X-Ray Crystallographic Determination of a Derivative of a New Flavin Compound, Roseoflavin

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Summary The structure of a derivative of a new flavin compound, roseoflavin, has been determined by *X*-ray crystallography; the compound was found to have an 8-dimethylamino-7-methylisoalloxazine nucleus.

ONE of us recently isolated from *Streptomyces davawensis* a new photosensitive, dark red compound, $C_{18}H_{23}N_5O_6$, m.p. 276—278°, which was found to have weak antibiotic activity.† Attempts to crystallize this compound in a good crystalline form for *X*-ray analysis were unsuccessful. We now report on the crystal structure of a degradative derivative of the compound.

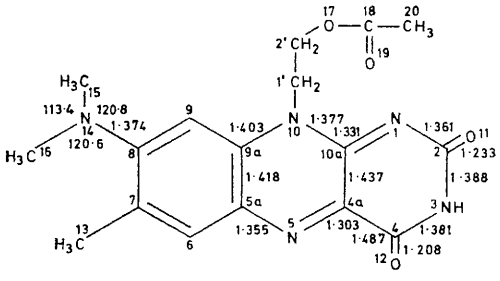
Roseoflavin was treated with sodium periodate followed by sodium borohydride reduction in aqueous solution. The reaction product was acetylated with acetic anhydride and pyridine to afford a monoacetate, $C_{17}H_{19}N_5O_4$, M_{obs} 357·1443 (high resolution mass spectrum), M_{calc} 357·1437, m.p. 243—245°, λ_{max} (MeOH) 219 nm (ϵ 15,000), 258·5 (44,700), 300sh (67,000), 496 (3900). An *X*-ray crystallographic analysis of this monoacetate was undertaken.

Crystal data: $C_{17}H_{19}N_5O_4$, $M = 357·63$, triclinic, $a = 9·080(5)$, $b = 9·212(9)$, $c = 10·556(8)$ Å, $\alpha = 110·03(8)$, $\beta = 92·11(8)$, $\gamma = 93·38(11)°$, $U = 826·6(4)$ Å^3, $D_m = 1·43$ g cm^{-3} (by flotation), $Z = 2$, $D_c = 1·436$ g cm^{-3}, $F(000) = 376$, space group $P\bar{1}$.

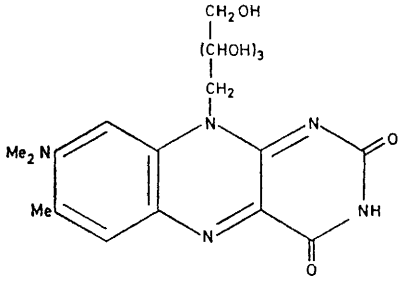
The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares procedures to $R = 0·11$ with 3215 reflections measured visually from equi-inclination Weissenberg photographs. All hydrogen atoms were located on difference Fourier maps.

† The isolation and the antibiotic activity of this compound will be reported elsewhere.

The result of the analysis indicates that this derivative is the new flavin compound (I).



(I)



(II)

Most of the angles and distances in the isoalloxazine nucleus are in fair agreement with those previously found in oxidized and neutral forms.[1] In this structure N(3)H and O(11) are hydrogen-bonded intermolecularly forming a dimer in which the two molecules are related to each other by a centre of symmetry. N(14) lies 0·19 Å above the plane defined by C(8), C(15), and C(16) and this value is small for sp^3 hybridization. The plane of the atoms N(14), C(15), and C(16) is twisted by 23·1° from the aromatic ring plane defined by C(5a), C(6), C(7), C(8), C(9) and C(9a). The length C(8)–N(14) (1·374 Å) is short for a C(sp^2)–N single bond. These facts indicate that a diffuse delocalization involves the isoalloxazine ring and the nitrogen atom of the dimethylamino-group. This is consistent with the reddish colour of the present compound or the parent compound compared with the yellowish colour of riboflavin.

Naturally occurring flavin species commonly contain two methyl groups at positions 7 and 8 of the isoalloxazine ring. Both the molecule in question and presumably roseoflavin are novel in that they carry a dimethylamino-group at position 8.

The molecular formula of roseoflavin ($C_{18}H_{23}N_5O_6$) suggests that the substituent at N(10) is a pentosyl group as represented in (II). This is also supported by the spectral properties of roseoflavin itself and its tetra-acetate, $C_{26}H_{31}N_5O_{10}$, m.p. 279—280°.

We thank Prof. F. Yamada of Kansai University for the measurement of the high resolution mass spectrum.

(*Received*, 18*th June* 1973; *Com.* 860.)

[1] B. L. Trus, J. L. Wells, R. M. Johnstone, C. J. Fritche, and R. E. Marsh, *Chem. Comm.*, 1971, 751; M. Glehn, P. Kierkegaard, and R. Norrestam, *Acta Chem. Scand.*, 1970, **24**, 1490; P. Kierkegaard, R. Norrestam, P.-E. Werner, I. Csöregh, M. von Glehn, R. Karlson, M. Leijonmarck, O. Rönnquist, B. Stensland, O. Tillberg, and L. Torbjörnsson, 'Flavins and Flavoproteins,' University Park Press, Baltimore, 1971, p. 1.