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THE STRUCTURE OF OCHROMYCINONE

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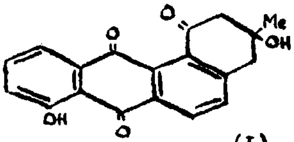
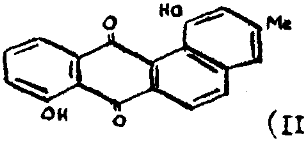
The recent report (1) of the structures of tetrangulol (I) and tetrangomycin (II) prompts us to present a preliminary account of the structure of ochromycinone, which has been isolated together with a series of rhodomycinones and pyrromycinones (2) from several Streptomyces strains (3).



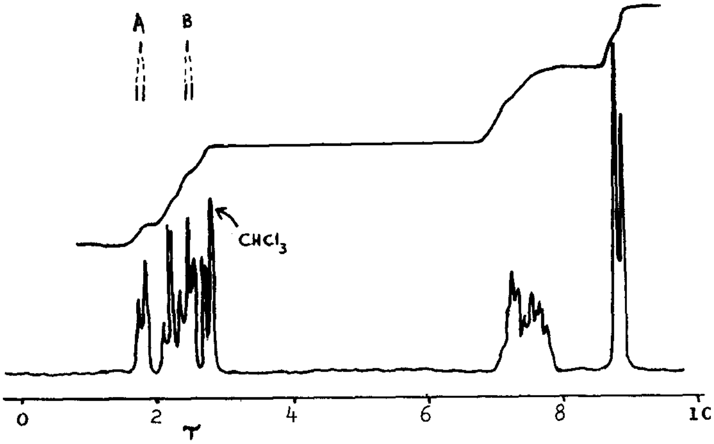
(I)



(II)

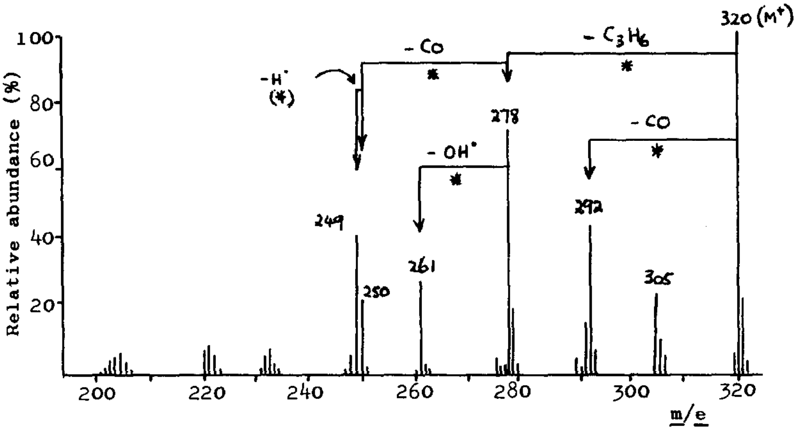
Ochromycinone, $C_{19}H_{14}O_4$, $[\alpha]_D^{25^\circ}$ 204.5° ($CHCl_3$), contains no methoxyl, ester, or non-bonded hydroxyl groups, and is stable both to acid and alkali. The ultraviolet spectrum ($\lambda_{max.}$ 265, 405 mμ; log ε 4.42, 3.55) is characteristic of a 1-hydroxyanthraquinone (4) containing an additional auxochromic substituent. Infrared carbonyl absorptions (1703, 1668, and 1638 cm.$^{-1}$) confirm both the presence of the 1-hydroxyanthraquinone moiety (5) and an additional conjugated carbonyl group. Aldehydic CH absorptions are absent in the infrared spectrum, and as ochromycinone forms a 2,4-dinitrophenylhydrazone under forcing conditions, the presence of a ketonic substituent on the anthraquinone is likely.

FIG. 1



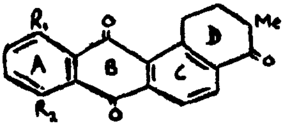
N.M.R. Spectrum (100 Mc.) of Ochromycinone in $CDCl_3$

FIG. 2



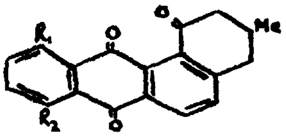
Mass Spectrum of Ochromycinone methyl ether

Ochromycinone forms a monomethyl ether and a monoacetate. The ultraviolet spectra of these derivatives lend additional support to the presence of the keto-1-hydroxyanthraquinone chromophore. The methyl ether exhibits infrared carbonyl absorptions at 1702 and 1678 cm.$^{-1}$, indicating that the phenolic group in ochromycinone is not adjacent to the α-keto group. The absence of strong absorption at 715 cm.$^{-1}$ in the infrared spectra of ochromycinone and its derivatives shows that both the terminal rings of the anthraquinone are substituted (5). Modified Kuhn-Roth oxidation of ochromycinone produces only acetic acid. Zinc dust distillation of ochromycinone yields 3-methylbenz[a]anthracene (identified by its absorption spectrum and R_F values in several solvents) (6). Assuming that methyl migration has not occurred during the zinc dust distillation, four structures (III - VI) can be written for ochromycinone.



(III) R_1 = OH, R_2 = H

(IV) R_1 = H, R_2 = OH



(V) R_1 = OH, R_2 = H

(VI) R_1 = H, R_2 = OH

The nuclear magnetic resonance spectra of ochromycinone (Figure 1) and of its derivatives shows a constant <u>ortho</u> AB splitting pattern (J_{AB} = 9.0 c.p.s.) due to the two protons of ring C, an unsymmetrical doublet due to the methyl protons, and a complex pattern due to the remaining protons of ring D.

The mass spectra of ochromycinone and its derivatives (see Figure 2 for the mass spectrum of ochromycinone methyl ether) are also informative structurally. These may be interpreted using a knowledge of the fragmentation modes of α-tetralones (7), as the fragmentation is only slightly complicated bv the anthraquinone moiety (8). An asterisk in Figure 2 represents the presence of an appropriate metastable peak for the process indicated and exact mass measurements establish the compositions of the major ions in the spectrum. The process $M^+ - C_3H_6 - CO - H^\bullet$ is changed to $M^+ - C_3H_4D_2 - CO - H^\bullet$ when the protons α- to the carbonyl group of ring D are exchanged with deuterium (MeOD/MeONa), thus establishing structure (V) or (VI) for ochromycinone. We prefer structure (VI) on biogenetic grounds, but hope to make the decision by syntheses of (V) and (VI) which are in progress.

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