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THE ANTIFUNGAL FACTORS IN BARLEY -
ISOLATION AND SYNTHESIS OF HORDATINE A.

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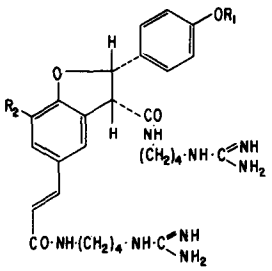
A recent communication (1) assigned structures to hordatine A (I, R_1=H) and hordatine B (II, R_1=H), which occur in barley as the glucosides (I or II, R_1= α-D-glucopyranosyl). Free hordatine A, already available as a methanolysis product (1), has now been found to occur naturally in the antifungal fraction (2) ranking next to the glucosides in abundance. Isolation required repeated counter-current distributions (1150 transfers) and further purification through the dipicrate**, identical with the dipicrate of carefully fractionated methanolysis product by uv and ir spectra. The syrupy diacetates, obtained by ion exchange of the dipicrates, were identical in optical rotation ($[\alpha]_D^{23^\circ}$ + 69°) and by all other available criteria (see below).



(I, R_2=H) (II, R_2=OMe)
(or enantiomers)

A biogenetic origin of the hordatines from phenylpropanoid precursors is indicated by their structures and also by the earlier isolation of coumaroylagmatine (3) as a cometabolite. Oxidative phenol coupling (4) of the latter could lead directly to hordatine A and precedent (5, 6, 7) was at hand for an

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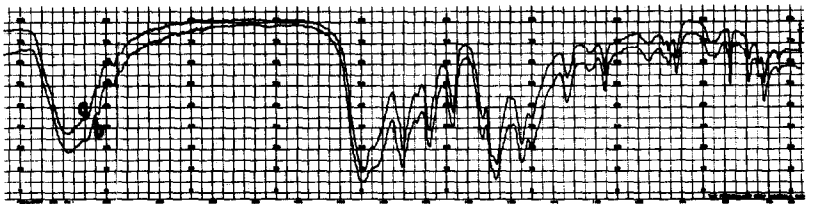
* Contribution No. 330

** $C_{40}H_{44}N_{14}O_{18}$ by elemental analysis.

analogous *in vitro* synthesis. Coumaroylagmatine proved an excellent substrate. It was readily oxidized by dilute hydrogen peroxide in the presence of catalytic amounts of horseradish peroxidase, under conditions approximating those of Freudenberg (7). No reaction was detectable in the absence of enzyme. The desired product, optically inactive, was isolated by countercurrent distribution in *ca* 35% yield. It was characterized as the dipicrate, identical with that of (I, R_1=H) by elemental analysis and uv spectrum. The ir spectra (KBr) of the optically active and the racemic forms were very similar (Fig. 1).

FIG. 1.



Infrared spectra of hordatine A dipicrate: a) natural b) synthetic

The syrupy diacetate of (±)-hordatine A was identical with that of the natural product in uv and nmr spectra, inhibition of *Monilinia fructicola* and behaviour in four chromatographic systems. Identity was further established by quantitative hydrogenation to (±)-dihydrohordatine A (1), which was characterized by uv and nmr spectra. Methylation of the synthetic dihydro derivative, followed by alkaline hydrolysis, gave the "lactone II" (1), identified by m.p. and mixed m.p.

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