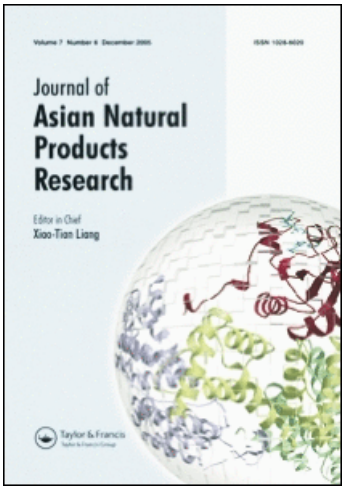

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Two new lignans from *Mentha spicata* L.

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Two new lignans named spicatolignan A **(1)** and spicatolignan B **(2)** have been isolated from the whole herbs of *Mentha spicata* L.

Keywords: *Mentha spicata* L; Lignan; Spicatolignan A; Spicatolignan B

1. Introduction

Mentha spicata L. is a plant of *Mentha* genus, which is one of the most well known oil-producing plants. Its volatile oil as an aromatic stimulant is usually added into candies or toothpastes in many places, especially in European countries [1,2]. According to modern research, it has shown activity such as anti-inflammation, styptic, relief of pain, and so on [3]. To further study this plant, research on its activities and chemical constituents from the active parts were carried out, and two new lignans named spicatolignan A and spicatolignan B were isolated. In this paper we report their isolation and structural elucidation.

2. Results and discussion

Spicatolignan A **(1)** was obtained as colourless needles (MeOH) with mp 175–177°C. It showed a positive Molish reaction. The glucose was examined after the acid hydrolysis. The molecular formula $C_{27}H_{30}O_{13}$ was determined on the basis of ESI-MS (*m/z* 561.0 $[M - H]^-$, 585.1 $[M + Na]^+$) together with ^1H NMR and ^{13}C NMR spectral data. The ^{13}C NMR spectrum exhibited 27 carbon signals, including three overlap signals (δ 148.3, 105.0, 56.3), a conjugated carbonyl, 16 olefinic, three methoxy groups, one alkyl carbon. The ^1H NMR spectrum showed a pair of *trans*-olefinic protons [δ_H 6.62 (1H, d, $J = 16.0$ Hz), 7.67 (1H, d, $J = 16.0$ Hz)], four aromatic protons [δ_H 7.15 (2H, s), 7.32 (1H, s), 7.65 (1H, s)] belonging to

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two benzene rings, two methoxyl protons [δ_H 3.87 (6H, s)]. The ^{1}H NMR and ^{13}C NMR spectra indicated the presence of a symmetrical benzene ring. The location of substituents in the two benzene rings and the glucose were confirmed by the HMBC spectrum. HMBC correlations between H-4 (δ_H 7.65), H-6 (δ_H 7.32) and C-10 (δ 144.9), H-10 (δ_H 7.67) and C-6 (δ 106.2), as well as H-11 (δ_H 6.62) and C-12 (δ 168.0) suggested the *trans*-double bond and the carbonyl group were positioned at C-5 and C-11, respectively. The glycoside linkage was determined to be at the C-3a position based on the ^3J long-range coupling between the anomeric proton (δ_H 4.39) and C-3a (δ 59.7) in the HMBC spectrum. Furthermore, the anomeric configuration of the sugar moiety was determined to be the β-form on the basis of the coupling constant for H-1′ ($J = 7.6$ Hz). On the above evidence, the structure of **1** was elucidated as 2-(3,5-dimethoxyl-4-hydroxyphenyl)-5-*trans*-carboxylethylene-7-methoxyl-benzofuran-3-methyl-*O*-β-D-pyranoglucoside **(1)**, and named spicatolignan A (figure 1).

