

## A Novel Terpenoid from *Lappula anocarpa*

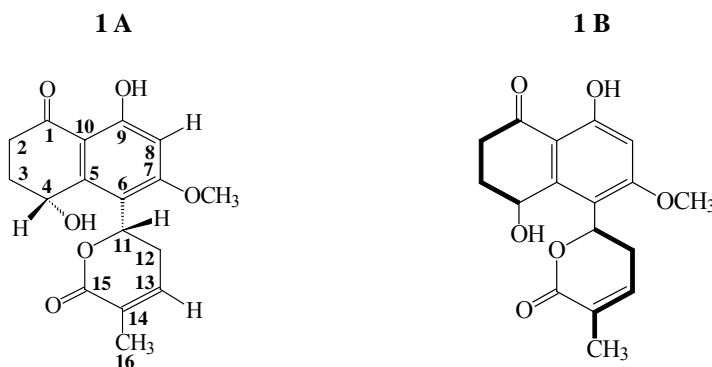
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**Abstract :** A novel terpenoid, named lappulanocarpine A **1** was isolated from the alcoholic extract of the whole plant of *Lappula anocarpa*. Its structure was characterized by 1D-, 2D-NMR and HR-ESIMS.

**Keyword:** *Lappula anocarpa*, Boraginaceae, terpenoid, lappulanocarpine A.

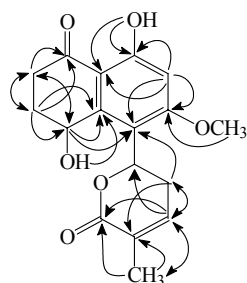
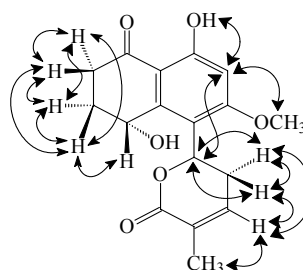
The genus *Lappula* (Boraginaceae) consists of about 61 species distributed throughout the world, particularly, in the dry and desert zone. Among them, *L. myosotis* and *L. heteracantha* have been used as an important folk medicine for anti-inflammatory and anti-bacteria agents<sup>1,2</sup>. In order to find bioactive principles, the chemical constituents of *Lappula anocarpa* C. J. Wang were investigated and a novel terpenoid **1** was isolated from the alcoholic extract of the whole plant. In this paper, we report the structural elucidation of the compound **1** (Figure 1A).



Compound **1** is a brown gum,  $[\alpha]_D^{25} -158$  (c 0.25, CHCl<sub>3</sub>). The molecular formula was assigned as C<sub>17</sub>H<sub>18</sub>O<sub>6</sub> by HR-ESIMS (M+NH<sub>4</sub><sup>+</sup> = 336.1454; Calcd. 336.1442), <sup>13</sup>C- and DEPT NMR experiments showed 2×CH<sub>3</sub>, 3×CH<sub>2</sub>, 4×CH and 8×C. Its UV spectrum showed bands at 210 nm (log ε 4.65) and 368 nm (log ε 3.99). The IR spectrum (film) indicated the presence of hydroxyl (3452 cm<sup>-1</sup>) and carbonyl (1722 cm<sup>-1</sup>) and phenyl

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groups and double bond ( $1643, 1594\text{ cm}^{-1}$ ). The  $^1\text{H}$  NMR spectrum indicated the presence of a methyl group (1.98, brs, 3H) linking to double bond, a methoxyl group ( $\delta 3.89$ , s, 3H), a phenolic hydroxyl group ( $\delta 12.24$ , s, 1H) and two proton signals for double bond ( $\delta 7.43$ , s, 1H;  $6.67$ , brd, 1H,  $J = 6.4\text{Hz}$ ), as well as two proton signals due to oxymethine ( $\delta 5.26$ , t, 1H,  $J = 4.4\text{Hz}$  and  $5.78$ , dd, 1H,  $J = 12.4, 3.6\text{Hz}$ ). In the  $^{13}\text{C}$  NMR spectrum, there were a ketone carbonyl ( $\delta 205.42$ ), an  $\alpha,\beta$ -unsaturated  $\delta$ -lactone carbonyl ( $\delta 165.91$ ) groups, a typical methoxyl group and eight signals due to one penta-substituted phenyl ring and one olefinic bond (Table 1).

