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## Correction to Three Novel Alkaloids from *Portulaca oleracea* L. and Their Anti-inflammatory Effects

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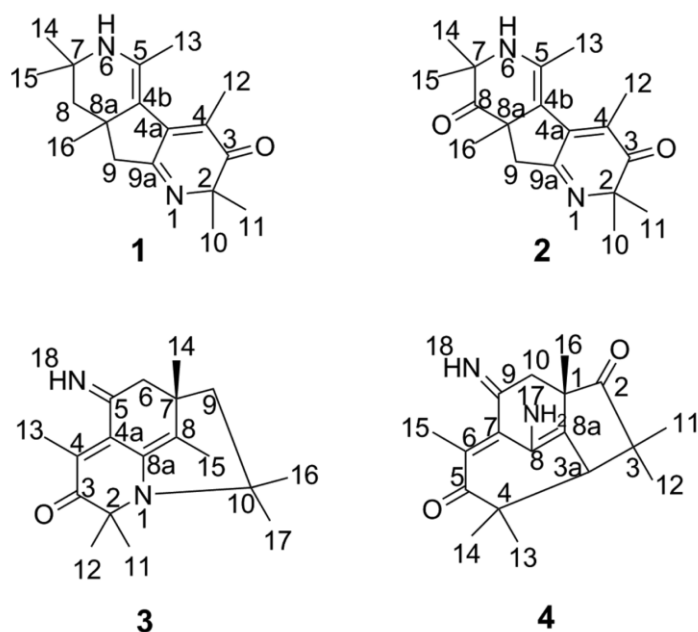
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**ABSTRACT:** Oleracimine and oleracimine A were isolated from *Portulaca oleracea* L. and described in the J. Agric. Food Chem, but the alternative structures of the two compounds are proposed on the basis of NMR analyses.

**KEYWORDS:** oleracimine, *Portulaca oleracea* L., structure elucidation

## INTRODUCTION

In the search for anti-inflammatory agents from *Portulaca oleracea* L., our group has conducted a well-kept purification work aiming at isolating and characterizing minor constituents of this plant. 1 New alkaloids have been isolated, among which are tricyclic metabolites named oleracimine (**1**) and oleracimine A (**2**). However, the proposed structures of two compounds (Figure 1) were erroneous, as commented by Dr. Didier Stien, and were therefore revised on the basis of the NMR analyses. Because of Dr. Stien's significant contribution to correcting our original work, he has been added as an author in the above listing.



**Figure 1.** Structures of compounds **1** and **2** isolated from *Portulaca oleracea*: **1**, revised structure of oleracimine; **2**, revised structure of oleracimine A; **3**, published structure of oleracimine; **4**, published structure of oleracimine A.

