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PHOTOCRINAMINE: A PHOTOTRANSFORMATION PRODUCT OF AN <u>AMARYLLIDACEAE</u> ALKALOID, CRINAMINE

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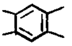
Contrary to the alkaloids of lycorine group which are considerably photosensitive, those of crinine group are believed to be stable to light[1] and none of the phototransformation product of this group has been hitherto characterized. Here we present the first example of phototransformation of an <u>Amaryllidaceae</u> alkaloid, crinamine, one of the representative alkaloid of crinine group.[1]

Irradiation of crinamine (1) in methanol under N_2 with high pressure mercury lamp (200W, with Pyrex filter) for 1.5 hr yielded a crystalline product, photocrinamine (2, m.p. 189-190°) of empirical formula $C_{17}H_{21}NO_4$ (M^+ 303) in ca. 10% yield with 20% recovery of crinamine; UV λ_{max}(MeOH) 235 sh. (logε 3.54), 295 nm (3.66); ^1H NMR($CDCl_3$) δ3.37(s, 3H, OCH_3), 4.17(s, 2H, $ArC\underline{H}_2N$), 5.88(s, 2H, $CH_2{<}^{O}_{O}$), 6.50(s, 1H, ArH), 6.56 ppm(s, 1H, ArH); ^{13}C NMR($CDCl_3$) δ(ppm) 146.3s, 146.0s, 135.4s, 132.2s, 108.6d, 107.1d(), 100.8t($CH_2{<}^{O}_{O}$), 81.1d, 69.1d (2 × $>$CH-O), 61.9t, 56.8t-q(2 × N-CH_2-), 57.9d(N-CH$<$), 51.3d(Ar-CH$<$), 49.3q (OCH_3), 39.4d($-$CH$<$), 37.1t, 36.5t(2 × CH_2). It formed the monoacetate (3), m.p. 152°; ^1H NMR($CDCl_3$) δ5.03 ppm (m, 1H, $>C\underline{H}$-OAc).

The spectral data of 2 and 3 indicated that the change had taken place at rings B and C as suggested from disappearance of both the double bond and the quaternary carbon in crinamine.

These results suggested the structure 2 for photocrinamine, which was confirmed by a single crystal <u>X</u>-ray analysis.

The crystals of photocrinamine (2) are orthorhombic, space group $\underline{P}2_12_12_1$, with $\underline{a}$=12.612, $\underline{b}$=18.725, $\underline{c}$=6.138 Å, and $\underline{Z}$=4. The intensity data were collected on a Philips PW-1100 diffractometer using graphite-monochromated Cu-$\underline{K}\alpha$ radiation. The structure was solved by direct methods with the MULTAN program.[2] Block-diagonal least-squares refinement of positional and thermal parameters reduced

R to 0.086 for 1451 observed reflections. The structure thus resulted is shown in the Figure.

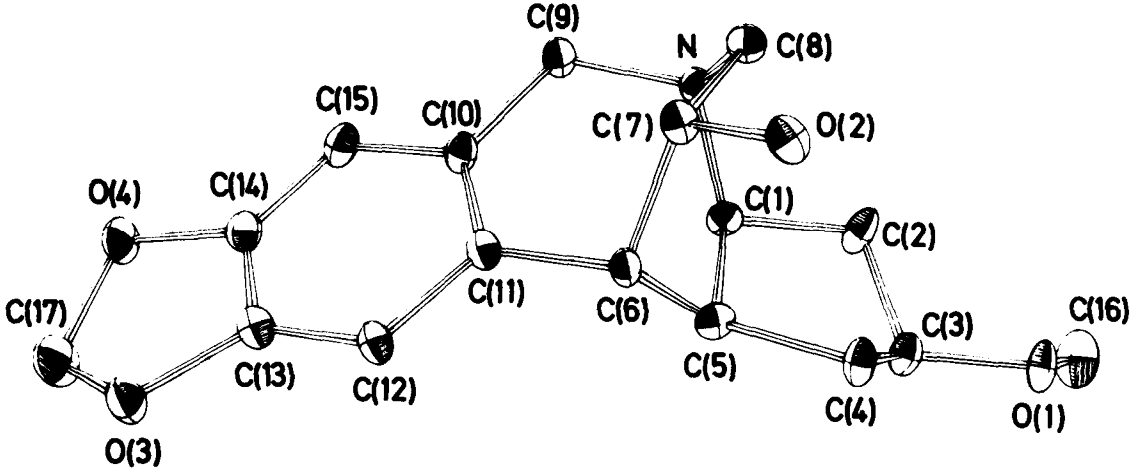
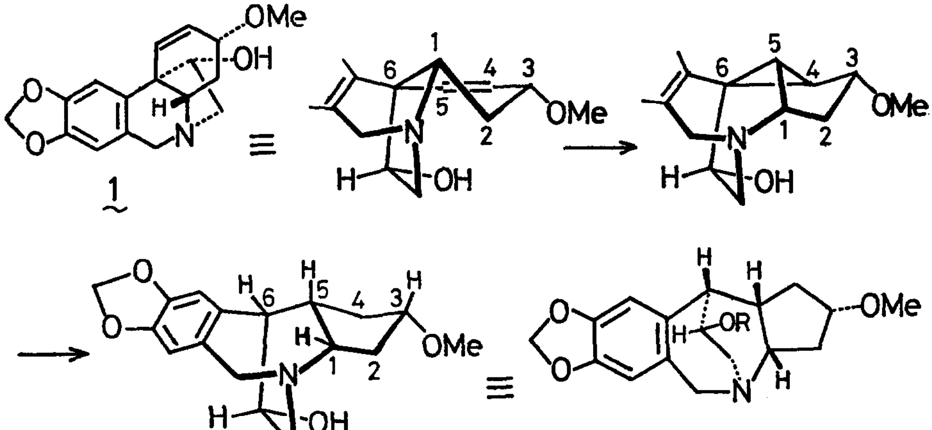


Figure. ORTEP[3] drawing of the molecular structure of photocrinamine (2).

We consider that the reaction proceeded in [π2a + σ2a] manner followed by photo-reduction of the intermediate aryl-conjugated cyclopropane, though there is no example of the latter reaction.



1

2 : R = H

3 : R = Ac

REFERENCES AND NOTES

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