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Erythrinarbine, a Novel nor-A ring Erythrina Alkaloid from *Erythrina arborescens*

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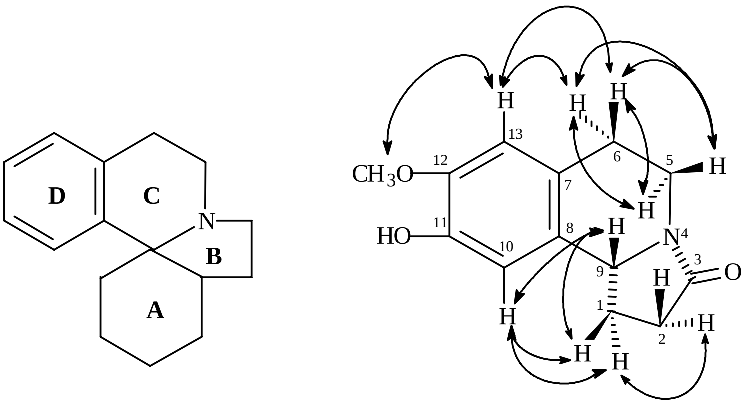
Abstract: Erythrinarbine **2**, a novel alkaloid was isolated from the stem of *Erythrina arborescens* Roxb. Its structure and stereochemistry were elucidated on the basis of the spectral analysis (^{13}C -^{1}H COSY, ^{1}H -^{1}H COSY, NOESY and HMBC).

Keywords: *Erythrina arborescens*; erythrinarbine; nor-A ring erythrina alkaloid.

Erythrina arborescens Roxb. belongs to *Erythrina* genus of Papilionaceae family plants, and is widely distributed in tropical and subtropical regions of the world, as well as in the south and south-west of China[1]. As a Chinese folk medicine, its root and stem are used to treat rheumatism and dysentery[2]. The Erythrina alkaloids, normally a C_{16} tetracyclic spiroamine system, erythrinane **1**, are the characteristic constituents in *Erythrina* genus and about 100 erythrina alkaloids have been so far reported from this genus plants[3-7]. Most of these Erythrina alkaloids have a tetrahydroisoquinoline or hexahydroindolizine skeleton. In the present paper, we report the isolation and structure elucidation of a nor-A ring erythrina alkaloid, a new alkaloid-erythrinarbine **2** from the stem of *Erythrina arborescens*.

Erythrinarbine **2** was obtained as white plate crystals (MeOH) from the extract of EtOH, mp. 193-194℃, optically inactive. The molecular weight was indicated as $C_{13}H_{15}NO_3$ by HR-EI mass spectroscopy, which gave the M^+ ion at m/z 233.1051 (calcd. 233.1052). The presence of hydroxyl and carbonyl of amide were confirmed by a broad absorption at 3440 cm^{-1} and a strong absorption at 1670 cm^{-1} in the IR spectrum. The down field carbon signal at δ 173.36 in the ^{13}C NMR confirmed the presence of the carbonyl of amide too. Six signals at δ 110.59, 110.97, 124.77, 130.06, 144.67 and 145.57 in the ^{13}C NMR showed presence of a benzene ring. ^{1}H NMR of **2** exhibited two *para* signals in the aromatic region at δ 6.60 (l H, s) and 6.67 (1H, s), which are related with carbon signals δ 110.97 and 110.59 in ^{13}C-^{1}H COSY, respectively. The carbon signal δ 55.97, related with δ 3.87 (3H, s) in ^{13}C-^{1}H COSY, is a methoxyl group (CH_3O) at the benzene ring. Another signal in middle field, δ 56.54, related with δ 4.69 (1H, t, 7.6) in ^{13}C-^{1}H COSY, which was coupled with δ 2.58 (1H, m) and 1.82 (1H, m) in ^{1}H-^{1}H COSY, showed the presence of the moiety of ph-CH (CH_2)-N-C=O. Four carbon signals δ 27.63, 31.75, 37.20 and 28.12, related with four pairs of protons, eight signals δ 2.58, 1.82; 2.60, 2.48; 4.28, 3.03 and 2.88, 2.68 in ^{13}C-^{1}H COSY, respectively, showed the presence of four methylene (CH_2)×4 moieties. Among them, the carbon signal δ 37.20, related with δ 4.28 and 3.03 in ^{13}C-^{1}H COSY, showed the presence of the moiety of CH_2-N-C=O. The above data showed a four substituted benzene ring, with two *para*-aromatic protons, a methoxyl and a hydroxyl groups on the one side in *ortho* position, and the other in *ortho* position was connected with a saturated cyclic system. ^{1}H-^{1}H COSY showed two groups of aliphatic proton signals which have no relation each other. One is δ 4.28, 3.03, 2.68 and 2.88, and the other is δ 4.69, 2.58, 1.82, 2.60 and 2.48. According to above data, we proposed the structure of **2**.

