UDC 547.972

PINOCEMBRIN AND PINOSTROBIN FROM THE HEARTWOOD OF PINUS SIBIRICA

V. I. Lutskii, N. A. Tyukavkina, and M. F. Shostakovskii

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 6, p. 383, 1968

From the wood of the Siberian pine, we have previously isolated three substances, two of which proved to be flavones [1]. Subsequently, by preparative chromatography on a polyamide sorbent from an acetone extract we have isolated two more compounds of a flavonoid nature which we denote by (I) and (II).

Substance (I) forms crystals with a yellowish tinge, mp 194–195° C (methanol). Its IR spectrum contains absorption bands at 1490, 1600 (C_6H_5-), 1638 (C=O of a flavanone nucleus), 1170, 1220 (C–O–C), 3100–3120 (hydroxy groups in ring A), 700 and 765 cm^{-1} (nonplanar vibrations of the CH groups of ring B bearing no hydroxy substituents) [2]. UV spectrum: λ_{max} 294 mμ (log ε 4.23); $\lambda_{max}^{AlCl_3}$ 310 mμ. The acetate of (I) melted at 117–118° C (ethanol). The IR spectrum of the acetate of (I) showed that it lacked free hydroxy groups and had acetate groups (1696 and 1768 cm^{-1}). UV spectrum: λ_{max} 315 and 260 mμ (log ε 3.58 and 4.02). Substance (I) was identified as 5,7-dihydroxyflavanone (pinocembrin) [3,4].

Substance (II) formed crystals with a faint pink tinge, mp 111–112° C (methanol), $[\alpha]_D^{20}$ –55° (c 2.1; chloroform). IR spectrum: 1520 cm^{-1}, 1575 (C_6H_5-), 1649 (C=O of a flavanone nucleus), 1155, 1190, 1244 (C–O–C), 1380, 1450, 2861 ($-OCH_3$), 700, and 770 cm^{-1} (nonplanar vibrations of the CH groups of ring B bearing no hydroxy substituents); no distinct bands of the vibrations of hydroxy groups. UV spectrum: λ_{max} 294 mμ (log ε 4.55); $\lambda_{max}^{AlCl_3}$ 302 mμ. Substance (II) was identified as 5-hydroxy-7-methoxyflavanone (pinostrobin) [5]. A chromatographic comparison of substance (II) with a sample of pinostrobin sent by Prof. Erdtman (Sweden) showed their complete identity. For both the substances isolated and for the acetate of (I) the results of elementary analysis agreed with the theoretical calculations.

5,7-Dihydroxy- and 5-hydroxy-7-methoxyflavanones are the hydrogenated analogs of the 5,7-dihydroxy- and 5-hydroxy-7-methoxyflavones isolated previously from the heartwood of the Siberian pine [1].

REFERENCES

1. N. A. Tyukavkina, V. I. Lutskii, A. K. Dzizenko, and V. A. Pentegova, KhPS [Chemistry of Natural Compounds], 4, 249, 1968.
2. L. H. Briggs and L. D. Colebrook, Spectrochim. Acta, **18**, 939, 1962.
3. H. Erdtman, Svensk Kem. Tid., **56**, 26, 1944.
4. H. Erdtman, Svensk. Kem. Tid., **56**, 95, 1944.
5. G. Linstedt, Acta Chem. Scand., **4**, 1042, 1950.

12 June 1968

Irkutsk Institute of Organic Chemistry, Siberian Division AS USSR

UDC 668.53

A CHROMATOGRAPHIC ANALYSIS OF THE HIGH-BOILING FRACTIONS OF THE EXTRACTION TURPENTINES FROM PINUS SILVESTRIS

I. I. Bardyshev, A. L. Pertsovskii, and V. I. Kulikov

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 6, p. 384, 1968

By the gas-liquid chromatographic (GLC) method, we have studied the composition of the pine flotation oils marketed by four Russian wood-chemical factories.

The samples of the oils corresponded to the requirements of the GOST [State Standard] [1]. Their GLC was carried out on packed and capillary columns. The identification of the components was effected by the addition of the authentic pure substances during GLC and from the relative retention times (RRT) of the substances. The GLC of the hydrocarbon fraction of the oils was carried out by the method described previously [2,3].

The contents of the components of the mixture were calculated by the method of internal standardization (with *l*-carvone as the standard).

