[M-C_6H_{11}O_5-OH]^+$. The ^1H NMR spectrum (**Table 1**) indicated the presence of two 1,2,4-trisubstituted benzene rings [δ 7.04 (d, 1H, $J = 2.1$ Hz), 6.91 (dd, 1H, $J = 8.3$, 2.1 Hz), 7.13 (d, 1H, $J = 8.3$ Hz); 6.98 (d, 1H, $J = 1.8$ Hz), 6.82 (dd, 1H, $J = 8.2$, 1.8 Hz), 6.78 (d, 1H, $J = 8.2$ Hz)], two methoxyl groups [3.83, 3.85 (s, each 3H)] and an anomeric proton of glucopyranoside [δ 4.90 (d, $J = 7.1$ Hz)], acid hydrolysis of **1** gave glucose

identified by TLC comparing with authentic sample. Furthermore, the ^1H NMR signals at δ 3.08 (m, 2H, H-1, 5), 4.66 (d, 2H, H-2, 6, $J = 4.3$ Hz), 4.20 (dd, 2H, H-4 α , 8 α , $J = 9.0, 6.6$ Hz), 3.85 (dd, 2H, H-4 β , 8 β , $J = 9.0, 2.4$ Hz), suggested **1** to be a lignan containing 3, 7-dioxabicyclo [3.3.0] octane ring system^{2,3}.

In the ^1H - ^1H COSY spectrum of **1**, there were significant cross-peaks between 3.08 (H-1, 5) and 3.85 (H-4 β , 8 β) and 4.20 (H-4 α , 8 α), H-1 and H-2; H-5 and H-6. This further testified the presence of furofuran ring in **1**. In the NOESY spectrum of **1**, there were significant cross-peaks between H-1 and H-8 α , H-2 and H-8 β , H-5 and H-4 α , H-6 and H-4 β , indicating H-1, 5 as α -orientation and H-2, 6 as β -orientation. Now, the only problem left was to ascertain the locations of glucose, hydroxy and two methoxyl groups. The HMBC spectrum exhibited related peaks at δ 3.85 (OCH₃), 4.66 (H-2), 7.04 (H-3') and 156.65 (C-2'); 3.83 (OCH₃), 4.71 (H-6), 6.98 (H-3'') and 156.73 (C-2''); 7.13 (H-6'), 4.66 (H-2) and 124.60 (C-1'); 6.78 (H-6''), 4.71 (H-6) and 122.96 (C-1''); 6.82 (H-5''), 6.98 (H-3'') and 155.97 (C-4''); 6.91 (H-5'), 7.04 (H-3'), 4.90 (the glucosyl C-1 proton signal) and 157.25 (C-4'), suggesting that the sites of attachment of the glucose, hydroxy and two methoxyl groups were at C-4', C-4'', C-2' and C-2'', respectively. Consequently, the structure of **1** was established. This is the first time to report occurrence of a lignan in the genus *Serratula*.

Table 1 ^1H and ^{13}C NMR data of compound **1** ((CD₃)₂CO, TMS, δ ppm)*

No.	δ_{H} (J Hz)	δ_{C}	No.	δ_{H} (J Hz)	c
1	3.08 m	55.09	2"		156.73
2	4.66 d (4.3)	86.56	3"	6.98d (1.8)	108.14
4	4.20 dd (9.0, 6.6) 3.85 dd (9.0, 2.4)	72.17	4"		155.97
5	3.08 m	55.21	5"	6.82dd (8.2, 1.8)	110.22
6	4.71 d (4.2)	86.30	6"	6.78d (8.2)	130.50
8	4.20 dd (9.0, 6.6) 3.85 dd (9.0, 2.4)	72.26	2"-OCH ₃	3.83 s	56.20
1'		124.60	Glu		
2'		156.65	1	4.90 d (7.1)	102.48
3'	7.04d (2.1)	107.31	2	3.44 dd (7.1, 8.0)	74.47
4'		157.25	3	3.83 t (8.0)	77.70
5'	6.91dd (8.3, 2.1)	109.57	4	3.46 t (8.0)	71.06
6'	7.13d (8.3)	130.13	5	3.50 ddd (8.0, 4.9, 1.1)	77.54
2'-OCH ₃	3.85 s	56.39	6a	3.67 dd (11.8, 4.9)	62.42
1"		122.96	6b	3.80 dd (11.8, 1.1)	

*Assignment from ^1H - ^1H COSY, HMQC, HMBC and NOESY

Table 2 ^1H and ^{13}C NMR data of compound **2** ($(\text{CD}_3)_2\text{CO}$, TMS, δ ppm)*

