

ULTRAVIOLET ABSORPTION SPECTRUM OF LACTONE-CONJUGATED POLYENE ANTIBIOTICS

Sir:

The "lactone-conjugated" subgroups of polyene macrolide antibiotics dissolved in protic solvents show "anomalous" UV absorption spectra:^{1,2,3,4} they exhibit two broad maxima instead of the sharp series of absorptions characteristic of polyenes.⁵ The visualization of this series of absorptions of this chromophore type, which is a conjugated system of a C=O and several (five or six) C=C double bonds, could be accomplished by low temperature (-185 or -173°C) UV measurements.^{4,6} The C=C double bond chain could be demonstrated by the UV spectrum of the LiAlH_4 reduction product of the antibiotic.^{3,6} In this case, however, it is a substantially different degradation product and not the original macrolide investigated. A further disadvantage of this method is that the α, β C=C double bond may also be attacked during the LiAlH_4 reduction which complicates the UV spectrum.

In the present study it was found that the peracetyl derivatives of flavofungin and flavomycoin, two representatives of the "lactone-conjugated" pentaenes, in cyclohexane solution exhibit UV spectra characteristic of the "classical" hexaenes⁵ (Fig. 1.).

This observation suggests that in the UV spectrum of "lactone-conjugated" polyenes dissolved in polar (both protic and aprotic) solvents the appearance of the fine structure is prohibited by intermolecular interaction between the solvent and the carbonyl group

site of solute. By minimizing this interaction the fine structure characteristic of "classical" polyenes appears. The broadening of the individual bands reflects some straining of the conjugated all-trans system.

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V. POZSGAY

BIOGAL Pharmaceutical Works,
4042-Debrecen, Hungary

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Fig. 1. UV spectrum of peracetyl flavofungin at $+25^{\circ}\text{C}$.

Peracetyl flavomycoin exhibited similar spectrum with somewhat smaller molecular extinction values.