The flotation oils studied had the following compositions (%, in the order of issuance of the substances in GLC on a column of PEG-600): α-pinene (0.3–0.9); camphene (traces-0.4); β-pinene (traces-0.8); β-myrcene (traces-0.1); 3-carene (0.3–8.0); α-terpinene (0.3–0.8); dipentene (1.5–3.0); β-phellandrene (0.2–0.5); p-cymene (0.3–2.0); γ-terpinene (0.2–0.5); terpinolene (1.7–11.0); x_1 (traces-0.3); m-1, 3(8)-menthadiene (traces-0.1); x_2, x_3 (traces-0.1); trans- and cis-alloocymenes (traces-0.1); x_4 (traces-0.1); fenchol (0.3–0.5); x_5 (ketone) (0.3–0.6); x_6, x_7, x_8, x_9, x_{10} (traces-0.1); camphane (1.4–3.4); methylchavicol (1.3–1.9); x_{11} (traces-0.1); trans-dihydro-α-terpineol (4.2–16.2); α-fenchol (1.3–2.8); β-terpineol (traces-0.1); x_{12} (alcohol) (0.4–0.7); 4-terpinenol (11.8–14.5); x_{13} (traces-0.1); γ-terpineol (3.0–3.5); x_{14}, x_{15}, x_{16} (0.1–0.2); isoborneol (traces-0.1); x_{17}, x_{18} (0.1–0.3); sylveterpineol (7.0–16.0); α-terpineol (9.5–10.6); verbenone (0.5–1.0); and other high-boiling substances (12.5–28.6).

Samples of the flotation oils from different factories possess similar qualitative compositions. Differences in the quantitative compositions of the oils are apparently due to differences in the raw materials used by the factories and the degree to which the hydrocarbons are distilled off from the alcoholic part of the turpentines. (Variations in quantitative composition are also observed in different batches of the flotation oils marketed by the same factory.)

REFERENCES

1. Pine Flotation Oil [in Russian], GOST, 6792-61.
2. I. I. Bardyshev, E. P. Dontsova, and A. L. Pertsovskii, KhPS [Chemistry of Natural Compounds], **3**, 347, 1967.
3. I. I. Bardyshev, V. I. Kulikov, and A. L. Pertsovskii, Lesokhim. i gidrolizn. prom., no. 8, 16, 1966.
4. B. A. Arbuzov, ZhPKh, **2**, 586, 1929; ZhPKh, **2**, 595, 1929.
5. V. N. Krestinskii, F. T. Solodkii, and G. Tol'skii, ZhPKh, **3**, 691, 1930.
6. B. A. Arbuzov, ZhRFKhO, **62**, 2023, 1930.
7. I. I. Bardyshev and R. I. Livshits, ZhPKh, **25**, 1289, 1952.
8. S. V. Dudenkov, Flotation Reagents [in Russian], Moscow, 1964.

26 February 1968

Institute of Physical Organic Chemistry, AS BSSR

UDC 547-341:633.88

ARTEMIN — A NEW SESQUITERPENE LACTONE FROM *ARTEMISIA TAURICA*

L. P. Tolstykh, V. I. Sheichenko, A. I. Ban'kovskii, and K. S. Rybalko

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 6, pp. 384–385, 1968

From *Artemisia taurica* we isolated three sesquiterpene lactones: tauremisin, taurin, and mibulactone. Structural formulas were proposed for the first two and the third lactone was identified as mibulactone [1]. However, the NMR spectrum recorded did not agree with the structure of mibulactone in view of which a detailed study of this lactone has been carried out. As now established, it is isomeric with mibulactone. We proposed for it the name artemin and the structural formula (I) as the most probable.

The dehydrogenation of artemin over selenium at 280–320° C for 30 hr gave 7-ethyl-1-methylnaphthalene, identified as the picrate, mp 94–96° C (from ethanol) and by the absence of a depression of the melting point with an authentic sample. Thus, artemin has the same structure of the carbon skeleton as tauremisin and other lactones of the eudesmane type.

Artemin contains two hydroxyls, one of which is readily acetylated giving a monoacetyl derivative $C_{17}H_{24}O_5$ with mp 220–222° C (from ethanol) and it is oxidized by chromic anhydride to a hydroxy keto lactone $C_{15}H_{20}O_4$ with mp 260–262° C (decomp., from ethanol). It follows from this that one hydroxyl in artemin is secondary and the other is tertiary. Artemin contains one double bond. On hydrogenation over a Pt catalyst (from PtO_2), both in ethanol and in glacial acetic acid, dihydroartemin $C_{15}H_{24}O_4$ with mp 234–236° C (from ethanol) was obtained.

The NMR spectrum of artemin has the signal of quaternary and tertiary methyls (singlet at 0.89 ppm and doublet at 1.25 ppm, respectively); two broad signals (each of one proton unit in the regions 4.98 and 5.03 ppm), correspond to the