ANALYSIS OF COMPOSITION OF THE NEUTRAL FRACTION OF THE OLEORESIN OF Abies sibirica USING A SCHEME OF GROUP SEPARATION

V. A. Raldugin, O. V. Sudakova, L. I. Demenkova,
and V. A. Pentegova

UDC 547.593.2

Information has been published on the composition of the acid fraction [1-3], the volatile components [4, 5] and the neutral diterpenoids [1, 6-8] of the oleoresin of the Siberean fir Abies sibirica Ledb., which is produced on the industrial scale. In view of the tendency of one of its components – cis-abienol [1, 6] – to undergo isomerization [9, 10] and polymerization [1], the facts relating to the neutral diterpenoids require refinement under conditions of analysis excluding the use of high-temperature facuum distillation. We have separated the neutral fraction of the oleoresin collected in the Maslyanino region of Novosibirsk province by the scheme of the group separation of conifer oleoresins [11]. In this way we obtained fractions of hydrocarbons (40%; here and below, on the neutral part), of carbonyl compounds and oxides (22%), of tertiary nonpolar alcohols (31%), of polar monohydric alcohols (3%), and of polyfunctional compounds (3%). In addition, we isolated a small fraction (1%), eluted before the combined nonpolar alcohols, that consisted of a mixture (1:1) of caryophyllene α-oxide [5] and 6,7-epoxyhumulene [12], which were identified from their PMR spectra after their separation.

The total hydrocarbons, according to GLC (5% SE-30, 3 mm × 2 m column) consisted of monoterpenes (82.0%), sesquiterpenes (17.7%), and diterpenes (0.3%). The latter contained 63.0% of abietadiene, 14.8% of isopimaradiene and not less than six other hydrocarbons, present in minor amounts.

The fractions of oxygen-containing compounds were investigated by the scheme of [11]. Bornyl acetate [5] amounted to ~80% of the fraction of carbonyl compounds and oxides, which also contain 15% of aldehydes and 5% of oxides. The main oxide (~70% of the combined oxides) was manoyl oxide [8], and the aldehydes were represented by abietinal [6], isopimarinal (the main component), and dihydroabietinal.

The fraction of tertiary nonpolar alcohols was represented by cis-abienol (~83% of the fraction), (+)-nerolidol ($[\alpha]_D^{19}$ +13° (c 2.26; $CHCl_3$)), and α-bisabolol [5]. There were no neoabienol [8], isoabienol [6], or trans-abienol [13]. Polar monohydric alcohols were represented by acetylated (65%) and nonacetylated (15%) alcohols. The latter were, in the main, sesquiterpene alcohols that have been described previously [5]. By chromatography on SiO_2, the acetates were separated into two fractions homogeneous according to TLC (in a ratio of ~1:3). The first of them, according to its PMR spectrum, consisted of a mixture of the acetates of isopimarinol (main component), of abietinol, of isopimara-8,15-dien-18-ol, of levopimarinol, and, in traces, of dehydroabietinol. The second fraction consisted of a mixture of bornyl acetate and the acetates of other monoterpene alcohols described in [5].

In view of its small amount, the fraction of polyfunctional compounds was not investigated in detail. The absence from it of polyabienol and of 15,16-bisnorlabd-18(14),11-dien-13-one, which have been found previously [6, 7] in the neutral fraction of the oleoresin that had been subjected to high-temperature vacuum distillation, was shown by TLC.

Thus, in the oleoresin of the Siberian fir, as in the oleoresins of other fir species [14, 15], cis-abienol is the main neutral diterpenoid. It is accompanied by abietane and isopimarane derivatives and all the other labdanoids described for this oleoresin apart from manoyl oxide are secondary, not native, compounds.

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 601-602, July-August, 1988. Original article submitted January 4, 1988.

