

parent that the unusual proclivity toward disproportionation in neutral aqueous solution and the decreased thermal stability of PG endoperoxides in aqueous solution vs. nonpolar solvents is characteristic of the conformationally rigid, strained, bicyclic peroxide nucleus **5** of PG endoperoxides. In fact, the rates of decomposition in aqueous solution observed for the model endoperoxide **5** and PG endoperoxides are almost identical.

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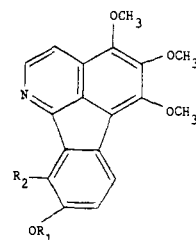
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## X-Ray Crystal Structure of Norrufescine

Sir:

We report herein the x-ray crystal structure of the azafluoranthene alkaloid norrufescine and thereby provide the first

covalent bonding parameters for the azafluoranthene nucleus. Norrufescine ( $\text{C}_{18}\text{H}_{15}\text{NO}_4$ ) occurs naturally in the stems of the Amazonian vines *Abuta imene* and *Abuta rufescens*.<sup>1</sup> Two azafluoranthene alkaloids, imeluteine (**1**) and rufescine (**2**), have been previously isolated and characterized.<sup>2</sup> Norrufescine



- 1,  $R_1 = \text{CH}_3$ ,  $R_2 = \text{OCH}_3$
- 2,  $R_1 = \text{CH}_3$ ,  $R_2 = \text{H}$
- 3,  $R_1 = \text{H}$ ,  $R_2 = \text{H}$

(**3**) differs from rufescine in that one of the four rufescine methoxy groups is replaced by a phenolic hydroxyl group. However there has been some ambiguity as to the position of this phenolic function.<sup>2</sup> This study has confirmed the predicted structure of norrufescine.

Small brown crystals of norrufescine were grown from a  $\text{CHCl}_3$ -methanol solution of this compound. The density of the crystals was not measured because only a very small amount of norrufescine was available. A crystal measuring  $0.08 \times 0.11 \times 0.13$  mm was used for x-ray measurements. Precession photographs revealed a monoclinic lattice. Systematic absences of  $hkl$  reflections for  $h + k$  odd and of  $h0l$  reflections for  $l$  odd indicated the space group to be either  $Cc$  or  $C2/c$ . The calculated density of norrufescine assuming the space group to be  $C2/c$  is in good agreement with known densities of alkaloids with similar composition. This assumption of space group was subsequently confirmed by the successful refinement of the structure.

X-ray diffraction data were measured on a Picker FACS-I diffractometer equipped with a graphite monochromator and employing  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.7093$  Å). The unit cell parameters, which were determined by the least-squares fit of the angular positions of 12 reflections, are  $a = 27.18$  (8),  $b = 8.57$  (2),  $c = 16.07$  (4) Å;  $\beta = 127.8$  (1)°. The x-ray reflections were measured to the limit  $2\theta = 50^\circ$  using the  $\theta$ - $2\theta$  scan mode with a scan rate of  $1^\circ \text{ min}^{-1}$ . The three reflections that were monitored after every 50 intensity measurements showed no significant decay during the data collection process.

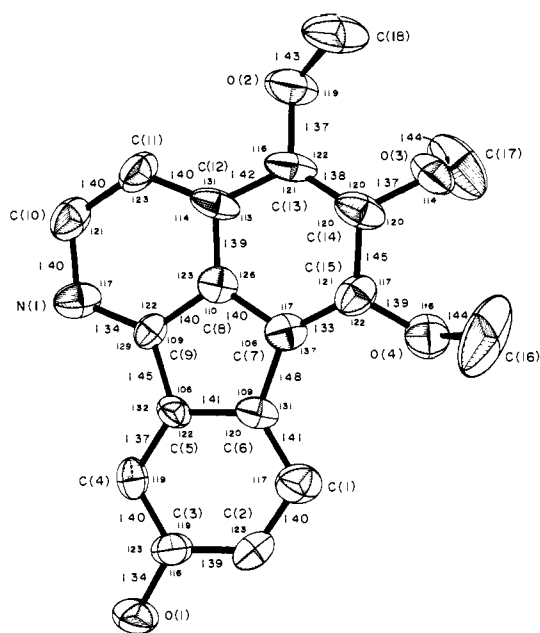
The measured intensities,  $I$ , were corrected for Lorentz and polarization effects. Standard deviations,  $\sigma(I)$ , were calculated according to Stout and Jensen<sup>3</sup> assuming an instrumental instability factor of 0.05. Of the 2355 measured unique reflections 1166 had  $I < 2.33 \sigma(I)$  and were therefore considered to be unobserved.

The structure of norrufescine was uneventfully solved by direct methods using the program MULTAN.<sup>4</sup> The structure was refined by least-squares procedures in which the quantity minimized was  $\sum w(|F_o| - |F_c|)^2$  where  $w = I/\sigma^2(I) = 1/\sigma^2(F_o)$ . The atomic scattering factors used were those of Cromer and Waber<sup>5</sup> for non-H atoms and those of Stewart, Davidson, and Simpson<sup>6</sup> for H atoms. The least-squares refinement, in which the thermal parameters of the non-H atoms were varied isotropically, converged at  $R = 0.156$ . This was followed by a refinement in which the thermal parameters were varied anisotropically. A difference Fourier map at this stage revealed the positions of the hydroxyl hydrogen and four of the five ring hydrogens. The methyl hydrogens could not be located. A final refinement in which non-H atoms were varied anisotropically and H atoms were varied isotropically con-

