UDC 547.913-14

NEUTRAL SUBSTANCES OF THE OLEORESIN OF ABIES SIBIRICA

II. Structure of Neoabienol

M. A. Chirkova and V. A. Pentegova

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 4, pp. 247-251, 1969

In the high-boiling neutral fraction of the oleoresin of Abies sibirica Ledeb. (Siberian fir) have been found—in addition to substances isolated previously [1, 2]—mannoyl oxide [3, 4] and a new diterpene alcohol with the composition $C_{20}H_{34}O$, n_D^{20} 1.5266, $[\alpha]_D^{20}$ +12.95, which we have called neoabienol (I).

The dehydrogenation of neoabienol gave 1, 2, 5-trimethylnaphthalene (II) [5], which permitted the alcohol obtained to be assigned to the group of bicyclic diterpene compounds [6, 7].

The IR spectrum of the alcohol has absorption bands of a trans-disubstituted double bond (970 cm^{-1}), a trisubstituted double bond (830 and 1665 cm^{-1}), and a tertiary hydroxyl group (1080 and 3590 cm^{-1}) [8].

In the UV spectrum, the absorption maximum at 238 mμ (log ε 4.46) shows the presence of a conjugated system of double bonds.

The hydrogenation of neoabienol gave tetrahydroabienol (III) [1, 9], the dehydration of which led to a hydrocarbon (IV) identical with labd-8(20)-ene [1, 10].

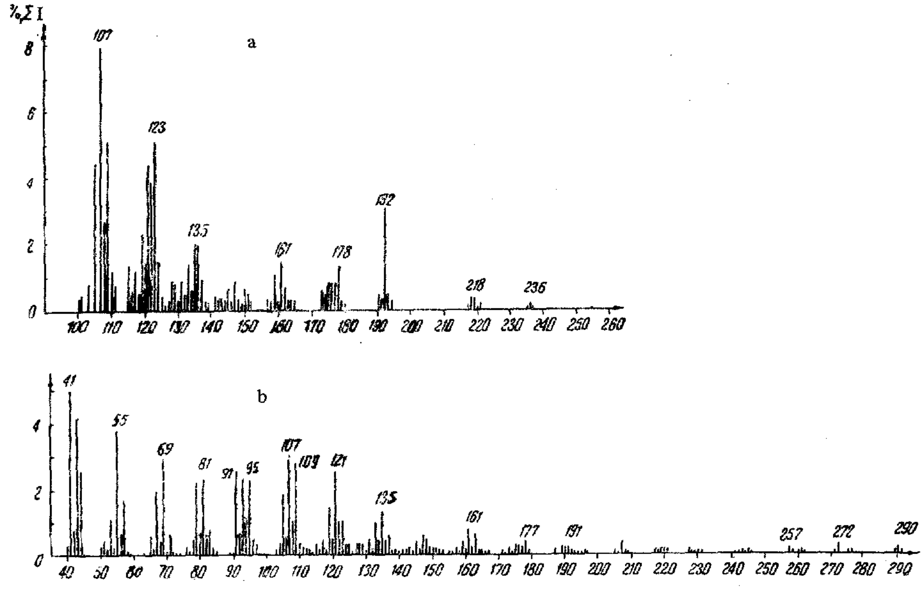
The ozonization of neoabienol gave a hydroxyacid with the composition $C_{15}H_{26}O_3$ (V), mp 143–144° C. From its melting point and its IR and mass spectra (figure, a), the hydroxyacid is identical with the hydroxyacid that we isolated from the products of the ozonolysis of the hydroxyketone described in a previous paper [2].

The mass spectrum of neoabienol (figure, b) shows the same fragmentary ions as for diterpene compounds containing a hydroxyl group and eight carbon atoms [11].

In the NMR spectrum of neoabienol (in CCl_4, from HMS, on a JNM-4H-100 instrument), in the region of a strong magnetic field there are signals at 0.78 ppm relating to a methyl group at C_{10} and at 0.93 and 0.94 ppm corresponding to two methyl groups at C_4. The chemical shift at 1.08 ppm is characteristic for a methyl group attached to the same carbon atom as a hydroxyl (C_8) [12]. The signal at 1.73 ppm relates to a methyl group at C_{14} [13], and that at 1.78 ppm to a methyl group attached to an unsaturated carbon atom bearing no hydrogen (C_{13}) [14].

In the weak magnetic field, signals at 5.28 ppm (quartet), 5.51 ppm (quartet) and 6.4 ppm (doublet) correspond to protons at C_{14}, C_{11}, and C_{12}, respectively.

On standing in the air, neoabienol is readily oxidized to a hydroxyketone (VI) the melting point and IR, NMR, UV, and mass spectra of which are identical with those of the hydroxyketone that we studied previously [2].

