THE QUESTION OF THE CONTENT OF ARCTIIN IN THE SEEDS OF Arctium leiospermum

L. D. Yakhontova and P. N. Kibal'chich

UDC 547.918

Arctiin, which is a monoglucoside of the lignane aglycone arctigenin, is widely distributed in plants of the family Compositae [1] and is also found in representatives of other families [2, 3]. It was first isolated from the seeds of Arctium lappa L. and then from Ar. minus (Hill) Bernh. and Ar. tomentosum (Mill) [1].

There is no information on the content of arctiin in Ar. leiospermum Juz. et Serg. in the literature. However, I. A. Kharlamov, R. L. Khazanovich, and Kh. Kh. Khalmatov [4] have reported the isolation from the fruit of Arctium leiospermum of a compound with the composition $C_{15}H_{18}O_6$, mp 98-100°C, having in the IR spectrum absorption bands at (cm^{-1}) 3400 (OH), 2925, 2850, 1465 (CH_2), and 1760 (C=O). The substance was characterized as the sesquiterpene lactone arctin. We have further purified the sample of arctin sent to VILR [All-Union Scientific-Research Institute for Medicinal Plants] by the authors mentioned above by recrystallizing it from aqueous ethyl acetate. A substance was obtained with the composition $C_{27}H_{34}O_{11} \cdot H_2O$, mp 110-112°C, $[\alpha]^{20}_D -49.3°$ (c 0.45; ethanol); UV spectrum: λ_{max} 230, 280 nm (log ε 4.17, 3.75); IR spectrum, cm^{-1}: 1785 (C=O), 1595, 1525 (aromatic C=C); NMR spectrum (in CD_3OD), δ: 3.69, 3.73 (9 p.u., 3 CH_3O), 6.6-7.0 (6 p.u., multiplet, aromatic H).

The results of a comparison of the physicochemical characteristics of this substance with those described in the literature for arctiin [2] permitted the hypothesis that arctin is arctiin. A mixture with a sample of arctiin which we isolated from the seeds of Ar. lappa gave no depression of the melting point, and the IR spectra of the two substances coincided (Fig. 1).

The methylation of arctigenin with dimethyl sulfate and subsequent oxidation of the O-methyl derivative with potassium permanganate in acetone in the presence of acetic acid led to veratric acid [mp 178-179°C; IR spectrum: 1690 cm^{-1} (C=O)], shown to be identical with an authentic sample. The facts presented give us grounds for stating that arctin is actually the known lignane glucoside arctiin.

EXPERIMENTAL

Purification of Arctin. With heating, arctin was dissolved in the minimum amount of ethyl acetate containing about 1% of water. The crystals that deposited on standing were filtered off, washed with ethyl acetate, and dried; composition $C_{27}H_{34}O_{11} \cdot H_2O$, mp 110-112°C, $[\alpha]^{20}_D -49.3°$ (c 0.45; ethanol). The analytical results for this and all the following substances corresponded to the calculated figures.

Isolation of Arctiin from the Seeds of Ar. lappa. The comminuted seeds (0.5 kg) were defatted with petroleum ether, after which they were extracted with ether and then with chloroform. The chloroform extract was evaporated to dryness. The residue was treated with ethanol, and after a short time of standing crystals were obtained (~ 15 g). After recrystallization from ethyl acetate containing about 1% of water, the substance had mp 110-111°C; the melting point of a mixture with the recrystallized arctin was 109-111°C. The IR spectra of the two substances coincided completely.

Preparation of Arctigenin. A mixture of 0.1 g of arctiin and 15 ml of 0.2 N sulfuric acid was heated in the water bath at 80°C for 1 h. The resinous substance that deposited was separated off, washed with water to neutrality, dried, and recrystallized from ethanol. Composition $C_{21}H_{24}O_6$, mp 98-99°C.

All-Union Scientific-Research Institute for Medicinal Plants. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 299-301, May-June, 1971. Original article submitted December 22, 1970.

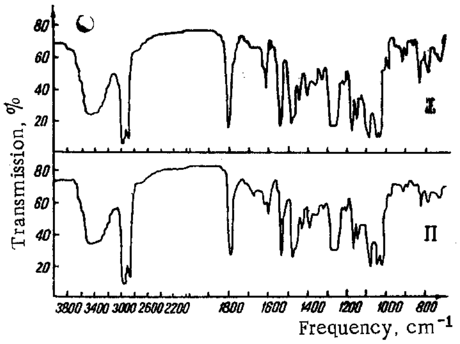

Fig. 1. IR spectra of arctin (I) and arctiin (II).

Methylation of Arctigenin and Oxidation of the Methyl Ether with Potassium Permanganate. A solution of 0.25 g of arctigenin in 2.5 ml of 4% KOH in methanol was treated with 1.5 ml of dimethyl sulfate, the mixture was heated to the boil, and a 50% solution of KOH in water was slowly added. The methanol was distilled off in vacuum, the residue was treated with 5% sulfuric acid, and the mixture was boiled for 5 min. The arctigenin methyl ether was extracted with chloroform, and the chloroform solution was dried with sodium sulfate and evaporated in vacuum.

The residue (0.24 g) was dissolved in 50 ml of acetone and, at room temperature, portions of 0.1 g of finely ground $KMnO_4$ and 0.25 ml of CH_3COOH were added. A total of 0.6 g of $KMnO_4$ and 1.5 ml of CH_3COOH was added. The reaction mixture was filtered, and the filtrate was evaporated to dryness in vacuum.

The residue was treated with chloroform, and the chloroform extract was washed with sodium bicarbonate solution. The acidification of the bicarbonate solution gave 0.1 g of veratric acid, $C_9H_{10}O_4$, mp 178-179°C (from water). The melting point of a mixture with an authentic sample was 177-178°C.

SUMMARY

It has been established that the arctin isolated from the seeds of *Arctium leiospermum* and described earlier as a sesquiterpene lactone is actually the known lignane glucoside arctiin.

LITERATURE CITED

1. R. Hänsel and H. Schulz, Z. Naturforschung, **19**, No. 8, 727 (1964).
2. Suco Hisada, Chem. Pharm. Bull., **16**, No. 11, 2308 (1968).
3. H. Thieme and H. J. Winkler, Pharmazie, **23**, No. 7, 402 (1958).
4. I. A. Kharlamov, R. L. Khazanovich, and Kh. Kh. Khalmatov, Khim. Prirodn. Soedin., **3**, 350 (1967).