partially relaxed spectra, in which a slower relaxation was observed for them than for the other monosaccharide residues [3].

The structure of (I) was also confirmed by the fact that when it was treated with a deacetylating agent (0.1% solution of NH_3 in 50% C_2H_5OH, 20 h), it gave (III) in quantitative yield, while the analogous treatment of the initial total glycosides did not change the impurity glycosides present in the initial fraction but converted (I) into the considerably more polar cucumarioside A_4-2 (IV) [1].

Thus, the structure of the aglycon, the sequence of linkage of the monosaccharide residues in the carbohydrate chain, and the position of the acetate group were established by a comparative study of (II) and (III), while the position of the sulfate group became clear after the formation of (IV), as described above. It follows unambiguously from this that cucumarioside A_1-2 (I) is 3β-O-{O-(6-O-acetyl-β-D-glucopyranosyl)-(1→3)-O-β-D-glucopyranosyl-(1→4)-[O-β-D-xylopyranosyl-(1→2)]-O-β-D-quinovopyranosyl-(1→2)-(4-O-(sodium sulfato)-β-D-xylopyranosyl)}holosta-7,25-dien-16-one.

LITERATURE CITED

1. S. A. Avilov, V. A. Stonik, and A. I. Kalinovskii, Khim. Prir. Soedin., No. 6, 787 (1990).
2. H. Ishii, S. Seo, K. Tori, T. Tozyo, and Y. Yoshimura, Tetrahedron Lett., No. 14, 1227 (1977).
3. A. I. Kalinovskii, Khim. Prir. Soedin., No. 4, 605 (1988).

A GLYCOSIDE OF SYRINGARESINOL FROM A TISSUE CULTURE OF *Scorsonera hispanica*

O. V. Bryanskii, V. V. Tolstikhina, and A. A. Semenov

UDC 547.914.4

Continuing a study of the chemical composition of a callous tumor tissue culture from *Scorsonera hispanica* [1], we have isolated syringaresinol O-β-D-glucopyranoside (I). The filtered cell mass was exhaustively extracted with 50% aqueous ethanol. The evaporated extract was fractionated in a continuous liquid–liquid extractor in the following systems: a) hexane–methanol (7:4) and b) chloroform–methanol–water (5:6:4). Glucoside (I) was isolated by droplet countercurrent chromatography in system (b) from the fraction of polar glycosides.

In nature, syringaresinol and its derivatives exist in the form of various stereoisomers or mixture of them [2]. The cells of *S. hispanica* produce a single stereoisomer, as follows from a consideration of chromatograms of an aqueous ethanolic extract of the tissue culture obtained by high-performance liquid chromatography. The structure of the syringaresinol glycoside was deduced from an analysis of the NMR spectra of its aglycon (II). These spectra showed that the molecule was completely symmetrical and agreed with literature information for a stereoisomer with the cis-linkage of the tetrahydrofuran rings and the pseudoequatorial arrangement of the aromatic substituents [3-6].

The aglycon (II) was obtained by the hydrolysis of (I) in boiling 5% caustic soda solution in an inert medium.

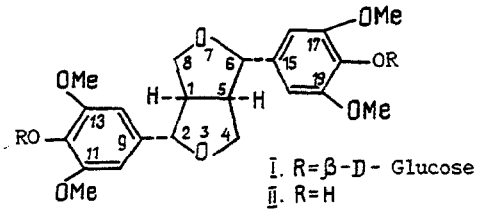
Contradictory information is given in the literature about the physicochemical constants of glycoside (I), and we therefore give our results in the scheme on the following page.

Syringaresinol O-β-D-glucopyranoside (I), $C_{28}H_{36}O_{13}$, white crystals, mp 177-179°C (ethanol), $[\alpha]_{546}^{25}$ −7° (c 0.72, ethanol). IR spectrum; ν_{max}^{KBR}, CM^{-1}: 3250-3500 (OH), 2830

Irkutsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences.

Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 591-592, September-October, 1992. Original article submitted November 26, 1991.

