IRIDOIDS OF THE BARK OF *Viburnum opulus*

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Viburnum opulus L. (European vibernum) family Caprifoliaceae has long been used in medicine. Viburnum bark is an officinal agent and is used in the treatment of internal bleedings, and it also possesses spasmolytic, cardiotonic, and sedative properties [1].

In a study of the chemical composition of viburnum bark, in addition to other compounds, we have detected no fewer than nine substances of iridoid nature, denoted as substances (I-IX), the main representatives being compounds (I), (VI) and (VII).

To isolate the iridoid compounds, the air-dry comminuted bark was treated with 10% sodium carbonate in order to bind the free organic acids and it was extracted with a tenfold amount of 95% ethanol. The extract was evaporated until the solvent had been eliminated completely, and the residue was mixed with boiling water and filtered. To free the iridoids from accompanying substances, the resulting filtrate was passed through a column of alumina in a ratio of 1:10. Then the column was washed with water. The iridoids were extracted from the combined eluates with a mixture of chloroform and ethanol (9:1), and the extract obtained was evaporated to dryness.

The iridoids were separated on a column of silica gel. The ratio of total iridoids to solvent was 1:50. As the eluent we used chloroform and a mixture of chloroform and acetone with a gradual increase in the amount of the latter to 50%. Chloroform eluted substance (I), mixtures of chloroform with 25-30% of acetone eluted substance (VI), and an increase in the concentration of acetone to 35-40% led to the isolation of substance (VII). All the substances isolated gave a blue-green coloration with the Stahl reagent [2], and a brown coloration in daylight and a yellow fluorescence in UV light with the Bacon—Edelman reagent [3]. After additional purification by activated carbon, substance (I), $C_{33}H_{46}O_{16}$, was obtained in the form of colorless acicular crystals with mp 90-92°C, $[\alpha]_D^{20} - 44°$ (c 1.0: methanol), and substances (VI) $C_{29}H_{42}O_{14}$, $[\alpha]_D^{20} - 65°$ (c 3.5; chloroform) and (VII), $C_{27}H_{40}O_{16}$, $[\alpha]_D^{20} - 55°C$ (c 2.0; methanol) were obtained in the form of amorphous hydroscopic masses.

When substances (I), (IV), and (VII) were boiled on the water bath with 10% hydrochloric acid in methanol for 1 h, they were converted into 7-formyl-4-methylcyclopenta[c]pyran with mp 90-93°C ($C_{10}H_8O_2$), which shows the presence of carbohydrate-containing substituents in positions 4 and 7 of the iridoid nucleus [4].

On treatment with 5% methanolic solutions of ammonia, substances (I), (VI), and (VII) underwent degradation with the formation of a greenish-blue precipitate, which indicates the substitution of the acetyl hydroxyl at C-1 of the iridoid nucleus by acyl residues.

In a hydrolysate after enzymatic hydrolysis, a sugar was detected which was identified by paper chromatography in various solvent systems as D-allose, and acetic and isovaleric acids were also detected.

The acetylation with acetic anhydride in pyridine of substances (VI) and (VII) led to the same compound $C_{33}H_{46}O_{18}$ with mp 111-113°C, $[\alpha]_D^{20} - 46°$ (c 1.0; methanol), which shows that substances (VI) and (VII) differ from one another in their degrees of acetylation.

The results obtained permit substances (VI) and (VII) to be identified as allosides of iridoids (I) and (II), which have been isolated previously from the leaves of *Viburnum opulus* L. [5].

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Thus, we have detected nine compounds of iridoid nature for the first time in the bark of the European viburnum, and of these we have isolated substances (I), (VI), and (VII). These substances are based on 7-formyl-4-methylcyclopenta[c]pyran, which is close in structure to baldrinal, isolated from valerian roots [6]. Substances (VI) and (VII) have been identified as allosides of iridoids (I) and (II), respectively, which have been isolated previously from the roots of the European viburnum. Some physicochemical properties of substance (I), not agreeing with the properties of known natural compounds, have been determined.

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SESQUITERPENE LACTONES OF *Artemisia pauciflora*

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The flower heads of *Artemisia pauciflora* Web. (oliganthous wormwood) collected in August, 1980, in the mountains of Karkarala, Karaganda province, Kazakh SSR, were exhaustively extracted with acetone. The concentrated extract was treated with 60% ethanol. The precipitate that deposited was filtered off, and the filtrate was treated with chloroform. The resin obtained after evaporation of the chloroform was separated on a column of type KSK silica gel with successive elution with benzene, benzene–ether (5:1) and (1:1), and ether.

The benzene–ether fractions yielded a new sesquiterpene lactone with the composition $C_{15}H_{22}O_3$ (I), mp 155-157°C (ethanol), M^+ 250, which has been called artepaulin.

The IR spectrum (tablets with KBr) showed absorption bands in the 1770 and 1700 cm^{-1} regions (γ-lactone carbonyl and cyclohexanone group, respectively).

The presence of a ketone group was shown by the formation of an oxime of (I) with the composition $C_{15}H_{23}O_3N$, mp 221-223°C (ethanol). IR spectra, ν_{max}^{KBr}, cm^{-1}: 3290 (–OH); 1765 (C=O of a γ-lactone), 1665 (C=N–).

The NMR spectra of (I) (Varian HA-100D, $CDCl_3$, δ scale, 0 – TMS) contained the following signals: singlet at 1.16 ppm (3 H) – angular methyl group; doublets with their centers at 1.16 ppm (3 H, J = 6 Hz) and 1.20 ppm (3 H, J = 6 Hz) – methyl groups at C_4 and C_{11}; triplet in the 3.92 ppm region (1 H, J = 10 Hz) – lactone proton.

The dehydrogenation of artepaulin at 280-310°C over Se for 30 h yielded 7-ethyl-1-methylnaphthalene, which was identified through its picrate with the composition $C_{19}H_{17}O_7N_3$, mp 94-96°C (ethanol).

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