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Two new nonacosanetriols from the pollen of *Typha angustifolia*

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Abstract

Chemical investigation of the pollen of *Typha angustifolia* Linn. has led to the isolation of two new nonacosanetriols, 7,8,10-nonacosanetriol (**1**) and 7,9,10-nonacosanetriol (**2**). Their structures were elucidated by chemical reaction and spectral analysis. Compounds **1** and **2** exhibited weak activity of antiplatelet aggregation *in vitro*.

Keywords: *Typha angustifolia*; Nonacosanetriol; Antiplatelet aggregation

The genus *Typha* (Typhaceae) consists of 18 species distributed throughout the world, and about 10 species are found in China [1]. Pollen Typhae is the pollen of all species of *Typha* such as *T. angustifolia* Linn., *T. latifolia* Linn., and *T. orientalis* Presl. Pollen Typhae has the function of hemostasis and removing stasis, and is often used in the treatment of dysmenorrheal, stranguria, and injuries in traditional Chinese medicine. Modern studies have found that Pollen Typhae mainly contains sterols, terpenoids, flavones, and long chain hydrocarbons, and possesses the pharmacological action of immunosuppressive activity, raising cAMP level, lowering cholesterol, and anticoagulation [2–4]. In our present study different solvent extracts of the pollen of *T. angustifolia* Linn. were screened, in which the ethyl acetate extract showed the important activities. From the ethyl acetate extract, two new nonacosanetriols (**1** and **2**) were successively separated by means of SiO_2 column chromatography. In this paper, we dealt with the isolation and structural elucidation of two new compounds, and their antiplatelet aggregation activity.

The pollen of *T. angustifolia* Linn. was collected from Jiangsu, China, in September 2008, and identified by Pro. De-kang WU, Nanjing University of Chinese Medicine, China. A voucher specimen (No. NJUTCM - 20080923) was deposited at Herbarium in Nanjing University of Chinese Medicine, China.

Compound **1**, $[\alpha]_D^{20}$ +24 (*c* 0.01, MeOH), was obtained as a white amorphous crystal (EtOAc). The molecular formula of **1** was determined to be $C_{29}H_{60}O_3$ by high-resolution negative ion ESI-MS (*m/z* 455.4459 [M−H], calcd. 455.4464). The ^{1}H NMR (CD_3OD) of **1** (Table 1) showed the presence of two terminal methyls at δ 0.88 (t, 6H, J = 7.1 Hz), methylenes at δ 1.20–1.33 (br. m, 48H), and three oxygenated CH groups at δ 3.36 (dt, 1H, J = 7.8, 4.3 Hz), 3.67 (m, 1H), and 3.79 (m, 1H). In the ^{13}C NMR spectrum of **1** (Table 1), three oxygenated C-atom signals at δ 70.1, 72.8, and 76.4 were recognized. These data inferred the existence of a straight-chain compound with three

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Table 1
NMR spectral data of compound **1** in CD_3OD.

Position	δ_H (J in Hz)	δ_C	^1H–^1H COSY	HMBC
1	0.88 (t 7.1)	14.8	H-2	C-2, C-3
2	1.33 (m)	24.1	H-1	C-1, C-3, C-4
3–4	1.20–1.28 (br. m)	28.9–31.0		
5	1.23 (m)	26.1	H-6	C-6, C-7
6	1.46 (m)	39.5	H-5, H-7	C-5, C-7, C-8
7	3.36 (dt 7.8, 4.3)	76.4	H-6, H-8	C-5, C-6, C-8, C-9
8	3.67 (m)	72.8	H-7, H-9	C-6, C-7, C-9, C-10
9	1.58 (m) Ha	42.1	H-8, H-10	C-7, C-8, C-10, C-11
	1.48 (m) Hb	42.1	H-8, H-10	C-7, C-8, C-10, C-11
10	3.79 (m)	70.1	H-9, H-11	C-8, C-9, C-11
11	1.46 (m)	39.5	H-11, H-12	C-9, C-10, C-12
12	1.23 (m)	26.1	H-11	C-10, C-11
13–27	1.20–1.28 (br. m)	28.9–31.0		
28	1.33 (m)	24.1	H-29	C-26, C-27, C-29
29	0.88 (t 7.1)	14.8	H-28	C-27, C-28

