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MONOCOTYLEDONAE

GRAMINEAE

THE IDENTIFICATION OF *p*-HYDROXYBENZYLAMINE IN BARLEY AND MALT

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Abstract—A phenolic compound obtained by vacuum distillation of water extracts of barley seed and malt has been identified as *p*-hydroxybenzylamine on the basis of its chromatographic behaviour and its reaction with ninhydrin

INTRODUCTION

A NUMBER of volatile amines are known to occur in malt,[1-5] the range of compounds identified being quite wide Most authors are agreed on the presence of at least the simple aliphatic primary amines—methylamine, ethylamine, *n*-butylamine, *iso*butylamine and *iso*amylamine, and the secondary amine, dimethylamine, has also been commonly recognized. The present paper describes the identification for the first time of *p*-hydroxybenzylamine as a component of the volatile amine fraction of barley and malt

RESULTS AND DISCUSSION

The volatile amine fraction derived from malt contains two compounds which react with ninhydrin to give a yellow colour,[2] one being identified as pyrrolidine The other, whose colour changed from yellow to purple after a few hours, reacted faintly with the Ehrlich reagent[6] and strongly with the Folin reagent.[7] These results indicated that the compound contained a phenolic group as well as being an amine The only compound reported in the literature to give the characteristic yellow to purple reaction with ninhydrin was benzylamine, but this compound was ruled out on the grounds of R_f (Table 1) Phenethylamine, tryptamine and tyramine as well as several pyrrole derivatives were also eliminated on grounds of both R_f and colour reaction with ninhydrin

Since the unknown compound was probably an hydroxylated derivative of benzylamine, the *o*-, *m*- and *p*-hydroxy derivatives of benzylamine were synthesized All three reacted with ninhydrin to give a yellow colour which gradually turned to purple However, the rate of colour change varied with the isomer under test· *m*-hydroxybenzylamine became purple within 30 min, *p*-hydroxybenzylamine became purple after 3 hr whereas the *o*-isomer took about 6 hr before becoming completely purple The rate of colour change of the unknown closely approximated to that of authentic *p*-hydroxybenzylamine

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TABLE 1 CHROMATOGRAPHIC DATA ON BENZYLAMINE DERIVATIVES

Compound	R_f	t_R*
Benzylamine	0 75	—
o-hydroxybenzylamine	0 67	1 21
m-hydroxybenzylamine	0 63	1 39
p-hydroxybenzylamine	0 60	1 21
unknown	0 60	1 21

* The GLC retention times (t_R) are relative to the retention time for *n*-butylamine (t_R = 1 00).

Co-chromatography on paper of the authentic compounds and the volatile amine fraction of the malt showed that *o*-hydroxybenzylamine was clearly separated from the unknown compound Co-chromatography in the GLC system showed a clear distinction between *m*-hydroxybenzylamine and the unknown compound. However, in both chromatographic systems authentic *p*-hydroxybenzylamine was indistinguishable from the unknown compound (see Table 1) and on the basis of this evidence and of the colour with ninhydrin, the unknown compound in the malt was identified as *p*-hydroxybenzylamine.

Ethyl acetate extracts of the water-soluble fraction of malt[7] have been shown to contain *p*-hydroxybenzylamine using paper chromatography and ninhydrin staining, indicating that this compound is not an artefact due to the alkaline distillation step used in the majority of experiments.

p-Hydroxybenzylamine has also been identified in aqueous extracts of whole ungerminated barley corns.

EXPERIMENTAL

The preparation of the volatile amine fraction and the paper chromatographic system have been described previously [2] Whole barley corns ground in a Casella mill were extracted in water in the same proportions as used for malt A Pye 104 gas chromatograph with flame ionization detectors was used for GLC analysis The column packing was Carbowax 400 on acid washed Celite (100–150 mesh) pretreated with polyethyleneimine [8] All determinations were made isothermally at 60° with N_2 flow of 25 ml/min Solutions of the amine HCl salts were made alkaline with excess KOH immediately before injection of 1 μl samples

p-Hydroxybenzylamine was prepared from *p*-hydroxybenzaldehyde, *m*-hydroxybenzylamine from *m*-hydroxybenzaldehyde and *o*-hydroxybenzylamine from salicylaldehyde oxime In the case of the *p*- and *m*-isomers the oxime was first synthesized by reaction with hydroxylamine followed by recrystallization from benzene [9] The oximes were converted to the amines by reduction with sodium amalgam in glacial acetic acid and ethanol at 60° [10]

Barley (*Hordeum sativum* var Golden Promise) was obtained from R F Bell & Son Ltd , Edinburgh and the malt was a gift from Campbell, Hope and King, Edinburgh

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Key Word Index—Hordeum vulgare, Graminae, barley, *p*-hydroxybenzylamine