SUMMARY

1. The comparative influence of substituting groups on the chemical shifts of the C-methyl groups of sesquiterpene alcohols of the carotane and humulane series in dependence on the nature and position of the substituent has been studied.

2. On the basis of the results obtained, a relative configuration of akitschenol has been put forward.

LITERATURE CITED

1. A. Sh. Kadyrov and G. K. Nikonov, Khim. Prirodn. Soedin., 59 (1972).
2. A. I. Saidkhodzhaev and G. K. Nikonov, Khim. Prirodn. Soedin., 559 (1972); 28 (1973); 166 (1964); 525, 526 (1974); 105 (1976).
3. A. Sh. Kadyrov, A. I. Saidkhodzhaev, and U. Rakhmankulov, Khim. Prirodn. Soedin., 284 (1977).
4. T. Kh. Khasanov, A. I. Saidkhodzhaev, and G. K. Nikonov, Khim. Prirodn. Soedin., 528 (1974).
5. A. Sh. Kadyrov, A. I. Saidkhodzhaev, and G. K. Nikonov, Khim. Prirodn. Soedin., 102 (1976).
6. G. V. Sagitdinova and A. I. Saidkhodzhaev, Khim. Prirodn. Soedin., 790 (1977).
7. L. A. Golovina and A. I. Saidkhodzhaev, Khim. Prirodn. Soedin., 796 (1977).
8. A. I. Saidkhodzhaev, Khim. Prirodn. Soedin., 70 (1978).
9. A. Sh. Kadyrov and A. I. Saidkhodzhaev, Khim. Prirodn. Soedin., 137 (1978).
10. A. I. Saidkhodzhaev, N. D. Abdullaev, T. Kh. Khasanov, G. K. Nikonov, and M. R. Yagudaev, Khim. Prirodn. Soedin., 517 (1977).
11. A. Sh. Kadyrov, A. I. Saidkhodzhaev, and G. K. Nikonov, Khim. Prirodn. Soedin., 152 (1975).
12. M. S. Sriraman, B. A. Nagasampagi, R. S. Pandey, and Sukh Dev, Tetrahedron, 29, 985 (1973).
13. M. E. Perel'son, A. A. Kir'yanov, A. I. Ban'kovskii, N. P. Kir'yalov, and T. V. Bukreeva, Khim. Prirodn. Soedin., 442 (1976).

TRITERPENES FROM THE LEAVES OF *Betula ermanii*

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Continuing a study of Far Eastern species of the genus *Betula* [1], from the leaves of *Betula ermanii** we have isolated two new triterpenes (I) and (II) (in order of increasing polarity).

The IR spectrum of triterpene (I) has the bands of hydroxyl absorption at 3570 and 3620 cm^{-1}, and also an absorption band at 1725 cm^{-1}, which is characteristic for an ester carbonyl. A fragment with m/e 143 (100%) in the mass spectrum of (I) showed the presence of a side chain in the form of a substituted tetrahydrofuran ring [2]. In the PMR spectrum of (I) there are the signals of the protons of eight tertiary methyl groups with δ (ppm): 0.78 (3H, s), 0.94 (6H, s), 0.98 (3H, s), 1.04 (3H, s), 1.12 (6H, s), and 1.21 (3H, s), and the signal of the protons of the methyl group of an acetate residue at 1.98 ppm (3H, s).

In the weak-field region a signal appears at 5.08 ppm (1H, multiplet), which could not be assigned solely with the aid of PMR spectroscopy to a definite proton. In the same region there are signals at 3.18 ppm (1H, triplet, $J \sim 8$ Hz), due to an axial proton, and at

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*The leaves were collected by V. I. Baranov, a post-graduate student in the chemotaxonomy laboratory, on August 12, 1975, in the Kamchatka oblast.

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3.72 ppm (1H, triplet) which, by analogy with the spectra of 20(S),24(R)-epoxydammarane-3α,12β,25-triol [3] and 20(S),24(R)-epoxydammarane-3α,12β,17α,25-tetraol [1] have been assigned to the protons at C-3 and C-24, respectively. The value of the chemical shift and the value of the spin—spin coupling constants of the C-3 proton of the triterpene (I) show the β configuration of the hydroxy group at this carbon atom. In the ^{13}C NMR spectrum of (I), the C-3 signal at 76.2 ppm also confirms the β configuration of the OH group at C-3 [4].

