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Structure of Xanthocidin

Sir:

We wish to propose the structure (I), 4,5-dihydroxy-5-isopropyl-4-methyl-2-methylene-3-oxocyclopentanecarboxylic acid, for xanthocidin, the antibiotic isolated in our laboratory.

Xanthocidin (I), $C_{11}H_{16}O_5$, ¹⁾ mp 185°C (dec.), $[\alpha]_D^{25} + 16.7$, is an acidic compound ($pK'a$, 3.8) and soluble in lower alcohols, esters and ketones. It is, however, slightly soluble in chloroform and water, and insoluble in benzene. Xanthocidin (I) shows λ_{max}^{MOH} 227 m μ (ϵ , 6420; cyclopentanone conjugated with exocyclic methylene)^{2a)} and infrared peaks (nujol) at 3480 (OH), 1733 (conjugated cyclopentanone), 1714 (COOH, it shifts to 1580 cm^{-1} by the formation of Rb salt), 1635 cm^{-1} (double bond).

The NMR spectrum of xanthocidin (I) is most informative, as represented in Fig. 1. The equivalent two-methyl protons of isopropyl group³¹ appear as a doublet ($J=6.9$ Hz) at δ 1.15, which is collapsed to a singlet by the irradiation of isopropyl-methine proton multiplet centered at δ 2.43. The irradiation of isopropyl-methyl protons collapses the methine proton multiplet to a singlet. In addition, the long-range couplings between H(1) and H(2a) ($J=2.1$ Hz) and between H(1) and H(2b) ($J=1.8$ Hz) have been confirmed by decoupling experiments.

I on hydrogenation with Pd/C consumed one mole-equivalent of hydrogen to give colorless crystalline dihydroxanthocidin (II),* $C_{11}H_{18}O_5$ (*Anal.* Found: C, 57.44; H, 7.62).

FIG. 1. NMR Spectrum of Xanthocidin ((CD₃)₂CO).

- 1) K. Asahi, J. Nagatsu and S. Suzuki, *J. Antibiotics*, **A19**, 195 (1966).
- 2) (a) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, London, 1964, p. 67. (b) *ibid.*, pp. 29 and 33.
- 3) The facile loss of 61 mass units from the mole-

cular ion ($M-H_2O-C_3H_7$) also indicates the presence of an isopropyl substituent.

* NMR data show that II is an almost equimolar crystal mixture of diastereomers due to α - and β -methyl group formed by the reduction.

SCHEME I.

The structure of II is supported by the facts: (a) The UV spectrum is similar to that of unconjugated cyclopentanone^{2b)} [$\lambda_{\max}^{\text{MeOH}}$ 295 $m\mu$ (ϵ , 36)]. (b) In the IR spectrum, $\nu_{\text{C}=\text{C}}$ 1635 cm^{-1} disappears and shift of $\nu_{\text{C}=\text{O}}$ is observed (to 1760 cm^{-1}). (c) The NMR spectrum shows that II has no olefinic proton and C-CH₃ was formed (centered at δ 1.05).

According to NMR data, the carbon atom which has methyl or isopropyl group contains no proton. Therefore methyl (isopropyl) group must attach to C₄(C₅) or C₅(C₄). If methyl (isopropyl) attaches to C₄, oxidation

of I or reduced trioxyderivative (III) with NaIO₄ would give acetic acid (isobutyric acid). I was reduced by NaBH₄ in ethanol to afford colorless needles (III), C₁₁H₁₈O₅, mp 184°C. (Anal. Found: C, 57.04; H, 8.17. The UV absorption of conjugated cyclopentanone and $\nu_{\text{C}=\text{O}}$ 1733 cm^{-1} in the IR spectrum disappeared). III was oxidized with NaIO₄ to give acetic acid (0.7 mole per mole of I). Prolonged treatment of I with NaIO₄ (4 days) also gave acetic acid (0.8 mole-equivalent) (Scheme I). *p*-Bromophenacyl ester of acetic acid was identified by comparison of its mass spectrum, TLC, and retention times on two different columns (VPC) with those of an authentic sample.

These results are consistent with the structure I of xanthocidin.

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