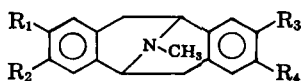


## Structure of Bisnorargemonine

Sir:

Bisnorargemonine,  $C_{19}H_{21}NO_4$ ,  $[\alpha]_D^{25} -265.8^\circ$  ( $CH_3OH$ ), is an alkaloid first isolated by Kier and Soine (1) from *Argemone munita* subsp. *rotundata* (Rydb.) G. B. Ownb. It was originally given the trivial designation of *rotundine* which was later changed to *bisnorargemonine* when it became evident that the original name was already in use (2). Bisnorargemonine was found to be closely related to argemonine (2) since it produced the latter on diazomethylation. The structure of argemonine has recently been elucidated by us (3) and independently confirmed by Stermitz and co-workers (4), thus establishing the basic ring structure as that of *N*-methylpavine (I), the structure of which had previously been established by Battersby and Binks (5) on the synthetic compound.



- I.  $R_1, R_2, R_3, R_4 = OCH_3$   
 II.  $R_1, R_3 = OH; R_2, R_4 = OCH_3$   
 III.  $R_1, R_2 = OH; R_3, R_4 = OCH_3$   
 IV.  $R_1, R_4 = OH; R_2, R_3 = OCH_3$

As a continuation of our interest in the *Argemone* alkaloids, we have examined the structural possibilities for bisnorargemonine and assign II as the structure based on the evidence cited below.

Bisnorargemonine possesses two phenolic groups and two methoxyl groups. Our previous findings have ruled out a vicinal catechol arrangement of the hydroxyls (2) such as in structure III because 4-ethoxy-5-methoxy-phthalic acid and *N*-methyl-4-ethoxy-5-methoxy-phthalimide have been demonstrated as oxidation products from treatment of diethylbisnorargemonine with potassium permanganate and

manganese dioxide-dilute sulfuric acid, respectively. The remaining structural possibilities would be II and IV.

We have utilized the nuclear magnetic resonance spectrum of bisnorargemonine to establish our structural assignment. Considering the two possibilities, it is evident that a decision can readily be made on the basis of the aromatic proton and methoxyl proton absorptions. Structure II has four aromatic protons, all of which differ and, therefore, should be resolvable into four singlets of one proton each. Likewise, the methoxyl groups in II are dissimilar and should show two singlets of three protons each. On the other hand, structure IV has two pairs of identical aromatic protons and two identical methoxyl groups. This should result in two aromatic proton singlets of two protons each and one methoxyl proton singlet of six protons. The nuclear magnetic resonance spectrum of bisnorargemonine<sup>1</sup> showed four nicely separated aromatic proton singlets of one proton each at 3.10, 3.25, 3.34, and 3.44 $\tau$  and two methoxyl singlets of three protons each at 6.13 and 6.19 $\tau$ . This establishes the structure of bisnorargemonine as II.

- (1) Kier, L. B., and Soine, T. O., *THIS JOURNAL*, **49**, 187 (1960).  
 (2) *Ibid.*, **50**, 321 (1961).  
 (3) Martell, M. J., Jr., Soine, T. O., and Kier, L. B., *J. Am. Chem. Soc.*, **85**, 1022 (1963).  
 (4) Stermitz, F. R., Lwo, S., and Kallos, G., *ibid.*, **85**, 1551 (1963).  
 (5) Battersby, A. R., and Binks, R., *J. Chem. Soc.*, **1955**, 2888.

TAITO O. SOINE  
 LEMONT B. KIER<sup>†</sup>

Department of Pharmaceutical Chemistry  
 College of Pharmacy  
 University of Minnesota  
 Minneapolis 14

<sup>†</sup> Department of Pharmaceutical Chemistry  
 College of Pharmacy  
 Ohio State University  
 Columbus

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