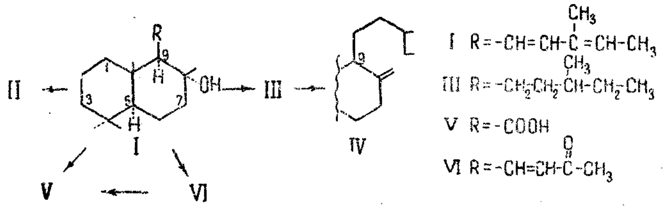


Mass spectra of the hydroxyacid (a) and of neoabienol (b).

The results obtained permit structure I to be put forward for neoabienol which therefore belongs to compounds of the labdane type.

Investigations carried out previously [1, 2] and also the results given in the present paper show that the main components of the high-boiling neutral fraction of the oleoresin of the Siberian fir are bicyclic diterpene compounds with a hydroxyl group at C_8.

The presence of these compounds in the oleoresin of the Siberian fir is undoubtedly of interest for the taxonomy of the botanical species Abies.



Experimental

The oxygen-containing diterpene compounds were isolated from the oleoresin of the Siberian fir by the method described previously [1].

The mixture of oxygen-containing compounds (21.0 g) was separated on neutral alumina (activity grades II and III) at a ratio of 1:50. A mixture of petroleum ether and benzene (9:1) gave a fraction (4.0 g) from which on chromatography, petroleum ether eluted crystalline manoyl oxide (0.5 g) and benzene eluted crude neoabienol (3.2 g).

Manoyl oxide. After four recrystallizations from isopropanol, the manoyl oxide has the composition $C_{20}H_{34}O$, mp 25.5–2.6° C, $[\alpha]_D^{20}$ +30° (c 3.0; chloroform). Literature data: mp. 24.5–26° C, $[\alpha]_D^{20}$ +23° [13]. The NMR, IR, and mass spectra of the manoyl oxide isolated were identical with the corresponding spectra of manoyl oxide given in the literature [14] and [11].

Manoyl oxide trihydrochloride [15]. A solution of manoyl oxide (150 ml) in glacial acetic acid (5.0 ml) was saturated with gaseous hydrogen chloride at 20° C for 3 hr. The crystals of the trihydrochloride that deposited had mp 124.5–125° C (from petroleum ether). Literature data: mp 124–125° C [16]. A mixture with authentic manool trihydrochloride gave no depression of the melting point (125° C).

Neoabienol (I). The crude neoabienol was chromatographed on silica gel (KSK-200, ratio 1:50) with a mixture of petroleum ether and benzene (1:1). This yielded pure neoabienol (2.9 g) with n_D^{20} 1.5268, $[\alpha]_D^{20}$ +12.95° (c 3.85; chloroform).

Found, %: C 82.32; H 11.84; H* 0.32; mol. wt. 290 (mass spectrometry). Calculated for $C_{20}H_{23}O$, %: C 82.75; H 11.72; H* 0.32; mol. wt. 290.

Dehydrogenation of neoabienol. Neoabienol (I) (1.0 g) was heated with selenium (1.5 g) and 300–320° C for 20 hr. The dehydrogenation product was purified by the usual method. A picrate with mp 139–140° C was obtained. In admixture with an authentic sample of 1, 2, 5-trimethylnaphthalene picrate, no depression of the melting point was observed (139° C).

The IR spectrum of the aromatic hydrocarbon had maxima at 228, 288, and 324 mμ (log ε 4.81, 3.72, and 2.85, respectively), which are characteristic for 1, 2, 5-trimethylnaphthalene [17].

Hydrogenation of neoabienol. Neoabienol (188.5 g) was hydrogenated in ethyl acetate (5.0 ml) on a PtO_2 catalyst (18.8 mg). The consumption of hydrogen was 26.0 ml (0° C, 760 mm), corresponding to two double bonds (the theoretical consumption of hydrogen for two double bonds is 29.0 ml). After chromatography, the hydrogenation product (140 mg) had n_D^{20} 1.5015. The IR spectrum of the saturated alcohol was identical with that of tetrahydroabienol [9].

Found, %: C 81.50; H 12.60; mol. wt. 294 (mass spectrometry). Calculated for $C_{20}H_{38}O$, %: C 81.63; H 12.96; mol. wt. 294.

Dehydration of tetrahydroabienol. Tetrahydroabienol (100 mg) was dehydrated with acetic anhydride (0.12 ml) and glacial acetic acid (0.12 ml) by Enzell's method [18]. The reaction product was extracted with ether and chromatographed on alkaline alumina (activity grade I–II). Petroleum ether eluted a hydrocarbon (50.0 mg) with n_D^{20} 1.4978. The IR spectrum of the hydrocarbon obtained was identical with that of labd-8(20)-ene [1, 10].

