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1,4-BENZOXAZINE DERIVATIVES IN PLANTS
A NEW GLUCOSIDIC DERIVATIVE FROM ZEA MAYS

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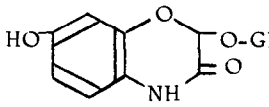
In previous paper on 1,4-benzoxazine derivatives in plants, three new unidentified glucosides of this type were mentioned (1); for one of these,"I-Glc.",the structure of a 2-(2,7-dihydroxy-1,4/2H/-benzoxazin-3/4H/-one)ß-D-glucopyranoside,(I), is now proposed. The quantities of"I-Glc."in various plants are found to be by one order of magnitude smaller than those of 2-(2,4-dihydroxy-7-methoxy-1,4/2H/-benzoxazin-3/4H/-one)ß-D-glucopyranoside (DIMBOA-Glc.) and its lactam form (HMBOA-Glc.). -"I-Glc." was isolated from corn seedlings by gel filtration on Sephadex G-10 (1). Recrystallisation from absolute ethyl alcohol leads to colourless needles, m.p. 262-3°C (decomp.),



(I)

with the following characteristic properties : Anal.calc.for $C_{14}H_{17}NO_9$: C,48.99; H, 4.98; N, 4.08; found : C, 49.25; H, 5.06; N, 3.93. UV spectra : $\lambda_{max(H_2O)}$ 262 nm with shoulder 282 nm, $\varepsilon^{262}_{H_2O}$ = 9 200. No coloured complex with $FeCl_3$ is formed. In descending paper chromatography in system n-BuOH, EtOH, H_2O (4:1:5), Whatman No.3, the value R_F O.3 was observed (the same as for "II-Glc."(1), which, however, gives strong blue coloration with $FeCl_3$).

On infrared spectra (Fig. 1) the ketone stretching vibration for 6-membered ring lies at 1705 cm^{-1}. Vibrations of heterocycle of 1,4-benzoxazine (1222, 1052 cm^{-1}) (2) are not so distinct as with aglucones of 1,4-benzoxazine (1,3).

On the mass spectrum, the relative abundances of fragment ions m/e 181, 165, 164, 142, 124 and 96 and of the molecular ion, 343, resemble closely the relative abundances of ions heavier by 14 mass units in spectrum of HMBOA-Glc., molecular weight 357 (4). This indicates the presence of a 7-hydroxyl group instead of the 7-methoxyl group in

HMBOA-Glc. (However, ions m/e 179 to which the structure of the glucosidic portion was ascribed (4) are missing while ions m/e 165 appear to occur instead).

The NMR spectrum was obtained by using deuterated dimethylsulphoxide as the solvent and hexamethyldisiloxane as an internal standard. The substance does not contain the methoxyl group. Splitting of signals of protons C-5 (6.68 ppm-doublet, J=8 cps), C-8 (6.44 ppm-doublet, J=3 cps), C-6 (6.34 ppm quartet), C-2 (5.57 ppm singlet) proves that the position C-7 is occupied by a hydroxyl group (9.04 ppm-singlet). The anomeric proton absorbs at 4.55 ppm (doublet) and amide proton at 10.55 ppm (singlet).

An increase of concentration of (I) in corn seedlings was found caused by the influence of the herbicide 2-chloro-s-triazine (atrazine); this increase was also described for HMBOA-Glc. (1).

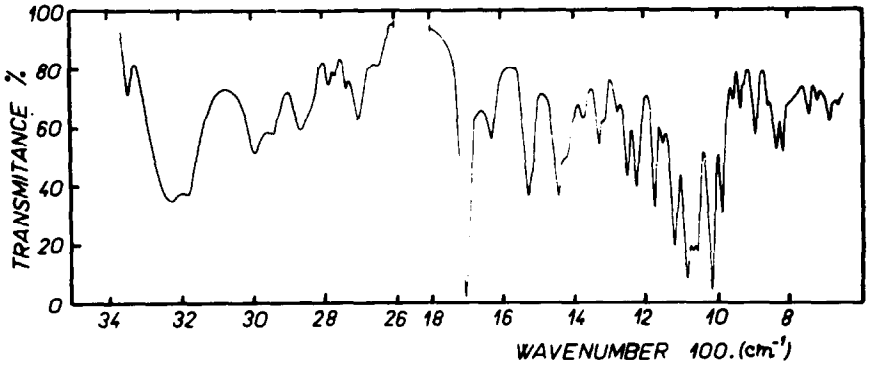


Fig. 1. Infrared spectra of (I) in KBr pellets.

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