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THE ISOLATION OF THE CYANOGENIC GLYCOSIDE PRUNASIN FROM PTERIDIUM AQUILINUM (L.) KÜHN

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Cyanogenic glycosides have been isolated from numerous species within angiospermae (1) and gymnospermae (2,3). Although the leaves of several ferns are known to be cyanophoric (4,5) no hydrogen cyanide producing glycoside has so far been identified in material originating from pterophyta.

The present communication reports the isolation and identification of prunasin (O-β-D-glucopyranosyl-D-mandelonitrile) from Pteridium aquilinum (L.) Kühn. Careful examination for other cyanogenic substances was negative. Prunasin appears to be the only glycoside responsible for the distinct smell of hydrogen cyanide, produced almost spontaneously, when the fresh leaves are crushed.

The isolation procedure, including a combined application of column- and thin-layer chromatography will be described elsewhere.

Prunasin (1270 mg from 790 g of fresh leaves) was identified as follows. Crystallized from benzene/99 % ethanol it had a m.p. 150-151° C (corr.); Lit.: 149-150° C (6). $[\alpha]_D^{28}$ = -30.1° (c 0.418 in water); Lit,: $[\alpha]_D^{21}$ = -27.0 (in water) (6). Found:

C 57.09; H 5.87; N 4.72 %. Calc. for $C_{14}H_{17}O_6N$: C 56.94; H 5.80; N 4.74 %.

The IR-spectrum of prunasin (KBr pellet) showed bands at 2920-3600 (strong), 1505, 1465 (medium) and several strong and medium bands in the range 1000-1400 cm^{-1}. The C≡N stretching band at 2270 cm^{-1} was scarcely detectable owing to the presence of the many oxygen-containing groups in the molecule (7).

Emulsin-catalysed hydrolysis of the compound indicated the release of hydrogen cyanide (picric acid reaction). Glucose was identified in the hydrolysate by thin layer- and paper chromatography; in an ether extract of the hydrolysate benzaldehyde was identified as such and as the 2,4-dinitrophenylhydrazone by thin layer chromatography.

Acetylation of prunasin with acetic anhydride in pyridine at room temperature for 48 h gave a tetraacetate, which crystallised from water/99 % ethanol in fine, colourless needles m.p. 139-140° C (corr.); Lit.: 139-140°C (6). Found: $[\alpha]_D^{27}$ = -22.2° (c 0.540 in ethanol); Lit.: $[\alpha]_D^{20}$ = -24.0° (in dry ethyl acetate) (6). Found: C 57.13; H 5.40; N 2.99 %. Calc. for $C_{22}H_{25}O_{10}N$: C 57.01; H 5.44; N 3.02 %. The NMR-spectrum of prunasin tetraacetate (110 mg dissolved in 500 µl $CDCl_3$) was consistent with the spectrum of prunasin tetraacetate reported by TOWERS et al. (3).

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