The Nuclear Magnetic Resonance Spectra of Some Aconite Bases: Lucaconine and Lucidusculine

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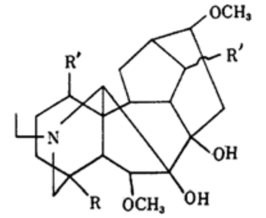
An alkaloid lucaconine has beeen isolated from *Aconitum lucidusculum*, Nakai[1]. Recently, the alkaloid was identified[2] as delcosine[3] obtained from *Delphinium conolida* L. Based on several reactions of delcosine, Marion and others[4] assumed that the alkaloid possesses the same carbon-nitrogen framework and oxygen pattern as lycoctonine II[5] and suggested a tentative structure I. However, there has been no direct evidence for this substance bearing the CH_2OCH_3 group for R.



I $R=CH_2OCH_3$
$R'=OH$
II $R=CH_2OH$
$R'=OCH_3$

In *Aconitum* and *Delphinium* alkaloids, R is generally the methyl, hydroxymethyl or methoxymethyl group[6]. However, the possibility of the presence of the hydroxymethyl group in lucaconine can be excluded, since corresponding aldehydic or acidic products have not been obtained by the oxidation conditions which are expected to lead to these products[1,4,7]. The observation of NMR spectrum of lucaconine has been made to determine whether R is methyl or methoxymethyl. The NMR spectrum at 40 Mc. of lucaconine in pyridine solution is shown in Fig. 1. In this figure, although the other *Aconitum* alkaloids in which R is methyl have a strong singlet absorption characteristic of

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[1] H. Suginome, S. Kakimoto, J. Sonoda and S. Noguchi, *Proc. Japan Acad.*, **22**, 122 (1946); H. Suginome and S. Furusawa, This Bulletin, **32**, 352 (1959); S. Furusawa, ibid., **32**, 399 (1959); T. Amiya and T. Shima, ibid., **31**, 1083 (1958).

[2] T. Amiya and T. Shima, in preparation.

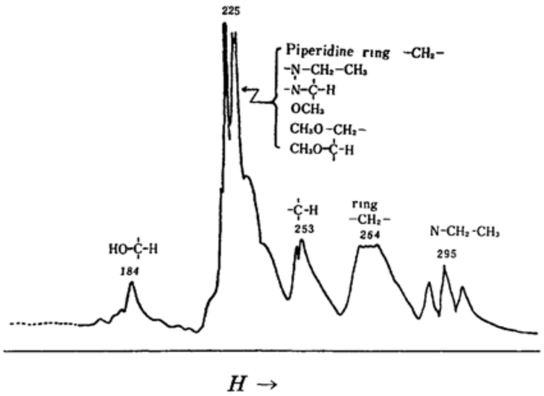
[3] L. N. Markwood, *J. Am. Pharm. Assoc.*, **13**, 696 (1924).

[4] R. Anet, D. W. Clayton and L. Marion, *Can. J. Chem.*, **35**, 397 (1957); R. Anet and L. Marion, ibid., **36**, 766 (1958); V. Skaric and L. Marion, *J. Am. Chem. Soc.*, **80**, 4434 (1958).

[5] M. Przybylska and L. Marion, *Can. J. Chem.*, **34**, 185 (1956).

[6] O. E. Edwards, L. Marion and K. H. Palmer, *Can. J. Chem.*, **36**, 1097 (1958); K. Wiesner, D. L. Simmons and L. R. Fowler, *Tetrahedron Letters*, **No. 18**, 1 (1959).

[7] E. Ochiai, T. Okamoto and M. Kaneko, *Chem. Pharm. Bull.*, **6**, 730 (1958).

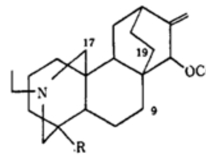


Relative area	Found	1.6	19	4.8	7.6	3
	(Calcd. on formula I)	(2)	(18)	(4)	(8)	(3)

Fig. 1. The proton spectrum of lucaconine (taken on Varian 40 Mc. instrument).

$-\overset{|}{\underset{|}{C}}-CH_3$ group at about 318 c.p.s. from the signal of α-proton of pyridine[8], such absorption can not be recognized for lucaconine. Accordingly, R is concluded to be CH_2OCH_3 in lucaconine. The anticipated singlet peak due to the methylene group of $-\overset{|}{\underset{|}{C}}-CH_2-OCH_3$ is, however, obscure[9] in Fig. 1, probably because of the overlapping with strong peaks of methoxyl groups, and of possible broadening due to the unequivalence of two methylene protons caused by the neighbouring asymmetric carbon atom[10]. A tentative interpretation based on the suggested structure I is also given in Fig. 1[11].

We next examined NMR spectrum of an aconite base lucidusculine[12]. Recently, one of us (T. A.) proposed formula III for the partial structure of lucidusculine on the basis of some chemical transformations[13].



III $R=CH_2OH$, one secondary OH group on the ring. Possible linkage between C_{17}-C_{19} or C_{17}-C_9.

IV $R=CH_3$, two secondary OH groups on the ring. Possible linkage between C_{17}-C_{19} or C_{17}-C_9.

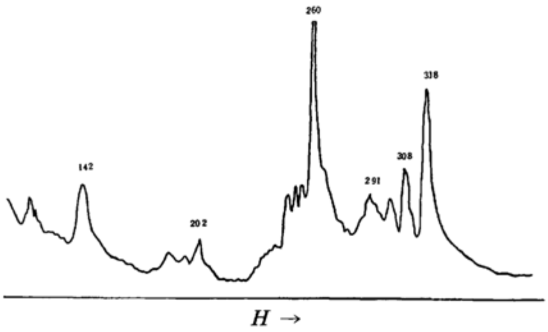


Fig. 2. The proton spectrum of lucidusculine.

The NMR trace at 40 Mc. of lucidusculine in pyridine is shown in Fig. 2. Clearly, the singlet band at 318 c.p.s. is to be ascribed to the methyl group on a quaternary carbon atom. This observation forces one to the conclusion that in lucidusculine R is actually the methyl group. The two hydroxyl groups in lucidusculine may both be secondary, since they are easily acetylated[12]. From above described results, a modified formula IV is now suggested as the partial structure of lucidusculine.

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[8] A. Suzuki, T. Amiya, K. Takahashi and T. Matsumoto, unpublished work.

[9] In the NMR spectrum of lycoctonine[8], the absorption due to methylene group of $-\overset{|}{\underset{|}{C}}-CH_2OH$ is also obscure.

[10] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, London (1959), p. 102.

[11] The signal of the methine proton of methoxycyclohexanes (H-C-OCH_3) has been shown to appear at a position very close to the methoxyl group. R. U. Lemieux, R. K. Kullning, H. J. Bernstein and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958).

[12] R. Majima and S. Morio, *Ber.*, **65**, 599 (1932); H. Suginome, S. Kakimoto and J. Sonoda, *J. Fac. Sci. Hokkaido Univ.*, Ser. III, Chem., **4**, 25 (1950); H. Suginome and S. Kakimoto, This Bulletin, **32**, 352 (1959): T. Amiya, ibid., **32**, 1133 (1959).

[13] T. Amiya, This Bulletin, **33**, 1175 (1960).