Signals were assigned by heteronuclear single-quantum coherence (HSQC), heteronuclear multiple-bond correlation (HMBC), and ^1H–^1H COSY experiments.

hydroxyl functions in **1** [5]. In the mass spectrum (ESI-MS–MS), a set of diagnostic fragment ions at *m/z* 159 → 141 → 123, 189 → 171 → 153, 297 → 279, and 267 were formed by α-fission and loss of H_2O. This suggested the hydroxyl group to be located at C-10. Other diagnostic fragment ions at *m/z* 115, 145 → 127 → 109, 341 → 323 → 306, 371 → 353 → 335 → 317, and 311 → 293 are shown in Fig. 1, which allowed us to propose locations of hydroxyl groups at C-7, C-8, and C-10. In the ^1H–^1H COSY spectrum of **1**, the correlations between H-6 at δ 1.46 (m) and H-7 at δ 3.36, H-7 and H-8 at δ 3.67, H-8 and H-9a at δ 1.58 (m), H-8 and H-9b at δ 1.48 (m), H-9a and H-10 at δ 3.79, H-9b and H-10, H-10 and H-11 at δ 1.46 (m) were observed in **1**. These correlations strongly confirmed that **1** contained the partial structure –CH_2–CH(OH)–CH(OH)–CH_2–CH(OH)–CH_2–. Furthermore, the corresponding correlations were observed in HSQC and HMBC[0] spectra (Table 1). From these data, compound **1** was identified as 7,8,10-nonacosanetriol.

To further prove the structure, compound **1** was subjected to acetylation. A solution of **1** (about 2.0 mg) in Ac_2O/pyridine (1:1) was kept at room temperature for 48 h to yield a crude product, to which 3 mL of water was added and then extracted with EtOAc (3× 3 mL) [5]. The final reaction product was analyzed by ESI-MS–MS (Fig. 2) (relative intensity %): *m/z* 605 ($[M+Na]^+$, 87), 545 ($[M+Na-AcOH]^+$, 100), 497 (3), 485 ($[M+Na-2\times AcOH]^+$, 14), 426 ($[M+Na-2\times AcOH-AcO]^+$, 6), 425 (7), 403 ($[M-2\times AcOH-AcO]^+$, 41), 353 (6), 339 (8), 315 (9), 267 (2), 243 (5), 229 (3), 157 (5).

Compound **2**, $[\alpha]_D^{20}$ +3.5 (*c* 0.04, MeOH), was obtained as a white amorphous crystal (EtOAc). The molecular formula of **2** was determined to be $C_{29}H_{60}O_3$ by high-resolution negative ion ESI-MS (*m/z* 455.4460 $[M-H]^-$, calcd. 455.4464). The ^1H NMR (CD_3OD) of **2** (Table 2) showed the presence of two terminal methyls at δ 0.88 (t, 6H,

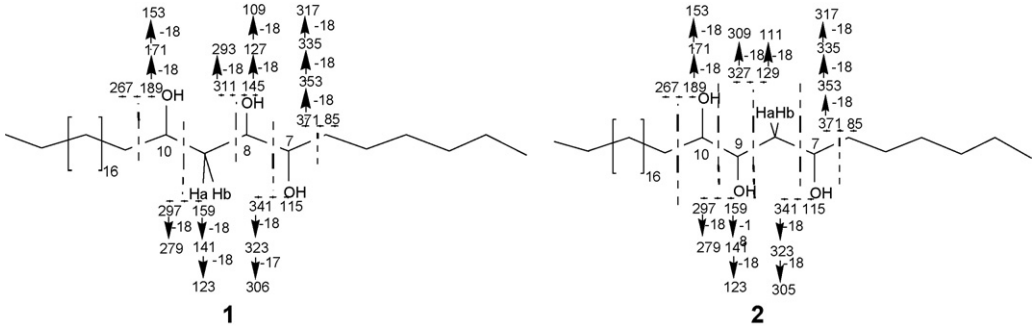

Fig. 1. ESI-MS/MS fragmentation of compounds **1** and **2**.