STRUCTURE AND PROPERTIES OF ELEUTHEROCIDE B, THE GLYCOSIDE OF Eleutherococcus senticosus Maxim

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The wide biological action spectrum of eleutherocides has been noted earlier, these being glycosides from the root of <u>Eleutherococcus</u> <u>senticosus</u> <u>Maxim</u> [1]. In particular the high protective effect of eleutherocide B against radiation sickness [2] was indicated. We have prepared six eleutherocides from the root of Eleutherococcus, and the structure of five of these was established [3-5]. In this article we describe the properties of eleutherocide B, which is one of the main glycosides of eleutherococcus, and show that it is identical with syringa, this being a β -glucoside of sinapic alcohol which has been produced previously from the syringa root (Syringa sp. L) [6, 7].

The main syring a sample was obtained from the root of syren (Syring vulgaris L.) using a somewhat modified method [8]. It should be noted that the syringide is isolated after aqueous extraction in the form of a crystalline hydrate, whereas eleutherocide B is obtained by extraction of the eleutherococcus root with methanol, and its molecule is devoid of water of crystallization. Both glucosides are identical in the remaining properties (see Table 1). Both glucosides behave identically in paper and thin-layer chromatography. With concentrated H_2SO_4 they both give a characteristic blue coloration followed by the deposition of a blue residue.

Eleutherocide B, as also the syringide, easily undergoes hydrolysis with dilute acids and bases with the formation of one mole of glucose and the very labile substance henin, which like sinapic alcohol easily undergoes further change with the formation of dimers and polymers. The specific rotation of both glucosides indicates the presence of a β -glucoside bond. On treatment of eleutherocide B with β -glucosidase from Gorki almond, sinapic alcohol is formed as the main product, together with two products resulting from its further transformation. Acetylation of the enzyme hydrolysis products and subsequent chromatography yielded the acetate of the main product, which according to NMR and mass spectrographic data (Fig. 1) is the diacetate of sinapic alcohol. The infrared, ultraviolet, and NMR spectra (Fig. 2) of both glucosides are identical and confirm the presence of the phenylpropane ring in the molecule of henin, with a symmetrical arrangement of both methoxyl groups, and a double bond in the side chain. This indeed is

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Analytical data		Eleutherocide B	Syringin
Empirical formula Temperature mp, °C		$\begin{array}{ c c }\hline C_{17}H_{24}O_9\\ 188-190\\ (From alcohol - CHCl_3)\end{array}$	$\begin{array}{c} C_{17}H_{24}O_{9} \cdot H_{2}O\\ 189-190\\ (From alcohol - CHCl_{3})\end{array}$
$[\alpha]_D^{20}$		—21,13 (в СН ₃ ОН)	—17,34 (в H ₂ O)
C, %	Found	54,62; 54,68	52,22; 52,20
	Calculated	54,84	52,30
Н, %	Found	6,51; 6,43	6,67; 6,81
	Calculated	6,45	6,66
OCH3, %	l'ound	16,54; 16,67	16,55; 16,4 6
	Calculated	16,66	15,89
Mol. wt.	Found *	583	583
Acetates	Calculated	582	582
Glucose,%	Found	44,8	44,2
	Calculatd	43,8	41,8

TABLE 1. Analytical Data for Eleutherocide B and Syringin

*The molecular weight was determined by the mass spectrometric method.

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Fig. 1. NMR spectrum (1) and mass spectrum (2) of acetylated henin B.

confirmed by the positive Müller reaction at the pyrogallol grouping, with a basic melt of cleutherocide B, which leads to the formation of gallic and syringic acids, and also by the rapid absorption of bromine without evolution of hydrogen bromide and easy hydrolysis in aqueous ethanol at room temperature with the formation of the dihydro derivative.

EXPERIMENTAL METHOD

Apart from the general experimental conditions described earlier in [3] it should be noted that the NMR spectra were obtained with a type JNM-C-60 radiospectrometer, the mass spectra with a standard MKh-1303 instrument, the ultraviolet spectra with a type SF-4A spectrophotometer, the specific rotation with a type SPY-E spectropolarimeter, and the melting point on a Boietius table. The method described in [9] was used for the quantitative determination of glucose [9].



Fig. 2. NMR spectra (in CD_3OD) of eleutherocide B (1), Syringin (2), and the dihydro derivative of eleutherocide B (3).

The production of eleutherocide B is described in [3]. On acetylation with acetic anhydride in pyridinc the acetate of eleutherocide B is formed, mp 105-106.5°C (from ethanol). Found: C 55.81, 55.80; H 5.93, 6.21; OAc 35.40, 35.39%. $C_{27}H_{34}O_{14}$. Calculated: C 55.67; H 5.84; OAc 36.94%.

<u>Hydrogenation</u>. A solution of 1.082 g of eleutherocide B in 50 ml of ethanol was stirred for 39 h with 254 mg of a Pt/C catalyst saturated with hydrogen. This resulted in the absorption of 79 ml of II_2 and the formation of the dihydro derivative of the glucoside, mp 149.5-150.3°C (CHCl₃). Found: C 54.46, 54.52; H 7.41, 7.20; OCH₃ 15.98, 15.94%. C₁₇H₂₆O₉. Calculated: C 54.54; H 6.95; OCH₃ 16.55%.

Enzymolysis. Two hundred ml of the glucoside was treated for three days at 37°C with excess β -glucosidase. The enzymolysis product was extracted with ether, acctylated, and purified by chromatography on SiO₂ [3]. This gave 45 ml of the diacetate of sinapic alcohol.

CONCLUSIONS

It is shown that eleutherocide B is identical with syringin, and is the β -glucoside of sinapic alcohol.

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