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THE STRUCTURE OF AUREO-ALCOHOL, A NOVEL DEGRADATION PRODUCT OF AUREOTHIN

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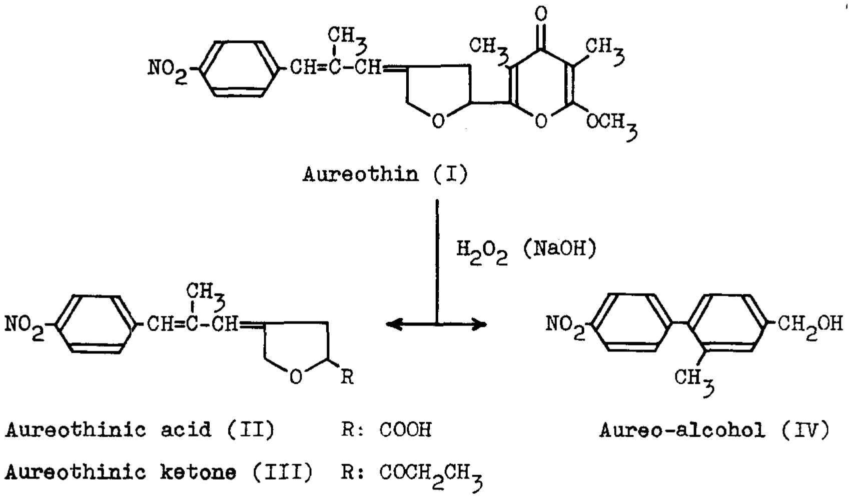
During the course of the structure elucidation studies of aureothin (I)(1), we have carried out the alkaline hydrogen peroxide oxidation reaction, and obtained aureothinic acid (II) and aureothinic ketone (III) as two major oxidation products (2). A careful fractionation of the residual reaction mixture further afforded a small amount of a new degradation product, aureo-alcohol (IV), the properties of which are very peculiar and in marked contrast to those of II or III. The present paper describes the structural assignment of this compound mainly from spectroscopic evidences.

Aureo-alcohol (IV), m.p. 108 - 109°, is an optically inactive, neutral substance and is relatively stable to acids and bases. Its molecular formula, $C_{14}H_{13}O_3N$ (Found: C, 69.21; H, 5.49; N, 5.89 %. Calcd. C, 69.12; H, 5.39; N, 5.76 %), was confirmed by the mass spectrometric measurement (Mol. Wt. 243). The infrared spectrum shows no carbonyl absorption around 1700 cm^{-1}, but three strong peaks at 1598, 1513, and 1344 cm^{-1} are indicative of an aromatic nitro group. A broad hydroxyl absorption at 3320 cm^{-1} is



Aureothin (I)

Aureothinic acid (II) R: COOH

Aureothinic ketone (III) R: $COCH_2CH_3$

Aureo-alcohol (IV)

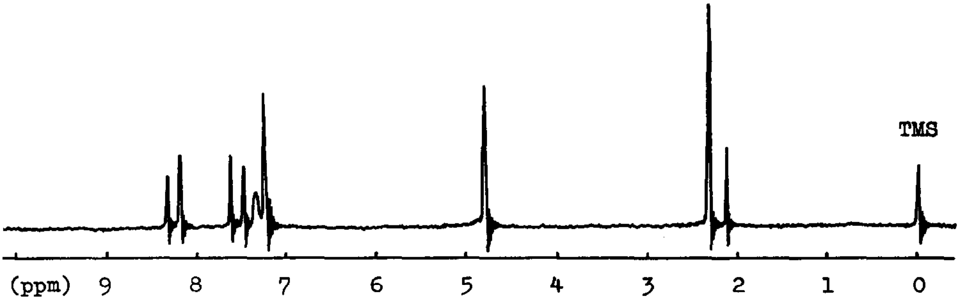
also observed. On treatment with acetic anhydride and pyridine, it gives a mono-acetate (V), m.p. 87 - 88°, $C_{16}H_{15}O_4N$ (Found: C, 67.34; H, 5.20; N, 4.78 %. Calcd. C, 67.36; H, 5.30; N, 4.91 %), the acetate band being at 1732 cm^{-1}.