Figure 1. The skeleton of erythrinane **1** and NOESY correlation of the protons in erythrinarbine **2**

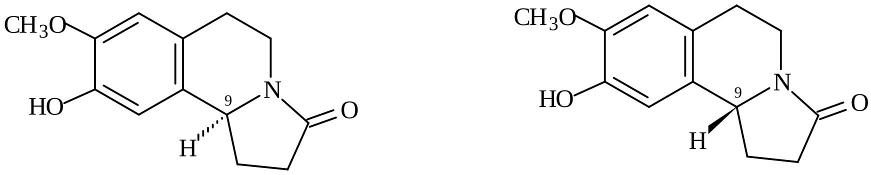


1 **2**

In the NOESY, the aromatic proton δ 6.67, acted with δ 4.69 (H-9) and 2.58, 1.82 (H-1) is H-10, while the other aromatic proton δ 6.60 is H-13. The signal of OCH_3 δ 3.87 (3H, s) which was acted with δ 6.60 (H-13) should substitute in C-12. Thus OH which showed a broad signal in δ 4.3-5.6 (1H, br, in $CDCl_3$) and δ 8.89 (1H, s, in DMSO-d_6), should substitute in C-11.

As the above data, **2** was characterized as 10-hydroxy-11-methoxy-benzo[g] hexahydroindolizin-3-one, named erythrinarbine. It has a chiral carbon center, C-9. Because of its optical inactive, $[\alpha]_D$ 0 (c 2.22, $CHCl_3$), it is a racemic modifications of **2A** and **2B** as follow.

Figure 2. The structure of erythrinarbine **2**



2A **2B**

The EI-MS spectroscopy showed the characteristic fragmental ions at m/z 233 (M^+, 58), 322 (M^+-1, 100), 218 (3), 217 (9), 216 (8), 202 (7), 190 (3), 189 (1), 188 (2), 177 (8), 176

(11) and 162 (8). These fragmental ions were confirmed by exact mass measurement and elemental composition of the fragments from **2** (see **Table 2**). The base ion at m/z 232.0975 ($C_{13}H_{14}NO_3$, 100) is M^+-1, which confirmed the presence of a -CH-N-moiety in the *ortho* position of the atom N. The molecular ion can lost CH_3 and CH_3, CO and get the two fragments, m/z 218.0779 ($C_{12}H_{12}NO_3$) and 190.0857（$C_{11}H_{12}NO_2$）respectively. At the same time, the base fragment ion can lost CH_3 and CO, and also get two fragments, m/z 217.0737 ($C_{12}H_{11}NO_3$) and 189.0794 ($C_{11}H_{11}NO_2$). These proved the presence of OCH_3 on benzene ring. The molecular ion can also lost OH and get the fragment, m/z 216.1029 ($C_{13}H_{14}NO_2$). It is because the presence of carbonyl group on the cyclic amide, which loses hydroxyl by enolazation. The cyclic-B in the molecular ion breaks and then appears fragment ions m/z 177.0783 and 176.0706 (composition $C_{10}H_{11}NO_2$ and $C_{10}H_{10}NO_2$).

Table 1. ^{1}H and ^{13}C-NMR spectral data of compound **2**

C/H	C δ ($CDCl_3$)*	H δ (J in Hz, $CDCl_3$)*	H δ (J in Hz, DMSO-d_6)
1	27.63	2.58 (1H, m)	2.23 (1H, ddd, 15, 8.0, 1.5)
		1.82 (1H, m)	1.58 (1H, ddd, 15, 12.5, 8.0)
2	31.75	2.60 (1H, m), 2.48 (1H, m)	2.63 (1H, m), 2.40 (1H, m)
3	173.36	—	—
5	37.20	4.28 (1H, ddd, 12.5, 6.0, 2.0)	4.00 (1H, ddd, 12.5, 5.0, 3.4)
		3.03 (1H, ddd, 12.5, 9.4, 4.2)	2.93 (1H, ddd, 12.5, 12.0, 7.8)
6	28.12	2.88 (1H, ddd, 15.0, 9.4, 6.0)	(1H, m)
		(1H, ddd, 15.0, 4.2, 2.0)	2.53 (1H, m)
7	124.77	—	—
8	130.06	—	—
9	56.54	4.69 (1H, t, 7.6)	4.61 (1H, t, 8.0)
10	110.59	6.67 (1H, s)	6.69 (1H, s)
11	144.67	—	—
12	145.57	—	—
13	110.97	6.60 (1H, s)	6.56 (1H, s)
OCH_3	55.97	3.87 (3H, s)	3.73 (3H, s)
OH	—	4.3-5.6 (1H, broad)	8.89 (1H, s)

*According to ^{13}C-^{1}H COSY and ^{1}H-^{1}H COSY in 100 and 400 MHz, respectively.

IR ν (KBr) cm^{-1}: 3400 (OH), 1670 (C=O), 1620, 1575, 1520, 1460, 1440, 1292, 1262, 1218, 1110. UV λ_{max}^{MeOH} 286nm. Data of ^{1}H NMR and ^{13}C NMR are listed in **Table 1**, and data of exact MS are listed in **Table 2**.

Table 2. Exact Mass Measurement and Elemental Composition

Fragment ion m/z	Composition	Fragment ion m/z	Composition
233.1051 (58)	$C_{13}H_{15}NO_3$	190.0857 (3)	$C_{11}H_{12}NO_2$
232.0975 (100)	$C_{13}H_{14}NO_3$	189.0794 (1)	$C_{11}H_{11}NO_2$
218.0779 (3)	$C_{12}H_{12}NO_3$	188.0689 (2)	$C_{11}H_{10}NO_2$
217.0737 (9)	$C_{12}H_{11}NO_3$	177.0783 (8)	$C_{10}H_{11}NO_2$
216.1029 (8)	$C_{13}H_{14}NO_2$	176.0706 (11)	$C_{10}H_{10}NO_2$
202.0918 (7)	$C_{12}H_{12}NO_2$	162.0612 (8)	$C_9H_8NO_2$

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