(OCH_3), 1580, 1605, 1405 (Ar), 885 (β-glycosidic bond). UV spectrum: λ_{max} (ethanol), nm: 209, 233, 272. FAB mass spectrum, m/z: 581 $[M + H]^+$, 418 $(M + H - 163]^+$, 401 $[M+H-163 - OH]^+$.



NMR spectral characteristics for the aglycon (II): PMR spectrum (200 MHz, $CDCl_3$): 3.07 (m, H-1, H-5), 4.77 (d, J = 4 Hz, H-2, H-6), 3.96 (dd, J = 9 and 3.5 Hz, H-4_a, H-8_a), 4.32 (dd, J = 9 and 7 Hz, H-4_b H-8_b), 6.59 (s, H-10, H-14, H-16, H-20), 3.83 (s, OCH_3). ^{13}C NMR spectrum (200 MHz, $CDCl_3$): 56.37 (OCH_3), 54.34 (C-1, C-5), 71.80 (C-4, C-8), 86.06 (C-2, C-6), 102.71 (C-10, C-14, C-16, C-20), 132.11 (C-9, C-15), 134.31 (C-12, C-18), 147.15 (C-11, C-13, C-17, C-19).

The analysis of the aqueous-ethanolic extract of the biomass of S. hispanica by the HPLC method was conducted on a Milikhrom-1 chromatograph using a Nucleosil-5, C_{18} column; UV detection at a wavelength of 210 nm.

LITERATURE CITED

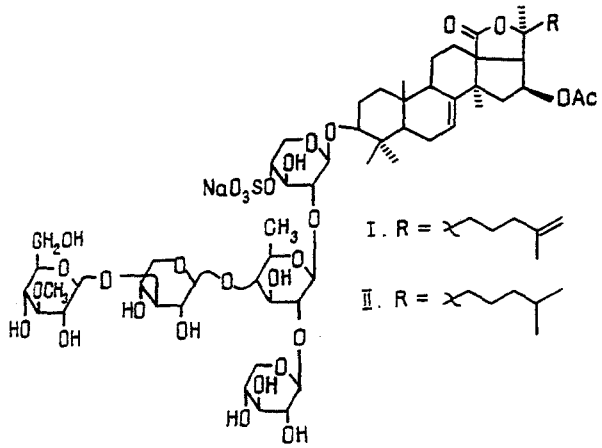
1. V. V. Tolstikhina, O. V. Bryanskii, A. I. Syrchina, and A. A. Semenova, Khim. Prir. Soedin., No. 5, 763 (1988).
2. S. D. Jolad, J. J. Hoffmann, J. R. Cole, M. S. Tempesta, and R. B. Bates, J. Org. Chem., 45, 1327 (1980).
3. C. H. Ludwig, B. J. Nist, and J. L. McCarthy, J. Am. Chem. Soc., 86, No. 6, 1186 (1964).
4. H. A. Arfmann, W. Kohl, and V. Wray, Z. Naturforsch., 40C, 21 (1985).
5. T. Deyama, T. Ikawa, and S. Nischibe, Chem. Pharm. Bull., 33, No. 9, 3651 (1985).
6. P. K. Agzawal and R. S. Thakur, Magn. Reson. in Chem., 23, No. 6, 389 (1985).

MINOR GLYCOSIDE FROM THE HOLOTHURIAN Cucumaria japonica

O. A. Drozdova, S. A. Avilov, A. I. Kalinovskii, and V. A. Stonik

UDC 547.996.593.96

With the aid of HPLC (Silasorb C-18, 10 × 150 mm, 45% C_2H_5OH, 3 ml/min) we have isolated from a fraction of weakly polar glycosides of the holothurian Cucumaria japonica a minor glycosidic component which has been called cucumarioside A_0-2 (I), mp 231-233°C, $[\alpha]_{578}$ −44° (c 0.1; pyridine).



Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Branch, Russian Academy of Sciences, Vladivostok.

Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 593, September-October, 1992. Original article submitted January 10, 1992.

0009-3130/92/2805-0520$12.50