

THE STRUCTURE OF DICTYOCARPINE

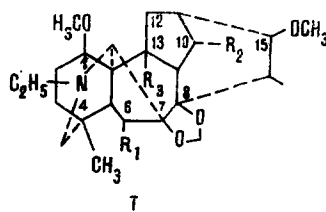
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We have previously reported the isolation from *Delphinium dictyocarpum* of a new alkaloid, dictyocarpine, for which a structure was proposed, although the position of one of the methoxy groups remained undetermined [1].

We suggested that the hydroxy group was located at C₁₃ on the basis of the shift in the signal of the C₁₀ proton. This shift was explained by the deshielding influence of a hydroxy group at C₁₃. To confirm this hypothesis, we have performed the passage from eldeline (I, R₁=OAc, R₂=OCH₃, R₃=OH) to delpheline (I, R₁=OH, R₂=OCH₃, R₃=H), which differs from the former by the absence of a hydroxy group at C₁₃ [2, 3]. For this purpose we obtained acetyldeline (I, R₁=R₂=OAc, R₃=OCH₃), C₂₉H₄₃NO₉, mp 155-156°C. The pyrolysis of acetyldeline at 210-220°C for 30 min in vacuum gave dehydroacetyldelpheline (I, R₁=OAc, R₂=OCH₃, Δ¹²), C₂₇H₃₉NO₇, mp 146-148°C. Catalytic hydrogenation of dehydroacetyldelpheline over platinum in ethanol led to acetyldelpheline (I, R₁=OAc, R₂=OCH₃, R₃=H), C₂₇H₄₁NO₇, mp 120-123°C. Hydrolysis of the latter with methanolic caustic soda gave delpheline (I, R₁=OH, R₂=OCH₃, R₃=H), C₂₅H₃₉NO₆, mp 215-217°C.

According to the NMR spectrum (see Table 1), the removal of the hydroxy group from C₁₃ leads to a displacement of the signal of the C₁₀ proton to the normal value. The facts given show that the C₁₃-hydroxy group does actually exert a deshielding influence on the C₁₀-β-proton. The shielding influence of an acetoxyl group at C₆ on the protons of the tertiary methyl and methylenedioxy groups can be seen from the same table.



For a final proof of the structure of dictyocarpine, we methylated dictyocarpine (I, R₁=R₂=R₃=OH) and eldelidine (I, R₁=R₃=OH, R₂=OCH₃) with methyl iodide in the presence of sodium hydride. The methylation products of the two bases were identical. The correlation performed showed that the remaining methoxy group in dictyocarpine is located at C₁₅.

TABLE 1. Chemical Shifts (δ scale)

| Substance | C-CH ₃ , ppm | CH ₃ O ₂ , ppm | α-Proton at C ₆ , ppm | β-Proton at C ₁₀ , ppm |
|------------------------------|----------------------------|-----------------------------------------|----------------------------------------|-----------------------------------------|
| Eldeline | 0.85 | 4.80 | 4.85 | 5.41 |
| Eldelidine | 0.90 | 4.99 | 5.06 | 4.22 |
| Dictyocarpine | 0.81 | 4.87 | 4.92 | 5.42 |
| Dictyocarpine | 0.91 | 5.02 | 5.14 | 4.20 |
| Dehydroacetyl- delpheline | 0.83 | 4.89 | 4.89 | 5.40 |
| Dehydrodelpheline | 0.91 | 5.03 | 5.13 | 4.18 |
| Acetyldelpheline | 0.79 | 4.82 | 4.85 | 5.34 |
| Delpheline | 0.86 | 5.01 | 5.08 | 4.14 |

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LITERATURE CITED

1. A. S. Narzullaev, M. S. Yunusov, and S. Yu. Yunusov, *Khim. Prirodn. Soedin.*, 498 (1972).
2. M. Carmack, D. W. Mayo, and J. P. Ferris, *J. Amer. Chem. Soc.*, 81, 4110 (1959).
3. A. D. Kuzovkov and T. F. Platonova, *Zh. Obshch. Khim.*, 29, 3840 (1959).