LITERATURE CITED

1. G. V. Pigulevskii and V. G. Kostenko, Questions of the Chemistry of Terpenes and Terpenoids [in Russian], Vilnius (1960), p. 147.
2. É. N. Shmidt, N. K. Kashtanova, L. N. Vol'skii, M. A. Chirkova, and V. A. Pentegova, Izv. Sib. Otd. Akad. Nauk SSSR, Series No. 5, Issue No. 12, 118 (1970).
3. V. A. Raldugin, O. V. Sudakova, V. I. Bol'shakova, N. I. Yaroshenko, É. N. Shmidt, and V. A. Pentegova, Khim. Prir. Soedin., 517 (1968).
4. M. A. Chirkova and V. A. Pentegova, Izv. Sib. Otd. Akad. Nauk SSSR, 145 (1962).
5. T. F. Titova, V. A. Khan, Zh. V. Dubovenko, and V. A. Pentegova, Khim. Prir. Soedin., 460 (1987).
6. M. A. Chirkova, A. E. Gorbunova, A. I. Lisina, and V. A. Pentegova, Khim. Prir. Soedin., 99 (1966).
7. M. A. Chirkova, A. K. Dzizenko, V. A. Pentegova, Khim. Prir. Soedin., 86 (1967).
8. M. A. Chirkova and V. A. Pentegova, Khim. Prir. Soedin., 187 (1960) [sic].
9. V. A. Raldugin and V. A. Pentegova, Khim. Prir. Soedin., 595 (1971).
10. P. F. Vlad, M. N. Koltsa, and A. G. Russo, Zh. Obshch. Khim., 43, 68 (1973).
11. V. A. Raldugin, V. A. Khan, Zh. V. Dubovenko, and V. A. Pentegova, Khim. Prir. Soedin., 609 (1976).
12. S. Dev, Tetrahedron, 24, 4113 (1968).
13. P. F. Vlad, A. G. Russo, and Chan Kuang Fan, Zh. Obshch. Khim., 39, 451 (1969).
14. É. N. Shmidt, Z. A. Isaeva, Zh. V. Dubovenko, and V. A. Pentegova, Khim. Prir. Soedin., 395 (1981).
15. P. S. Gray and J. S. Mills, J. Chem. Soc. Suppl. I, 5822 (1964).

TRITERPENOIDS AND STEROIDS OF SOME SPECIES OF THE ORDER ERICALES

G. A. Fokina, N. E. Zaitseva, and N. E. Fokina

UDC 547.913

Plants of the order Ericales (Ericaceae) are producing agents of substances of phenolic nature and also of compounds of the isoprenoid class [1]. We have investigated 17 species of the families Ericaceae, Pyrolaceae, Monotropaceae, and Empetraceae. It was found that all the plants studied contained triterpenoids both of neutral nature and of the acid type. On GLC analysis of methylated extracts of the materials under investigation [2], two triterpene acids were detected — oleanolic and ursolic. The relative amounts of the latter ($K_{ol/urs}$) expressed as the ratio of the areas of the peaks of the methyl esters of these acids were determined:

Plant	$K_{ol/urs}$
Family Ericaceae Juss.	
Andromeda polifolia L. (bog rosemary andromeda)	0.80
Arctostaphylos uva-ursi (L.) Spreng. (bearberry)	2.70
Arctous alpina (L.) Niedenzu (arctic ptarmiganberry)	0.35
Calluna vulgaris (L.) Hull. (Scotch heather)	0.22
Cassiope ericoides (Pall.) D. Don	0.54
Chamaedaphne calyculata (L.) Moench. (leatherleaf)	0.65
Oxycoccus palustris Pers. (cranberry)	0.59
Phyllodoce caerulea (L.) Bab. (blue mountain heath)	0.39
Vaccinium arctostaphylos L. (Caucasian whortleberry)	0.22
V. ovalifolium Smith (ovalleaf whortleberry)	2.65
V. uliginosum L. (bog blueberry)	0.75
V. vitis-idaea L. (cowberry)	0.50

(continued on following page)

V. L. Komarov Botanical Institute, Academy of Sciences of the USSR, Leningrad. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 602-603, July-August, 1988. Original article submitted July 9, 1987; revision submitted March 14, 1988.

0009-3130/88/2404-0516 $12.50