

	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
β -D-Mannopyranose	101.5	71.6	72.9	77.85	77.5	62.0
β -D-Glucopyranose	103.7	74.45	76.6	80.0	75.4	62.0

Weak signals with CSs of 21.7 and 173.5 ppm relating to the CH₃ and CO atoms of ester groups were detected in the spectrum.

Thus, the results of a chemical study and ¹³C NMR spectroscopy permit the conclusion that the polysaccharides investigated were natively acetylated glucomannans possessing unbranched or only slightly branched chains the hexopyranose residues of which are linked to one another by β -(1 → 4) bonds and they differed from known polysaccharides [8] by their ratios of monosaccharides and degrees of polymerization.

LITERATURE CITED

1. D. A. Rakhimov, M. I. Igamberdieva, and Z. F. Ismailov, *Khim. Prir. Soedin.*, 85 (1976).
2. W. N. Haworth, *J. Chem. Soc.*, 107, 8 (1915).
3. T. Purdie and J. Irvine, *J. Chem. Soc.*, 83, 1021 (1903).
4. M. I. Igamberdieva, D. A. Rakhimov, and Z. F. Ismailov, *Khim. Prir. Soedin.*, 189 (1977).
5. D. A. Rakhimov, M. I. Igamberdieva, and Z. F. Ismailov, *Khim. Prir. Soedin.*, 466 (1979).
6. J. Hoffmann, B. Linndberg, and S. Svensson, *Acta Chem. Scand.*, 26, 661 (1972).
7. A. Dzhurmuratova, D. A. Rakhimov, A. S. Shashkov, and E. S. Kondratenko, *Khim. Prir. Soedin.*, 14 (1982).
8. N. K. Shcherbukhina, *Usp. Biol. Khim.*, 11, 226 (1970).

ACIDS OF AN AQUEOUS EXTRACT OF THE WOODY VERDURE OF THE PINE *Pinus sylvestris*

Z. A. Karepova, S. M. Repyakh,
and V. L. Levdikova

UDC 581.19.2:674.87

Interest in the chemical composition of aqueous extracts of woody verdure is due to their use as a nutrient medium in the cultivation of protein-producing microorganisms. Aqueous extracts of the woody verdure of the pine and the spruce contain compounds necessary for the nutrition of microorganisms [1]. In addition to sugars, probable sources of carbon may also be organic acids [2]. We have studied the degree of assimilation of individual acids by the yeast *Candida krusei* VEH-11, which is capable of accumulating biomass on aqueous extracts of conifer needles. It was found that the culture studied assimilates as sources of carbon such acids as acetic, malic, succinic, and lactic. On the cultivation of aqueous extracts of woody verdure these acids could become an additional source of nutrient for microorganisms [3, 4]. In the study of the organic acids of an aqueous extract of the woody verdure of the pine *Pinus sylvestris*, we obtained the following results:

Acid	Amount, % of the total amount
Glyceric	13.5
Oxalic	0.4
Succinic	3.2
Benzoic	15.3
Fumaric	3.2
Malic	10.6
Glutaric	3.9
Cinnamic	0.4
Tartaric	2.0
Citric	5.2
Hemimellitic	0.6
Trimellitic	0.5

The aqueous extract of the woody verdure of the pine contained aliphatic mono-, di-, and tricarboxylic acids and benzenecarboxylic acids. Of the aromatic acids, the benzoic acid, which was found in the largest amounts, may lower the nutritional value of the extract. The aliphatic acids were represented by malic, citric, glutaric, and others. The concentration of malic acid amounted to 10% of the total acids, and the amount of

citric was half this. The presence of such acids permits the more intensive assimilation of sugars by the microorganism, which, in the final account, leads to an increase in the weight of the fodder product obtained from aqueous extracts of the verdure.

The comminuted woody verdure of the pine *Pinus sylvestris* was extracted at 18–20°C for 15–20 min. The filtered extract was passed through KU-2 cation-exchange resin to eliminate impurities and to convert the acids into the free form. The total content of acids, calculated as malic, was determined by titration with 0.1 N NaOH. The concentrated eluate was extracted with ether, followed by repeated treatment with 5% sodium bicarbonate solution, decomposition of the salts with 2 N HCl, and extraction of the free acids with ether. The chromatographic investigation was carried out on a LKhM-72 chromatograph using a thermal conductivity detector. The acids were analyzed in the form of their methyl esters under the following conditions: rate of flow of carrier gas (He) 37 ml/min; column 200 × 0.4 cm; solid support Chromaton N-AWGMS (0.16–0.20 nm); stationary phase Silicone SE-30, 5% on the mass of the solid support. Temperature of the detector 300°C. The temperature was programmed at the rate of 3.6°C per minute in the interval of 60–290°C. Identification was performed by the method of adding the pure substances.

LITERATURE CITED

1. Z. A. Karepova, S. M. Repyakh, and V. L. Levdkova, *Khim. Prir. Soedin.*,
2. B. I. Osipov, *The Hydroaromatic Acids of Conifers* [in Russian], Novosibirsk (1979), p. 111.
3. G. A. Evdokimova et al., *Khim. Drev.*, **3**, 113 (1976).
4. Inventor's Certificate No. 765,359. *Byull. Izobret.*, No. 28 (1977).

HYDROXYCOUMARINS OF *Phaseolus vulgaris*

V. I. Dikhtyarev, V. N. Kovalev,
and N. F. Komissarenko

UDC 547.99:635.652

We have previously [1] reported on the isolation of the hydroxycoumarin scopoletin from the herbage of *Phaseolus vulgaris* L. (kidney bean). Continuing a study of the coumarins of the epigeal part of this plant, we have isolated four substances, preliminarily designated compounds A–D.

Substance A fluoresced pale blue in UV light on a paper chromatogram, with color of the fluorescence changing to orange after treatment with an ethanolic solution of caustic soda [3]. It had the empirical formula $C_{10}H_8O_4$ and was amorphous. In view of the identical elementary compositions and close R_f values in a number of solvent systems of the substance isolated and scopoletin, it was assumed that it was an isomer of scopoletin – 6-hydroxy-7-methoxycoumarin [3]. The isomer of scopoletin was obtained by methylating esculin with dimethyl sulfate in dry acetone in the presence of dry potassium carbonate followed by enzymatic hydrolysis with rhamnodiastase.

A comparison of the physicochemical properties of substance A with the 6-hydroxy-7-methoxy coumarin obtained showed their identity.

Substance B had the empirical formula $C_9H_6O_3$, mp 228–230°C and fluoresced bright blue in UV light. Its methylation gave a compound with the composition $C_{10}H_8O_3$, mp 117–118°C, identical with herniarin (7-methoxycoumarin). From its physicochemical properties, substance B was identified as umbelliferone (7-hydroxycoumarin) [2].

Substance C has the composition $C_9H_6O_4$, mp 268–272°C. On chromatograms it was revealed in UV light in the form of a blue spot which, after treatment with an ethanolic solution of caustic soda, fluoresced yellow. By its chromatographic behavior in various solvent systems and the absence of a depression of the melting point of a mixture with authentic material, substance C proved to be identical with esculetin (6,7-dihydroxycoumarin) [2].

Substance D had the composition $C_{15}H_{16}O_9$, mp 204–205°C. A preliminary study permitted its assignment to

Khar'kov Pharmaceutical Institute. Translated from *Khimiya Prirodnikh Soedinenii*, No. 3, p. 384, May–June, 1983. Original article submitted February 2, 1983.