No.	δ_{H} (J Hz)	δ_{C}	DEPT	No.	δ_{H} (J Hz)	δ_{C}	DEPT
1		137.93	C	8'	1.75 m	29.79	CH_2
2	6.62 d (1.4)	113.11	CH	9'	3.83 t (6.0)	69.21	CH_2
3		148.24	C	glu			
4		144.56	C	1	4.68 d (7.3)	103.87	CH
5	6.96 d (8.2)	116.71	CH	2	3.20 dd (7.3, 8.0)	74.19	CH
6	6.51 dd (8.2, 1.4)	119.98	CH	3	3.41-3.77 m	76.93	CH
7	2.67 t (6.6)	32.37	CH_2	4	3.41-3.77 m	70.70	CH
8	2.53 t (6.6)	45.26	CH_2	5	3.41-3.77 m	77.17	CH
9		175.26	C	6	3.41-3.77 m	62.03	CH_2
1'		134.16	C	1'	4.26 d (7.6)	104.30	CH
2'	6.74 d (1.1)	115.57	CH	2'	3.34 dd (7.6, 8.1)	74.49	CH
3'		148.30	C	3'	3.41-3.77 m	77.47	CH
4'		145.56	C	4'	3.41-3.77 m	71.12	CH
5'	6.65 d (8.0)	119.00	CH	5'	3.41-3.77 m	77.68	CH
6'	6.56 dd (8.0, 1.1)	121.46	CH	6'	3.41-3.77 m	62.37	CH_2
7'	2.61 t (7.5)	32.11	CH_2				

*Assignment from ^1H - ^1H COSY, HMQC and HMBC.

Compound **2** was obtained as a colourless gum. The IR spectrum (KBr) showed the presence of hydroxyl (3389cm^{-1}), aromatic rings ($3008, 1600, 1510\text{ cm}^{-1}$) and carbonyl group (1708 cm^{-1}). FABMS exhibited the $[\text{M}]^+$ peak at m/z 670. The ^{13}C NMR and DEPT spectrum (**Table 2**) indicated that compound **2** possesses $16\times\text{CH}$, $7\times\text{CH}_2$, $1\times\text{CH}_3$ and seven quaternary carbon atoms. Thus, the molecular formula of **2** was determined as $\text{C}_{31}\text{H}_{42}\text{O}_{16}$, which was confirmed by HR-FABMS (m/z 670.2469; Calc.: 670.2473). The ^1H NMR spectrum displayed resonances at δ 6.96 (d, 1H, $J = 8.2\text{ Hz}$), 6.62 (d, 1H, $J = 1.4\text{ Hz}$), 6.51 (dd, 1H, $J = 8.2, 1.4\text{ Hz}$), 6.74 (d, 1H, $J = 1.1\text{ Hz}$), 6.65 (d, 1H, $J = 8.0\text{ Hz}$), 6.56 (dd, 1H, $J = 8.0, 1.1\text{ Hz}$), indicating the presence of two 1,2,4-trisubstituted benzene rings. The ^1H NMR spectrum also showed the presence of two anomeric proton of glucopyranoside [δ 4.68 (d, $J = 7.3\text{ Hz}$), 4.26 (d, $J = 7.6\text{ Hz}$)]. These data together with ^{13}C NMR signals at δ 103.87 (CH), 74.19 (CH), 76.93 (CH), 70.70 (CH), 77.17 (CH), 62.03 (CH_2), and δ 104.30 (CH), 74.49 (CH), 77.47 (CH), 71.12 (CH), 77.68 (CH), 62.37 (CH_2), indicated that compound **2** has two β -glucosyl moieties⁴.

In the ^1H - ^1H COSY spectrum of **2**, there were significant cross-peaks between δ 2.67 (H-7) and 2.53 (H-8), 1.75 (H-8') and 2.61 (H-7') and 3.83 (H-9'), suggesting the presence of the partial structures $-\text{CH}_2-\text{CH}_2-$ and $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, respectively. The HMBC spectrum exhibited related peaks at 2.67 (H-7) and 6.62 (H-2) and 6.51 (H-6) and δ 137.93 (C-1); 6.96 (H-5) and 4.68 (the glucosyl C-1 proton signal) and 144.56 (C-4);

3.83 (OCH₃) and 6.62 (H-2) and 148.24 (C-3); 2.53 (H-8) and 3.83 (H-9) and 175.26 (C-9); 2.61 (H-7') and 6.74 (H-2') and 6.56 (H-6') and 134.16 (C-1'); 6.65 (H-5') and 4.26 (the glucosyl C-1' proton signal) and 148.30 (C-4). Furthermore, in its FABMS spectrum, the fragment ions at m/z 342 (C₁₆H₂₁O₈⁺) and 358 (C₁₆H₂₁O₉⁺) was due to the α -fragmentation around carbonyl group. Thus, the structure of **2** was deduced.

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