Compound **2** was white amorphous powder (MeOH) with mp 150–152°C. The molecular formula $C_{20}H_{20}O_7$ was deduced by HRFAB-MS at *m/z* 395.1091[M + Na]$^+$. The ^{1}H NMR, ^{13}C NMR and DEPT spectra indicated the presence of the three methylenes (δ 88.0, 52.7, 62.8), two methoxyl groups (δ_H 3.74, 3H, s; 3.82, 3H, s), a carbonyl group (δ 168.1) and 14 olefinic carbons. The ^{1}H NMR spectrum exhibited a large coupling constant between δ_H 6.40 (1H, d, $J = 15.9$ Hz) and 7.52 (1H, d, $J = 15.9$ Hz), showing the *trans*-configuration for the double bond, a pair of *meta*-coupled aromatic protons (δ_H 7.24, 1H, br.s; 7.21, 1H, br.s) and an ABX system (δ_H 6.92, 1H, d, $J = 1.8$ Hz; 6.76, 1H, dd, $J = 8.1$, 1.8 Hz; 6.74, 1H, d, $J = 8.1$ Hz), indicating there were two benzene rings. The ^{1}H NMR and ^{13}C NMR spectra also exhibited a —CH—CH—CH_2OH moiety. In the HMBC spectrum, the long-range correlations of H-4 (δ_H 7.21), H-6 (δ_H 7.24) with C-10 (δ 144.0), and H-10 (δ_H 7.25) with C-6 (δ 112.4), C-12 (δ 168.1) suggested the *trans*-double bond and the carbonyl group were placed in C-5 and C-11, respectively. The correlations between δ_H 6.91/δ_H 3.74 and δ_H

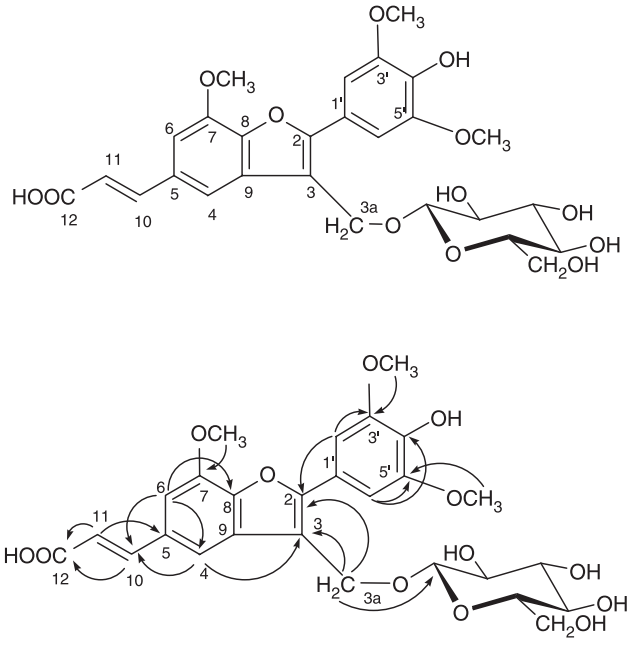

Figure 1. Structure and key HMBC correlations of **1**.

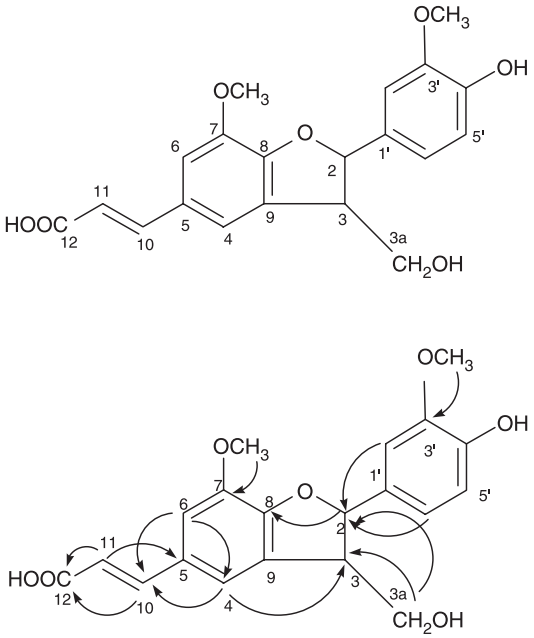

Figure 2. Structure and key HMBC corrections of **2**.

7.24/δ_H 3.82 in the NOESY spectrum proved the methoxyl groups at δ_H 3.74 (3H, s) and 3.82 (3H, s) were located at C-3′ and C-7, respectively. Finally, the structure of **2** was concluded to be 2-(3-methoxyl-4-hydroxyphenyl)-3-hydroxylmethyl-5-*trans*-carboxylethylene-7-methoxyl-2, 3-dihydrobenzofuran, and named spicatolignan B (figure 2).

