Tetraenol, a Novel Sesquiterpenoid from the Relict Plant *Tetraena mongolica* in China

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A novel furansesquiterpenoid, tetraenol, was isolated from a relict shrub plant, *Tetraena mongolica,* collected from the northern desert of the Ningxia Hui Autonomous Region. The structure of the new compound was elucidated on the basis of spectroscopic analysis.

Key words: Tetraena mongolica, Furansesquiterpenoid, Tetraenol

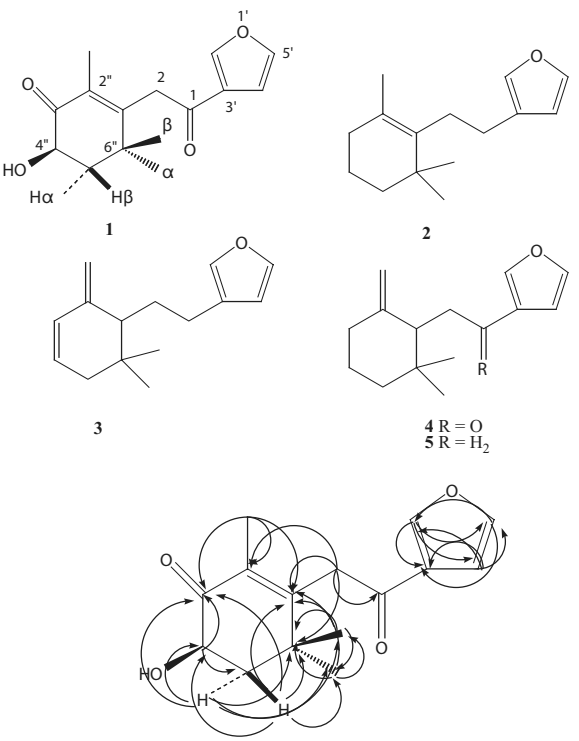
Introduction

To search for bioactive compounds from extreme environments in the northwestern parts of China, a few characteristic species of the region were collected and analyzed. *Tetraena mongolica* Maxim. (Zygophyllaceae) is a relict species specifically distributed in the northern dry plateau areas of northern China (mainly the Inner Mongolia and the Ningxia Hui Autonomous Regions). The species is a tough dwarf shrub, which is extremely drought tolerant. Thus far no phytochemical study has been carried out on this shrub. In this study, we collected the aerial parts of *T. mongolica* from the Ningxia Hui Autonomous Region, China. Analysis of its constituents resulted in the characterization of a new furanosesquiterpenoid.

Results and Disscussion

The powdered aerial parts of *Tetraena mongolica* were exhaustively extracted with MeOH and the extract was partitioned between EtOAc and H_2O. The EtOAc-soluble portion was repeatedly chromatographed over silica gel and Sephadex LH-20 column to afford **1**.

Tetraenol (**1**) was obtained as a white crystalline compound, m.p. 58.5–59 °C, $[\alpha]_D$ + 108° (*c* 0.25, MeOH). The molecular formula of **1** was deduced from its HREIMS data (*m/z* 262.1188 $[M]^+$, $C_{15}H_{18}O_4$ requires 262.1205). Its IR absorption at 3448, 1678 cm^{-1} and ^{13}C NMR signals at δ 199.8 (C-3″), 189.0 (C-2), 69.3 (C-4″) indicated the presence of two carbonyl groups and a hydroxyl group. Compound **1** containing a 3-carboxyfuranyl group



HMBC correlations for **1**

Fig. 1. Structures of tetraenol (**1**), pallescensins-1 (**2**), pallescensins-2 (**3**), pallescensene (**4**), penlapallascensin (**5**) and HMBC correlations for **1**.

was revealed in the ^1H NMR spectrum at δ 8.13, 7.49 and 6.80 ppm (Table I) and by fragment ion at *m/z* 95 (Cambie *et al.*, 1987). The ^1H NMR spectrum also showed three methyl signals (δ 1.73,

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Table I. ^1H and ^{13}C NMR data for compound **1** in $CDCl_3$ (500 MHz).