Found, %: C 87.00; H 12.95; mol. wt. 276 (mass spectrometry). Calculated for $C_{20}H_{36}$, %: C 86.86; H 13.02; mol. wt. 276.5.

The presence of an exomethylene double bond was confirmed by ozonization [19]. This gave 0.16 mg of formaldehyde (the theoretical amount of formaldehyde per methylene double bond is 0.21 mg).

Ozonization of neoabienol [20]. Neoabienol (600 mg) in 10 ml of methylene chloride was ozonized at −70° C for 2 hr. The ozonide was decomposed by being boiled with water; after the elimination of the methylene chloride the reaction product was extracted with ether. The ozonolysis product (590 mg) in glacial acetic acid (6.5 ml) was treated with a solution of potassium permanganate (590 mg in 8.5 ml of water). After standing at room temperature for 48 hr, the reaction mixture was treated as described by Hochmanova and Herout [21]. The acid fraction was chromatographed on silica gel (KSK, 200 μ; ratio 1:50). Petroleum ether eluted a hydroxy acid (V) with mp 143–144° C. The IR spectrum of the hydroxyacid had absorption bands at 960, 1080, 1270, 1370, 1390, and 1740.

Found, %: C 70.08; H 9.90; mol. wt. 254 (mass spectrometry). Calculated for $C_{15}H_{26}O_3$, %: C 70.86; H 10.23; mol. wt. 254.

We obtained a hydroxyacid with the same properties by the ozonization of the hydroxyketone isolated previously from the oleoresin of Siberian fir [2]. A mixture of these acids gave no depression of the melting point (143° C).

Oxidation of neoabienol. Neoabienol (400 mg) was allowed to stand in the air for 2 months and was then chromatographed on neutral alumina (activity grade II–III) at a ratio of 1:50. Elution was carried out successively with petroleum ether and with mixtures of benzene and ether. From the benzene–ether (1:1) eluate was isolated a crystalline hydroxyketone with mp 124–125° C. Its NMR, IR, and UV spectra were identical with those for 14,15-bis-nor-8α-hydroxy-labd-11-en-13-one.

A mixture of the hydroxyketone isolated (VI) with an authentic sample gave no depression of the melting point (125° C).

Conclusions

From the oleoresin of Abies sibirica Ledeb. have been isolated manoyl oxide and a new diterpene alcohol with the composition $C_{20}H_{34}O$ (I) which we have called neoabienol. It has been established that it is labd-11,13-dien-8α-ol.

REFERENCES

1. M. A. Chirkova, A. E. Gorbunova, A. I. Lisina, and V. A. Pentegova, KhPS [Chemistry of Natural Compounds], 2, 99, 1966.
2. M. A. Chirkova, A. K. Dzizenko, and V. A. Pentegova, KhPS [Chemistry of Natural Compounds], 3, 86, 1967.
3. J. R. Hosking and C. W. Brandt, Ber., 68, 37, 1935.
4. M. Belardini, G. Scuderi, and L. Mangoni, Gazz., 94, 829, 1964.
5. L. Ruzicka and M. Janot, Helv. Chim. Acta, 14, 645, 1931.
6. D. H. R. Barton, Quart. Rev., 3, 36, 1949.
7. B. Klyne, J. Chem. Soc., 3072, 1953.
8. M. Hinder and M. Stoll. Helv. Chim. Acta, 36, 1997, 1953.
9. G. V. Pigulevskii and V. G. Kostenko, DAN, 128, 305, 1959.
10. G. V. Pigulevskii, V. G. Kostenko, and L. D. Kostenko, ZhOKh, 31, no. 9, 3143, 1961.
11. C. R. Enzell and R. Ryhage, Arkiv vör kemi, 23, no. 33, 367, 1965.
12. I. M. Lehn, Bull. Chem. Soc., France, 10, 1962.
13. S. Bory, M. Fetizon, and P. Laszlo, Bull. Soc. Chem., France, no. 10, 2310, 1963.
14. C. W. L. Bewan, D. Ekong, and J. I. Okogun, Chem. Commun. no. 2, 44, 1966.
15. R. M. Garman and P. K. Grant, J. Chem. Soc., no. 5, 2187, 1961.
16. R. M. Garman and N. Dennis, Austr. J. Chem., 20, 163, 1967.
17. Elsevier's Encyclopedia of Organic Chemistry, NY-Amsterdam, 12B, 166, 1948.
18. C. Enzell, Acta Chem. Scand., 15, 1303, 1961.
19. J. Naves, Helv. Chim. Acta, 32, 1151, 1949.
20. J. Haeuser, R. Lombard, F. Lederer and G. Ourisson, Tetrah., 12, 205, 1961.
21. J. Hochmanova and V. Herout, Coll., 29, 2369, 1964.

15 February 1968

Novosibirsk Institute of Organic Chemistry, Siberian Branch
AS USSR