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A new lignan from the seeds of *Arctium lappa*

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A new compound, neoarctin A (**1**), together with nine known compounds (**2**–**10**), were obtained from the ethanolic extract of the seeds of *Arctium lappa*. The structure of **1** was elucidated on the basis of spectral and chemical evidence.

Keywords: *Arctium lappa*; Seeds; Lignans; Neoarctin A

1. Introduction

The seeds of *Arctium lappa* are used in folk medicine as diuretics, anti-inflammatory or detoxifying agents, while its roots are used as food. In our research, a new lignan, named neoarctin A (**1**) together with nine known compounds were obtained. The known compounds were identified by comparison with literature values and confirmed by 2D NMR data. This paper describes the isolation and structure elucidation of the new compound.

2. Results and discussion

Column chromatography on silica gel, Sephadex LH-20 and preparative HPLC of the n-BuOH phase from the ethanolic extract of the seeds from *Arctium lappa* resulted in the isolation of ten compounds. The known compounds: mairesinol (**2**) [1], arctiin (**3**) [2], lappaol A (**4**), E (**5**), F (**6**) [3] and H (**7**) [4], arctignan A (**8**), G (**9**) and H (**10**) [5] were identified by comparing their NMR data with those in the literature.

Compound **1**, obtained as amorphous powder from MeOH, showed a positive reaction with 5% H_2SO_4. Its HRFAB-MS afforded a quasimolecular ion peak at *m*/*z* 537.1956 $[M - H]^-$ which indicated the molecular formula of $C_{26}H_{34}O_{12}$, also confirmed by NMR data. The ^{1}H NMR spectrum exhibited six olefinic protons, including two ABX systems at δ

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7.14 (1H,d, $J = 7.9$ Hz, H-5), 7.08 (1H, br.s, H-2), 6.97 (1H, d, $J = 7.9$ Hz, H-6), 7.10 (1H, d, $J = 7.9$ Hz, H-5′), 6.99 (1H, br.s, H-2″) and 6.76 (1H,d, $J = 7.9$ Hz, H-6″). The upfield region of the spectrum exhibited eight proton signals at δ 4.66 (1H, d, $J = 7.5$ Hz, H-7), 4.57 (1H, d, $J = 8.1$ Hz, H-7″), 4.27 (1H, dd, $J = 9.0$, 4.5 Hz, H-9″β), 3.90 (1H, dd, $J = 9.0$, 7.5 Hz, H-9″α), 3.79 (1H, dd, $J = 11.1$, 4.5 Hz, H-9a), 3.69 (1H, dd, $J = 11.1$, 6.4 Hz, H-9b), 2.63 (1H, m, H-8″) and 2.28 (1H, m, H-8). Two methoxyl groups at δ 3.88 (3H, s, 3″-OC$\underline{H}_3$), 3.85 (3H, s, 3-OC$\underline{H}_3$) were also found. The ^{13}C NMR spectrum showed that apart from the 12 aromatic and two methoxyl carbons, there were six other carbon atoms, four of them bearing oxygen. In the ^{1}H–^{1}H COSY spectrum, the presence of two 3,4-disubstituted phenyl groups was observed. Since the two methoxylgroups showed cross peaks with H-2 and H-2″ in the NOESY spectrum of **1**, the two phenyl groups were considered to form guaiacyl structures. In the aliphatic region, two three-carbon units, composed of a benzylcarbon bearing oxygen, a methine carbon and a methylene carbon bearing oxygen (C-7, 8, 9; C-7″, 8″, 9″) were connected at the methine carbons (C-8, 8″). The signals in the ^{13}C NMR spectrum were also consistent with these combinations. Based on the degree of unsaturation, one of the three oxygen atoms in the alphatic portion of **1** was considered to form a furan ring. The sugar moiety of **1** was determined to be β-glucose, based on the coupling constant at δ 4.89 ($J = 6.8$ Hz) in the ^{1}H NMR spectrum and the ^{13}C NMR data (δ: 102.7, 77.8, 77.3, 74.9, 71.3, 63.2). Based on the cross peak between H-1″ and C-4 in the HMBC spectrum (figure 2), the glycosidic linkage of **1** was determined to be at C-4. The HMBC spectrum of **1** also showed that protons 3,3′-OC$\underline{H}_3$ (δ: 3.85, 3.88) correlated with C-3,3′. A *trans*-orientation of configuration at C-7/C-8 and C-8/C-8′ bonds were assigned, based on the chemical shifts of H-7 at δ 4.66 [6], C-8 at δ 55.8 and C-8′ at δ 52.7 [7–9]. The coupling constant $J_{H7',H8'} = 8.1$ Hz implied a *trans*-orientation of configuration for these two protons [9]. Furthermore, the NOESY experiment revealed clear correlations between H-7′/H-8,9′ β and H-8/H-7′,2′, suggesting a closer proximity of the guaiacyl group of C-7′ to C-8 than C-9′. Therefore the configuration of C-7′ was determined to be *S*, relative to C-8′(*S*), C-8(*R*) and C-7(*S*) [10]. From the above evidence, the structure of **1** was established as shown in figure 1.