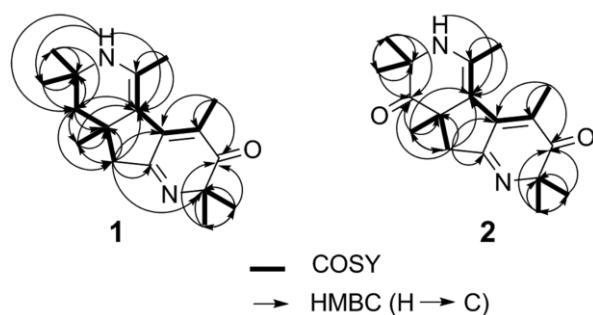
## DISCUSSION

The  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and DEPT spectra of compound **1** showed 18 carbon resonances, including 7 methyls, 2 methylenes, and 9 quaternary carbons including 1 carbonyl, 5 olefinic carbons, and 3 aliphatic carbons. Additionally, one active hydrogen ( $\delta_{\text{H}} = 6.408$ , 1H, br s) was observed. The  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) data are listed in Table 1. Compound **1** had two gem-dimethyl systems univocally identified on the basis of HMBC correlations of H-10/C-11 and H-11/C-10 and H-14/C-15 and H-15/C-14 couplings. Because all methyl signals were singlet, it was concluded that these two pairs of methyl groups were linked to quaternary carbons. The HMBC (Figure 2) spectrum showed cross-peaks of H<sub>1</sub>-6/C-4b, C-8, and C-15; H<sub>a</sub>-8/C-7, C-8a, C-9, and C-16; H<sub>b</sub>-8/C-4b, C-7, C-8a, and C-16; H<sub>a</sub>-9/C-2, C-8, C-8a, C-9a, and C-16; H<sub>b</sub>-9/C-2, C-4a, C-4b, C-8a, C-9a, and C-16; H<sub>3</sub>-13/C-4b and C-5; H<sub>3</sub>-14/C-7, C-8, and C-15; H<sub>3</sub>-15/C-7, C-8, and C-14; and H<sub>3</sub>-16/C-4b, C-8, C-8a, and C-9. It can be concluded that two methyls (C-14, C-15) were located at C-7 and that methyl C-13 was located at C-5. According to the identified methyls and their neighboring carbons, a six-membered ring and a five-membered ring sharing the same two carbon (C-4b

and C-8a) atoms were indicated, among which N was connected between C-5 and C-7 because of the downfield  $^{13}\text{C}$  NMR chemical shifts ( $\delta_{\text{C-5}}$  141.0,  $\delta_{\text{C-7}}$  50.6). The first ring had three aliphatic carbons, two olefinic carbons, and a nitrogen atom; the second ring had two aliphatic carbons and three olefinic carbons. The HMBC showed the cross-peaks of  $\text{H}_3\text{-10/C-2}$ , C-3, and C-11;  $\text{H}_3\text{-11/C-2}$ , C-3, and C-10; and  $\text{H}_3\text{-12/C-3}$ , C-4, and C-4a, suggesting two methyls (C-10, C-11) were located at C-2; methyl C-12 was located at C-4. In a similar way, a second six-membered ring fragment having two identical (C-4a, C-9a) atoms with the five-membered ring aforementioned was figured out. To satisfy the molecular formula, the presence of the nitrogen atom in this ring was reasonable, considering the downfield chemical shift of C-9a ( $\delta_{\text{C}}$  169.4) and C-2 ( $\delta_{\text{C}}$  65.7). The overall structure of compound **1** was further confirmed by additional 2D NMR data (Figure 1). The relative configuration was confirmed by the NOE spectrum, according to the correlations of  $\text{H}_3\text{-16/Hb-8}$ , Hb-9, and  $\text{H}_3\text{-14}$ ; Ha-8/Ha-9 and  $\text{H}_3\text{-15}$ ,  $\text{H}_3\text{-12/H}_3\text{-13}$ , and  $\text{H}_1\text{-6/H}_3\text{-15}$ , as illustrated in Figure 3. Thus, the structure of compound **1** was elucidated as 2,2,4,5,7,7,8a-heptamethyl-2,6,7,8,8a,9-hexahydro-3H-cyclopenta[1,2-b:3,4-c']dipyridin-3-one, named oleracimine, **1**.

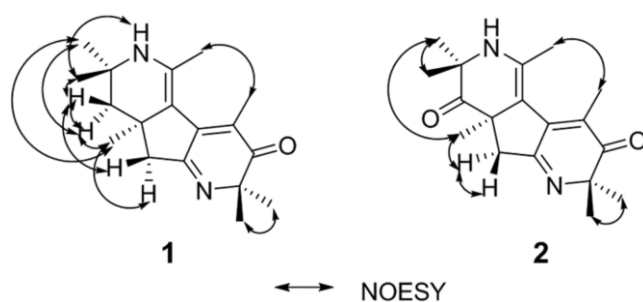
Table 1.  $^1\text{H}$  NMR (500 MHz) and  $^{13}\text{C}$  NMR (125 MHz) Data of Compounds **1** and **2** in  $\text{CDCl}_3$

