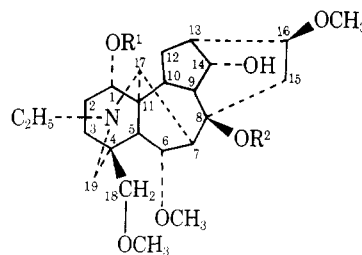


were made on 56 reflections which were particularly sensitive to a change of enantiomorph ($|F_c(hkl)| > 20$, $|F_2(hkl)| / |F_c(hkl)| > 1.05$ or < 0.95). In all cases, the ratio of integrated intensities confirmed the original assignment of the absolute configuration.

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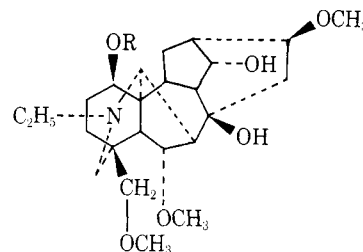
- 1, $R^1 = R^2 = H$
2, $R^1 = CH_3$; $R^2 = H$
9, $R^1 = R^2 = CH_3$

Structure of Neoline, Chasmanine, and Homochasmanine

Sir:

Neoline ($C_{24}H_{39}NO_6$), mp 161° , was first isolated from amorphous aconitine by Freudenberg and Rogers.¹ Careful studies led Wiesner, *et al.*,² to assign structure **1**, with a C-1 α -hydroxyl, to the alkaloid. Marion, *et al.*,³ subsequently correlated neoline with chasmanine, an alkaloid reported^{4,5} to have structure **3**, and, on this basis, assigned structure **4**, with a C-1 β -hydroxyl, to neoline.

In the accompanying communication⁶ we have described the isolation of a new alkaloid, delphisine, from the seeds of *Delphinium staphisagria* and the assignment of its structure as **5** by an X-ray crystallographic analysis of the hydrochloride. Delphisine has, by three routes, been converted to a pair of C-1 epimers, **1** and **4** Scheme I. Also mild hydrolysis of delphisine affords epimer **1**, which by exhaustive comparison, is identical with neoline. This correlation of neoline with delphisine demonstrates that Wiesner's original structural assignment² **1** for neoline is correct and that the revised structure **4**³ is the fact in error. Also the

