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A New Bisesquiterpene from *Ligularia macrophylla*

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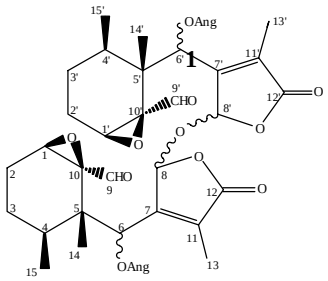
Abstract: From the roots of *Ligularia macrophylla*, a bisesquiterpene, ligumacrophyllal was isolated and its structure was elucidated on the basis of spectroscopic methods.

Keywords: *Ligularia macrophylla*, Compositae, bisesquiterpene, ligumacrophyllal.

There have been several reports about chemical studies of *Ligularia macrophylla*[1,2]. From the roots of this plant collected in Xinjiang, a new bisesquiterpene was isolated and determined as a dimer of 6-angeloyloxy-10α-aldehyde, 1β, 10β-epoxy-8, 9-seco -eremophila-7 (11)-en-8, 12-olide, named as ligumacrophyllal (**1**).



Compound **1**, colorless gum, $[\alpha]_D^{20}$ +12.83 (*C* 0.78, $CHCl_3$), displayed IR bands at 1766, 1727, 1690 and 1645 cm^{-1}, which suggested the presence of α, β-unsaturated γ-lactone, conjugated ester and aldehyde groups. Its ^{1}H-NMR spectrum (**Table 1**) gave the signals of two aldehyde groups at quaternary carbon, and two angeloyls. Except for these signals, the six methyl protons in the highfield could be divided into two groups, which showed the similarities to those of eremophilanolide. The corresponding ^{13}C-NMR and DEPT spectra (**Table 1**) of **1** exhibited 20 pairs of carbons. Apart from the carbon signals of two angeloyloxys, the rest ones just constituted two identical sesquiterpenolide units. The quasi-molecular ion peak at *m/z* 739 $[M+1]^+$ and the ion peak at *m/z* 379 $[M+H-360]^+$ in FABMS spectrum indicated that the two sesquterpenolide units were linked to each other by an oxygen. Thus, the molecular formula of compound **1** was established as $C_{40}H_{50}O_{13}$ with sixteen unsaturations.

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The sesquiterpene unit of **1** was similar to the aldehydes reported[3,4]. In comparison NMR data of **1** with those of reported compounds, the difference was that the 1, 10 doubled bond in reported compounds was replaced by an epoxy in the unit of **1**, which was confirmed by HMBC correlations (C-10/H-1/H-9 and C-1/H-2/H-3). In the ^{1}H-^{1}H NOESY spectrum, the correlations from H-4α to H-1 and H-2α, and from H-1 to H-2α and H-9 showed that H-1 and H-9 were α-orientation. H-14β was determined based on the NOESY correlation of H-14 with H-15. Consequently, the structural unit of **1** was elucidated as an 8, 9-secoeremophilanolide derivative. Two units were joined through the 8, 8'-ether bond because of the unit as an acetal for the absence of IR hydroxyl band and HMBC correlations from H-8' to C-8 and H-8 to C-8'. Therefore, compound **1** was confirmed as shown.

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

No.	δ_H	δ_C
1/1'	3.49/3.49 (1H, d, 1.6)	59.6/59.5 (CH)
2α, 2β/2'α, 2'β	1.26, 1.38/1.26 (1H, m), 1.38 (1H, m)	24.5/24.4 (CH_2)
3α, 3β/3'α, 3'β	1.41, 1.89/1.42 (1H, m), 1.88 (1H, m)	23.7/23.6 (CH_2)
4/4'	2.22/2.22 (1H, m)	31.7/31.7 (CH)
5/5'	----	43.1/43.0 (C)
6/6'	6.45/6.42 (1H, brs)	72.6/72.3 (CH)
7/7'	----	161.0/160.6 (C)
8/8'	5.87/5.82 (1H, brs)	97.8/97.5 (CH)
9/9'	8.69/8.67 (1H, s)	197.1/197.0 (CH)
10/10'	----	64.6/64.5 (C)
11/11'	----	126.6/126.6 (C)
12/12'	----	169.2/169.1 (C)
13/13'	2.18/2.18 (3H, brs)	13.0/12.7 (CH_3)
14/14'	1.12/1.12 (3H, s)	15.6/15.6 (CH_3)
15/15'	0.76/0.73 (3H, d, 7.2)	18.3/18.3 (CH_3)
OAng 1	----	166.8/166.4 (C)
2	----	126.7/126.5 (C)
3	6.12/6.08 (1H, qq, 7.2, 1.2)	140.9/140.4 (CH)
4	1.96/1.94 (3H, dq, 7.2, 1.0)	16.0/15.8 (CH_3)
5	1.89/1.88 (3H, dq, 1.4, 1.2, 1.0)	20.6/20.6 (CH_3)

Acknowledgment

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