

## TRITERPENOIDS OF THE LEAVES AND BARK OF THE BLACK-BARK FORMS OF THE WHITE BIRCHES *Betula pendula* AND *B. pubescens*

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Continuing a study of the chemical composition of the leaves and bark of birches, we have determined the triterpene compositions of specimens of the black-bark forms of *Betula pendula* Roth. and *B. pubescens* Ehrh. growing wild in the forest-steppe of the trans-Urals region, which is of great importance for selection and systematization. As is known black-bark birches are found sporadically, and only a few examples have been detected in Kurgan province. Samples of leaves and bark were collected on June 13, 1989.

During analysis, the leaves were extracted with ether, and the extracts were worked up by a known procedure [1]. There were no triterpenoids in the unsaponifiable part of the ethereal extract of *B. pubescens* leaves, which is characteristic for birches of this species [2]. As has been shown previously [3], the qualitative and quantitative compositions of the triterpenoids in the leaves of *B. pendula* depend essentially on the collection site. Therefore, in order to compare the composition of the leaves of a black-bark birch with those of a corresponding white-bark *B. pendula*, we collected leaves of a white bark *B. pendula* from the same region at the same time. The results of the analyses are presented in Table 1. The levels of triterpenoids are given as percentages on the weight of the air-dry leaves. Minor components were not determined. It can be seen from Table 1 that the chemical compositions of the leaves of the white- and black-bark birches differed little from one another and the amounts of the main component — betulafolienetetraol (2) — practically coincided. Of those studied earlier, the closest to them in the qualitative composition of the triterpenoids was *B. pendula* growing in the environs of Semipalatinsk, but the amount of triterpenoids in this was considerably lower [3].

Samples of bark from the black-bark forms of *B. pendula* and *B. pubescens* were extracted with chloroform, and the extracts were analyzed by GLC. The analysis was conducted on a Tsvet instrument with a flame-ionization detector in a steel column (0.4 × 150 cm) containing 3% of SE-30 on Chromaton N-AW HMDS (0.200-0.250 mm), with the carrier gas helium (50 ml/min). The temperature was raised from 230 to 275°C at a rate of heating of 3°C/min. The amounts of triterpenes were estimated by the internal-standard method, with cholestane as the internal standard. Before analysis, all the samples were esterified with diazomethane since they contained triterpene acids (betulinic and oleanolic acids (6 and 7), the ratio of which was not determined, since they were not separated under the analytical conditions used). The results obtained are presented in Table 2.

Minor components were not determined. The chemical compositions of the barks of the white-bark forms of *B. pubescens* and *B. pendula* have been described in detail in [4]. The black-bark birches have the same qualitative composition of the triterpenoids, but their amount is considerably less (by a factor of 2-3). It may be noted that in the white-bark and black-bark forms of *B. pubescens* the amount of betulin (4) was far lower than in the corresponding samples of *B. pendula*. If we compare the composition of the bark of the specimens studied with the chemical composition of the bark of the far-eastern black-bark birch *B. davurica* the difference will be at the qualitative level, since a high content of oleanolic acid and its derivatives is characteristic for *B. davurica* [5].

Thus, from the point of view of phylogeny, the results of the study of the triterpenoids in the leaves and bark of black-bark forms of *Albae* birches show that the probability of their close relationship with far-eastern black-bark birches of the

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TABLE 1. Compositions of Ethereal Extracts of *B. pendula* Leaves

Form of birch	Unsaponifiable part of the ethereal extract	Betulafo- lienetriol (1)	Betulafo- lienetetraol (2)	Dammar-25-ene- 3 $\alpha$ ,12 $\beta$ ,17 $\alpha$ , 20(S), 24-pentaol (3)
Black-bark	3.46	0.09	0.32	0.044
White-bark	3.39	0.18	0.33	0.096

TABLE 2. Compositions of Chloroform Extracts of Birch Bark

Species of birch	Chloroform extract, % on the weight of the bark	Amount of triterpenes in the extract, %		
		Betulin (4)	Lupeol (5)	Triterpene acids (6, 7)
<i>B. pendula</i>	12.13	28.4 $\pm$ 1.3	2.86 $\pm$ 0.07	7.2 $\pm$ 0.5
<i>B. pubescens</i>	9.16	8.5 $\pm$ 0.5	2.75 $\pm$ 0.04	5.5 $\pm$ 0.3

*Dahuricae* section is extremely problematical. It is most likely that their origin was the result of spontaneous mutations affecting the chemical composition of the bark more profoundly.

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