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GLYCOSIDES OF *Dorema hyrcanum*

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UDC 547.918

In a study of *Dorema hyrcanum* growing in the region of the town of Kara-Kala, Turkmen SSR, we found two phenolic glycosides. For their isolation, the dried roots were extracted with methanol, and the concentrated extracts were diluted with water and were extracted with ether and then with butanol. When the butanolic fraction was chromatographed on silica gel (0.25 mm) and eluted in the benzene–propanol (10 : 1 and 1 : 1) systems, two substances were isolated.

Substance (I), $C_{15}H_{20}O_9$, mp 200-202°C (water–methanol), $[\alpha]_D^{20}$ – 95° (c 1.12; ethanol), R_f 0.6 [BAW (4 : 1 : 5) system, Silufol], giving on acidic hydrolytic cleavage D-glucose and an aglycone $C_9H_{10}O_4$, M^+ 182. Acetylation formed a pentaacetate with mp 140-145°C. On the basis of the physicochemical constants of the substance itself and its derivatives and from its spectral characteristics, the glycoside isolated was identified as pleoside [1].

Substance (II), $C_{21}H_{30}O_{14}$, mp 218-220°C (methanol–water), $[\alpha]_D^{20}$ –11.1° (c 1.11; water), R_f 0.3 [BAW (4 : 1 : 5) system, Silufol], proved to be a new bioside. We have called it hyrcanoside. It is readily soluble in water. Its IR spectrum shows the following maxima: λ_{max} 220-227 nm (shoulder), 285 nm (log ε 2.02, 2.15), which demonstrates the presence in its molecule of the same chromophore as in pleoside. The IR spectrum has bands at 3450 cm^{-1} (hydroxy groups), 1630, 1590, 1510 cm^{-1} (aromatic nucleus), and 1050 and 860 cm^{-1} (β-glycosidic bond).

The acetylation of (II) yielded an octaacetate with mp 158-160°C, which confirms its bioside nature. The acid hydrolysis of (II) yielded an aglycone identical with that from pleoside, and D-glucose was detected in the hydrolyzate by chromatography.

The NMR spectrum of the glycoside showed the signals of the following protons: singlet (3H) at 2.83 ppm – the protons of methylacetophenol; singlet, (3H) 3.58 ppm – methoxy group in an aromatic nucleus; doublets at 6.22 and 6.71 ppm (1H) – meta protons of an aromatic nucleus. In the 4.0-4.5 ppm region there are the signals of protons of two sugar residues (12H). A doublet at 5.48 ppm (J = 7 Hz) shows that one of the anomeric centers has the β configuration. The signal of the second anomeric proton is masked by other signals, but according to a calculation by Klyne's method, the second residue has the α configuration.

The NMR spectrum of the octaacetate has the signals of seven acetyl groups attached to sugar residues – singlet at 1.90 (21H) – and of one attached to the aromatic nucleus – singlet at 2.10 ppm (3H). The signals of the aromatic proton in the acetate of (II) are shifted downfield, as in the acetate of (I), by 0.27 and 0.36 ppm. The nature of the NMR spectrum of the acetate shows the possibility of a 1 → 6 bond between the sugars [2]. This hypothesis was confirmed by the results of the Hakomori methylation of the bioside followed by the hydrolysis of the polymethyl ether, which gave 2,3,4-tri-O-methyl- and 2,3,4,6-tetra-O-methyl-D-glucose, which were identified by chromatography on "Silufol" plates in the chloroform–methanol (25 : 1) system with markers. Thus, it has been established that hyrcanoside has the structure of 2-[O-α-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyloxyl-6-hydroxy-4-methoxyacetophenone.

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THE STRUCTURE OF AKICHENOL AND AKICHENIN

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Continuing a study of plants of the genus Ferula [1-3], from the roots of Ferula akitschensis B. Fedsch. gathered in July, 1974, in the Susamyr valley, Kirghiz SSR, we have isolated a substance $C_{27}H_{36}O_6$, M^+ 456, mp 162-163°C, $[\alpha]_D^{20}$ −8.3° (c 0.9; $CHCl_3$). It is readily soluble in ethanol and chloroform, sparingly soluble in petroleum ether, and insoluble in water; its UV spectrum has a maximum at 260 nm (log ε 4.16), which is characteristic for an aromatic nucleus, and its IR spectrum shows absorption bands at 1520, 1590, 1625 cm^{-1} (aromatic nucleus), 1695-1710 cm^{-1} (ester carbonyl), and 3200-3600 cm^{-1} (hydroxy group). The substance is new, and we have called it akichenin (I).

When compound (I) was hydrolyzed by being heated with 5% caustic potash for 2 h, from the acid part of the hydrolyzate we isolated p-hydroxybenzoic acid (II) and by chromatography, and also by NMR spectroscopy, we identified angelic acid (III). From the neutral fraction we obtained a previously unknown triol – akichenol (IV), $C_{15}H_{26}O_3$, M^+ 254, mp 155-156°C, $[\alpha]_D^{20}$ +37.5° (c 1.33; $CHCl_3$), the IR spectrum of which showed absorption bands at 1660 cm^{-1} (double bond) and 3200-3600 cm^{-1} (hydroxy group). On acetylation it formed a diacetate $C_{19}H_{32}O_5$ (V) with mp 105-106°C having in its IR spectrum the absorption band of a hydroxy group, which is tertiary. This is also confirmed by the fact that when the IR spectrum of the deuterated acetate of akichenin (V) was recorded, an absorption band characteristic for the −O−D bond was observed at 2650 cm^{-1} and the intensity of the absorption band at 3590 cm^{-1} had decreased.

The presence, according to the NMR spectrum, of only one double bond in the triol showed its bicyclic structure. When the NMR spectrum of (IV) was compared with that of ferutinol (VI) [4], it was seen that the two compounds are similar. Judging from the nature of the multiplicity and the values of the chemical shifts of the signals of the hemihydroxyl and the olefinic protons and of the C-methyl groups, (IV) differs from (VI) only

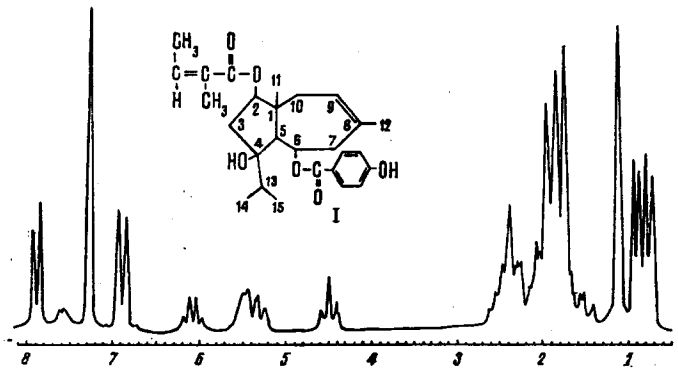

Fig. 1. NMR spectrum of akichenin (in $CDCl_3$).

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