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A new lipophilic monosaccharide from *Erigeron annuus*

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Abstract

A new lipophilic monosaccharide, erigearide A (**1**), was isolated from the aerial parts of *Erigeron annuus* (Linn.) Pers. Its structure was elucidated by analysis of spectroscopic evidence.
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Keywords: *Erigeron annuus*; Lipophilic monosaccharide; Erigearide A

The genus *Erigeron* (Compositae) comprises more than 200 species in the world, of which 35 are widely distributed in China [1]. Some of them have a long history of applications in Chinese folk medicine, especially *Erigeron annuus* (Linn.) Pers. This plant has been used as a traditional medicine for the treatment of indigestion, enteritis, epidemic hepatitis, and hematuria [2]. Previously investigation revealed that this plant contains monoterpenoids, sesquiterpenoids, diterpenoids, triterpenoids, and phenolic derivatives [3–6]. In the course of our study on searching bioactive constituents from this plant, a new lipophilic monosaccharide, erigearide A (**1**), together with nodosin [7], quercetin [8], luteolin [8], tamarixetin [9], apigenin [10], isovanillin [11] and citrusin C [12], was isolated from the aerial parts of *E. annuus*. In this paper, we presented the isolation and structure elucidation of **1** based on the spectral analysis.

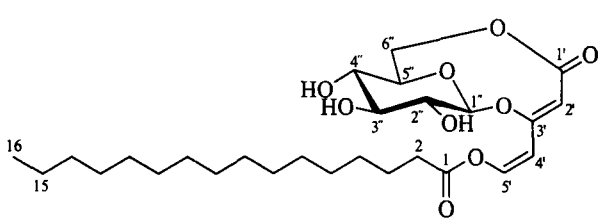

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Table 1
NMR data of **1** in DMSO-d_6 (^{1}H: 500 MHz; ^{13}C: 125 MHz)

Position	δ_H (mult., J, Hz)	δ_C (mult.)	HMBC
1		172.4 (s)	
2	2.25 (t, 7.4)	33.5 (t)	C-3, 1
3	1.47 (m)	24.4 (t)	C-2, 1
4–13	1.21–1.22 (overlapped)	28.4–29.0 (t)	
14	1.22 (m)	31.3 (t)	
15	1.25 (m)	22.1 (t)	
16	0.84 (t, 6.3)	14.0 (q)	C-15, 14
1′		172.7 (s)	
2′	8.12 (s)	155.7 (d)	C-1′, 5′
3′		145.8 (s)	
4′	6.39 (d, 5.5)	116.2 (d)	C-1, 3′, 2′,
5′	8.10 (d, 5.5)	144.1 (d)	C-1, 2′, 3′, 4′
Glc			
1″	4.83 (d, 7.2)	100.0 (d)	C-3′, 5″
2″	3.20 (overlapped)	73.0 (d)	C-1″, 3″
3″	3.21 (overlapped)	76.3 (d)	C-2″, 4″
4″	3.11 (m)	69.7 (d)	C-3″, 6″
5″	3.35 (t, 8.8)	73.8 (d)	C-1″, 4″, 6″
6″a	4.28 (d, 11.7)	63.1 (t)	C-1′, 4″
6″b	4.03 (m)		C-1′, 5″
HO-2″	5.46 (d, 5.5)		C-1″, 2″, 3″
HO-3″	5.21 (d, 4.6)		C-2″, 3″, 4″
HO-4″	5.28 (d, 5.5)		C-4″, 5″

The air-dried and powdered aerial parts of *E. annuus* (4.5 kg) were percolated with 70% aqueous Me_2CO (3× 10 L) at room temperature to yield an extract. The EtOAc soluble fraction (110 g) was subjected to silica gel and Sephadex LH-20 column chromatography, and semipreparative HPLC to afford compound **1** (13 mg) and seven known compounds.

Compound **1** was isolated as white powder, with UV (MeOH) λ_{max} (log ε) at 313 (2.87), 261 (4.26) and 213 (4.26) nm. $[\alpha]_D^{28.2}$ + 22.12° (c 0.11, MeOH/$CHCl_3$, 1:1); its molecular formula of $C_{27}H_{44}O_9$ was established on the basis of positive HRESIMS analysis ($[M+Na]^+$, m/z 535.2875) and its ^{13}C NMR spectrum, indicating 6° of unsaturation. The IR spectrum showed absorption bands of hydroxy (3451 cm^{-1}) and carbonyl groups (1735 and 1637 cm^{-1}). The ^{1}H NMR spectral data (Table 1) displayed a characteristic resonance for a terminal methyl (δ_H 0.84, t, J = 6.3 Hz) linked to methylene groups of aliphatic chains. The broad singlet between δ_H 1.21 and 1.22 (20H), two signals at δ_H 8.10 and 6.39 (each d, 1H, J = 5.5 Hz) and 8.12 (1H, s) suggested 10× $-CH_2-$ groups and three olefinic protons. The ^{13}C NMR spectral data (Table 1) showed resonances for twenty-seven carbons: two lactone carbons, a quaternary carbon, eight methines (including three olefinic and five oxygenated carbons), fifteen methylenes, and a methyl, of which sixteen were assigned to a long-chain fatty acid, confirmed by the MS data, the remaining was ascribed to a sugar moiety (δ_C 63.1, 69.7, 73.0, 73.8, 76.3, and 100.0), and a 1,3-dien-pentanoic acid. Apart from two double bonds, a sugar moiety, and two lactone carbonyl groups, the remaining elements of the unsaturation in **1** were assumed to be another ring. Extensive analysis of HSQC, ^{1}H–^{1}H COSY, and HMBC spectral data led to the establishment of the functional groups (Fig. 1). The HMBC correlations of H-4′ with C-2′ and C-3′, and of H-2′ with C-1′ and C-5′, along with a proton spin

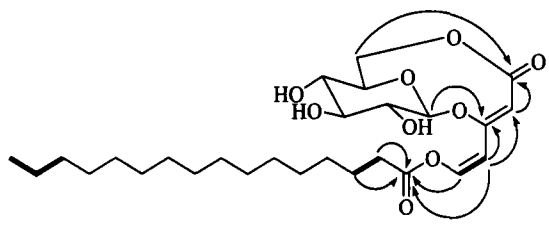

Fig. 1. Key ^{1}H–^{1}H COSY (—), and HMBC (→) correlations of **1**.

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system (H-4′/H-5′), led to the establishment of the substructure, 1,3-dien-pentanoic acid. In addition, the splitting pattern and the respective J (H, H) values (5.5 Hz) of H-4′ and H-5′ confirmed the Z-configurated double bond between C-4′ and C-5′. ^{1}H-NMR and ^{13}C NMR data indicated that the monosaccharide unit was a β-glucopyranosyl (H-1″, δ_H 4.83, d, J = 7.2 Hz). From the HMBC correlations from H-4′ and H-5′ to C-1, from H-1″ to C-3′, and from H_2-6″ to C-1′, the connections of three substructures through ether bridges were concluded. Thus, the structure of **1** (erigearide A) was determined.

Seven known compounds were identified by comparing their spectroscopic data with those reported [7–12].

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