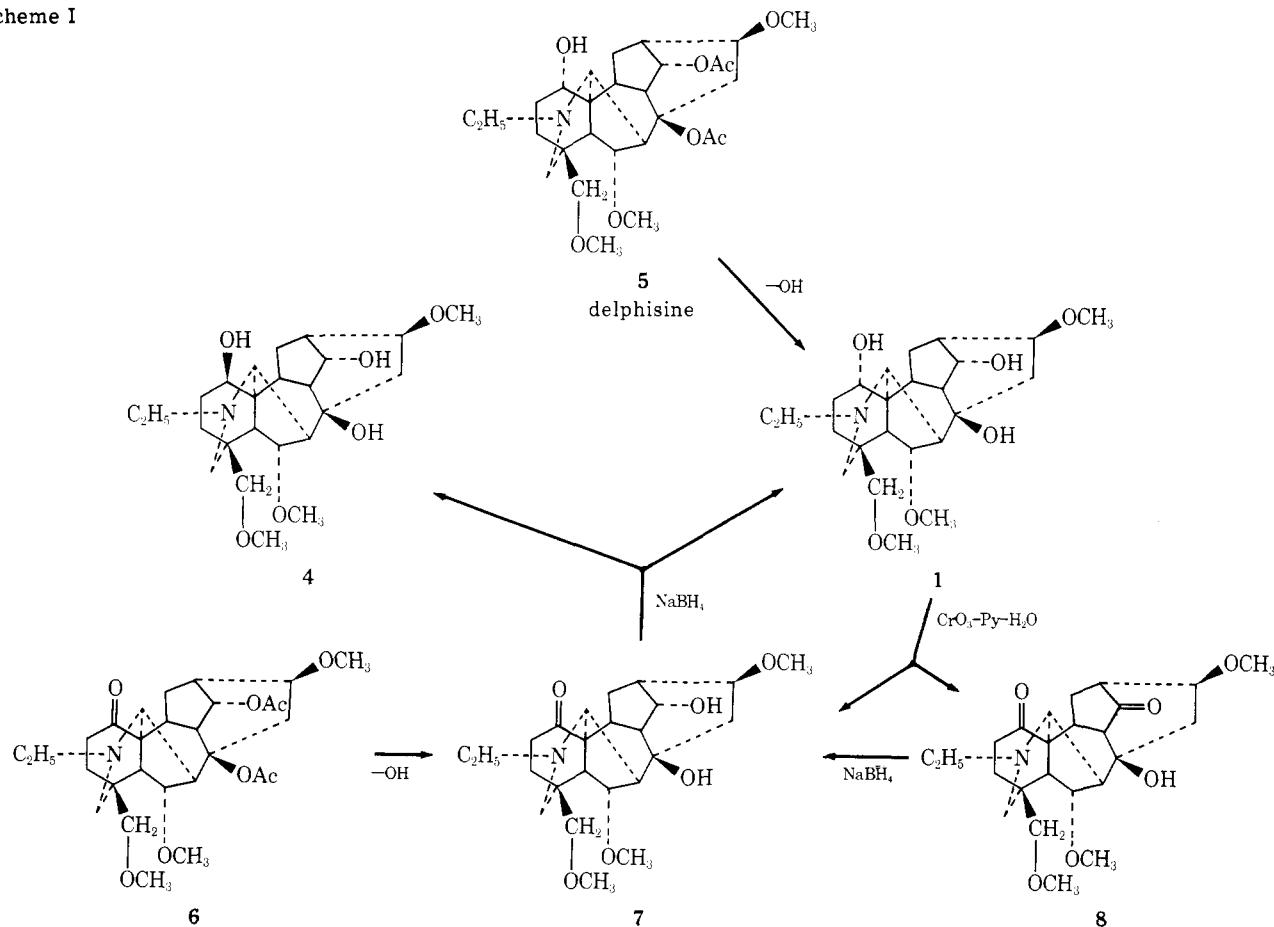


- 3, $R = CH_3$
4, $R = H$

structures of chasmanine and homochasmanine must now be revised to **2** and **9**, respectively.

Oxidation of delphisine **5** ($C_{28}H_{43}NO_8$) with Cornforth reagent (CrO_3 -Py- H_2O) afforded 1-ketodelphisine⁷ (**6**), mp 171° , which was subsequently hydrolyzed with alkali to the 1-keto-8,14-diol derivative **7** ($C_{24}H_{37}NO_6$), mp 150 – 152° . The latter also was prepared from delphisine **5** by the reverse procedure. Hydrolysis of **5** to the corresponding triol

Scheme I



1 ($C_{24}H_{39}NO_6$), mp 159–160°, followed by oxidation with Cornforth reagent gave **7** as well as the 1,14-diketo derivative **8** ($C_{24}H_{35}NO_6$), mp 170–171°, ν_{\max} 1740 and 1690 cm^{-1} . The diketo derivative **8** was reduced with 1 equiv of sodium borohydride to a product which is identical with **7** by ir, nmr, melting point, and mixture melting point. The stereo-specificity of this reduction is anticipated, because the β side of the 14-keto group is less hindered, thereby favoring an α -oriented 14-hydroxyl group. Similar arguments cannot be applied to the reduction of the 1-keto function where both sides are essentially equally hindered. Reduction of **7** with sodium borohydride proceeded without stereo-specificity, to afford a mixture of two epimeric triols **1** and **4** in a ratio of 1:2, respectively, which could be separated by preparative tlc over silica gel. The less polar triol **4** crystallized from chloroform, as a chloroformate, mp 100–105°, $[\alpha]^{26D} + 6.0^\circ$ (c 5.3, ethanol). The more polar epimer was shown to be identical with the hydrolysis product of delphisine by ir, nmr, melting point, and mixture melting point and therefore may be assigned structure **1**.

The ir spectra of the epimeric triols **1** and **4** were different, especially in the hydroxyl region. Triol **1** showed broad absorption between 3620 and 3000 cm^{-1} , with a sharp peak at 3515 and well-defined peak at 3290 cm^{-1} , indicative of a hydrogen bonded hydroxyl group. In contrast triol **4** showed hydroxyl absorption between 3600 and 3210 cm^{-1} centered at 3430 cm^{-1} . The nmr spectra of the triols were also different, especially the signals of the C-1 protons. Compound **1** displayed a multiplet at δ 3.82; compound **4** showed a multiplet at δ 4.00.

