

THE STRUCTURE OF CAMMACONINE FROM *ACONITUM VARIEGATUM*

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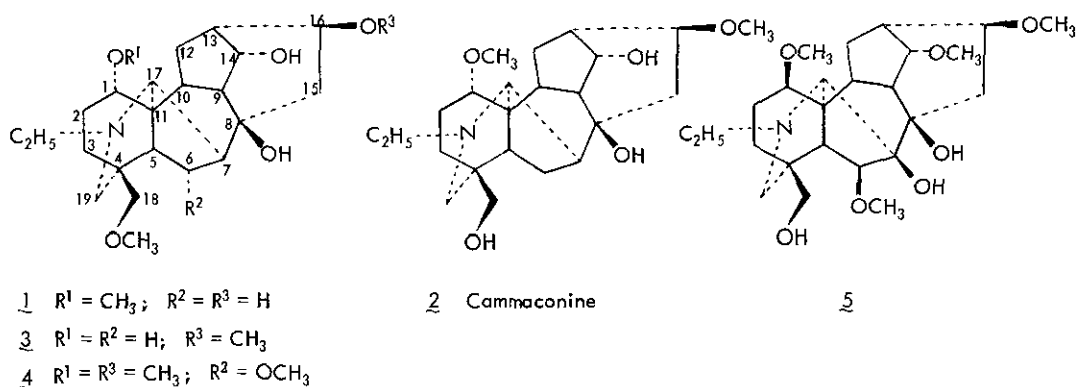
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The novel structure assigned earlier to the C_{19} -diterpenoid alkaloid, cammaconine, contained a C(16) hydroxyl and a C(18) methoxyl group. On the basis of ^{13}C NMR spectral analysis, these assignments have been reversed.

In 1971 Mollov and co-workers¹ 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 alkaloids² 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 analysis²⁻⁵ of ^{13}C NMR spectra of more than 100 *Aconitum*- and *Lycotonia*-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), lycotonia (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.

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. ¹³C 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, CDCl₃. * Values within any vertical column are interchangeable.

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