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Abstract

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THE GLYCOSIDE AMORPHIN

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Amorphin was the name given to a glycoside found by Acree, Djecoboson, and Haller ([1]) in the fruits of the plant *Amorpha fruticosa* L. (fam. Leguminosae). By hydrolysis with concentrated hydrochloric acid they obtained the aglycone—amorphigenin. Later Yashchenko ([2]), among the products of hydrolysis of amorphin, detected *d*-glucose and presented data indicating that one more molecule of sugar is bound to the aglycone, which apparently is a pentose.

In addition to *Amorpha fruticosa*, we found amorphin in the fruits of six other species of *Amorpha* ([3]). The glycoside isolated by us had m.p. 151—152°, $[\alpha]_D^{20} = -67.9°$ (in pyridine), and in its physicochemical properties coincided with the substance described in ([1,2]). The analytical data spoke more in favor of the formula $C_{33}H_{38}O_{16}$, which is lower by 2 hydrogen atoms than the formula proposed for amorphin by the previous authors.

On heating with 20% sulfuric acid, amorphin (I) underwent complete hydrolysis. From the hydrolysate, after removal of the aglycone, crystalline *l*-arabinose was isolated with m.p. 155° (diphenylhydrazone, m.p. 202—203°) and *d*-glucose (osazone, m.p. 203—204°). To determine the order of linkage of the sugars, amorphin was subjected to exhaustive methylation and then hydrolyzed. In the hydrolysate, by paper chromatography, 2,3,4-trimethyl-1-arabinose was detected. This indicates that, in the sugar chain, *l*-arabinose occupies the terminal position ([4]).

The aglycone of amorphin, amorphigenin $C_{22}H_{20}O_7$ (II), is a crystalline substance with m.p. 191—192°, $[\alpha]_D^{20} = -200.9°$ (in benzene); acetate (III) $C_{24}H_{22}O_8$, m.p. 152—154°. The authors who first described amorphin and amorphigenin ([1]) already pointed out that both compounds give the color reaction with Duram' s reagent characteristic of rotenoids. The rotenoid structure of amorphigenin was also confirmed by us ([3,4]) by comparison of the ultraviolet absorption spectra of amorphigenin and rotenone (λ_{max}238 mμ, $\lg\varepsilon$4.1, and λ_{max}295 mμ, $\lg\varepsilon$4.2). Amorphin is the first instance of the occurrence, among the rotenoids, of a substance of glycosidic character.

In addition to the acetylatable hydroxyl group which in the glycoside is bound to the sugar residue, amorphigenin, like rotenone, contains two methoxyl groups and a carbonyl group (oxime, m.p. 225—227°). On oxidation of amorphigenin

reaction scheme

Figure 1: reaction scheme

(II) with iodine in alcoholic solution (in the presence of sodium acetate), dehydroamorphigenin $C_{22}H_{18}O_7$ (IV) is formed, a yellow crystalline substance with m.p. 224—225°, $[\alpha]_D^{20} = -50 \pm 5°$ (in chloroform); acetate $C_{24}H_{20}O_8$ (V) with m.p. 172—175°. The character of the ultraviolet spectrum of dehydroamorphigenin ($\lambda_{\max} 240, 280, 210$ mμ), analogous to the spectrum of dehydrorotenone, shows that this reaction is connected with the introduction of a double bond between C-7 and C-8.

On heating with an alcoholic solution of caustic potash and zinc dust, dehydroamorphigenin (IV), adding two molecules of water, is converted into amorphigenic acid (XII) of composition $C_{22}H_{22}O_9$, m.p. 130—132°, $[\alpha]_D^{20} = -64.7°$ (in methanol). Its methyl ester $C_{23}H_{24}O_9$ has m.p. 96—98°. A positive reaction with ferric chloride indicates the appearance

phenolic hydroxyl. Oxidation of amorphigenic acid with hydrogen peroxide in alkaline medium leads to the dicarboxylic acid $C_{12}H_{14}O_7$ (X) with m.p. 166-167° (dimethyl ester (XI) with m.p. 66-67°), which proved to be identical with derric acid ([5]). On heating with acetic anhydride, amorphigenic acid (XII), undergoing the reverse transformation, forms dehydroamorphigenin acetate (V).

(I) –O-D-glucose + L-arabinose

(II) –OH

(III) –OAc

(IV) –OH

(V) –OAc

(VI) R = H

(VII) R = Ac

(VIII) R = H

(IX) R = CH_3

(X) R = H

(XI) R = CH_3

The reversible reaction dehydroamorphigenin–amorphigenic acid and the oxidation of the latter to derric acid are highly reminiscent of the analogous reactions of dehydrorotenone and derric acid ([5-7]). The commonality in the structure of the carbon skeleton of rotenone and amorphigenin in the part concerning rings A, B, and C is quite evident. However, they already differ in that amorphigenin $C_{22}H_{20}O_7$ contains one carbon atom less than rotenone $C_{23}H_{22}O_6$ and also contains a hydroxyl group that is absent in rotenone.

