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THE ALKALOIDS OF DELPHINIUM BICOLOR NUTT.

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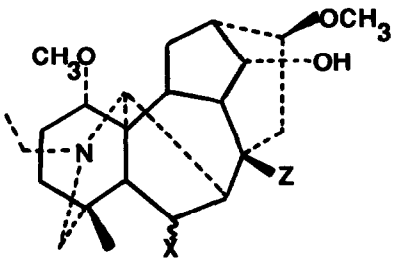
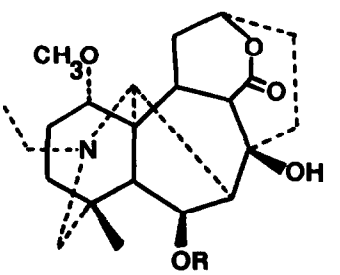
The structures of alkaloid-A and -B were established via X-ray crystallography of the former as its HI salt, and its chemical conversion to the latter.

An investigation of the alkaloids of Delphinium bicolor Nutt. resulted in the isolation and identification of three known diterpenoid alkaloids, delcosine, lycoctonine, and isotalatizidine, and two new bases designated alkaloid-A, and -B. Originally these compounds were assigned structures 1 and 2.[1,2] However, as a result of a detailed re-examination of the ^{13}C-nmr spectra of the alkaloids, and comparison with other model compounds, these structures were subsequently revised: alkaloid-A being assigned structure 3, and, by implication, alkaloid-B structure 4.[3]

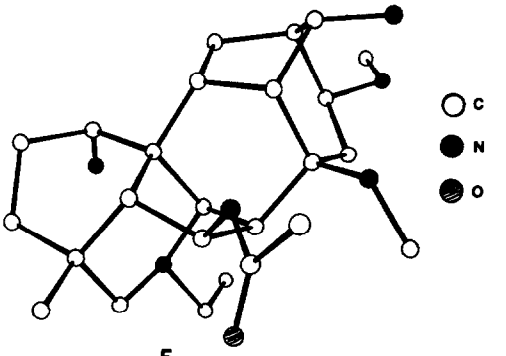




1 X = OCH_3 , Z = $OCOCH_3$
2 X = Z = OH
3 X = α-$OCOCH_3$, Z = OCH_3
4 X = α-OH , Z = OH
5 X = β-$OCOCH_3$, Z = OCH_3
6 X = β-OH , Z = OH

7 R = H
8 R = $COCH_3$

We have now completed an X-ray crystallographic analysis of alkaloid-A as its hydroiodide salt which revealed that its structure is 5[4], i.e., the 6β epimer of 3. Re-examining our previous conclusions, we realised that although we correlated the ^{13}C signal for C-6 with that of heteratisine 7, and its 6-acetate 8, compounds known to be 6β-substituted[5], the structure drawn showed a 6α-orientation: an error which has subsequently been consistently reproduced.



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Given that alkaloid-B probably possessed the structure 6, it appeared likely that it might be derivable from alkaloid-A by hydrolysis. Accordingly we dissolved the free base 5 in 3M aqueous sulfuric acid and heated the solution on a steam-bath overnight. Basification of the reaction mixture followed by column chromatography of the chloroform soluble material (on Woelm alumina, Grade 2, neutral) gave a crystalline product, m.p. 190-191°, identified as alkaloid-B by direct comparison (i.r., m.p., tlc) with the authentic compound.

Thus alkaloids-A and -B have the structures 5 and 6 respectively.

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REFERENCES AND NOTES

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2. A. J. Jones and M. H. Benn, Can. J. Chem., 51, 486 (1973).
3. S. W. Pelletier, N. V. Mody, A. J. Jones, and M. H. Benn, Tetrahedron Lett., 3025 (1976).
4. Full details of this work will be published elsewhere. The final R value is 0.042.
5. R. Aneja, D. M. Locke, and S. W. Pelletier, Tetrahedron, 29, 3297 (1973).

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