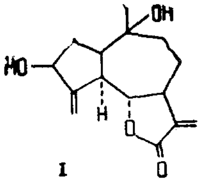
pyrethroidinin structure corresponds to 3,10-dihydroxy-1,5α,7α(H)6β(H)-guaia-4(15),11(13)-dien-6,12-olide.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LITERATURE CITED

1. B. Kh. Abduazimov, A. I. Yunusov, and G. P. Sidyakin, Khim. Prir. Soedin., 649 (1983).
2. B. Kh. Abduzimov, N. D. Abdullaev, A. I. Yunisov, M. R. Yagudaev, and G. P. Sidyakin, Khim. Prir. Soedin., 792, (1984).
3. U. A. Abdullaev, Ya. V. Rashkes, M. I. Yusupov, and Sh. Z. Kasymov, Khim. Prir. Soedin., 796 (1980).
4. U. A. Abdullaev, Ya. V. Rashkes, I. D. Sham'yanov, and G. P. Sidyakin, Khim. Prir. Soedin., 56 (1982).
5. H. Voshioka, T. J. Mabry, M. A. Irwin, T. A. Geissman, and Z. Samek, Tetrahedron, 27, 3317 (1971).
6. F. Bohlmann and C. Zdero, Phytochemistry, 16, 778 (1977).
7. A. G. Gonzales, J. Bermejo, I. Cabrera, G. M. Massanet, H. Mansilla, and A. Galindo, Pytochemistry, 17, 955 (1978).
8. P. S. Kalsi, V. B. Sood, A. B. Masih, D. Gupta, and K. K. Talwar, Phytochemistry, 22, 1387 (1983).
9. S. Das, R. N. Baruan, R. P. Sharma, I. N. Baruan, and P. Kulanthivel, W. Herz, Phytochemistry 22, 1980 (1983).
10. P. S. Kalsi, Sunila Sharma, and Gurdeep Kaur, Phytochemistry, 22, 1993 (1983).
11. S. Oksur and E. Putun, Phytochemistry, 22, 2615 (1983).
12. K. Ito, T. Iido, and T. Kobayashi, Phytochemistry, 23, 188 (1984).

α-BISABOLOL IN NEEDLES OF THE FAMILY Pinacae

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The sesquiterpence alcohol α-bisabolol has been found in the needles of a number of conifers of the family Pinaceae [1] . However, no attention was devoted to which of the four stereoisomers was present in a particular oleoresin. In some cases — for example, for the biogenesis of bisabolol, for the chemotaxonomy of conifers, and for synthetic organic chemistry — the stereoisomeric forms of α-bisabolol may play an important role. The determination of the configurations of the asymmetric carbon atoms of α-bisabolol is a fairly complex problem, but it has been solved by a number of workers using synthesis from known compounds [2]. It follows from these investigations that (+)-α-bisabolol has the 6S configuration, and the (—) form the 6R configuration. The configuration at the carbinol carbon atom (C_7) can be determined from the position of the C_7 methyl group in the PMR spectrum — for 6S,7R- and 6R,7S-α-bisabolols the signals of this group are observed in a weaker field than for the other diasteromers of α-bisabolol (the 6S,7S- and 6R,7R-isomers) [2].

On investigating; the α-bisabolols isolated from six species of conifers: Pinus sibirica ($[\alpha]_D^{19}$ +50° (c 4,8; $CHCl_3$)) ; Pinus koraiensis ($[\alpha]_D^{20}$ +49,4° (in the pure form)); Picea ajanensis ($[\alpha]_D^{24}$ +43° (c 3,25; $CHCl_3$)) ; Abies sibirica ($[\alpha]_D^{20}$ +62° (in the pure form)); Abies semenovii ($[\alpha]_D^{22}$ +62° (in the pure form)), and Abies nephrolepis ($[\alpha]_D^{22}$ +70° (c 1,7; $CHCl_3$)),— we found that all the oleoresins mentioned contained dextrorotatory α-bisabolol. Thus, they must have the 6S configuration in all cases. In the PMR spectra of the α-bisabolols isolated

