

The contents of the components of the mixture were calculated by the method of internal standardization (with *l*-caryone 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):  $\alpha$ -pinene (0.3-0.9); camphene (traces-0.4);  $\beta$ -pinene (traces-0.8);  $\beta$ -myrcene (traces-0.1); 3-carene (0.3-8.0);  $\alpha$ -terpinene (0.3-0.8); dipentene (1.5-3.0);  $\beta$ -phellandrene (0.2-0.5); p-cymene (0.3-2.0);  $\gamma$ -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- $\alpha$ -terpineol (4.2-16.2);  $\alpha$ -fenchol (1.3-2.8);  $\beta$ -terpineol (traces-0.1);  $x_{12}$  (alcohol) (0.4-0.7); 4-terpinenol (11.8-14.5);  $x_{13}$  (traces-0.1);  $\gamma$ -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);  $\alpha$ -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 turpentine. (Variations in quantitative composition are also observed in different batches of the flotation oils marketed by the same factory.)

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#### ARTEMIN — A NEW SESQUITERPENE LACTONE FROM *ARTEMISIA TAURICA*

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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

protons of an exocyclic methylene group which can be present only in the  $C_4-C_{14}$  position since at the  $C_{11}-C_{13}$  position these signals would be shifted to the low field by approximately 1 ppm [2]. The lactone proton appears in the form of a doublet at 4.30 ppm, which shows that it is located at  $C_5-C_6$ . A quartet in the 4.21 ppm region ( $J = 5$  and 11 Hz) is due to a proton present in the geminal position to the OH group, i.e., artemin contains one secondary hydroxyl, which agrees with the results of acetylation.

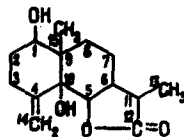
The NMR spectrum of the acetyl derivative retains the signals of quaternary and tertiary methyls (singlets at 0.98 ppm and doublet at 1.23 ppm), of the exocyclic methylene group (broadened signals in the 5.01 and 5.06 regions), and of the lactone proton (doublet at 4.27 ppm); the signal of an acetyl group appears (singlet at 2.01 ppm) and the signal of its geminal proton, as was to be expected, is displaced in the weak field direction (quartet at 5.41 ppm).

In the dihydro derivative, the signals of the exocyclic protons have disappeared; in place of them a new doublet has appeared in the 0.97 ppm region.

Three positions are possible for the tertiary hydroxyl: at  $C_{10}$ ,  $C_{11}$ , and  $C_6$ . The position at  $C_{11}$  is excluded because in the NMR spectrum the  $CH_3$  group appears in the form of a doublet, and of the remaining two possible positions the less likely is that at  $C_{10}$ , which agrees with the NMR spectrum of artemin. While the chemical shift between the  $H_6$  and  $H_{11}$  protons will be comparatively large or the proton at  $C_6$  will be absent, the signal from  $CH_3$  at  $C_{11}$  must appear in the form of a well-defined doublet; in artemin and its derivatives the trough between the lines of the methyl doublet approaches half the height of the signal, which is connected with the combination lines arising from the interaction of the methyl proton at  $C_{11}$  with the proton on the neighboring carbon atom.

Several positions are possible for the secondary hydroxyl. We give our preference to the position at  $C_1$  because the signal of the angular methyl group in the oxidized product—dehydroartemin—is shifted to the weak field, as we have also observed in the NMR spectra of tauremisin and taurin. On the basis of the biogenesis of the sesquiterpene lactones, we consider that the position of the OH group at  $C_8$  is unlikely.

Thus, structure (I) is the most likely for artemin.



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## AMBROSIN—A SESQUITERPENE LACTONE FROM CYCLACHAENA XANTHIFOLIA

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From the total sesquiterpene lactones of *C. xanthifolia* Fresen, family Compositae (rag sumpweed), we have obtained (yield 0.15%), by fractional crystallization from benzene, a substance  $C_{15}H_{18}O_3$ , chromatographically homogeneous on a thin layer of alumina [ $R_f$  0.63, carbon tetrachloride—chloroform—ethanol (10:30:1)] and silica gel G [ $R_f$  0.80, benzene—acetone (4:1)]; mp 144–146° C (from benzene);  $[\alpha]_D^{20} -122^\circ$  (c 8.7; chloroform). The IR spectrum (UR-10, KBr) exhibited absorption bands at 1760 ( $\gamma$ -lactone), 1640, 820 ( $>C=CH_2$ ), 1710, 1585, and 1406  $cm^{-1}$  (CO