3. Experimental

3.1 General experimental procedures

NMR specta were recorded at 400 MHz for ^{1}H and 100.0 MHz for ^{13}C on a Bruker AM-400 spectrometers with TMS as internal standard. Optical rotations were measured with a Horiba

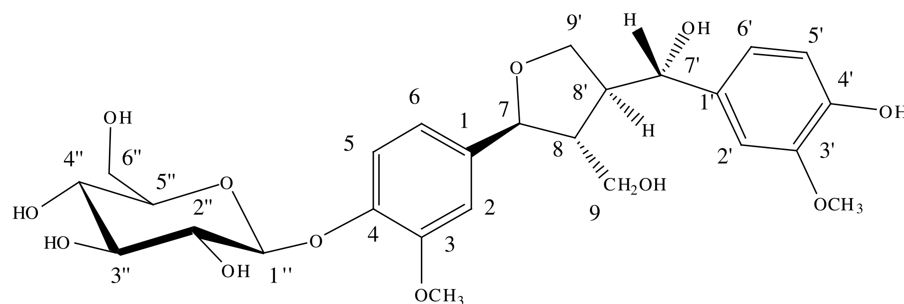

Figure 1. Structure of compound **1**.

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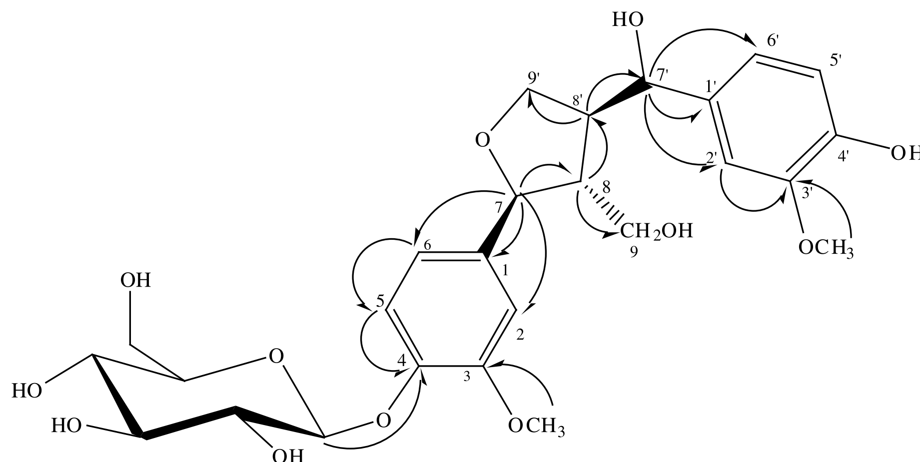

Figure 2. Important HMBC correlations of **1**.

SEAP-300 spectropolarimeter in CH_3OH. UV spectra were determined on a Hitachi U-2000 spectrophotometer. MS data were recorded on a VG-AUTOSPEC-3000 spectrometer. HPLC was performed on a Shimadzu LC-20A liquid chromatograph. IR spectra were recorded on a Shimadzu IR-450 spectrometer with KBr pellets. Merk lobar lichroprep RP-18 and Silica gel (200–300 mesh, Qingdao, China) were used for column. Sephadex LH-20 (Pharmacia) was used for molecular exclusion chromatography. TLC employed precoated Si gel GF254 plates (Qingdao, China).

3.2 Plant material

The seeds of *Arctium lappa* were purchased from the herbal market of Kunming, Yunnan Province, China. It was identified by Professor Zhang Weng Jin. A voucher specimen (20041015) is deposited at the Laboratory of Photochemistry-try, Kunming Institute of Botany.

