

New Eudesmenes from *Erigeron annuus*

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Abstract: Chemical investigation of *Erigeron annuus* afforded two new eudesmenes, which were identified as 1 β , 5 α -dihydroxyeudesma-4(15)-en (**1**) and 1 β , 7 α -dihydroxyeudesma-4(15)-en (**2**). Their structures were established by spectroscopic methods including 2D NMR experiments.

Keywords: *Erigeron annuus*, compositae, eudesmene, sesquiterpene.

Plants of the genus *Erigeron* have applied in folk medicine for a long time. *E. annuus* was also a useful traditional medicine for the treatment of indigestion, enteritis, epidemic hepatitis and hematuria¹. In the research for its biologically active constituents, we found two new sesquiterpenes from its EtOAc extract.

Compound **1** was isolated as colorless oil, $[\alpha]_D^{17} +51$ (*c* 0.4, CHCl₃). The IR spectrum showed absorption bands for hydroxyl group (3374 cm⁻¹) and double bond (1645 cm⁻¹). The EIMS showed [M]⁺ peak at *m/z* 238, corresponding to the molecular formula C₁₅H₂₆O₂. In the ¹H-NMR spectrum, a signal at δ 4.06 (dd, *J*=11.7 Hz, 5.1 Hz) attributable to an axial proton (geminal to a hydroxyl group) was observed. Two double signals at δ 4.85 and δ 4.75 (*J*=1.5 Hz) confirmed the presence of an exomethylene group². Together with three signals for methyl groups δ 0.76 (s, 3H), δ 0.91 (d, 3H, *J*=6.6 Hz) and δ 0.87 (d, 3H, *J*=6.6 Hz), compound **1** can be deduced as an eudesmane sesquiterpene derivative. In the HMBC spectrum, the correlations of the olefinic protons with C-3 (δ 29.91) and C-5 (δ 76.16), the angular methyl protons with C-5, C-10 (δ 42.23), C-1 (δ 73.12) and C-9 (δ 29.76), and the carbinol proton with C-3 showed that the exocyclic double bond laid at 4(15) and the hydroxyl groups at C-1 and C-5. The signal of H-14 at δ 0.76 was characteristic of *trans*-fused eudesmanes³. If H-7 was presumed to be α -orientation, the configurations of other substituted groups should be 1 β , 5 α -dihydroxy and 10 β -methyl by the NOESY cross-peaks observed between H-1 α and H-9 α , Me-14 protons and H-8 β , H-7 α and H-1 α , 3 α . The upfield shift in the ¹³C-NMR absorption of the angular methyl carbon to δ 12.70 further confirmed that the hydroxyl group at C-1 was equatorial and β -configuration⁴. Therefore, the structure of **1** was identified as 1 β , 5 α -dihydroxyeudesma-4(15)-en. The ¹H and ¹³C NMR signals were completely assigned on

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the basis of ^1H - ^1H COSY and HMQC spectra (**Table 1**).

Compound **2**, $[\alpha]_{\text{D}}^{17} +30$ (c 0.1, CHCl_3), was colorless oil and its molecular formula also was $\text{C}_{15}\text{H}_{26}\text{O}_2$, deduced from its EIMS spectrum ($[\text{M}]^+$ peak at m/z 238). Two fragment peaks at 220 $[\text{M}-\text{H}_2\text{O}]^+$ and 202 $[\text{M}-2\text{H}_2\text{O}]^+$ revealed the presence of two hydroxyl groups, corresponding to the absorption band at 3374 cm^{-1} in the IR spectrum. Its NMR data were similar to those of **1** except for the obvious downfield shift of C-8 and C-11 (**Table 1**), indicating that a tertiary hydroxyl group was at C-7. This was further confirmed by the cross-peaks observed between H-12, 13 (δ 0.95, d, 6H, $J=6.3$ Hz) and C-11 (δ 41.70) and C-7 (δ 73.35) in the HMBC spectrum. Thus compound **2** was deduced to be $1\beta, 7\alpha$ -dihydroxyeudesma-4(15)-en.

Figure 1 Structures of compounds **1**, **2**

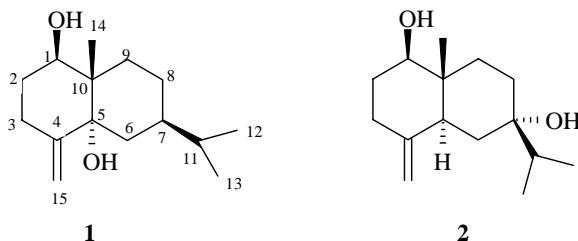


Table 1 ^1H -NMR (300 MHz) and ^{13}C -NMR (75 MHz) data of **1,2** (CDCl_3 , δ ppm)

C	1 δ_{C}	2 δ_{C}	H	1 δ_{H}	2 δ_{H}
1	73.12	78.97	1 α	4.06 (dd, $J=11.7, 5.1$)	3.50 (dd, $J=11.7, 5.1$)
2	30.54	31.41	2 β	1.54 (m)	--
			2 α	1.81 (m)	
3	29.91	34.25	3 β	1.25 (m)	--
			3 α	2.12 (m)	--
4	150.59	148.91	--	--	--
5	76.16	39.02	5 α	--	--
6	34.28	32.02	6 β	2.17 (m)	--
			6 α	1.64 (m)	--
7	38.25	73.35	7 α	2.71 (m)	--
8	23.65	31.81	8 β	1.56 (m)	--
			8 α	1.85 (m)	--
9	29.76	29.00	9 β	1.60 (m)	--
			9 α	1.83(m)	--
10	42.23	38.59	--	--	--
11	32.78	41.70	11	1.53 (m)	--
12	20.00	16.80	12	0.87 (d, $J=6.6$)	--
13	19.99	16.00	13	0.91 (d, $J=6.6$)	0.95 (d, $J=6.3$)
14	12.70	9.08	14	0.76 (s)	0.95 (d, $J=6.3$)
15	108.66	106.56	15a	4.85 (d, $J=1.5$)	0.66 (s)
			15b	4.75 (d, $J=1.5$)	4.47 (d, $J=1.5$)
					4.76 (d, $J=1.5$)

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