By hydrogenation of amorphigenin (II) in alkaline medium over nickel (Raney), tetrahydroamorphigenin $C_{22}H_{24}O_7$ (VI) was obtained, m.p. 197-198°, $[\alpha]_D^{20} = +37.6^\circ$ (in methanol); oxime $C_{22}H_{25}O_7N$, m.p. 227-229°. As in the case of rotenone ([5]), hydrogenation is presumably accompanied by opening of the dehydrofuran ring. Tetrahydroamorphigenin (VI), being a phenol, dissolves in alkalis, although it gives no color reaction with ferric chloride. If tetrahydroamorphigenin (VI) is oxidized under conditions analogous to the dehydrogenation of amorphigenin (II), tetrahydrodehydroamorphigenin $C_{22}H_{22}O_7$ (VII) is formed, m.p. 187-189°; diacetate $C_{26}H_{26}O_9$ (VIII), m.p. 151-153°. The order of the reactions may be changed, i.e., tetrahydrodehydroamorphigenin (VII) may be obtained by direct hydrogenation over nickel of dehydroamorphigenin (IV). Analogously to dehydrorotenoids, tetrahydro-

Dehydroamorphigenin (VII), like all derivatives of dehydroamorphigenin, is yellow in color.

When amorphigenin (II) is oxidized with permanganate in an acidic medium, formaldehyde is formed. When tetrahydroamorphigenin (VI) is oxidized under the same conditions, formaldehyde was not detected. This makes it possible to assume the presence in amorphigenin of a vinyl group connected with the dihydrofuran ring, since, if the double bond were located in the furan nucleus (isorotenoic) ([5]), opening of the ring would not occur under the hydrogenation conditions used.

Analysis of the experimental material presented leads to the conclusion that amorphigenin is 24-noroxyrotenone (II), while dehydroamorphigenin (IV), tetrahydroamorphigenin (VI), tetrahydrodehydroamorphigenin (VII), and amorphigenic acid (XII) have the structures corresponding to those shown in the scheme.

The reduction of amorphigenin proceeds in an entirely different way if it is carried out not in an alkaline medium, but in glacial acetic acid in the presence of platinum black. Unexpectedly, in the product obtained, of composition $C_{22}H_{22}O_6$ (IX), m.p. 154-155°, $[\alpha]_D^{20} = -130^\circ$ (in chloroform), simultaneously with reduction of the double bond there was one oxygen atom less. Comparison of the IR spectra of the deoxydihydroamorphigenin (IX) obtained and amorphigenin (II) showed that the hydroxyl band (3510 cm^{-1}) present in amorphigenin had disappeared. At the same time, the spectrum of deoxydihydroamorphigenin, like the spectrum of amorphigenin, indicates retention of the carbonyl group (1684 and 1679 cm^{-1}, respectively). The oxime of deoxydihydroamorphi-

genin was also obtained, with m.p. 238-240°.

Exactly the same structure as (IX), as shown in the scheme, is possessed by d,l-nordihydrorotenone (m.p. 150-152°), synthesized by Miyano and Matsui ([8]). For greater certainty, starting from deoxydihydroamorphigenin (IX), deoxydihydrodehydroamorphigenin $C_{22}H_{20}O_6$ (XIV) was obtained, m.p. 220-222°, $[\alpha]_D^{20} = -60 \pm 5^\circ$ (in chloroform), corresponding in its structure to d,l-nordihydrodehydrorotenone, m.p. 220° ([8]), and by reduction on platinum of amorphigenic acid (XII)—deoxydihydroamorphigenic acid $C_{22}H_{24}O_8$ (XV), m.p. 160-162°, $[\alpha]_D^{20} = -62 \pm 5^\circ$ (in acetone), corresponding to d,l-nordihydrodehydrorotenic acid, m.p. 162-163° ([8]). The coincidence of the melting points and analytical data of compounds (IX), (XIV), and (XV) with the same data for d,l-nordihydrorotenone and its derivatives shows with the greatest obviousness that compound (IX) is the levorotatory form of nordihydrorotenone.

For the final establishment of the structure of amorphigenin, it is necessary to clarify the question of the position of the hydroxyl group. For the time being it is entirely clear only that it is absent from rings A, B, and C.

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Note: Figure translations are in progress. See original paper for figures.