# STRUCTURE OF 14-ACETYLNUDICAULIDINE

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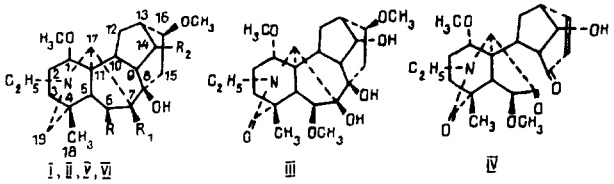
The structure of 14-acetylnudicaulidine has been confirmed by chemical transformations and spectral studies. A correlation has been made of nudicaulidine and demethylenedelpheline.

We have previously reported [1] the isolation from the chloroform-soluble alkaloids of the epigeal part of the plant Delphimium confusum of a new alkaloid – 14-acetylnudicaulidine, for which structure (I) was proposed on the basis of a study of its spectral characteristics. Because of the absence of an authentic sample of nudicaulidine (II), we have made a number of chemical transformations that have confirmed structure (I) as 14-acetylnudicaulidine. The oxidation of nudicaulidine (II) with potassium permanganate in aqueous acetone led to a compound of nonbasic character – oxonudicaulidine (III), $C_{24}H_{37}NO_7$, having a lactam carbonyl in a seven-membered ring (1640 $cm^{-1}$). The mass spectrum of the lactam was characteristic for a 19-oxo compound with a lycoctonine skeleton. The oxidation of oxonudicaulidine with periodic acid yielded oxosecodemethanolnudicaulidine (IV), $C_{23}H_{31}NO_6$. The IR spectrum of (IV) contained absorption bands at 1640, 1700, and 1753 $cm^{-1}$, showing the position of one carbonyl group in a five-membered ring and of another in a six-membered or larger ring [2]. Analysis of the mass spectrum (M+417) and the PMR spectrum (3H, singlets, $2OCH_3$, 3.22, 3.36 ppm) showed that the reaction had not only disrupted the diol system but had also involved the elimination of a methanol molecule. The UV spectrum ($\lambda_{max}C_2H_5OH$ 228 nm; log ε 3.8) and the IR spectrum (1700 $cm^{-1}$) showed that the double bond formed was conjugated with a carbonyl group in a six-membered ring. The ready elimination of a methanol molecule showed that one of the methoxy groups was present in the β-position with respect to a keto group [3]. The PMR spectrum of compound (IV) contained signals from two olefinic protons in the form of a one-proton doublet at 5.98 ppm (J = 9 Hz), with additional splitting of ~1.5 Hz, and a one-proton quadruplet at 6.81 ppm with $J_{AX}$ = 9 Hz and $J_{BX}$ = 7 Hz.



I, II, V, VI  III  IV

I. R = $OCH_3$; $R_1$ = OH; R = OAc
II. R = $OCH_3$; $R_1$ = $R_2$ = CH
V. R = $R_1$ = OH; $R_2$ = $OCH_3$
VI. R = $R_1$ = $R_2$ = $OCH_3$

The presence in the mass spectrum of (I) of the maximum peak of the $M^+ - OCH_3$ ion showed the location of a second methoxy group at C-1 [4].

To establish the position of the remaining methoxy group, we effected a transition from demethylenedelpheline (V) to nudicaulidine. When (V) was methylated with methyl iodide in the presence of sodium hydride we obtained compound (VI), which was identical with the product of the methylation of nudicaulidine under the same conditions.

We obtained additional confirmation of the structure of 14-acetylnudicaulidine by studying its $^{13}C$ NMR spectrum with complete decoupling from protons, which contained signals from

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26 carbon atoms and coincided completely with the corresponding characteristics of 14-acetylnudicaulidine isolated simultaneously by Pelletier and Kulanthaivel [5].

## EXPERIMENTAL

The homogeneity of the substances was checked by chromatography in a thin layer of alumina (for chromatography) in the ether, chloroform, chloroform–ethanol (50:1), and ether–methanol (50:1) systems. IR spectra were taken on a UR-20 instrument (tablets with KBr), PMR spectra on a BS-567A (δ scale, CDCl, HMDS), $^{13}C$ NMR spectra on a Bruker WM-300 spectrometer ($CDCl_3$, TMS), and mass spectra on a MKh-1310 mass spectrometer (with a SVP5 system for direct sample introduction).

Oxonudicaulidine (III). A mixture of 0.08 g of nudicaulidine, 10 ml of acetone, and 5 ml of water was treated with 0.3 g of potassium permanganate in 30 ml of 50% aqueous acetone. The reaction mixture was shaken for 15 min. The excess of potassium permanganate was decomposed with sodium sulphite, and the manganese dioxide was separated off. The acetone was evaporated off, and the aqueous residue was acidified with 5% sulfuric acid and was shaken with chloroform. The residue after the distillation of the solvent was chromatographed on a column (1.8 × 30 cm) of deactivated alumina. Elution of the reaction product with hexane–ether yielded 0.05 g of homogeneous amorphous oxonudicaulidine.

Oxosecodemethanolnudicaulidine (IV). A mixture of 0.05 g of oxonudicaulidine and 0.08 g of periodic acid in 15 ml of water–methanol (1:3) was left at room temperature for 12 days. The methanol was evaporated off and the aqueous solution was made alkaline with sodium carbonate and extracted with chloroform. The solvent was distilled off, giving 0.03 g of homogeneous amorphous (IV).

6,7-Di-O-methyldemethylenedelpheline (VI). A mixture of 0.1 g of demethylenedelpheline, 3 ml of freshly redistilled methyl iodide, and 0.1 g of sodium hydride in 15 ml of freshly redistilled dioxane was boiled for 6 h. The reaction mixture was filtered, and the filtrate was evaporated. The residue was dissolved in 5% sulfuric acid. The acid solution was washed with ether, made alkaline with sodium carbonate, and extracted with chloroform. The alkaline chloroform fraction, after evaporation of the solvent, was separated on a column of alumina. Elution with hexane–ether (5:1) yielded 0.08 g of the homogeneous amorphous product (VI). Mass spectrum $M^+$ 465; PMR spectrum: 3.20, 3.28, 3.31, 3.38, 3.57 ppm (3H each, singlets, $5OCH_3$).

7,14-Di-O-methylnudicaulidine (VI). The methylation of 0.1 g of nudicaulidine and the working up of the product obtained were carried out by above-described procedure, giving 0.04 g of homogeneous amorphous (VI).

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