activation reaches a maximum along the diagonals of the diamond.

It was further noted that all nuclei were circular in crystals which had been formed or dehydrated rapidly. This means that, apart from the re-assessment of the free energy of activation for slow growth, no modifications need be applied to the earlier work on precipitated samples, for with such materials only circular nuclei are expected. A more detailed discussion of slow growth in azides will be presented elsewhere.

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[1] Thomas and Tompkins, *J. Chem. Phys.*, **20**, 662 (1952). Wischin, *Proc. Roy. Soc.*, A, **172**, 314 (1939).
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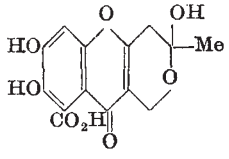
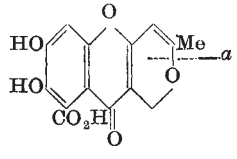
Fulvic Acid: its Structure and Relationship to Citromycetin and Fusarubin

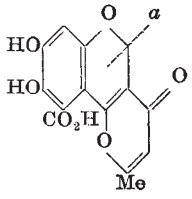
Fulvic acid, $C_{14}H_{12}O_8$, is a yellow acidic metabolite produced by several fungi including *Carpenteles brefeldianum* Dodge (Shear) and was first isolated and characterized by Oxford, Raistrick and Simonart[1]. Investigations which have been carried out in this Department and which will be published in detail elsewhere enable us to formulate fulvic acid as (I).



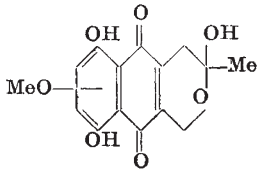
(I)



(II)



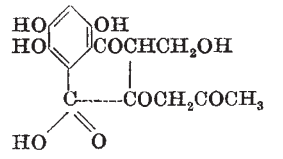
(III)



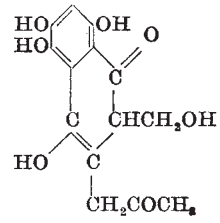
(IV)

Fulvic acid is readily dehydrated, giving anhydrofulvic acid (II), which is isomeric with citromycetin[2] (III) from *Penicillium glabrum*. Oxford *et al.* have shown that fulvic acid is a dihydric phenolic acid and noted a general resemblance to citromycetin (III), which is now clearly due to the benzenoid system. We have observed, however, that fulvic acid (I) has many reactions in common with fusarubin[3] (IV), a pigment from *Fusarium solani*, and that fulvic acid and fusarubin are in fact isomeric when allowance has been made for the presence in the latter of a methoxyl group instead of a hydroxyl group. This methoxyl group has not yet been definitely located, but the reactions we encountered (for example, the ready dehydration) are clearly due to the terminal pyran systems.

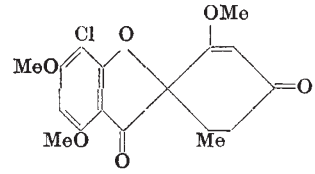
Because we were impressed by these resemblances, we analysed the structures of these metabolites into simpler patterns and found that all three could be reduced to the same fundamental structure (V), which, in this or an equivalent form, might therefore be considered a precursor of the three compounds. Structure (V) is reached from anhydrofulvic acid (II) or citromycetin (III) merely by conventional hydrolytic fissions of the pyrone rings and of the bonds marked (*a*). The connexion between (V) and fusarubin (IV) is less obvious, but consists chiefly in the linking of the carbon atoms connected by a dotted line in (V). For simplicity, one might suppose the carboxyl group in (V) to be reduced to hydroxymethyl (since there are many known sequences of natural products of which the members differ in the sense CH_3, CH_2OH, CHO, COOH), whereupon condensation of the new methylene group with the appropriate carbonyl group leads to a reduced naphthoquinone (VI) simply related to fusarubin (IV). It remains to be seen whether the methoxyl group does in fact occupy the position required by this hypothesis.



(V)



(VI)



(VII)

C. brefeldianum produces fulvic acid when grown on Raulin–Thom media. On Czapek–Dox media, however, fulvic acid is not produced, nor is citromycetin or fusarubin. Instead, the chief metabolite is now griseofulvin[4] (VII), which cannot be readily related to fulvic acid except at the lowest level of acetate hypothesis[5]. It is of interest that variations in the environment of the fungus have a more profound effect on its metabolism than have variations in the species.

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