When triterpene (I) was saponified with an ethanolic solution of caustic soda we obtained the triterpene (II), which gave no depression of the melting point in admixture with (II) isolated directly from the leaves of *Betula ermanii*.

The IR spectrum of (II) has bands of hydroxylic adsorption at 3470 and 3615 cm^{-1} (free OH). In the mass spectrum of (II) a peak with m/e 143 (100%) shows the presence of a side chain of the same type as in the triterpene (I). In the PMR spectrum of the triterpene (II) there are the signals of the protons of eight tertiary methyl groups with δ (ppm): 0.79 (3H, s), 0.90 (3H, s), 0.96 (6H, s), 1.03 (3H, s), 1.12 (6H, s), and 1.19 (3H, s), and also the signals of protons on carbon atoms bearing oxygen functions at δ (ppm): 3.18 (1H, triplet) and 3.72 (1H, triplet) from the protons at C-3 and C-24, respectively, and 3.80 (1H, multiplet, $\Sigma J > 20$ Hz), which shows the presence of an axial proton. It did not appear possible to assign this signal unambiguously to a definite proton.

The position of the third hydroxy group in (II) and, correspondingly, of the acetate group in (I) was established by comparing the ^{13}C NMR spectra of the triterpene (II) and of 20(S),24(R)-epoxydammarane-3α,12β,25-triol (betulafolienetriol oxide).

Below we give the signals of some of the carbon atoms in the ^{13}C NMR spectra of the triterpene (II) and betulafolienetriol oxide:

Carbon atom	C_3	C_5	C_6	C_{12}	C_{13}	C_{14}	C_{17}	C_{20}	C_{24}	C_{25}
Triterpene (II)	78.4	56.2	71.0		40-42	49.9	55.8	86.0	83.4	71.5
Betulafolienetriol oxide	76.2	49.8		71.2	48.2	50.5	52.3	86.6	85.5	70.2

On comparing the chemical shifts of the carbon atoms in the δ 45-60-ppm region, we came to the conclusion that the downfield shift of the C-17 signal in the spectrum of (II) by Δδ 3.5 ppm and the upfield shift of the C-13 signal by Δδ 8 ppm shows the absence of an OH group at C-12 in the triterpene (II) [5]. The downfield shift of the C-5 signal by Δδ 6.4 ppm may show the presence of an OH group at C-6. To confirm this, from (II) we obtained the diketone (III) and recorded its ^{13}C NMR spectrum, in which a characteristic downfield shift by Δδ 6 ppm of the C-5 signal as compared with the C-5 signal in the spectrum of (II) is observed [6].

The ease of formation of the diacetate (IV) indicates the α configuration of the hydroxy group at C-6. It is known that the 6α-OH group in zeorin is acetylated under mild conditions, while the 6β-OH group in epizeorin forms an acetate with far greater difficulty [7]. Shibata et al. [8], in determining the structure of panaxatriol, reported the ease of acetylation of the equatorial 6α-OH group.

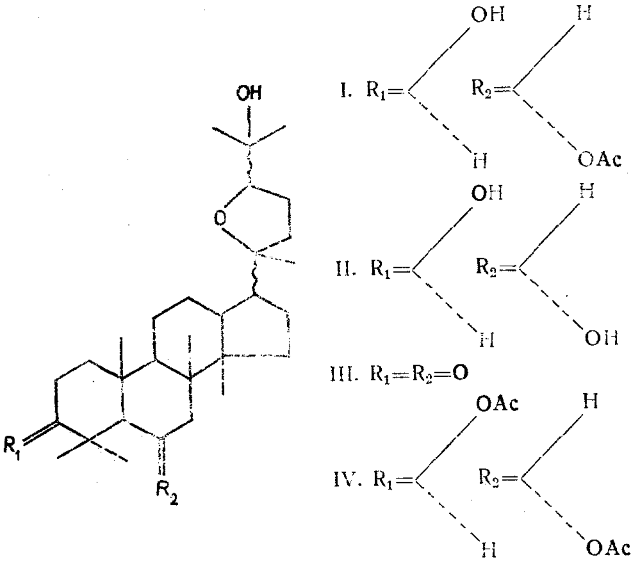
On the basis of these facts, for the triterpene (I) we propose the structure of 6α-acetoxy-20,24-epoxydammarane-3β,25-diol, and for (II) 20,24-epoxydammarane-3β,6α,25-triol.

