Microbial Degradation of Dehydroabietic Acid†

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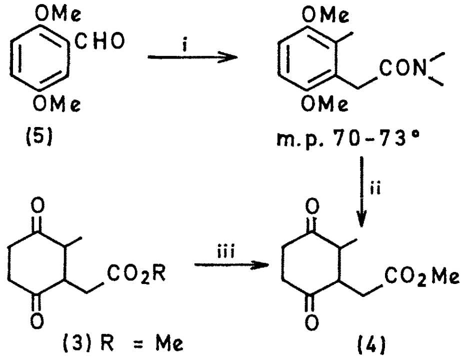
Summary The structure of acyclic and monocyclic metabolites of dehydroabietic acid has been established.

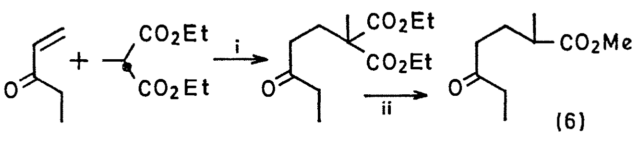
WE have shown[1] that incubation of dehydroabietic acid (**1**) with *Flavobacterium resinovorum* gave the ketone (**2**). Using the same experimental techniques as previously described,[2] we have isolated, as their methyl esters, new metabolites which could occur by further degradation of the ketone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



(*i*) $NaBH_4$; $CH_3C(OMe)_2NMe_2$.[3] (ii) OH^-; Li/NH_3; CH_2N_2. (iii) OsO_4; $NaIO_4$

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° (dioxan, *c* 0·13).



(i) EtONa. (ii) OH^-; H^+; CH_2N_2.

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.[4] [$\delta_{\beta H}$ 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*[5] (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:

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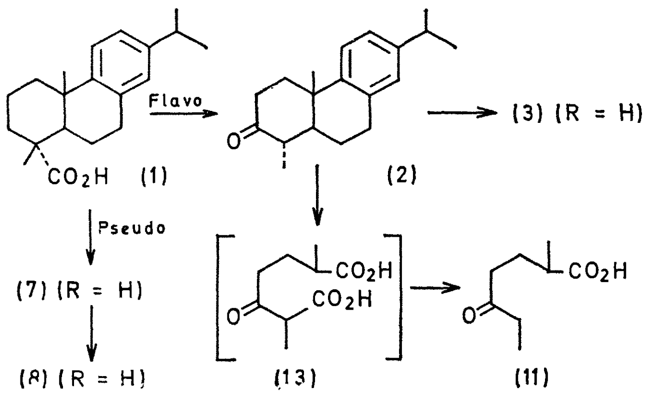
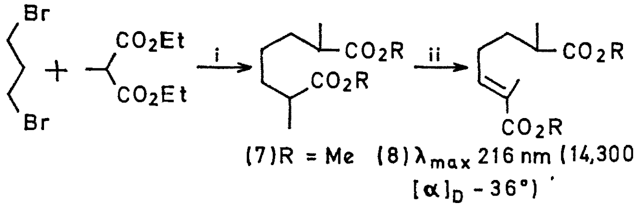
† We thank Dr. Sanderson, Hercules Powder Co., Wilmington, Delaware, U.S.A., for providing us with dehydroabietonitrile.

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



Other metabolites were found, but their structures have not yet been established with certainty.



(i) NaH; OH^-; H^+; CH_2N_2. (ii) H_2-Pt.

We did not find any compounds, except for the ketone (**2**), related to the metabolites which have been isolated by other investigators.[6]

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