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A New Sesquiterpene from *Ligularia Songarica*

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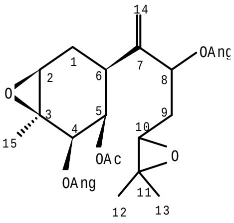
Abstract: A new bisabolane sesquiterpene, 5β - acetoxy - 4β, 8- diangeloyloxy - 2β, 3β, :10, 11-diepoxy-bisabola-7 (14)-ene, was isolated from the roots of *Ligularia songarica* and its structure was elucidated on the basis of spectroscopic methods, especially 2D-NMR techniques.

Keywords: Bisabolane; new sesquiterpene; *ligularia songarica*.

The chemical studies of *Ligularia songarica* have not been reported till now. In our preliminary study on the roots of this plant, a new bisabolane sesquiterpene was obtained and its structure was identified as 5β-acetoxy-4β, 8-diangeloyloxy-2β, 3β, : 10, 11-diepoxy-bisabola-7 (14)-ene **1**.



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Compound **1**, colorless needles, m.p. 90-90.5°C; $[\alpha]_D^{25}$-17.6 (c 0.5, $CHCl_3$). Its FAB-MS showed a quasi-molecular ion at m/z=491: $[M+H]^+$, together with elemental analysis suggested the molecular formula to be $C_{27}H_{38}O_8$ with nine unsaturation confirmed by the ^{1}H-NMR and ^{13}C-NMR (**Table 1**). IR (cm^{-1}) showed carbonyl groups at 1744 (OAc), 1717 ($C=CCO_2R$), double bond at 1650 (C=C) and 857 ($C=CH_2$). The FAB-MS exhibited main fragments at m/z: 391 (M^++H-AngOH), 291 (M^++H-2×AngOH), 231 (291-AcOH), 83 ($C_4H_7CO^+$), this indicated the presence of two angeloyl groups and an acetyl group which was supported by the ^{1}H-NMR and ^{13}C-NMR (**Table 1**). Except for the three ester groups, the ^{1}H-NMR spectra exhibited a terminal methylene, three methyls, two methylenes and six methines (five oxygenated). The ^{13}C-NMR and DEPT spectra also indicated that there were 15 skeleton carbons (3× CH_3, 3× CH_2, 6×CH, 3×C). Therefore, the compound **1** was confirmed as bisabolane sesquiterpene type[1, 2, 3]. In the HMBC experiment of **1**, the correlations of H-5 with δ_C 170.1 (OAc), C-3, C-4, C-6 and C-1; H-4 with δ_C 166.7 (OAng), C-5, C-3 and C-6; H-8 with δ_C 166.7 (OAng), C-7, C-14, C-10, C-9 and C-6 pointed to the acetyl group at C-5 and the two angeloyl groups at C-4 and C-8. The correlations of H-2 with C-3, C-6, C-1 and C-15; H-10 with C-8, C-9, C-12 and C-13 indicated two epoxy groups at C-2, C-3 and C-10, C-11, respectively. The relative stereochemistry of **1** was deduced by the coupling constants ($J_{1\alpha,\,2\alpha}$=5.2, $J_{4\alpha,\,5\alpha}$=4.8, $J_{5\alpha,\,6\alpha}$=2.4, $J_{6\alpha,\,1\alpha}$=4.0, $J_{6\alpha,\,1\beta}$=12.5, Hz) and the ^{1}H-^{1}H NOESY experiment. At first, if H-6 were α-oriented, in the NOESY spectra, the obviously correlated peaks of H-2 with H-1α, H-15; H-4 with H-5, H-15 and H-5 with H-6 revealed that the ester groups at C-4 and C-5 must be all β-configuration and the epoxy group must be 2β, 3β-configuration. Thus, the structure of **1** was determined.

Table 1. ^{1}H (400MHz) and ^{13}C-NMR (100MHz) data of Compound 1 ($CDCl_3$, δ, ppm, TMS)

	^{1}H-NMR[a]	^{13}C-NMR	DEPT
1α	1.98 (1H, m)		
1β	2.17 (1H, dd, 15.2, 12.5)	25.7	CH_2
2	3.17 (1H, brd, 5.2)	59.5	CH
3	—	56.5	C
4	5.35 (1H, d, 4.8)	71.8	CH
5	5.30 (1H, br dd, 4.8, 2.4)	68.3	CH
6	2.45 (1H, dddd, 12.5, 4.0, 2.4)	37.9	CH
7	—	145.9	C
8	5.38 (1H, dd, 11.6, 2.2)	74.6	CH
9	2.02 (1H, m),		
9’	1.83 (1H, m)	33.4	CH_2
10	2.71 (1H, dd, 6.6, 5.2)	60.7	CH
11	—	58.1	C
12	1.26 (3H, s)	24.6	CH_3
13	1.26 (3H, s)	24.6	CH_3
14	5.23 (1H, brs)		
14’	5.04 (1H, brs)	115.4	CH_2
15	1.28 (3H, s)	18.9	CH_3
OAng	6.10, 6.06 (3’-H, qq, 7.6, 1.2),	166.6, 166.7, 127.2, 127.4	C
	1.98, 1.88 (4’-H, dq, 7.6, 1.5),	139.1, 139.2	CH
	1.95, 1.83 (5’-H, dq, 1.5, 1.2)	15.7, 19.5, 20.5, 20.8	CH_3
OAc	2.01 (3H, s)	170.1	C
		20.4	CH_3

a. Coupling constants in parentheses in Hz.

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