**Table I.** Positional Parameters of Norrufescine Non-H Atoms ( $\times 10^4$ )<sup>a</sup>

|       | x        | y          | z         |
|-------|----------|------------|-----------|
| C(1)  | 3971 (6) | 5938 (12)  | 2172 (8)  |
| C(2)  | 3757 (6) | 6939 (13)  | 2578 (9)  |
| C(3)  | 3298 (5) | 6518 (11)  | 2669 (8)  |
| C(4)  | 3037 (5) | 5026 (12)  | 2355 (8)  |
| C(5)  | 3232 (5) | 4021 (10)  | 1943 (7)  |
| C(6)  | 3695 (5) | 4455 (10)  | 1843 (7)  |
| C(7)  | 3805 (5) | 3142 (11)  | 1378 (7)  |
| C(8)  | 3391 (5) | 1965 (10)  | 1197 (7)  |
| C(9)  | 3045 (5) | 2456 (10)  | 1528 (6)  |
| C(10) | 2500 (5) | 90 (12)    | 949 (7)   |
| C(11) | 2854 (6) | -407 (12)  | 633 (8)   |
| C(12) | 3323 (5) | 507 (11)   | 761 (7)   |
| C(13) | 3727 (6) | 225 (11)   | 494 (7)   |
| C(14) | 4151 (6) | 1332 (12)  | 678 (7)   |
| C(15) | 4160 (5) | 2851 (11)  | 1083 (7)  |
| C(16) | 4535 (8) | 4613 (19)  | 404 (11)  |
| C(17) | 5138 (7) | 368 (20)   | 1317 (10) |
| C(18) | 3617 (7) | -1404 (12) | -839 (8)  |
| N(1)  | 2598 (4) | 1565 (8)   | 1402 (6)  |
| O(1)  | 3135 (4) | 7558 (8)   | 3087 (6)  |
| O(2)  | 3706 (4) | -1244 (7)  | 131 (6)   |
| O(3)  | 4551 (4) | 1016 (8)   | 453 (5)   |
| O(4)  | 4610 (4) | 3895 (9)   | 1283 (5)  |

<sup>a</sup> The positional parameters are expressed as fractions of a unit cell edge. Standard deviations as determined from the variance-covariance matrix of the final cycle of least-squares refinement are given in parentheses and refer to the least significant digits of their corresponding parameters.



**Figure 1.** An ORTEP drawing illustrating the molecular structure of norrufescine together with the bond distances (Å) and bond angles (degrees) found in the crystal structure. The average standard deviations of these quantities are 0.01 Å and 0.9°, respectively. Hydrogen atoms have been omitted from the drawing.

verged at a final value of  $R = 0.109$  based on the 1175 observed unique reflections. The position of the highest peak in the final difference Fourier map, which had a height of  $0.49 e/\text{Å}^3$ , made no chemical sense.

Table I lists the final positional parameters of the non-H atoms. The molecular configuration of norrufescine in the crystal structure is illustrated in Figure 1 together with the atomic numbering scheme used in this report and the covalent bond angles and distances involving non-H atoms found in the structure.

It can be seen in Figure 1 that the phenolic hydroxyl group is substituent to atom C(3). The bond lengths and angles in norrufescine are identical to within experimental error with the corresponding quantities in fluoranthene.<sup>7</sup> There are no unusual bond lengths in the structure. However some angle strain is apparent, especially in the isoquinoline portion of the molecule. Similar angle strain in naphthalene groups attached to five-membered rings has been observed in the crystal structures of acenaphthalene,<sup>8</sup> the cis dimer of acenaphthalene<sup>9</sup> and fluoranthene.<sup>7</sup> Norrufescine, like fluoranthene, is a highly planar molecule. The root-mean-square deviation of the 16 ring atoms of norrufescine from their least-squares plane is 0.03 Å.

An intermolecular O—H...N hydrogen bond of length 2.71 Å is formed between the hydroxyl group and the nitrogen atom of a molecule related to that tabulated in Table I by a twofold rotation axis. There are no other intermolecular contacts in the structure that are less than their minimal van der Waals contact distances.

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**Supplementary Material Available:** Listings for norrufescine of the anisotropic thermal parameters for non-H atoms and the positional and thermal parameters for H atoms (2 pages). Ordering information is given on any current masthead.

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## Megalomicins. 6.<sup>1</sup> Tertiary Glycosidic Macrolide Antibiotics. A Structural Revision by Carbon-13 Nuclear Magnetic Resonance and X-Ray Crystallography

Sir:

Independent studies on the megalomicins<sup>1-3</sup> and on the XK-41 complex<sup>4</sup> have led to the assignment of structures for megalomicin A (XK-41-C) (1), megalomicin B (XK-41-B<sub>1</sub>) (2), megalomicin C<sub>1</sub> (XK-41-A<sub>2</sub>) (3), megalomicin C<sub>2</sub> (XK-41-A<sub>1</sub>) (4), and XK-41-B<sub>2</sub> (5). The novel amino sugar present in these antibiotics was thought to be D-rhodamine.<sup>5,6</sup> Subsequently the <sup>13</sup>C NMR data for megalomicin A (1) were published<sup>7</sup> and several anomalies, namely the chemical shifts of C<sub>12</sub> ( $\delta_c$  80.8) and C<sub>1''</sub> ( $\delta_c$  90.8),<sup>8</sup> as well as C<sub>2'''</sub> ( $\delta_c$  37.6), C<sub>5'''</sub> ( $\delta_c$  67.7), C<sub>3'''</sub> CH<sub>3</sub> ( $\delta_c$  19.2),<sup>9</sup> C<sub>3'''</sub> ( $\delta_c$  66.0), and C<sub>5'''</sub> ( $\delta_c$  59.9) were apparent to us.