Position	<b>1</b>		<b>2</b>	
	$\delta_{\text{C}}$ , type	$\delta_{\text{H}}$ , mult ( <i>J</i> in Hz)	$\delta_{\text{C}}$ , type	$\delta_{\text{H}}$ , mult ( <i>J</i> in Hz)
1	N		N	
2	65.7, C		65.9, C	
3	206.2, C		206.7, C	
4	121.3, C		122.2, C	
4a	143.5, C		140.3, C	
4b	110.7, C		110.6, C	
5	141.0, C		142.1, C	
6	NH	4.07 brs	NH	4.01 brs
7	50.6, C		60.2, C	
8	46.8, $\text{CH}_2$	a: 1.47 d (13.2) b: 2.02 d (13.2)	212.1, C	
8a	38.9, C		49.3, C	
9	52.3, $\text{CH}_2$	a: 2.28 d (15.3) b: 2.56 d (15.3)	43.3, $\text{CH}_2$	a: 2.85 d (17.1) b: 2.61 d (17.1)
9a	169.4, C		166.8, C	
10	29.1, $\text{CH}_3$	1.31 s	28.6, $\text{CH}_3$	1.34 s
11	27.4, $\text{CH}_3$	1.45 s	27.8, $\text{CH}_3$	1.44 s
12	14.3, $\text{CH}_3$	1.88 s	14.7, $\text{CH}_3$	1.95 s
13	21.1, $\text{CH}_3$	1.82 s	22.1, $\text{CH}_3$	2.03 s
14	28.6, $\text{CH}_3$	1.34 s	27.6, $\text{CH}_3$	1.49 s
15	32.5, $\text{CH}_3$	1.30 s	28.4, $\text{CH}_3$	1.37 s
16	28.8, $\text{CH}_3$	1.17 s	25.5, $\text{CH}_3$	1.32 s



**Figure 2.** Selected  $^1\text{H}$ - $^1\text{H}$  COSY and HMBC correlations of compounds **1** and **2**.

The  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and DEPT spectra of compound **2** showed 18 carbon resonances, which was of high similarity with that of compound **1** except for one more carbonyl and one less methylene, including 7 methyls, 1 methylene, and 10 quaternary carbons (2 carbonyls, 5 olefinic carbons, and 3 aliphatic carbons). One active hydrogen ( $\delta_{\text{H}}$  6.401, 1H, br s) was also observed.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) data are provided in Table 1. Similarly, the HMBC (Figure 2) spectrum of compound **2** showed cross-peaks of  $\text{H}_1$ -6/C-4b;  $\text{H}_a$ -9/C-8, C-8a, C-9a, and C-16;  $\text{H}_b$ -9/C-4a, C-4b, C-8a, C-9a, and C-16;  $\text{H}_3$ -10/C-2, C-3, and C-11;  $\text{H}_3$ -11/C-2, C-3, and C-10;  $\text{H}_3$ -12/C-3, C-4, and C-4a,  $\text{H}_3$ -13/C-4b and C-5;  $\text{H}_3$ -14/C-7, C-8, and C-15;  $\text{H}_3$ -15/C-7, C-8, and C-14;  $\text{H}_3$ -16/C-4b, C-8, C-8a, and C-9, were almost the same as those of compound **1**. Hence, it can be assumed these two compounds had the same carbon skeleton. The only difference is methylene replaced by carbonyl at C-8. The relative configuration was confirmed by NOE spectrum, as indicated by correlations of  $\text{H}_3$ -16/ $\text{H}_b$ -9 and  $\text{H}_3$ -14;  $\text{H}_a$ -9/ $\text{H}_b$ -9,  $\text{H}_3$ -14/ $\text{H}_3$ -15, and  $\text{H}_3$ -16, as illustrated in Figure 3. Therefore, the structure of compound **2** was elucidated as 2,2,4,5,7,7,8a-heptamethyl-6,7,8a,9-tetrahydro-2H-cyclopenta-[1,2-b:3,4-c']dipyridine-3,8-dione, named oleracimine A, **2**.



**Figure 3.** Selected  $^1\text{H}$ - $^1\text{H}$  NOESY correlations of compounds **1** and **2**.

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