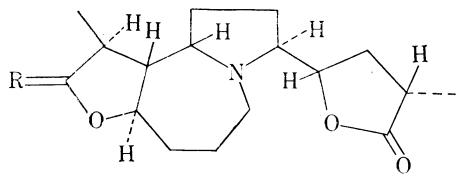
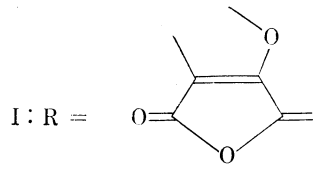
[Chem. Pharm. Bull. 21(2) 451—452 (1973)] UDC 547.94.02 : 543.422.8

X-Ray Crystallographic Determination of the Structure of the Alkaloid Protostemonine

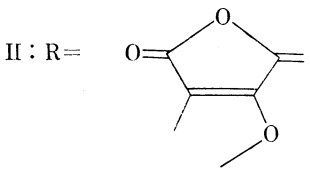
Previously the structure of protostemonine, an alkaloid isolated from *Stemona japonica* Miq. was shown to be represented by either I or II.[1]



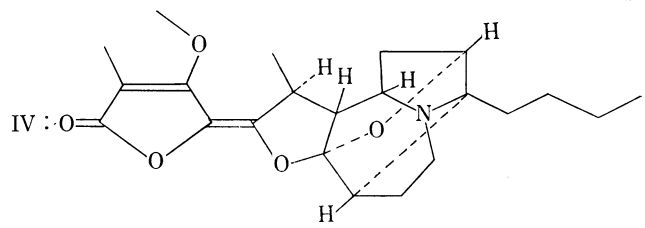


I : R =

III : R=



II : R=



IV :

Because of the inconclusive nature of the chemical and spectral data to select the correct one of these two alternative structures, it was decided to elucidate the structure of this alkaloid by X-ray crystallographic analysis of its methanol solvate.

Protostemonine methanol solvate, $C_{23}H_{31}O_6N$–CH_3OH, mp 172—173° (after sintering at 90—100°), crystallizes from methanol in monoclinic prisms with the cell dimensions, a= 11.685, b=10.335, c=10.028Å, β=101.80°, Dm=1.25 g·cm^{-3}, Dc=1.26 g·cm^{-3}, space group $P2_1$, Z=2.

Intensity data covering zones h01 to h71 and hk0 to hk5 were measured visually on the equi-inclination Weissenberg photographs. The trial structure solved by the usual symbolic addition procedure[2] was refined by the block diagonal least sqaures methods, with anisotropic thermal parameters for all non-hydrogen atoms, to an R-factor of 6.6% for 2441 reflections.

The perspective drawing of the molecule and bond lengths and angles are shown in Fig. 1 and 2, respectively.

Since the absolute configuration of the molecule can be deduced from the established configuration of stemonine (III)[3] which constitutes an essential part of the molecule of protostemonine, the structure of protostemonine is now formulated as I.

The geometry of the conjugated system in the molecule of protostemonine thus estabilshed is the same as that of stemofoline (IV),[4] the structure of which has been elucidated previ-

1) H. Irie, H. Harada, K. Ohno, T. Mizutani, and S. Uyeo, *Chem. Commun.*, **1970**, 268.
2) I.L. Karle and J. Karle, *Acta Cryst.*, **21**, 849 (1966).
3) H. Koyama and K. Oda, *J. Chem. Soc.* (*B*), **1970**, 1330.
4) H. Irie, N. Masaki, K. Ohno, K. Osaki, T. Taga, and S. Uyeo, *Chem. Commun.*, **1970**, 1066.

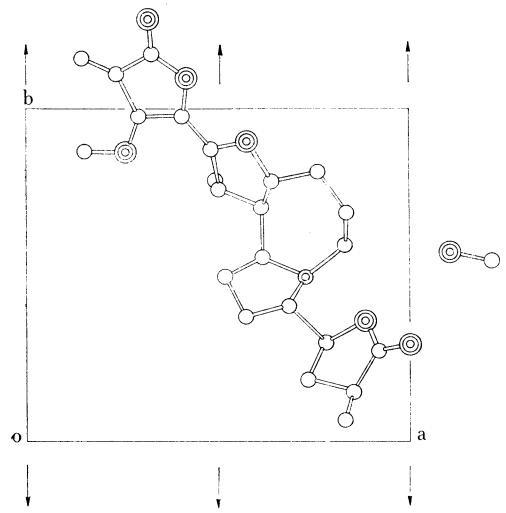


Fig. 1. The Molecule viewed in Projection along the c-axis

◉: O ◎: N ○: C

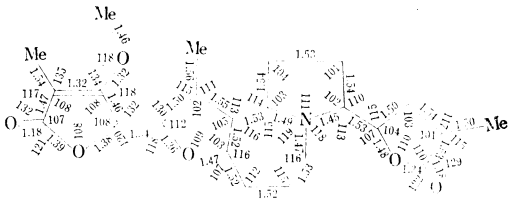


Fig. 2. Bond Lengths and Angles in the Molecule of Protostemonine

Estimated standard deviations are 0.01Å and 0.6°, respectively.

ously. It may be due to the two additional annelations including an ether linkage that the chemical properties of these two alkaloids are not quite similar. Thus protostemonine gave protostemonine hydrate hydrochloride[1] on treatment with cold concentrated hydrochloric acid, while stemofoline did not give any hydrate under the same conditions, only isolable product being demethylated product, isodemethylstemofoline hydrochloride, mp 100° (decomp.), in which the configuration of the methyl group attached to the allylic position is epimerized and accordingly it did not give stemofoline on remethylation with diazomethane, but an isomer, mp 123—127° whose nuclear magnetic resonance (NMR) and mass spectra were virtually identical with those of stemofoline though the amplitude of its circular dichroism (CD) curve is smaller than that of stemofoline.

Furthermore it is noteworthy that the difference of substle environmental factors around the conjugated system affected the UV absorption maxima of the alkaloids and protostemonine showed λ_{max}^{EtOH} 305 nm while stemofoline exhibited λ_{max}^{EtOH} 296 nm.

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