3. Experimental

3.1 General experimental procedures

Melting points were measured on a Yanaco MP-S3 apparatus without correction. The NMR spectra were run on a Bruker ARX-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) spectrometer; HRFAB-MS spectra were measured with a Bruker APEX mass spectrometer; TLC was performed on silica gel H (10–40 μ, Qingdao Marine Chemical Inc., China). Separation and purification were performed by column chromatography on silica gel (200–300 mesh, Qingdao Marine Chemical) or Sephadex-LH20 (25–100 μm, Pharmacia).

3.2 Plant material

Mentha spicata was obtained as whole herbs from Faku in Liaoning Province of China and identified by Professor Qi-shi Sun at the Department of Pharmacognosy of Shenyang Pharmaceutical University. The voucher specimen is deposited at same department.

3.3 Extraction and isolation

The whole herbs of *M. spicata* (7 kg) were extracted with water three times. The extracts were collected together and concentrated, then mixed with three times volume of EtOH

to cause precipitation. The supernatant was evaporated under pressure to obtain the crude extract (550 g), then the extract was dissolved in water and submitted to a macroporous resin AB-8 column, which eluted with water (20%) and ethanol (30%, 80%) successively. The 30% EtOH portion was subjected to column chromatography on silica gel and eluted with $CHCl_3$/MeOH/H_2O (75:25:2.5) solvent to afforded five fractions. Fraction three was further treated by CC over silica gel to yield compound **1** (10.0 mg). The 80% EtOH portion was subjected to column chromatography on silica gel eluting with a petroleum ether/acetone gradient system, to give seven fractions. Fraction four was treated by crystal to yield compound **2** (11.3 mg).

3.3.1 Spicatolignan A (1). Colourless needles (MeOH), mp 175–177°C; ESI-MS *m/z* 561.0 $[M-H]^-$, 585.1 $[M + Na]^+$; ^1H NMR and ^{13}C NMR data are given in table 1.

3.3.2 Spicatolignan B (2). White amorphous powder (MeOH), mp 150–152°C; HRFAB-MS *m/z* 395.1091$[M + Na]^+$ (calcd for $C_{20}H_{20}O_7Na$, 395.1101); ^1H NMR and ^{13}C NMR data are given in table 1.

Table 1. NMR data of compounds **1** and **2** (DMSO-d_6).

	1		***2***	
Position	δ_H	δ_C	δ_H	δ_C
2		155.6	5.53 (1H, d, $J = 6.6$ Hz)	88.0
3		111.0	3.49 (1H, m)	52.7
4	7.65 (1H, s)	113.2	7.21 (1H, br.s)	117.9
5		130.9		127.9
6	7.32 (1H, s)	106.2	7.24 (1H, br.s)	112.4
7		144.3		144.4
8		143.0		149.8
9		132.0		130.0
10	7.67 (1H, d, $J = 16.0$ Hz)	144.9	7.25 (1H, d, $J = 15.9$ Hz)	144.0
11	6.62 (1H, d, $J = 16.0$ Hz)	119.3	6.40 (1H, d, $J = 15.9$ Hz)	116.5
12		168.0		168.1
1′		118.9		132.1
2′	7.15 (1H, s)	105.0	6.92 (1H, d, $J = 1.8$ Hz)	110.6
3′		148.3		147.7
4′		137.2		146.7
5′		148.3	6.74 (1H, d, $J = 8.1$ Hz)	115.5
6′	7.15 (1H, s)	105.0	6.76 (1H, dd, $J = 8.1$, 1.8 Hz)	118.8
3a	4.86 (1H, d, $J = 11.5$ Hz)			
	5.03 (1H, d, $J = 11.5$ Hz)	59.7	3.66 (2H, m)	62.8
1″	4.39 (1H, d, $J = 7.6$ Hz)	101.6		
2″	3.06 (1H, m)	73.6		
3″	3.15 (1H, m)	77.2		
4″	3.06 (1H, m)	70.4		
5″	3.12 (1H, m)	77.0		
6″	3.49 (1H, m)			
	3.75 (1H, d, $J = 11.1$ Hz)	61.4		
7-OCH_3	4.02 (3H, s)	55.8	3.82 (3H, s)	55.9
3′-OCH_3	3.87 (3H, s)	56.3	3.74 (3H, s)	55.8
5′-OCH_3	3.87 (3H, s)	56.3		

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