

STRUCTURE OF VERMICULINE, A NEW NINE-MEMBERED LACTONE
FROM PENICILLIUM VERMICULATUM

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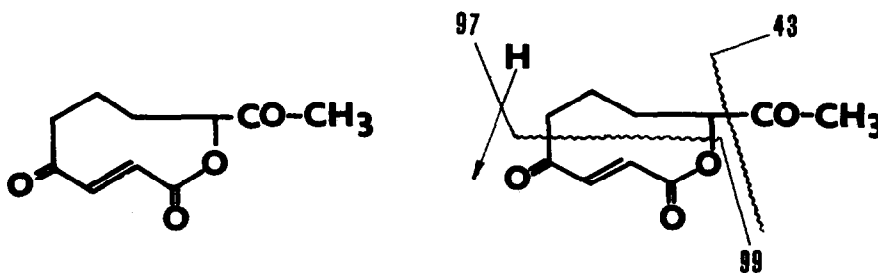
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To elucidate the structure of vermiculine (I), a recently described antibiotic¹, we measured its PMR and mass spectra. PMR⁺ (δ): 1.65 mt (2H), 2.16 s (3H, CH₃CO-), 2.30 - 3.02 mt (3H), 2.19 mt (1H), 5.41 mt (1H), 6.42 and 6.98 AB (J = 16.4 Hz, two trans-olefinic protons). Mass spectrum⁺⁺ (m/e): 197 (26%, C₁₀H₁₃O₄, M+1), 99 (30%, C₄H₅O₃), 97 (48%, C₆H₉O), 43 (100%, C₂H₃O). Hydrogenation on Pd/CaCO₃ affords the dihydroderivative (II) - PMR (δ): 1.95 mt (2H), 2.15 s (3H, CH₃CO-), 2.40 - 2.95 mt (8H), 5.19 mt (1H); MS (m/e): 199 (1.1%, C₁₀H₁₅O₄, M+1), 101 (30%, C₄H₅O₃), 97 (59%, C₆H₉O), 43 (100%, C₂H₃O).

None of the twelve vermiculine protons are exchangeable and its IR spectrum¹ does not contain any frequencies due to the OH or COOH groups. However, the strong $\nu_{C=O}$ bands indicate the presence of some C=O or COO groups. The AB pattern of the olefinic protons in the PMR spectrum of I requires the presence of two quarternary carbon atoms in both α -positions of the double bond. The ions m/e 99 and 101 in the mass spectra of I and II evidently involve the double bond. The comparison of their elemental composition leads to a conclusion that one COO and one C=O group are attached

to it. Consequently, the remaining oxygen atom is located in the CH_2CO -group. The signal of a single proton which appears at 5.41 and 5.19 ppm in the PMR spectra of I and II, respectively, can be assigned to a proton of the CHOCO type. To explain its multiplicity, at least one vicinal CH_2 group must be considered. Taking the formation of the $\text{C}_6\text{H}_9\text{O}$ ion into account, the alternative partial structures $-\text{COCH}=\text{CHCOOCH}-\text{CH}_2\text{CH}_2\text{CH}_2\text{COCH}_3$ and $-\text{COCH}=\text{CHCOOCH}(\text{COCH}_3)\text{CH}_2\text{CH}_2\text{CH}_2$ can be written. The molecular formula and the formation of a dihydroderivative indicate the presence of a ring in the molecule. Since this ring must contain a trans-double bond, the former structure should be rejected and the structure of vermiculine formulated as I. Its fragmentation pattern can be rationalized according to the scheme 1.



I

Scheme 1

- 1) J.Fuska, P.Nemec, I.Kuhr, J.Antibiotics 4, 208 (1972).
- +) Varian HA-100, 100 MHz, CDCl_3 , TMS as an internal standard.
- ++) Varian MAT-311, 70 eV, ion source 200°C , direct inlet at 130°C . High resolution mass determination was performed using the peak-matching procedure and PFK standard (accuracy 2 ppm).