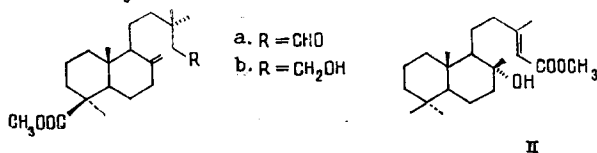


V. I. Bol'shakova, É. N. Shmidt,  
and V. A. Pentegova

UDC 547.914

Continuing a study of the chemical composition of the oleoresins of conifers growing in Transcarpathia [1], we have investigated the composition of the polyfunctional resin acids of the oleoresin of *Pinus mugo* K. (Swiss mountain pine) and of *Pinus strobus* Ledeb. (eastern white pine or Weymouth pine). Methylation of the acidic fraction of the oleoresin followed by chromatography of the combined methyl esters led to the isolation of three esters of bicyclic labdane acids not previously found in the oleoresins of domestic conifers.



From the oleoresin of *Pinus mugo* K. we isolated methyl 15-oxolabd-8-en-19-oate (Ia) and methyl 15-hydroxylabd-8-en-18-oate (Ib). The PMR spectra of the methyl esters (Ia and Ib) were identical with the spectra of the imbricatolalate and imbricatolate [2]. The reduction of (Ia) and (Ib) with  $\text{LiAlH}_4$  in ether gave imbricatodiol with mp 108-109°C,  $[\alpha]_D^{20} + 24.4^\circ$  (c 4.9;  $\text{CHCl}_3$ ), literature [3]: 113-114°C,  $[\alpha]_D^{20} + 24.4^\circ$ .

In the mixtures of methyl ethers of the polyfunctional acids from the oleoresin of the eastern white pine we identified methyl 15-hydroxydehydroabietate and methyl 15-hydroxyabietate (in a ratio of 1:1, GLC), the presence of which is characteristic for the oleoresins of certain pine species [4].

By adsorption chromatography we also isolated methyl 8 $\alpha$ -hydroxylabd-13E-ene-15-oate with mp 88-89°C,  $[\alpha]_D^{20} + 11.2^\circ$  (c 3.5;  $\text{CHCl}_3$ ), which, from its spectral characteristics was close to the methyl sclareolate (II) obtained previously by the oxidation of sclareol [5].

The reaction of (II) with  $\text{LiAlH}_4$  in ether gave labd-13E-ene-8 $\alpha$ ,15-diol with mp 128°C; according to the literature [6]: mp 130-131°C.

In this way, we have shown the presence of sclareolic acid in the acidic fraction of the oleoresin of the eastern white pine.

Thus, bicyclic polyfunctional acids that have not previously been detected in the oleoresins of conifers growing in the USSR have been found in the acidic fraction of the oleoresins of the Swiss mountain pine and the eastern white pine.

## LITERATURE CITED

1. V. I. Bol'shakova, L. I. Demenkova, É. N. Shmidt, and V. A. Pentegova, *Khim. Prir. Soedin.*, 212 (1987).
2. D. F. Zinkel, L. C. Zank, and M. F. Wasolowski, *Diterpene Resin Acids*, US Department of Agriculture/Forest Products Laboratory, Madison (1971).
3. G. Weismann, K. Bruns, and H. F. Grutzmacher, *Tetrahedron Lett.*, No. 51 4623 (1965).
4. V. Yu. Puzanova, É. N. Shmidt, B. A. Radbil', and V. A. Pentegova, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, No. 5, 129 (1986).
5. C. Asselineau, S. Bory, M. Fetizon, P. Laszlo, *Bull. Soc. Chim. France*, No. 7, 1429 (1961).
6. M. T. Calabuig, M. Cortes, C. G. Francisco, R. Hernandez, and E. Suarez, *Phytochemistry*, 20, No. 9, 2255 (1981).

Novosibirsk Institute of Organic Chemistry, Siberian Branch, USSR Academy of Sciences.  
Translated from *Khimiya Prirodnikh Soedinenii*, No. 2, pp. 302-303, March-April, 1988. Original article submitted August 10, 1987.