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1,4-BENZOXAZINE GLUCOSIDES FROM *ZEA MAYS*

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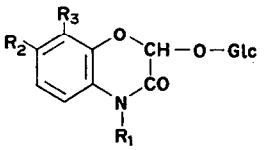
Key Word Index—*Zea mays*; Gramineae; 1,4-benzoxazine glucosides.

Abstract—One new benzoxazine glucoside has been found in corn and identified as 2-(2-hydroxy-7,8-dimethoxy-2H-1,4-benzoxazin-3[4H]-one)-β-D-glucopyranoside.

GLUCOSIDES of the 1,4-benzoxazine type have been found in corn and wheat plants[1–3] and we reported the isolation of one of these, 2-(2,4-dihydroxy-7,8-dimethoxy-2H-1,4-benzoxazin-3[4H]-one)-β-D-glucopyranoside (I), earlier.[4] Its degradation product, 6,7-dimethoxy-2(3)-benzoxazolinone, which was not found in the plant, has been isolated from dried corn tissue.[5] We have now identified a second substance as 2-(2-hydroxy-7,8-dimethoxy-2H-1,4-benzoxazin-3[4H]-one)-β-D-glucopyranoside (II). Thus, again, the hydroxam and lactam derivatives of the same 1,4-benzoxazine have been isolated, the hydroxam always in higher concentration.



(I) R_1 = OH; R_2 = OMe; R_3 = OMe
(II) R_1 = H; R_2 = OMe; R_3 = OMe
(III) R_1 = OH; R_2 = OMe; R_3 = H
(IV) R_1 = OH; R_2 = H; R_3 = H
(V) R_1 = OMe; R_2 = OMe; R_3 = H

Compounds (I) and (II) were isolated from corn extracts by means of gel filtration (GF) on aged Sephadex G10. The first peak contained (I), (IV) and (V) and the second (II) and (III), in contrast to the observations with fresh Sephadex G10.[1] Individual components were purified by TLC on silica gel.

(I) [m.p. 149–151°, λ_{max} (EtOH) 267, weak shoulder 289 nm; NMR δ 5·93 (*s*, 2-H), 7·01 (*d*, 5-H), 6·68 (*d*, 6-H), 3·80 (*s*, 7-MeO) and 3·83 ppm (*s*, 8-MeO)]; (II) [m.p. 171–174°, λ_{max} 259, weak sh. 288 nm; NMR δ 5·73 (*s*, 2-H), 6·69 (*d*, 5-H), 6·58 (*d*, 6-H), 3·78 (*s*, 7-MeO) and 3·83 ppm (*s*, 8-MeO)]. Reduction of (I) with Zn in AcOH gave (II). Treatment of (II) with β-glucosidase gave aglucones with identical m.p., UV, IR and NMR to synthetically prepared standard.

In base, the formation of anions ($-NO^- + H^+$) from hydroxam derivatives is accompanied by a shift of UV maximum to higher wavelengths. (I) λ_{max} (H_2O) pH 5·0 267

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nm and pH 8·0 289, isosbestic point 274 nm; (III) 262 and 289, iso. pt. 275 nm; (IV) 255 and 296, iso. pt. 270 nm; (V) 264 and 264 nm. The formation of anions is confirmed by the unchanged spectrum of the *N*-alkyl derivative (V).

EXPERIMENTAL

Synthesis of aglucone of (II). Reduction (Sn–HCl) of 2,3-dimethoxy-6-nitrophenol[6] gave 2,3-dimethoxy-6-aminophenol which was transformed into 2,3-dimethoxy-6-(dichloracetamido)-phenol with $CHCl_2COCl$. By means of the subsequent hydrolysis and cyclization in solution 0·2 M $NaHCO_3$ (100° for 30–60 sec), 2-hydroxy-7,8-dimethoxy-2H-1,4-benzoxazin-3[4H]-one was obtained. Satisfactory analytical data were obtained for all new compounds.

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