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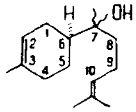

from the oleoresins of the spruce and three species of fir two signals of methyl groups attached to carbinol carbon atoms (1.12 and 1.0 ppm) were observed in a ratio of 4:1 with the predominance of the weak-field signal. Consequently, in the four oleoresins the main isomer is (+)-6S,7R-α-bisabolol and the minor isomer is the 6S,7S- compound. Only the oleoresins of the Siberial stone pine and the Korean pine contained a single diastereoisomer of (+)-α-bisabolol, which had the 6S,7R- configuration. Apart from the PMR spectra, the two diasteromers have small differences in the ^{13}C NMR spectra. For 6S,7R-α-bisabolol the following signals are characteristic ($CDCl_3$; ppm from TMS; internal standard $CDCl_3$, δ 76.9 ppm); 133.71 s, 131.58 s, 124.49 d, 120.67 d, 74.21 s, 43.24 d, 39.26 t, 30.97 t, 25.98 t, 25.58 q, 23.86 t, 23.89 q, 23.20 q, 22.19 t, 17.55 q; for 6S,7S-α-bisabolol – 134.00 s, 131.58 s, 124.50 d, 120.45 d, 74.19 s, 42.90 d, 40.01 t, 30.96 t, 26.82 t, 25.57 q, 23.85 t, 23.85 q, 23.19 q, 21.97 t, 17.55 q.

LITERATURE CITED

1. V. A. Khan, Zh. V. Dubovenko, V. A. Pentegova, Khim. Drev., No. 4, 34 (1983).
2. W. Knoll and C. Tamm, Helv. Chim. Acta, 58, 1162 (1975); A. Kergomard and H. Veschambre, Tetrahedron, 33, 2215 (1977); M. A. Schwartz and G. C. Swanson, J. Org. Chem., 44, 953 (1979).

STEROLS OF THE FAR EASTERN RED ALGA *Ahnfeltsia tobuchiensis*

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Red algae which are widely distributed in the Far Eastern zone, form one of the possible sources of the production of new and unusual sterols [1, 2]. It has been established previously that among the sterols of algae of the family *Rhodophycea* cholest-5-en-3β-ol predominates and there are considerable amounts of cholesta-5,24-dien-3β-ol and cholesta-5,22-dien-3β-ol [3, 4]. Among the sterols with more alkylated side chains from red algae have been isolated 24-ethylcholest-5-en-3β-ol ergosta-5,24(28)-dien-3β-ol, and (24E)stigmasta-5,24(28)-dien-3β-ol.

Continuing an investigation of Far Eastern algae [5], we have studied the sterol composition of the industrially harvested alga *Ahnfeltsia tobuchiensis*.

The dry and comminuted alga collected in November in Troits inlet, Peter the Great Bay, Sea of Japan, was extracted with chloroform–ethanol (1:1). After the saponification of the evaporated extract, the combined sterols, amounting to 0.0115% of the weight of the dry algal sample, were obtained by the usual working up procedure and chromatographic separation on silica gel. According to GLC and chromato-mass spectrometry, the main components of the fraction were cholest-5-en-3β-ol (59%) and 24-ethylcholest-5-en-3β-ol (32%). Fractions containing cholestadiene and cholestatriene made up 7% of the weight of the sterol fraction.

After the acetylation of the sterol fraction and chromatographic separation of the combined acetates on silica gel impregnated with $AgNO_3$, the acetates of 24-methylcholest-5-en-3β-ol (M – 60, 384; M – 75, 369; 260; 255; 247; 213) and of 5α-cholestan-3β-ol (M – 60, 370; M – 75, 355; 276; 275; 257; 230; 215) were characterized.

Thus, we have established that the sterol fraction of *Ahnfeltsia tobuchiensis* contains a set of Δ^5-sterols among which cholest-5-en-3β-ol and 24-ethylcholest-5-en-3β-ol predominate. An interesting fact is the considerable amount of di- and triunsaturated sterols.

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