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TRICORNINE, A NEW DITERPENOID ALKALOID FROM *DELPHINIUM TRICORNE*

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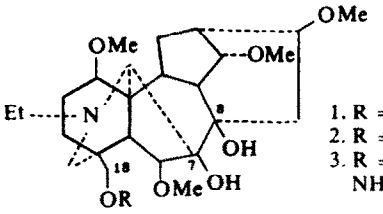
Our continued interest in the chemistry of diterpenoid alkaloids of the genus *Delphinium* led us to investigate *D. tricorne*, a relatively rare plant growing in the mountains of the Southeastern United States. To our knowledge, no chemical investigation of this plant has been reported in the literature. The total alkaloid extract from 1.1 kg of the whole plant, upon gradient pH separation, column chromatography and preparative TLC, yielded tricornine, $C_{27}H_{43}NO_8$, mp 187–189° (d), $[\alpha]_D^{22}$ + 47.3 (*c* 1.3, EtOH), and the known alkaloid, lycoctonine [1, 2]. In this communication, we wish to report the structure of tricornine as **1** on the basis of chemical and spectral evidence. It is interesting to note that although several C-18 esters of lycoctonine are known in nature [3], tricornine represents the only simple ester isolated so far. All the others are various *N*-substituted anthranilic acid esters of lycoctonine at C-18, e.g., avadharidine (3) [4].

The IR spectrum of tricornine in KBr shows bands at 3450 (OH), 3200 (OH, intramolecularly H-bonded), 1740 and 1235 (OCOMe), and 1090 (C—O—C) cm^{-1}. The ^{1}H NMR spectrum in $CDCl_3$ (TMS) shows four



1. R = Ac
2. R = H
3. R = COC_6H_4—(*o*) $NHCOCH_2CH_2CONH_2$

sharp 3H singlets at δ3.88, 3.98, 4.02 and 4.06 ppm for four OMe groups, a sharp 3H singlet at 2.46 ppm for a OAc and a 3H triplet at 1.26 ppm (J = 7 Hz) for —N—CH_2—CH_3. The integration of the remainder of the signals accounts for the rest of the protons in the molecule. The ^{13}C NMR spectrum (taken with a JEOL JMN/FX 60 spectrometer) of tricornine in $CDCl_3$ (TMS) shows 27 signals corresponding to 27 carbon atoms in the molecule. The spectrum very closely resembles that of lycoctonine [5, 6] with the following exceptions: The chemical shift of the C-18 in lycoctonine (67.5 ppm) appears significantly downfield at 69.2 ppm in the spectrum of tricornine. Also, the two additional carbons in the tricornine molecule appear at 20.8 and 170.9 ppm in the ^{13}C spectrum. The off resonance decoupled ^{13}C NMR spectrum of tricornine shows that the peak at 20.8 is a quartet and the one at 170.9 is a singlet. The downfield shift of the C-18 carbon and the presence of two additional carbons at 170.9 (C=O) and 20.8 (Me) in the ^{13}C NMR spectrum of tricornine suggests it to be a C-18 acetate of lycoctonine. The supporting chemical evidence for this conclusion comes from the mild alkaline hydrolysis of tricornine. The product is identical with lycoctonine in all respects (mp, mmp, IR, ^{1}H and ^{13}C NMR). Moreover, lycoctonine on treatment with Ac_2O in Py at room temp. produces tricornine (mp, mmp, IR, ^{1}H and ^{13}C NMR). As only the primary OH function of lycoctonine could be acetylated under the above conditions, tricornine must be represented by structure **1**.

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