Relative peaks in HMBC (H  $\longrightarrow$  C)Cross peaks in COSY (H  $\longleftrightarrow$  H)

**Table 1** Data of  $^1\text{H}$ - (400MHz),  $^{13}\text{C}$ -NMR (100MHz),  $^1\text{H}$ - $^1\text{H}$  COSY and HMBC for compound **1**\* ( $\delta_{\text{ppm}}$ ,  $J_{\text{Hz}}$ )

No.	$\delta_{\text{H}}$	$\delta_{\text{C}}$	COSY	HMBC
1	-	205.42 s	-	H <sub>2</sub> -2, H <sub>2</sub> -3
2 $\alpha$	3.07, ddd (17.6, 11.6, 4.8)	33.48 t	H-2 $\beta$ , H <sub>2</sub> -3	H-3 $\beta$ , H-4 $\beta$
2 $\beta$	2.56, dt (17.6, 4.4)		H-2 $\alpha$ , H <sub>2</sub> -3	
3 $\alpha$	2.56, dt (17.6, 4.4)	28.90 t	H <sub>2</sub> -2, H-3 $\beta$	H <sub>2</sub> -2
3 $\beta$	2.26, m		H <sub>2</sub> -2, H-3 $\alpha$ , H-4	
4 $\beta$	5.26, t (4.4)	61.61 d	H-3 $\beta$	H <sub>2</sub> -2, H <sub>2</sub> -3
5	-	115.25 s	-	H-3 $\alpha$ , H-4 $\beta$ , HO-9
6	-	130.90 s	-	H-4, H-8, H-12 $\alpha$
7	-	146.95 s	-	H-8, CH <sub>3</sub> O-7
8	7.43, s	117.26 d	CH <sub>3</sub> O-7, HO-9, H-11	-
9	-	152.13 s	-	H-8, HO-9
10	-	127.96 s	-	H-8, HO-9
11 $\beta$	5.78, dd (12.4, 3.6)	74.01 d	H-8, H <sub>2</sub> -12	H-8, H-13
12 $\alpha$	2.35, m	30.44 t	H-11 $\beta$ , H-12 $\beta$ , H-13	H-13
12 $\beta$	2.82, ddd (18.4, 5.6, 4.0)		H-11 $\beta$ , H-12 $\alpha$ , H-13	
13	6.67 brd (6.4)	139.52 d	H <sub>2</sub> -12, H <sub>3</sub> -16	H <sub>2</sub> -12, H <sub>3</sub> -16
14	-	128.45 s	-	H <sub>2</sub> -12, H <sub>3</sub> -16
15	-	165.91 s	-	H-13, H <sub>3</sub> -16
16	1.98, brs	17.00 q	-	H-13
7-OCH <sub>3</sub>	3.89, s	56.57 q	H-8	-
9-OH	12.24, s	-	H-8	-

\* Assignments were aided by spin splitting patterns, DEPT, HMQC, HMBC experiments, and chemical shift values ( $\delta$ ). The  $\delta$  values are in ppm and are referenced to either the residual  $\text{CHCl}_3$  (7.26 ppm) or  $\text{CDCl}_3$  (77.0 ppm) signals.

In the  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **1**, there were significant cross-peaks (**Table 1**), suggesting the presence of two partial structures (see **Figure 1B** indicated with bold bond). These substituents and partial structures could be put together by key relative peaks in HMBC (**Table 1**), such as C-6 ( $\delta$ 130.90) with H-4 ( $\delta$ 5.26), H-8 ( $\delta$ 7.43), and H-12 $\alpha$  ( $\delta$ 2.82); C-7 ( $\delta$ 146.95) with H-8 and 7-OCH<sub>3</sub> ( $\delta$ 3.89); C-9 ( $\delta$ 152.13) with H-8 and 9-OH ( $\delta$ 12.24); C-15 ( $\delta$ 165.91) with H-13 ( $\delta$  6.67) and H<sub>3</sub>-16 ( $\delta$ 1.98). The relative configuration of two chiral carbons (C-4 and C-11) in the molecule **1** can also be deduced by couple constants:  $J_{4\beta,3\alpha} = J_{4\beta,3\beta} = 4.4\text{Hz}$ ,  $J_{11\beta,12\alpha} = 12.4\text{ Hz}$  and  $J_{11\beta,12\beta} = 3.6\text{ Hz}$  in the  $^1\text{H}$  NMR, suggesting the 4-OH for  $\alpha$ -oriented and 11-H for  $\beta$ -oriented. Thus, the structure of compound **1** was elucidated as shown in **Figure 1A**, named lappulanocarpine A, the structure with a nor-carbons terpene skeleton.

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