

THE NATURE OF "DELSEMINE" FROM DELPHINIUM SEMIBARBATUM AND
D. TRICORNE MICHAUX (DWARF LARKSPUR)

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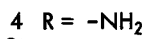
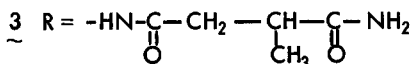
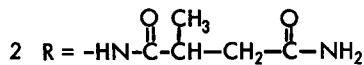
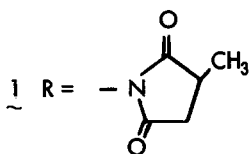
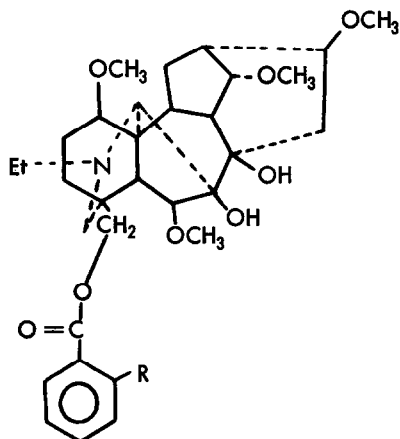
During the isolation of the alkaloids of Delphinium tricornis Michaux (Dwarf Larkspur) by the gradient pH separation technique, we were able to isolate, inter alia, two bases from the chloroform extract of the total alkaloids at pH 6 and pH 9 (NH₄OH), respectively. The bases, referred to as Alkaloid A and Alkaloid B, did not crystallize from various solvent mixtures used and formed salts which also did not crystallize. The purity of the bases was ascertained by repeated preparative TLC until they gave single spots on analytical TLC plates.

Mild alkaline hydrolysis of both Alkaloid A and Alkaloid B furnished lycoctonine.¹ The ¹³C NMR spectrum of Alkaloid A showed 37 signals corresponding to 37 carbon atoms in the molecule. The chemical shifts of 24 of these carbons are identical with those of lycoctonine.² The peak at 69.1 ppm definitely arises from C-18 of lycoctonine when the C-18-OH is esterified, as in tricorinine.³ The remainder of the peaks at 179.8(s), 175.8(s), 164.1(s), 133.6(d), 133.0(s), 131.0(d), 130.0(d), 129.4(d), 127.0(s), 37.0(d), 35.3(t), and 16.4(q) ppm are in agreement with the structure of Alkaloid A as methyllycaconitine (1), a well known alkaloid.¹ The ¹³C NMR spectrum of Alkaloid B on the other hand, showed 45 peaks of which 24 peaks correspond with the 24 carbons of lycoctonine.² The remaining peaks are at 176.0(s), 174.1(s), 172.4(s), 170.0(s), 168.1(s), 168.1(s), 141.9(s), 141.7(s), 134.9(d), 130.3(d), 122.5(d), 120.7(d), 114.8(s), 114.7(s), 69.5(t), 51.9(d), 51.7(d), 41.4(t), 39.0(t), 17.9(q), 17.1(q) ppm. The twin peaks at 141.9 and 141.7, 114.8 and 114.7, 51.9 and 51.7, 41.4 and 39.0, and 17.9 and 17.1 ppm along with six lowfield singlets for six carbonyl groups indicate that Alkaloid B is a mixture of compounds (2) and (3).

The alkaloid "delsemine", isolated by Yunusov and Abubakirov⁴ from D. semibarbatum was assigned⁵ alternative structures (2) or (3). The structure of "delsemine" rests mainly on its formation from methyllycaconitine (1) on treatment with NH₄OH and on its conversion to the known alkaloid, anthranoyllycoctonine (4), upon hydrolysis with aqueous 6N HCl at 90° for 1 hr. We treated pure methyllycaconitine (Alkaloid A) with NH₄OH following the procedure used by the previous workers,⁴ but the resulting product gave a ¹³C NMR spectrum identical with that of Alkaloid B. This is to be expected because NH₄OH will certainly attack the methyl-succinimido group on both the carbonyl centers, producing a mixture of compounds (2) and (3). Hydrolysis of Alkaloid B [(2) and (3)] with 6N HCl following the procedure used for hydrolysis of "delsemine"⁵ gave a product identical with anthranoyllycoctonine (4). Thus, the identity of "delsemine"

with Alkaloid B is established. It is obvious that "delsemine" is an apparently inseparable mixture of the closely-related compounds (2) and (3), which are artifacts resulting from both the Soviet workers' use and our use of NH_4OH during the isolation procedure. This case is an example of the great value of ^{13}C NMR spectroscopy in solving complex structural problems which otherwise are virtually impossible to resolve.

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