Sesquiterpenes from Stems of *Syringa pinnatifolia* var. *alashanensis*

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Abstract: **Objective** To study the chemical constituents of the volatile oil from the stems of *Syringa pinnatifolia* var. *alashanensis*. **Methods** The volatile oil from the stems of *S. pinnatifolia* var. *alashanensis* was obtained by steam distillation. They were isolated by chromatography on silica gel, Sephadex LH-20 columns and TLC, etc. The structures were elucidated by spectroscopic methods, including extensive 1D and 2D NMR techniques. **Results** Five sesquiterpenes were isolated from the volatile oil. **Conclusion** Compound **1** is a new sesquiterpene.

Key words: 15-norcadina-2-en-5, 9-diol; Oleaceae; sesquiterpene; *Syringa pinnatifolia* var. *alashanensis*; volatile oil
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Introduction

Syringa pinnatifolia Hemsl. var. *alashanensis* Ma. et S. Q. Zhou is a member of the family Oleaceae, and found predominantly in the spinney and scrub in upland of Helan Mountain, Inner Mongolia, China. The stems of *S. pinnatifolia* var. *alashanensis*, one of the best-known traditional herbal medicines, are frequently used to treat cardiovascular symptoms in Mongolian medicine (Nei, 1987; Ma, 1989; Qi, 2002). It is widely used in Mongolia as a substitute of the precious Chinese materia medica, *Lignum Aquilariae Resinatum*, which is used in treatment of asthma, cardiopalmus, and angina pectoris. The volatile oil from the stems of *S. pinnatifolia* var. *alashanensis* has a significant protective effect against experimental myocardial ischemia (Yan *et al*, 2010). The lignans (Ao *et al*, 2012a), neolignans (Wang *et al*, 2012), and sesquiterpenes (Ao *et al*, 2012b) have been isolated from this plant. As a part of our search for bioactive materials, we carried out a systematic chemical study on the volatile oils from the stems of *S. pinnatifolia* var. *alashanensis*, which resulted in the isolation of a new sesquiterpene, together with four known ones. Here, we report the structural characterization of the new compound by spectral analysis.

Materials and methods

General experimental procedures

The UV spectra were recorded on a Shimadzu UV—2201 Spectrometer. The IR spectra were recorded on a Thermo Nicolet 200 Double Beam Spectrophotometer with KBr pellets. Optical rotations were measured in $CHCl_3$ at 25 ℃ on a Perkin-Elmer 241 Polarimeter. The HR-ESI-MS spectra were measured on Bruker Daltonics MicroTOFQ. The NMR spectra were measured on a Bruker ARX — 600 NMR Spectrometer with tetramethylsilane (TMS) as the internal reference. Column chromatography was performed by using silica gel (200—300 mesh, Marine Chemical Factory, Qingdao, China) and Sephadex LH-20 (Pharmacia, Uppsala, Sweden). Fractions were monitored by TLC (silica gel GF_{254} 10—40 μm, Marine Chemical Factory, Qingdao, China), and spots were visualized by heating silica gel plates after spraying with 10% H_2SO_4 in EtOH.

Plant material

The stems of *Syringa pinnatifolia* Hemsl. var. *alashanensis* Ma. et S. Q. Zhou were collected in Inner Mongolia of China, in July 2010, and identified by Prof. Buhebateer (Inner Mongolia University for Nationalities). A voucher specimen (No. 20100726) was

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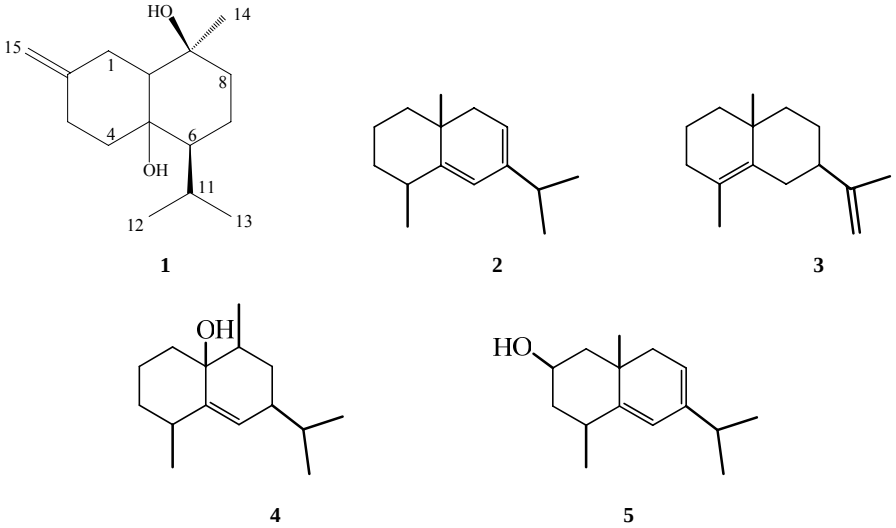
deposited in the School of Traditional Mongolian Medicine of Inner Mongolia University for Nationalities.

Extraction and isolation

The volatile oil from the stems of *S. pinnatifolia* var. *alashanensis* (200 g) was obtained by steam distillation. The volatile oil (5 mL) was subjected to silica gel column chromatography eluted with petroleum ether (PE)-EtOAc (80:1 to 10:1) to afford eight fractions (Frs. 1—8). Fr. 2 (200 mg) was purified by silica gel column eluting with PE-EtOAc (80:1 to 50:1) to yield four fractions (Frs. 2-1—2-4). Fr. 2-2 (40 mg) was further purified by silica gel column with PE-EtOAc (70:1) to give compound **2** (8 mg). Fr. 2-3 (40 mg) was further chromatographed over Sephadex LH-20 column eluting with $CHCl_3$-MeOH (1:1), and then separated over TLC (PE-acetone 10:1) to yield compound **3** (10 mg). Fr. 4 (300 mg) was subjected to a column of silica gel and eluted with PE-EtOAc (60:1 to 30:1) to give four fractions (Frs. 4-1—4-4). Fr. 4-2 (30 mg) was further purified over silica gel column with PE-EtOAc (50:1) to give compound **4** (9 mg). Fr. 4-3 (50 mg) was further chromatographed over Sephadex LH-20 column eluting with $CHCl_3$-MeOH (1:1), and then purified by TLC (PE-acetone 10:1) to yield compounds **1** (8 mg) and **5** (11 mg).

