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Dasycarine, a New Quinoline Alkaloid from *Dictamnus dasycarpus*

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Abstract: Dasycarine, a new quinoline alkaloid along with five known compounds, dictamine, dihydroobacunone, obacunone, fraxinellone and β-sitosterol, were isolated from *Dictamnus dasycarpus*. The structure of dasycarine was identified as 4, 5, 8- trimethoxyl –3- (3- methyl –2- butenyl)- 2- quinone by 1D and 2D NMR techniques.

Keywords: *Dictamnus dasycarpus*, Rutaceae, alkaloids, dasycarine.

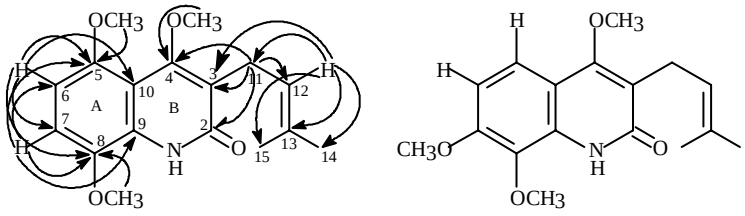
Dictamnus dasycarpus Turcz, which is mainly distributed in northern China, is used as traditional Chinese medicine for the treatment of rheumatism and virus infection *etc*[1]. Investigation on the roots of this plant led to the isolation of a new alkaloid named dasycarine and 5 known compounds, dictamine, dihydroobacunone, obacunone, fraxinellone and β-sitosterol.

Dasycarine, colorless needles, was crystallized from acetone, mp 172-173℃. HREIMS (found 303.1456, calc. 303.1470) suggested the molecular formula $C_{17}H_{21}NO_4$, which was consistent with the ^{13}C and ^1H-NMR spectral data. EIMS spectrum of dasycarine gave a molecular ion peak at *m*/*z* 303 $[M]^+$ (100) and fragment ion peaks at *m*/*z* 288 (94), 272 (25), 260 (82), 248 (86), 234 (45), 218 (20). Its NMR data showed the presence of three methoxyl groups, a four-substituted aromatic ring with two *ortho* coupled protons, two methyl groups, one double-bond and one amide group (**Table 1**). The UV absorptions at 220, 232, 251, 260, 296, 325, 338nm, together with NH (3078cm^{-1}) and amide (1640 cm^{-1}) absorptions in the IR spectrum showed characteristics of a 2-quinolone derivative[2]. The ^1H-NMR spectrum was very informative with an exchangeable (N-H) proton at δ 10.08, two *ortho* coupled aromatic protons at δ 7.47 and 7.02 (J = 9 Hz), methoxyl singlets at δ 3.97 (3H), 3.95 (3H) and 3.92 (3H), vinylic Me singlets at δ 1.65 and 1.79 and a one-proton triplet at δ 5.27 (J = 6.5 Hz) coupled to a two-proton doublet at δ 3.30. The ^1H-^1H COSY and HMQC spectra revealed the following partial structure: $–CH_2-CH = C (CH_3)_2$. The HMBC experiment indicated the relations between H-11, H-12 and C-3, between H-11 and C-2, and between H-11 and C-4, OMe and C-4, suggesting the 3-methyl -2-butenyl group and one methoxyl group were attached to C-3 and C-4, respectively.

The locations of the other two OMe groups at ring A were determined by HMBC

spectrum simultaneously (**Figure 1**.). The two OMe groups were easily confirmed to be connected with C-5 and C-8 due to the long-range correlations between H-6 and C-10, between H-7 and C-9. These assignments were also supported by comparison with the spectral data of preskimmianine[3, 4]. In the NMR spectra of dasycarine, the C-10 resonance signal shifted from δ 112.2 to 110.9, while an aromatic proton signal was downshifted from δ 6.85 to 7.02, when compared with those of preskimmianine. So dasycarine was elucidated to be 4, 5, 8- trimethoxyl -3- (3- methyl -2- butenyl) -2- quinone, and its ^{1}H- and ^{13}C-NMR spectra (**Table 1**) were completely assigned by detailed 2D-NMR experiments.

Figure 1. The ^{1}H-^{13}C long-range COSY of Dasycarine



dasycarine preskimmianine

Table 1. ^{1}H-(500MHz) and ^{13}C-(125MHz) NMR spectral data for dasycarine ($CDCl_3$, TMS)

Proton	δ , mult. J (Hz), int.	Carbon	δ	Carbon	δ
H-6	7.02, d, 9.0,1H	C-2	164.5	C-11	23.8
H-7	7.47, d, 9.0, 1H	C-3	121.0	C-12	123.1
H-11	3.30, d, 6.5, 2H	C-4	162.2	C-13	131.9
H-12	5.27, t, 6.5, 1H	C-5	135.0	C-14	18.0
H-14	1.79, s, 3H	C-6	108.2	C-15	25.8
H-15	1.65, s, 3H	C-7	119.1	OMe	56.5
OMe	3.97, s, 3H	C-8	153.7	OMe	61.1
OMe	3.95, s, 3H	C-9	133.0	OMe	62.0
OMe	3.92, s, 3H	C-10	110.9		

Signal assignments are based on 2D-NMR (^{1}H-^{1}H COSY, HMQC and HMBC) spectra.

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