

## Microbial Degradation of Dehydroabietic Acid†

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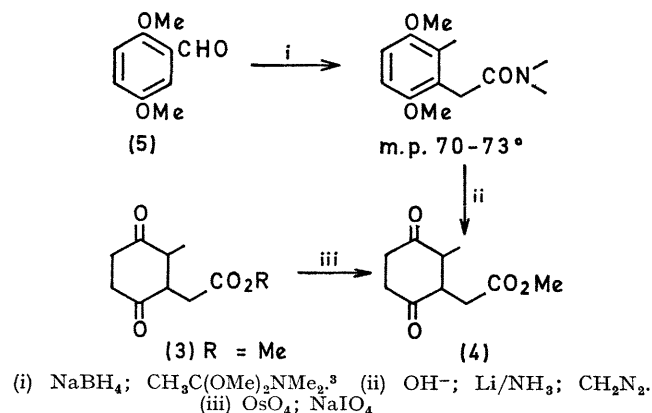
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**Summary** The structure of acyclic and monocyclic metabolites of dehydroabietic acid has been established.

We have shown<sup>1</sup> that incubation of dehydroabietic acid (1) with *Flavobacterium resinovorum* gave the ketone (2). Using the same experimental techniques as previously described,<sup>2</sup> we have isolated, as their methyl esters, new metabolites which could occur by further degradation of the ketone (2).

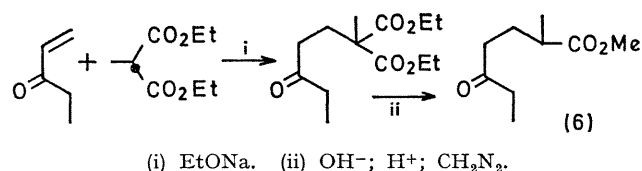
To one of the metabolites, occurring as a mixture of epimers, which we were unable to separate, we assigned structure (3; R = Me) on the basis of spectroscopic data and on the hypothesis that it derived from the ketone (2). The diketone (4), prepared by osmium tetroxide treatment of (3; R = Me) and cleavage of the diol with sodium metaperiodate was identical with a sample prepared from 2,5-dimethoxybenzaldehyde (5) by the route indicated:



† We thank Dr. Sanderson, Hercules Powder Co., Wilmington, Delaware, U.S.A., for providing us with dehydroabietonitrile.

‡ The determination of the absolute configuration of (6), (9), and (10) will be reported in the definitive paper.

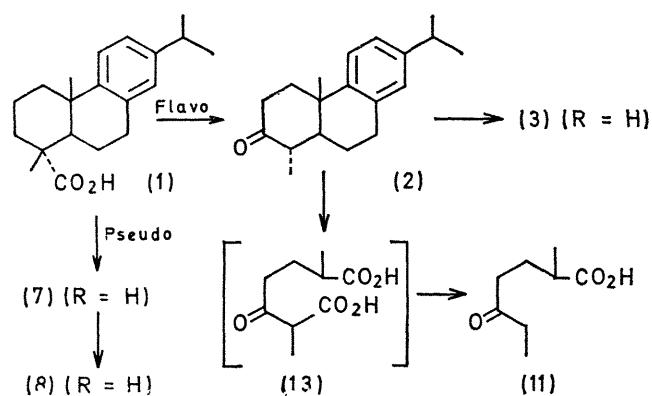
An acyclic compound was isolated and structure (6) was formulated on the basis of spectroscopic arguments. The synthesis of (6) was accomplished and the resulting product was identical with the material isolated from the culture, except that the latter was optically active‡:  $[\alpha]_D - 7.4^\circ$  (dioxan,  $c$  0.13).



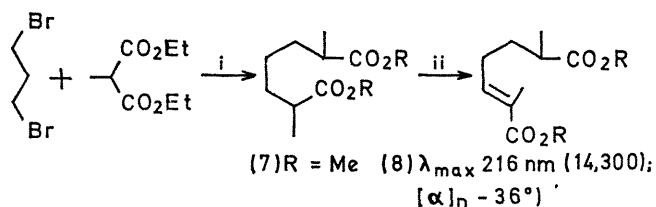
At the same time, we studied the metabolism of dehydroabietic acid (1) by *Pseudomonas resinovorans*, using similar experimental conditions. We isolated two acyclic products for which structures (7; R = Me) and (8; R = Me) seemed reasonable. We correlated (7; R = Me) and (8; R = Me) by hydrogenation of (8; R = Me), and synthesised (7; R = Me). The stereochemistry of the double bond in (8; R = Me) was established by n.m.r.<sup>4</sup> [ $\delta_{\text{PM}}$  in (8; R = Me): 6.75 p.p.m., in methyl angelate: 5.98 p.p.m., in methyl tiglate: 6.73 p.p.m.]. We have shown by conversion into its dianilide that compound (7; R = Me) is *meso*<sup>5</sup> (m.p. 184–185°).

It is interesting to note that the *Flavobacterium resinovorum* first oxidises the carbon at C-3 before degrading the aromatic nucleus. This was not found to be so in the case of *Pseudomonas resinovorans*.

If we assume that these products arise from dehydroabietic acid (1), the following partial degradation pathways may be written:



not yet been established with certainty.



(i) NaH; OH<sup>-</sup>; H<sup>+</sup>; CH<sub>2</sub>N<sub>2</sub>. (ii) H<sub>2</sub>-Pt.

We did not find any compounds, except for the ketone (2), related to the metabolites which have been isolated by other investigators.<sup>6</sup>

Other metabolites were found, but their structures have

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<sup>4</sup> G. Kresze, "Physikalische Methoden in der Organischen Chemie, I," W. de Gruyter, Berlin, 1962, p. 91; L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 1960, 2881, 2886.

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