Results and discussion

Compound **1** (Fig. 1): pale yellow oil, $[\alpha]_D^{25}$ + 26° (*c* 0.10, $CHCl_3$); IR ν_{max}^{KBr} (cm^{-1}): 3023, 2964, 2856, 1624, 1390, 1361, 1195, 997, 912; ^{1}H-NMR and ^{13}C-NMR data were given in Table 1. HR-ESI-MS: *m/z* 238.1307 $[M-H]^-$ (Calcd. for $C_{15}H_{26}O_2$, 238.1324). The molecular formula was assigned as $C_{15}H_{26}O_2$ by HR-ESI-MS at *m/z* 238.1307 $[M - H]^-$ (Calcd. for $C_{15}H_{26}O_2$, 238.1324). The ^{13}C-NMR data indicated the presence of three methyls, five methylenes, three methines, two quaternary carbons as well as one terminal double bond in the molecule of compound **1**. The ^{1}H-NMR spectra of compound **1** showed the presence of one methyl group linked to a quaternary carbon, one isopropyl group and two olefinic hydrogens (Table 1). The proton bearing carbon signals was assigned by analysis of the HMQC spectrum and the correlations observed in the HMBC spectrum (Fig. 2) confirmed the planar structure of compound **1**. The correlations of CH_3-13 (δ_H 0.93, d) and CH_3-12 (δ_H 0.90, d) with C-6 (δ 51.4), as well as CH_3-14 (δ_H 1.20, s) with C-10 (δ 54.1) and C-8 (δ 43.0) indicated the isopropyl group located at C-6, and the methyl group located at C-9; the correlations of Ha-15 (δ 4.85, s) with C-3 (δ 34.6) and Hb-15 (δ 4.74, s) with C-1 (δ 46.9) indicated that the terminal double bond was attached to C-2. In addition, the HMBC spectrum showed the correlations between H-1 and C-3, C-5, C-9, C-15; H-6 and C-4, C-8, C-10. The relative configuration at the chiral carbons in compound **1** was supported by the NOESY spectrum and the coupling constants. First, in its ^{1}H-NMR spectrum, the typical coupling constants, $J_{10,1\alpha}$ = 11.4 Hz, indicated that H-10 was with β-orientation (Bohlmann *et al*, 1984; Fang, Yu, and Mabry, 1988; Lago, Brochina, and Roque, 2000), in correspondence with NOESY correlation between H-10



1 **2** **3** **4** **5**

Fig. 1 Structures of compounds 1—5

Table 1 ^{1}H-NMR and ^{13}C-NMR data (600 and 150 MHz, in DMSO-d_6) of compound 1

Positions	δ_H	δ_C
1	2.51 (d, 1H, J = 13.2 Hz)	46.9
	1.94 (d, 1H, J = 11.4 Hz)	
2		146.1
3	2.38 (m, 1H); 1.96 (m, 1H)	34.6
4	2.94 (m, 1H); 1.32 (m, 1H)	22.8
5		75.0
6	1.13 (m, 1H)	51.4
7	1.52 (m, 2H)	19.4
8	1.85 (m, 1H); 1.46 (m, 1H)	43.0
9		72.5
10	1.39 (d, 1H, J = 11.4 Hz)	54.1
11	2.10 (m, 1H)	25.2
12	0.90 (d, 3H, J = 6.6 Hz)	18.4
13	0.93 (d, 3H, J = 6.6 Hz)	24.0
14	1.20 (s, 3H)	18.2
15	4.85 (s, 1H); 4.74 (s, 1H)	111.4

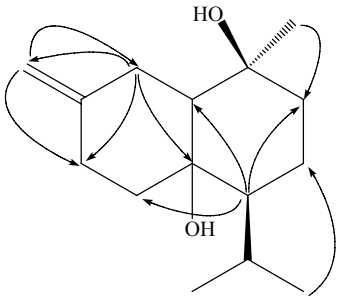


Fig. 2 Key HMBC correlations of compound 1

and H-1β (δ_H 2.51). The NOESY interaction from H-6 to CH_3-14 showed that these four protons were at the same side. When the H-10 took β-orientation and no correlation was observed between H-10 and CH_3-14 or H-6, CH_3-14 and H-6 should be in α-orientation, which was supported by the NOESY interaction from H-6 to CH_3-14. The configuration of C-5 has not been determined in the study because of the low yield of compound **1**. Thus, the structure of compound **1** was elucidated and named as 15-norcadina-2-en-5, 9-diol.

The comparison of ^{1}H-NMR and ^{13}C-NMR spectrum data for compound **2** with literature (Lago, Brochina, and Roque, 2002) indicated its structure as eudesma-5,7-diene. The sesquiterpenes eudesma-4,11-diene (**3**), eudesma-4,11-diene-10-ol (**4**), and eudesma-5,7-dien-2-ol (**5**) were identified by comparison of their ^{1}H-NMR and ^{13}C-NMR spectrum data with literature (Bohlmann *et al*, 1984; Fang, Yu, and Mabry, 1988; Lago, Brochina, and Roque, 2000).

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