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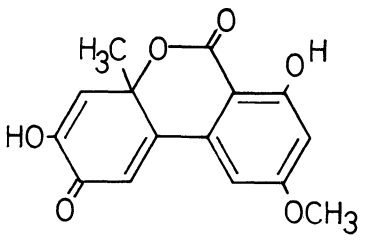
AN APROACH TO BIOGENESIS OF DEHYDROALTENUSIN BY ENZYMIC OXIDATION[1)]

Kiyoshi KAMEDA and Mitsuo NAMIKI
Faculty of Agriculture, Nagoya University, Nagoya 464

Dehydroaltenusin, a metabolite of Alternaria kikuchiana, was coverted from altenusin with homogenated potato and sweet potato extracts.

It has so far been shown that the phytopathogens, Alternaria species produce several analogous metabolites of dibenzo-α-pyrone derivatives as alternariol[2)], alternariol monomethylether[2)], altenuic acid II[3)], altenuene[4)] and altenuisol[5)]. Then, it seems of interest to elucidate the biogenetical relationships between these metabolites, but no work on the biogenesis of those has done except for alternariol and its monomethylether by Thomas et al. using ^{14}C-acetate[6)]. In the course of our investigations on the toxic meatbolites of A.Kikuchiana, two phenolic metabolites were recently isolated from the culture medium and determined to be identical with dehydroaltenusin and altenusin[7)], which were obtained from A.tenuis, by their chemical and physical properties. In respect to the structural relationship, dehydroaltenusin is assumed to be an oxidatively lactonized product of altenusin and that was demonstrated by the oxidation of the latter with ferric chloride[8)]. A similar oxidative lactonization of the carboxylic acid group has also been shown in the oxidation of geodoxin from geodin hydrate[9)]. On the other hand, an oxidation of griseophenone A into dehydrogriseofulvin with homogenized potato peelings-hydrogen peroxide was reported[10)]. These facts led us to attempt an enzymic transformation of altenusin into dehydroaltenusin in vitro as one of the biogenetical studies on these metabolites using peroxidase- hydrogen peroxide system and crude o-diphenol oxidase enzymes from potato and sweet potato extracts.



DEHYDRO-
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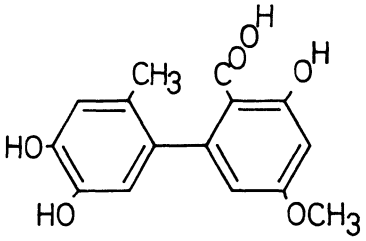
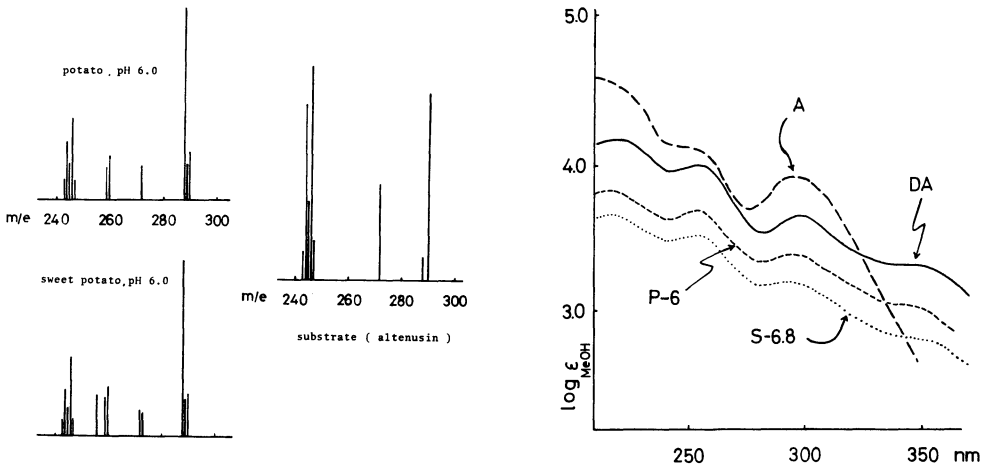


ALTENUSIN

To a phosphate buffer solution (pH 6.0 or 6.8) of altenusin (ca. o.1%) were added subsequently, a solution of peroxidase of horse radish (Worthington Biochemicals) and hydrogen peroxide and then added a catalase to decompose the excess of the hydrogen peroxide. On the other hand, in the cases of crude enzyme solutions prepared from potato and sweet potato according to the method of Hyodo et al.[11)], the reactions were

carried out aerobically in the absence of hydrogen peroxide at 30°C for 40 min and at 5°C for 3 days, respectively. Acidification of the reaction mixtures followed by the extraction with ethyl acetate gave some reaction products along with the unchanged starting material. In the cases of the experiments done with the crude enzymes, the main product (ca. 50% yield) was identified as dehydroaltenusin from the UV and MS[12] spectral data as shown in figures and was also confirmed by comparing the tlc data (silisic acid, chloroform:MeOH, 13:1, Rf 0.90, authentic sample 0.90, $FeCl_3$ and 2,4-DNP, positive, respectively and substrate Rf 0.35), but the peroxidase was less effective for the production of dehydroaltenusin (ca.5%). These results demonstrated that altenusin could be converted into dehydroaltenusin by the action of the oxidase or o-diphenol oxidase from potato and sweet potato and not of the peroxidase from horse radish. Therefore, it was suggested that such conversion was also brought about by a simmilar enzymic system of Alternaria spp.. Further works on their biogenetical relationships are being undertaken.



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References and Notes

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