It must be mentioned that the triterpene (I) together with (II) have been detected in the leaves of material collected in August, while the leaves collected at an earlier period (July 14) contained only the triterpene (II).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer, the mass spectra on an MKh-1303 spectrometer, and the PMR and ^{13}C NMR spectra on a Brüker HX-90E instrument in $CDCl_3$ with TMS as internal standard (δ scale).

For chromatography we used type-KSK silica gel. The individuality of the substance was characterized by thin-layer chromatography in silica gel in the following systems: 1) benzene—ethanol (10:1) and 2) petroleum ether—acetone (2:1). For detecting the triterpenes on the chromatograms we used a 10% solution of H_2SO_4 in methanol.



Isolation of the Triterpenes (I) and (II). The air-dry leaves of *Betula ermanii* (4 kg) were treated by the method of Fischer and Seiler [9]. This gave 22 g of an unsaponifiable fraction of the ethereal extract, which was chromatographed on silica gel, with elution by petroleum ether—acetone systems. Petroleum ether—acetone (20:1) yielded the triterpene (I), $C_{32}H_{54}O_5$, crystallizing with a molecule of acetone, yield 0.5 g (2.3%), mp 199-201°C (petroleum ether, acetone), $[\alpha]_D^{20}$ +14.8° (c 0.5, $CHCl_3$). Mass spectrum: M^+ 518, m/e 500 ($M^+ - H_2O$), 485 ($M^+ - CH_3 - H_2O$), 482 ($M^+ - 2H_2O$), 459 ($M^+ - [(CH_3)_2C^+{-}OH]$), 399, 207, 143 (100%). In the petroleum ether—acetone (10:1) system we obtained the triterpene (II), $C_{30}H_{52}O_4$, yield 1.22 g (55%), mp 216-218°C (petroleum ether) $[\alpha]_D^{20}$ +24.4° (c 0.5, $CHCl_3$). Mass spectrum: M^+ 476, m/e 461 ($M^+ - CH_3$), 458 ($M^+ - H_2O$), 443 ($M^+ - CH_3 - H_2O$), 440 ($M^+ - 2H_2O$), 417 ($M^+ - [(CH_3)_2C{-}OH]$), 339, 143 (100%).

Hydrolysis of the Triterpene (I). A solution of 33 mg of the sapogenin (I) in 1 ml of ethanol was treated with 4 ml of a 0.1 N ethanolic solution of KOH. Saponification was carried out with stirring at 20°C for 3 days. After the usual working up, the residue was chromatographed on silica gel.

The petroleum ether—acetone (20:1) system eluted 15 mg of the initial (I), and petroleum ether—acetone (8:1) eluted 12 mg of a substance (mp 216-218°C, from petroleum ether) which gave no depression of the melting point in admixture with compound (II).

Oxidation of the Triterpene (II). A solution of 47 mg of the product in 1 ml of pyridine was treated with 60 mg of CrO_3 in 1.5 ml of pyridine. Oxidation was continued at 20°C for 2 days. As a result of the reaction we obtained 35 mg of the diketone (III), mp 169-172°C (hexane), $[\alpha]_D^{20}$ +46° (c 0.5, $CHCl_3$).

Acetylation of the Triterpene (II). A mixture of 212 mg of compound (II) and 3 ml of pyridine was treated with 1.5 ml of acetic anhydride at 20°C for 7 days. After the usual working up, the residue was chromatographed in silica gel in the petroleum ether—acetone (45:1) system. This gave 27 mg of a chromatographically homogeneous syrupy substance the PMR spectrum of which showed the signals of the protons of the methyl groups of acetate residues with δ (ppm) 1.95 (3H, s), 1.98 (3H, s), 2.03 (3H, s), and 224 mg of the diacetate (IV), mp 133-135°C (petroleum ether), $[\alpha]_D^{20}$ +35.8° (c 1.0, $CHCl_3$). PMR spectrum (δ, ppm): 0.86 (6H, s), 0.94 (3H, s), 0.97 (3H, s), 1.00 (3H, s), 1.12 (6H, s), and 1.2 (3H, s) — the signals of the protons of Me groups; 1.96 (3H, s) and 2.04 (3H, s) — signals of the protons of acetate Me groups; and 3.66 (1H, triplet), 4.4 (1H, triplet), and 5.02 (1H, multiplet) — the signals of the protons at C-24, C-3, and C-6, respectively.