Both triols formed triacetates with acetic anhydride and *p*-toluenesulfonic acid. Epimer **1** gave 1 α ,8 β ,14 α -triacetate, mp 151°, identical with delphisine 1 α -monoacetate. Its nmr spectrum shows an *N*-ethyl group (3 H triplet, $J = 7$ Hz) centered at δ 1.12, three acetoxyl groups (δ 2.05 as 3 H singlet and δ 2.10 as 6 H singlet), three methoxyl groups (δ 3.36, 3.40, and 3.43 corresponding to 3 H singlets), and C-1, β -proton at δ 5.00 (quartet $J_1 + J_2 = 14$ Hz). The 1 β ,8 β ,14 α -triacyl compound was obtained as an oil. Its nmr spectrum shows an *N*-ethyl group (3 H triplet, $J = 7$ Hz) centered at δ 1.09, three acetoxyl groups (δ 2.05, 2.10, and 2.12 corresponding to 3 H singlets), three methoxyl groups (δ 3.36 corresponding to three protons and δ 3.40 corresponding to six protons), and a C-1 proton as a multiplet at δ 5.30.

It will be noted that the structure of neoline, as proposed by Wiesner, *et al.*,² corresponds to epimer **1**, while that proposed by Marion, *et al.*,³ corresponds to epimer **4**. The epimer **1**, mp 159–160°, $[\alpha]^{26D} + 21^\circ$ (c 4.0, ethanol) is identical with natural neoline, mp 161°², $[\alpha]^{26D} + 22^\circ$ (c 4.3, ethanol); thus a mixture of the two compounds produced a single spot in tlc and had an undepressed melting point (159°). The ir spectra, obtained in chloroform solution, KBr pellet, and Nujol mull, and the nmr spectra in $CDCl_3$ of both substances were respectively superimposable. Triol **1** and neoline also had identical ^{13}C nmr spectra. Thus neoline must be assigned structure **1** and the revised structure **4**, based on the reported correlation with chasmanine,³ is in error.

The structures previously assigned to chasmanine^{4,5} and homochasmanine⁸ must now be considered. Chasmanine has been correlated³ with neoline by treatment of each alkaloid with sodium hydride and methyl iodide in refluxing dioxan for 12 and 24 hr, respectively. The products, designated as 8,14-di-*O*-methylchasmanine and 1,8,14-tri-*O*-methylneoline, respectively, were shown to be identical by mixture melting point, rotation, behavior on tlc, infrared and nmr spectra, and by identical Debye-Scheerer diagrams. We have replicated this correlation, and there is no

doubt about the identity of the two products. Consequently on the basis of the correlation of chasmanine with neoline, chasmanine must also have a 1 α -substituent and accordingly be assigned structure **2**. A ^{13}C nmr study of chasmanine, delphonine, neoline, and delphisine when compared with published values⁹ for lycotoxine and browniine confirms this assignment.¹⁰ Because chasmanine diacetate has been converted to homochasmanine by treatment with methanol under pressure, followed by saponification, homochasmanine may be assigned structure **9**.

Because chasmanine, homochasmanine, and neoline have been related to delphisine, the absolute configuration of delphisine derived by X-ray analysis⁶ applies to these compounds as well.

Acknowledgment. It is a pleasure to express thanks to Professors T. Okamoto and Léo Marion for reference samples of neoline, to Dr. O. E. Edwards for a sample of chasmanine, to Professor K. Wiesner for infrared spectra of neoline and certain of its derivatives, and to Mr. Courtney Pape for providing the ^{13}C nmr spectra.

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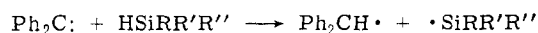
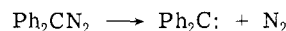
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Organosilicon Iminamino Radicals from the Addition of Silyl Radicals to Diphenyldiazomethane

Sir:

In an attempt to generate observable quantities of arylsilyl radicals *via* hydrogen abstraction by diphenylmethylene



solutions of diphenyldiazomethane in liquid organosilanes¹ were irradiated with ultraviolet light directly in the microwave cavity of an electron spin resonance spectrometer.² ESR signals were obtained from all silanes examined, but the presence of large nitrogen splittings in the ESR spectra immediately revealed that the radicals detected were *not* the desired silicon-centered radicals. Instead we had generated *N*-silyl derivatives of a new class of radicals, the iminamino radicals $>C=NN\cdot$, not previously detected by ESR spectroscopy.

The iminamino radical