orbitals. Either framework is, of course, sufficient, the point being to obtain the simplest heuristic model.
(6) If all the occupied localized orbitals were included, $P_{S_C S_N}$ would be invariant under the localizing unitary transformation.
(7) For reference, the squared INDO density matrix elements ($\times 10^4$) obtained from all the occupied orbitals, localized or delocalized, are for couplings (1)–(11): 395, 473, 542, 725, 726, 705, 795, 710, 1191, 2079, and 829, respectively.
(8) The small positive deviation for methylamine is large relative to its $^1J^{FC}$ (as is the case with pyridine and benzonitrile). On the other hand, for benzonitrile oxide the positive relative deviation is small and probably arises merely as a consequence of the least-squares fitting procedure, which requires both positive and negative deviations.
(9) For methyl isocyanide the corresponding expression would be (% S_N)(% $S_{\text{lone pair on carbon}}$).
(10) A similar observation was made in ref 4.
(11) For the above reasons we prefer this interpretation to the more general statement of a failure of the average energy approximation. The latter may, however, be appropriate to one exception we have found to eq 1 and Figure 1. The molecule ^{15}N-methylphenylpropynylamine has recently been reported to have a $^{15}N-^{13}C\equiv C-$ $|^1J_{CN}|$ of 36.2 Hz (T. Bottin-Strzalko, M. J. Pouet, and M. P. Simonnin, *Org. Magn. Reson.*, **8**, 120 (1976)). For the model system, planar $H_2N-C\equiv CH$ we obtain $J^{FC} = -29.5$, $J^{P} = 0.3$, and $J^{SD} = -0.03$ Hz, in reasonable agreement with experiment with only the contact term of consequence. The corresponding (% S_C)(% S_N) = 1650 places this $^1J_{CN}$ somewhat above the line in Figure 1. As with other systems, when the nitrogen is pyramidalized the positive lone-pair effect causes $^1J_{CN}$ to fall below the line.

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Received June 14, 1976

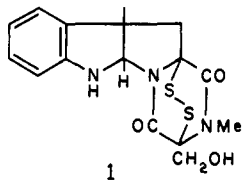
The Structure of Chetomin

Sir:

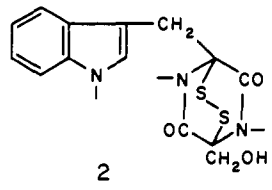
Chetomin, an antibiotic discovered more than 30 years ago,[1] is thought to be associated with poor growth in young ruminants.[2] Chemical degradation and spectroscopic studies,[3] suggested that the fragments **1** and **2** were present, linked by a bond between the quaternary β-indoline carbon of **1** and one of the three nitrogen atoms of **2.** The other nitrogen atoms of **2** bore methyl substituents. Evidence for the orientation of the substituents on the nitrogen atoms of **2** has now been obtained with the aid of ^{15}N labeling, and ^{15}N and ^{13}C NMR spectroscopy.

Chaetomium cocliodes (HLX 833)[3] was grown in shake flasks for 14 days at 25 °C on a medium containing (g/l.) glucose, 30; calcium carbonate, 3; potassium chloride, 0.5; magnesium sulfate, 0.5; dipotassium hydrogen phosphate, 1; trace metals;[4] and sodium nitrate, 2.44 (in the labeling experiments $Na^{15}NO_3$, 99 atom % was used). Chetomin ($[\alpha]^{20}D$ +257° (*c*, 0.1, $CHCl_3$), ϵ_{285nm} (MeOH) 11 800, 4 mg/l.) was isolated from extracts of the mycelium by partition chromatography.[3]

The broad band ^1H-decoupled ^{15}N NMR spectrum of ^{15}N enriched chetomin consisted of six resonances (δ_N 123.0, 117.4, 95.3, 91.1, 90.3, 51.0, referred externally to 4 M NH_4Cl in 2 N HCl). ^{13}C NMR spectra with ^1H broad band decoupling were recorded with concomitant single frequency irradiation ($\gamma H_2/2\pi$ 15–65 Hz) of each ^{15}N resonance. The ^{15}N resonance at δ_N 117.4 could be assigned to the indole nitrogen of **2,** for it was coupled ($^1J_{CN}$ = 13.8 Hz) to the carbon atom bearing a hydrogen substituent (δ_C 127.3, $^1J_{CH}$ = 186 ± 2 Hz)[3,5] in the five-membered indole ring. This nitrogen atom was also coupled to a quaternary aromatic carbon (δ_C 134.1, $^1J_{CN}$ = 14.5 Hz) and to the β-quaternary carbon atom of the five-membered ring of the indoline nucleus of **1** (δ_C 73.8, $^1J_{CN}$ = 11.9 Hz). This β-indoline quaternary carbon was long-range coupled to the pyrroline (δ_N 123.0, $^2J_{CN}$ = 3.7 ± 0.6 Hz) and



1



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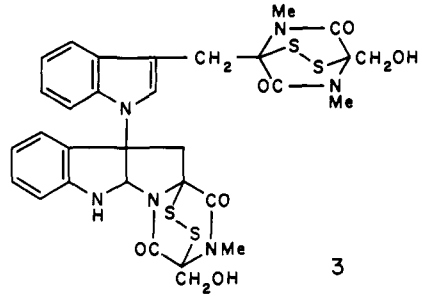

3

indoline (δ_N 51.0, $^1J_{NH}$ = 87.7 Hz, $^2J_{CN} \sim 1$ Hz) nitrogen atoms of the eserine system. The orientation **3** may therefore be assigned to chetomin, and this conclusion was confirmed by the following facts. The indoline nitrogen (δ_N 51.0) was coupled ($^1J_{CN}$ = 8.1 Hz) to a methine carbon (δ_C 80.2, $^1J_{CH}$ = 174 ± 1 Hz) which was also coupled ($^1J_{CN}$ = 5 ± 1 Hz) to the pyrroline nitrogen (δ_N 123.0). This pyrroline nitrogen atom was further coupled to a carbonyl carbon (δ_C 163.1, $^1J_{CN}$ = 14.6 Hz) and to two quaternary carbon atoms each bearing a sulfur substituent (δ_C 76.3, $^2J_{CN}$ = 6.2 Hz; δ_C 73.6, $^1J_{CN}$ = 5.0 Hz). The remaining three nitrogen atoms (δ_N 90.3, 91.1, 95.3) were coupled ($^1J_{CN}$ = 9.3 Hz) to methyl carbons (δ_C 27.5, 27.5, 28.3) and to ($^1J_{CN}$ = 13.7 Hz) carbonyl carbons (δ_C 165.6, 165.6, 166.8) and were therefore parts of amide systems as required by structure **3.** Other $^{15}N-^{13}C$ and $^{13}C-^1H$ couplings, not mentioned, were fully consistent with this structure.

This structural conclusion is of biosynthetic interest. In the ring closure reaction giving eserine metabolites a second tryptophan residue may be substituted at the β-position of its indole ring as in the chaetocin and verticillin groups[6] or at the ring nitrogen as in chetomin. A second ring closure does not occur in the latter case, thus providing an example in the same molecule of the two types of metabolite (gliotoxin[7] and hyalodendrin[8]) found in the phenylalanine series.

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Received June 1, 1976