Saponification of the Diacetate (IV). A solution of 45 mg of the acetate (IV) in 1.5 ml of ethanol was treated with 5 ml of 0.1 N ethanolic KOH. Saponification was carried out at 20°C for 24 h. After the usual working up, the residue was chromatographed on silica gel. The petroleum ether—acetone (15:1) system eluted 28 mg of a substance with mp 199-201°C (petroleum ether, acetone), which gave no depression of the melting point in admixture with (I). The petroleum ether—acetone (5:1) system eluted 13 mg of product (II).

SUMMARY

From the unsaponifiable fraction of an ethereal extract of the leaves of *Betula ermanii* a new triterpene of the dammarane series — 20,24-epoxydammarane-3β,6α,25-triol (II) — and its 6-O-acetyl derivative (I) have been isolated.

LITERATURE CITED

1. N. I. Uvarova, G. V. Malinovskaya, and G. B. Elyakov, Tetrahedron Lett., 4617 (1976).
2. M. Nagai, N. Tanaka, O. Tanaka, and S. Ichikawa, Chem. Pharm. Bull., 21, 2061 (1973).
3. M. Nagai, N. Tanaka, S. Ichikawa, and O. Tanaka, Tetrahedron Lett., 4239 (1968).
4. J. Asakawa, R. Kasai, K. Yamasaki, and O. Tanaka, Tetrahedron, 33, 1935 (1977).
5. H. Eggert, C. L. Van Antwerp, N. S. Bhacca, and C. Djerassi, J. Org. Chem., 41, 71 (1976).
6. S. A. Knight, Org. Magn. Res., 6, 603 (1974).
7. S. Huneck, Chem. Ber., 94, 614, 1151 (1961).
8. S. Shibata, O. Tanaka, K. Soma, Y. Iida, T. Ando, and H. Nakamura, Tetrahedron Lett., 207 (1965).
9. F. C. Fischer and N. Seiler, Lieb. Ann. Chem., 626, 185 (1959).

THE HYDROLYSIS OF THE SAPONINS OF *Aralia manchurica*

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The saponins of *Aralia manchurica* (Manchurian aralia) consist of glycosides of oleanolic acid (aralosides A, B, and C). In addition to a tincture, which is used in medicine as a tonic, the total preparation "Saparal" recommended for the same purposes, is obtained from the Manchurian aralia [1]. The latter includes all three aralosides. Oleanolic acid and its semisynthetic derivatives, which possess physiological activities of various types [2-4], may be widely introduced into the practice of the public health service.

It appeared of interest to study the hydrolysis of the saponin aralosides, since the industrial wastes from the production of "Saparal" may serve as an additional source for the production of oleanolic acid.

Literature information relating to the conditions of the hydrolysis of the saponins of the Manchurian aralia is contradictory: Various hydrolysis mixtures and temperature conditions are proposed [5]. Moreover, the aglycone obtained in the process of hydrolysis requires additional purification from the products of transformation of sugars. To solve the problem posed we have investigated the hydrolysis of samples of the technical preparation "Saparal" kindly provided by the experimental factory of the All-Union Scientific-Research Institute of Medicinal Plants.

Below we give details of hydrolysis in various systems. The analysis of the samples was carried out every 5 min by thin-layer chromatography ["Silufol" plates, solvent system chloroform—methanol—water (61:32:7)]

Hydrolizing Mixture ratio (1:1)	Temperature, °C	Time of Hydrolysis
Water — 10% H_2SO_4	120	More than 4 h
Water — 20% H_2SO_4	"	"
Water — 30% H_2SO_4	"	"
CH_3COOH — 10% H_2SO_4	"	1 h 30 min
CH_3COOH — 20% H_2SO_4	"	30 min
CH_3COOH — 30% H_2SO_4	"	30 min
Acetone — 10% H_2SO_4	80	More than 4 h
Acetone — 20% H_2SO_4	"	"

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