

STEPWISE HYDROLYSIS OF AMORPHIN

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It has been shown previously that amorphin, $C_{34}H_{40}O_{16}$, a rotenoid diglycoside from plants of the genus Amorpha, is a vicinoside of amorphigenin [1, 2]. However, the configuration of the glycosidic bond between the sugars was not strictly proved.

This can be done only by stepwise hydrolysis, although on acid hydrolysis both glycoside bonds of amorphin are cleaved simultaneously, with the formation of amorphigenin, D-glucose, and L-arabinose. For this reason, the intermediate hydrolysis product has not yet been detected [2]. Yashchenko's paper [3] on the isolation of an intermediate product does not agree with the already established structure of the sugar chain of amorphin.

In the course of a study of the stepwise hydrolysis of amorphin according to the concentration of the acids, the temperature, and the duration of heating, we selected conditions leading to the formation of the intermediate compound.

A solution of amorphin in 2% H_2SO_4 was heated to the boil for 40 min and then cooled. The precipitate was shown by TLC on silica gel [benzene-methanol (9:1)] to contain three substances in approximately equal amounts. The most polar of them proved to be unchanged amorphin, and the least polar was the aglycone of amorphin, amorphigenin $C_{23}H_{22}O_7$.

To obtain the substance with the intermediate polarity, the water-washed and dried precipitate was freed from amorphigenin by extraction with ether and then chromatographed on a column of silica gel in a benzene-methanol (6:1) system. A substance with the composition $C_{29}H_{34}O_{12}$, mp 165-166° C, $[\alpha]_D^{20} -122^\circ$ (c 0.1, ethanol) was isolated which was identical in its chemical properties and UV and IR spectra with amorphigenin β -D-glucopyranoside, which we found previously in some species of Amorpha [4]. The hydrolysis of this substance with 20% H_2SO_4 led to amorphigenin and D-glucose.

Similar results were obtained when a solution of amorphin was heated with Amberlite IR-120 (H^+ form) at 60-80° C for 2 hr. If we remember that the specific rotation of amorphin $[\alpha]_D^{20}$ is -98° (ethanol), the difference in the molecular rotations of amorphin $[M]_D -690^\circ$ and amorphigenin β -D-glucopyranoside $[M]_D -700^\circ$, is $+10^\circ$ C.

For methyl α -arabopyranoside $[M]_D$ is $+28^\circ$ (water) and for methyl β -arabopyranoside $[M]_D$ is 403° [5]. These facts show that the glycoside bond of the arabinose in amorphin has the α -configuration.

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