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THE STRUCTURE OF CAMMACONINE FROM *ACONITUM VARIEGATUM*

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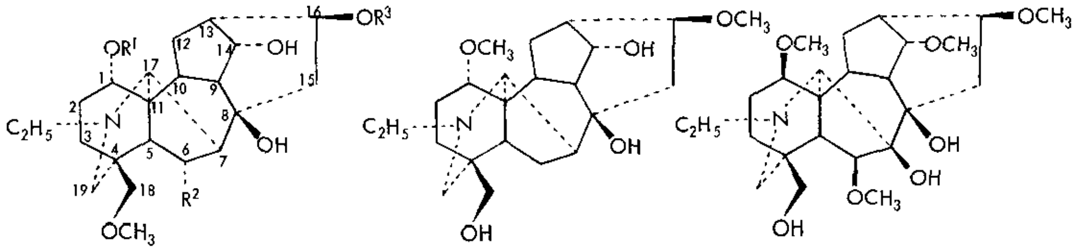
The novel structure assigned earlier to the C_{19}-diterpenoid alkaloid, cammaconine, contained a C(16) hydroxyl and a C(18) methoxyl group. On the basis of ^{13}C NMR spectral analysis, these assignments have been reversed.

In 1971 Mollov and co-workers[1] reported the isolation of a new alkaloid, cammaconine, from *Aconitum variegatum* and on the basis of chemical correlation with isotalatizidine, oxidation reactions, and spectral analysis, assigned structure 1 to cammaconine. Thus cammaconine would be the first member of the C_{19}-diterpenoid alkaloids[2] to bear a C(16)β- hydroxy instead of a C(16)β- methoxy group. This unusual feature prompted us to examine the ^{13}C NMR spectrum of cammaconine.

We report here a revision of the structure of cammaconine to 2 on the basis of ^{13}C NMR spectral analysis. A recent analysis[2-5] of ^{13}C NMR spectra of more than 100 *Aconitum*- and *Lycoctonine*-type alkaloids and their derivatives provides a foundation for unambiguous assignments of all resonances for cammaconine. A correlation of the ^{13}C NMR spectrum of cammaconine was made with isotalatizidine (3), chasmanine (4), lycoctonine (5) and other published ^{13}C NMR data for related alkaloids (Table 1). The presence of a primary hydroxy carbon signal at 68.8 ppm and the absence of a methoxy carbon signal at ~ 59 ppm indicated that a hydroxy group instead of a methoxy group is present at C(18) in cammaconine. Furthermore, the signals at 82.3 and 56.3 ppm also revealed the presence of a methoxy group at C(16) instead of at C(18) in cammaconine. All other signals are also in agreement with the new structure (2) assigned for cammaconine.



1 $R^1 = CH_3$; $R^2 = R^3 = H$

3 $R^1 = R^2 = H$; $R^3 = CH_3$

4 $R^1 = R^3 = CH_3$; $R^2 = OCH_3$

2 Cammaconine

5

The above evidence indicates that cammaconine possesses a C(18) hydroxyl rather than a C(16) hydroxyl group. It is therefore identical with the alkanolamine of the alkaloid aconorine.[5]

Table 1. ^{13}C Chemical shifts and Assignments for Cammaconine (2) and Related Alkaloids†

	2	3	4	5		2	3	4	5
C(1)	86.3	72.3	86.1	84.2	C(14)	75.6	75.6	75.5	84.0
C(2)	25.8	29.2	26.0	26.1	C(15)	38.3	42.3	39.2	33.7
C(3)	33.2	29.7	35.2	31.6	C(16)	82.3	82.4	82.2	82.7
C(4)	39.1	37.3	39.5	38.6	C(17)	63.0	63.7	62.4	64.8
C(5)	46.0	41.7	48.8	43.3	C(18)	68.8	79.0	80.8	67.6
C(6)	24.6	25.0	82.5	90.6	C(19)	53.1	56.6	54.0	52.9
C(7)	45.9	45.3	52.8	88.3	N-CH_2	49.5	48.4	49.3	51.1
C(8)	73.0	74.3	72.6	77.5	CH_3	13.7	13.0	13.6	14.1
C(9)	47.0	46.7	50.3	49.7	C(1')	56.5*	-	56.3	55.7
C(10)	37.6	40.4	38.4	38.0	C(6')	-	-	57.2	57.7
C(11)	48.8	48.7	50.4	48.9	C(14')	-	-	-	58.0
C(12)	27.7	26.8	28.6	28.8	C(16')	56.3*	56.2	55.9	56.2
C(13)	45.6	44.1	45.7	46.1	C(18')	-	59.3	59.2	-

† In ppm downfield to TMS; Solvent, $CDCl_3$. *Values within any vertical column are interchangeable.

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