A CHEMICAL STUDY OF Angelica ternata

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Angelica ternata Rgl. et Schmalh. is a high-mountain herbaceous plant which grows in the Tien-Shan at a height of 3600-4000 m above sea level and has not previously been studied chemically.

We have investigated the roots and epigeal part of the plant collected in September in the period of the ripening of the fruit (Zarafshanskii range, Remon Pass).

The dried and comminuted roots (1 kg) were treated with methanol. When the methanolic extracts were concentrated, a considerable amount of a substance with mp 178-180°C, identified by a mixed melting point as sucrose, deposited. The filtrate from this was concentrated, diluted with water, and treated with ether. The extract was distilled. This yielded 92.5 g (9.25%) of an oily residue with a specific odor which contained two components giving a red coloration with diazotized sulfanilamide (R_f 0.0 and 0.2) and one component (R_f 0.09) not giving this reaction but having a bright-blue fluorescence [n-hexane–benzene–methanol (5 : 4 : 1) system; paper impregnated with a 10% solution of formamide in methanol].

On chromatographic separation on alumina, elution with 5.5 liters of petroleum ether gave a fraction with R_f 0.95. This was then distilled in vacuum at 140-145°C/1 mm Hg. The distillate was rechromatographed on Al_2O_3, giving a yellow, oily, neutral substance with the composition $C_{12}H_{14}O_2$, readily soluble in carbon tetrachloride, benzene, and petroleum ether, and insoluble in water. On treatment with alkali, the substance underwent irreversible changes, from which it followed that it is neither a sesquiterpene lactone nor a coumarin lactone. The UV spectrum (in chloroform) had strong absorption in the 260-350 nm range with maxima on this background at 276 nm (inflection), 287, 294, and 325 nm (log ε 3.95, 3.96, 3.93, 3.91) and a minimum at 307-312 nm (log ε 3.52), which is specific for the chromophore of butylidenephthalides. The IR spectrum had absorption bands at 1760-1780 cm^{-1} (C=O of an unsaturated γ-lactone) and 1632 cm^{-1} (C=C bond in conjugation). The NMR spectrum (in CCl_4, taken on a JNM-4H-100/100 MHz instrument) had signals corresponding to the structure of ligustilide – doublets at 6.12 and 5.86 ppm, J = 10 Hz (olefinic protons in a six-member ring), triplet at 5.12 ppm, J = 8 Hz (olefinic proton in a side chain) – and three methylene groups adjacent to a double bond – multiplets in the 1.8-2.6 ppm region, together with methyl and methylene groups, 0.75-1.6 ppm. The results of a consideration and comparison of the spectroscopic findings showed that the substance was identical with ligustilide, a sample of which, isolated from Angelica sinensis [1] was kindly given to us by Dr. O. Motl. Fractional vacuum distillation at 80-100°C/1 mm and 140-160°C/1 mm yielded us another two phthalides with M^+ 204 and 220 having fragmentation in the mass spectra similar to that of ligustilide, which we have provisionally called ternin and ternitin. Their NMR spectra had the signals characteristic for ligustilide – a triplet at 5.06 ppm, J = 7.5 Hz, two doublets at 5.84 and 6.15 ppm, J = 10 Hz, and a multiplet in the 2.1-2.5 ppm region with an intensity of 6 H, but with a higher integral intensity of the signals of the methylene and methyl groups than in the case of ligustilide. These results permit the conclusion that ternin and ternitin are homologs of ligustilide and contain side chains consisting of five and six carbon atoms. In addition to this, a component with M^+ 192 was detected, in the mass spectrum of which the fragments were located two units higher than in ligustilide, which can be explained by the presence of dihydroligustilide in the plant. As accompanying substances we isolated β-sitosterol and a keto acid with mp 168-169°C (from ethyl acetate).

LITERATURE CITED

1. B. Trivide, L. Volicer, and O. Motl., Českosl. Farmacie, 1966, No. 4, 206.

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