The ultraviolet spectra of aureo-alcohol (IV) and its mono-acetate (V) are entirely different from those of other major oxidation products, II and III, as shown in Table I. This suggests that IV has a particular chromophoric system not encountered so far in our structural studies of aureothin.

TABLE I. Ultraviolet Absorption Spectra: λ_{max}^{EtOH} mμ (log ε)

Aureothinic acid (II)	249 (4.14), 345 (4.20)
Aureothinic ketone (III)	248 (4.20), 342 (4.28)
Aureo-alcohol (IV)	300 (4.07)
Aureo-alcohol mono-acetate (V)	295 (4.07)

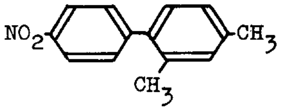
Fig. 1. The NMR Spectrum of Aureo-alcohol (IV) in $CDCl_3$



The proton NMR spectrum of IV (Fig. 1) is quite revealing, and we now assign the structure of this new degradation product as 2-methyl-4-hydroxymethyl-4'-nitro-biphenyl (IV).

A sharp singlet at 2.12 ppm (1H) is a hydroxyl signal, which disappears on deuteriation. A singlet at 2.32 ppm (3H) corresponds to a methyl group on the benzene nucleus, and a singlet at 4.80 ppm (2H) is assigned as benzylic hydrogen atoms of the type Ar-CH_2-O- (3). Two doublets (7.48, 7.62, 8.28, and 8.43 ppm)(4H) are the characteristic pattern of a p-substituted nitro phenyl group, while a singlet at 7.33 ppm (2H) and a broad singlet at 7.40 ppm (1H) originate from aromatic hydrogen atoms of the another benzene ring (4).

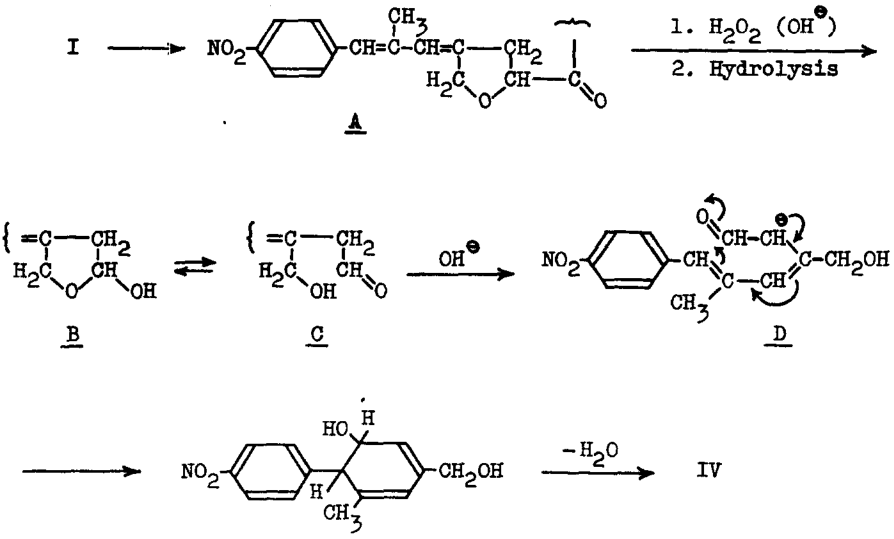
This structural assignment is also supported by the fact that the ultraviolet absorption of IV (Table I) agrees well with that of a synthesized model compound VI (5).



VI

Finally, the formation of this novel carbon skeleton from aureothin (I) would require explanation. Oxidative hydrolysis of the pyrone ring in I with alkaline hydrogen peroxide may give rise to a keto intermediate A, which then affords a cyclic acetal B through a Baeyer-Villiger type reaction (6) and a subsequent hydrolysis. The acetal B would exist as its open-chain tautomer C, and the conjugated carbanion D from the latter may give aureo-alcohol (IV) by an intramolecular aldole condensation.

The synthetic work of this compound is under progress and the result will be reported soon.



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