3.3 Extraction and isolation

The air-dried and milled seeds of *Arctium lappa* (10 kg) were extracted with 95% MeOH three times under reflux. After removal of the solvent *in vacuo*, the syrup (500 g) was suspended in water (1500 ml) and extracted with EtOAc (3 × 1000 ml) and n-BuOH (3 × 1000 ml) successively to give EtOAc-soluble fraction (275 g) and n-BuOH-soluble fraction (300 g), respectively. n-BuOH-soluble fraction (300 g)was subjected to column chromatography on silica gel (200–300 mesh) and eluted with a gradient $CHCl_3$/MeOH to afford four fractions. Fraction 1 was further repeatedly subjected to column chromatography (silica gel; 200–300 mesh) using a gradient $CHCl_3$/MeOH as eluent to yield fractions 2 (465 mg, 12:1), (5 g, 10:1) and 4 (1.3 g, 10:1). Fraction 2 was separated on a silica gel column with a gradient mixture of $CHCl_3$/MeOH to give three sub-fractions. Compound **5** (50 mg, 10:1) was obtained from sub-fraction 1. Sub-fraction 2 was subjected to preparative HPLC and eluting with 65% MeOH/H_2O to produce compounds **6** (30 mg, 15 min) and **7** (25 mg, 17 min). Fraction 3 was chromatographed on a Rp-18 column and eluted with 30%, 40%, 50%, 60%, 70% and 100% CH_3OH/H_2O successively. The 50% eluate was

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chromatographed by preparative HPLC and eluted with 60% CH_3OH/H_2O to produce compounds **8** (17 mg, 28 min) and **9** (23 mg, 35 min). The 40% eluate was further repeatedly subjected to column chromatography using a gradient $CHCl_3$/MeOH as eluent to yield compound **10** (47 mg, 8:1). Fraction 4 was chromatographed on a sephadex LH-20 column and eluted with MeOH to give 3 sub-fractions. Sub-fraction 3 was separated on a silica gel column eluting with $CHCl_3$/MeOH (5:1) to yield compound **1** (15 mg).

3.3.1 Neoarctin A (1). $C_{26}H_{34}O_{12}$, white amorphous powder. $[\alpha]_D^{20} -15.7$(c 0.11, CH_3OH). UV(CH_3OH) λ_{max}: 273, 268, 247 nm^{-1}. IR (KBr) cm^{-1}: 3400 (OH), 1600 (arom. C=C). ^1H NMR (400 MHz, CD_3OD) δ (ppm): 7.14 (1H, d, $J = 7.9$ Hz, H-5), 7.10 (1H, d, $J = 7.9$ Hz, H-5′), 7.08 (1H, br.s, H-2), 6.99 (1H, br.s, H-2′), 6.97 (1H, d, $J = 7.9$ Hz, H-6), 6.76 (1H, d, $J = 7.9$ Hz, H-6′), 4.89 (1H, d, $J = 6.8$ Hz, H-1″), 4.66 (1H, d, $J = 7.5$ Hz, H-7), 4.57 (1H, d, $J = 8.1$ Hz, H-7″), 4.27 (1H, dd, $J = 9.0$ Hz, 4.5 Hz, H-9″ β), 3.90 (1H, dd, $J = 9.0$ Hz, 7.5 Hz, H-9″ α), 3.88 (3H, s, 3″-OC$\underline{H}_3$), 3.85 (3H, s, 3-OC$\underline{H}_3$), 3.79 (1H, dd, $J = 11.1$ Hz, 4.5 Hz, H-9a), 3.69 (1H, dd, $J = 11.0$ Hz, 6.4 Hz, H-9b), 2.63 (1H, m, H-8″), 2.28 (1H, m, H-8). ^{13}C NMR (100 Hz, CD_3OD) δ (ppm): 150.8 (C-3), 149.0 (C-3″), 147.6 (C-4), 147.4 (C-4″), 139.6 (C-1), 134.0 (C-1″), 120.7 (C-26″), 120.6 (C-6), 117.5 (C-5), 116.0 (C-5″), 112.1 (C-2″), 111.2 (C-2), 102.7 (C-1″), 85.5 (C-7), 78.2 (C-7″), 71.1 (C-9), 62.5 (C-9″), 55.8 (C-8), 52.7 (C-8″), 77.8 (C-3″), 77.3 (C-5″), 74.9 (C-2″), 71.3 (C-4″), 63.2 (C-6″), 56.7 (3-O$\underline{C}H_3$), 56.4 (3″-O$\underline{C}H_3$). 2D-NOESY cross peaks: H-2/3-OC$\underline{H}_3$, H-7, 8; H-6/H-7, 8; H-7/H-9a, b, 9″ α; H-8/H-7″, 2″; H-2″/3″-OC$\underline{H}_3$, H-7″, 8; H-7″/H-8, 9″ β. FAB-MS m/z:537.1956 $[M - H]^-$(calcd for $C_{26}H_{33}O_{12}$, 537.1972).

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