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ISOPRENOIDS OF THE OUTER BARK OF THE FAR EASTERN BIRCHES Betula costata AND Betula ermanii

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Continuing an investigation of the chemical composition of Far Eastern birches [1, 2], we have studied extracts of the outer bark of Betula castata Trautv., which is widespread in the southern part of the Far East (samples 1-4) and B. ermanii Cham. (Erman's birch) growing on Kamchatka, Sakhalin, and the Kurile islands (sample 5). Both species of birch belong to the subgenus Neurobetula V. Vassil. [3].

The air-dried bark was extracted with chloroform in a Soxhlet apparatus for 14 h. The dry residue obtained by evaporation in vacuum was separated on a chromatographic column of KSK silica gel using the solvent system petroleum ether—acetone. This led to the isolation of β-sitosterol (I) and eight triterpenoids: 3β-acetyl-11α,12α-epoxyolean-28,13-olide (II) [4], the acetate of oleanolic acid (III), lupeol (IV), methyl oleanolate (V), betulin (VI), betulinic acid (VII), oleanolic (VIII), and betulin caffeate (IX). Compounds (VI-IX) were isolated after the acetylation of the fraction containing a difficultly separable mixture of these components.

Extracts of the bark of B. costata and B. ermanii (samples 2 and 5) showed antioxidant activity according to the method of Maximov et al. [5]. The activity of these samples is obviously connected with the presence of betulin caffeate [6], since this component was present only in summer samples of the bark. The results of the investigation are given in Table 1. The structures of the compounds isolated were confirmed by mixed melting points with authentic samples (no depression of the melting points was observed) and by comparison of their IR spectra.

TABLE 1.

Sample and time of collection	Yield of extract	Yield of the composition, % of the total air-dried bark								
		I	II	III	IV	V	VI	VII	VIII	IX
B. costata 9. V 1986	15,15	—	0,019	0,3	0,19	—	3,00	—	1,5	—
18. VI 1984	15,6	0,027	—	0,7	0,13	0,015	2,44	0,08	1,4	0,04
14. IX 1984	23,4	—	—	0,55	0,11	0,016	5,27	—	1,23	—
20. XII 1984	17,7	—	—	0,3	0,16	—	2,94	—	1,41	—
B. ermanii 26. VIII 1984	21,0	—	—	0,42	0,23	—	2,37	—	1,12	0,26

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METHYLATED STEROLS FROM POLYENE-RESISTANT STRAINS OF THE YEAST Saccharomyces cerevisiae

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Yeasts of the species *Saccharomyces cervisiae* are rich in sterols and form a source of ergosterol, 22,23-dihydroergosterol, and zymosterol [1]. An increase in resistance to polyene antibiotics leads to an accumulation of new sterols by the yeast cells [2]. The composition of the sterols from strains of the yeast resistant to polyene antibiotics and having functional disturbances of the $\Delta^8 \rightarrow \Delta^7$-isomerase or 22,23-dehydrogenase — enzymes regulating the biosynthesis of ergosterol — has been analyzed.

The sterol components were isolated from the unsaponifiable lipid fractions of yeast strains resistant to polyene antibiotics by thin-layer chromatography [Silufol plates impregnated with a 20% aqueous solution of $AgNO_3$ in the chloroform—acetone (95:5) system]. In nine strains the amount of compounds with R_f 0.73 detected was considerably greater than for other intermediates in the biosynthesis of ergosterol that we have identified previously [3]. The unknown sterols were identified by mass spectrometry on a Varian MAT instrument (temperature of the ion source 120°C; accelerating voltage 3.5 kV; ionization energy 70 eV).

Mass spectrum of compound (I) (direct introduction), m/z, %: 426 $[C_{30}H_{50}O]^+$, 87; 411 $[C_{29}H_{47}O]^+$, 100; 393 $[C_{29}H_{45}]^+$, 61; 383 $[C_{27}H_{43}O]^+$, 73; 327 $[C_{23}H_{35}O]^+$, 22; 245 $[C_{17}H_{25}O]^+$, 61.

Mass spectrum of compound (II) (direct introduction), m/z, %: 412 $[C_{29}H_{48}O]^+$, 35; 397 $[C_{28}H_{45}O]^+$, 100; 395 $[C_{28}H_{43}O]^+$, 30; 313 $[C_{22}H_{33}O]^+$, 12; 299 $[C_{21}H_{31}O]^+$, 25; 245 $[C_{17}H_{25}O]^+$, 49; 231 $[C_{16}H_{23}O]^+$, 72.

The presumed elementary compositions of the fragmentary ions formed on the breakdown of the molecules of compounds (I) and (II) were confirmed by the results of high-resolution mass spectrometry on a MKh-1320 instrument with direct introduction. The resolving capacity of the instrument was 10,000-12,000 at an accelerating voltage of 2.5 kV and an ionization energy of 70 eV.

Strong peaks of molecular ions with m/z 426 and 412, and also base peaks with m/z 411 and 397, respectively ($[M - 15]^+$) indicated that the compounds being analyzed were sterols methylated in positions 4 and 14 [4].

On comparing the mass spectra that we had obtained with the spectra given in [5] of 4,14-dimethylergosta-8,24(28)-dien-3β-ol ($m/z \geq 200$) (%): 426 (39); 411 (100), 393 (10), 383 (7), 327 (14), 245 (21); and 14-methylergosta-8,24(28)-diene-3β-ol ($m/z \geq 200$) (%): 412 (32), 397 (100), 379 (5), 369 (5), 313 (14), 299 (10), 245 (12.5), 231 (32); it was found that the spectra of compounds I and II contained the peaks of almost all the characteristic

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