Position	δ_H	δ_C
1		189.0
2	3.76	41.5
2′	8.13	147.0
3′		127.2
4′	6.80	108.7
5′	7.49	144.5
1″		157.2
2″		131.1
3″		199.8
4″	4.36 (dd, J = 14, 5.8 Hz)	69.3
5″	1.88 (β, t, J = 14 Hz), 2.16 (α, dd, J = 14, 5.8 Hz)	44.8
6″		37.1
2″-CH_3	1.73	12.3
6″-α-CH_3[a]	1.11	29.1
6″-β-CH_3[a]	1.25	25.0

[a] The data for 6″-α-CH_3 and 6″-β-CH_3 may be reversed.

1.11, 1.25, each 3H, s), a methylene singlet (δ 3.76, s), and an isolated spin system (δ 4.36, dd, J = 14, 5.8 Hz; 2.16, dd, J = 14, 5.8 Hz; 1.88, t, J = 14 Hz). All the above evidence with the aid of 2D NMR (HMQC, HMBC) (Fig. 1) led to structure **1** for compound **1**.

To our best knowledge, all other similar compounds reported so far (compounds **2**–**5**) were isolated from marine sponges (Cambie *et al.*, 1987; Cimino *et al.*, 1975; Guella *et al.*, 1983). Some of them exhibited antifeedant activity against fish (Thompson *et al.*, 1982).

Tetraenol was tested for the cytotoxicity against HL-60 human promyelocytic leukemic cells, but showed no significant bioactivity. Other bioassays of tetraenol are currently under way.

Experimental

General

Melting points were determined on a Fisher-Johns micromelting point apparatus and are uncorrected. Optical rotation was determined in MeOH on a Perkin-Elmer 241MC polarimeter. UV spectra were obtained on a Hitachi UV-300 spectrophotometer, and IR spectra were recorded on a Nicolet FT-IR Nexus 470 spectrophotometer with KBr disks. EIMS and HREIMS were obtained with a Finnigan-MAT-95 mass spectrometer. 1D- and 2D-NMR spectra were measured in $CDCl_3$ with a Bruker Advance 500 NMR spectrometer using TMS as internal standard (δ in ppm, J in Hz).

Plant material

The aerial parts of *Tetraena mongolica* Maxim. were collected from the Ningxia Hui Autonomous Region, China, and the plant was identified by Prof. Yu-Long Ding at Nanjing Forestry University. A voucher specimen is deposited in the Department of Biochemistry, School of Life Sciences, Fudan University, Shanghai.

Extraction and isolation

The aerial parts of *Tetraena mongolica* (dry weight 430 g) were extracted three times with MeOH at room temperature. The residue obtained by removal of the solvent *in vacuo* was partitioned between water and EtOAc. The EtOAc portion (12 g) was fractioned by silica gel (200–300 mesh) chromatography eluted with petroleum ether/EtOAc (from 100:0 to 0:100) to afford several fractions. The fraction (0.6 g) from petroleum ether/EtOAc (80:20 v/v) was purified by repeated silica gel chromatography and molecular filter (Sephadex LH-20) to give 6.2 mg of compound **1**.

Tetraenol (**1**): White crystals. M.p. 58.5–59 °C. – $[\alpha]_D$ + 108°(*c* 0.25, MeOH). – UV (MeOH): λ_{max} (log ε) = 247 nm (4.03). – HR-EIMS: *m/z* = 262.1188 $[M]^+$; for $C_{15}H_{18}O_4$: calcd. 262.1205. – EI-MS: *m/z* (rel. int) = 262 (12) $[M]^+$, 244 (8) $[M\text{-}H_2O]^+$, 218 (15), 190 (20), 175 (18), 95 (100) $[C_5H_3O_2]$. – IR: ν_{max} (KBr) = 3448, 2927, 1678, 1333, 1155 cm^{-1}. – ^1H and ^{13}C NMR: see Table I.

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