THE STRUCTURE OF THE SESQUITERPENE LACTONE ARSUBIN

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The isolation of a sesquiterpene lactone from Artemisia sublessingiana* with the composition $C_{15}H_{22}O_4$, mp 233-234°C, has been reported previously [1]. Its physicochemical properties differ from those of lactones with the same composition and similar functional groups that have been described [2-5]. We have called it arsubin (I).

Arsubin has two hydroxy groups (secondary and tertiary) and one double bond. The position and nature of the double bond were determined by a study of the NMR spectra of arsubin acetate (III) (Fig. 1a) and its dihydro derivative (IV) (Fig. 1b). Two broadened signals of one proton unit each at 4.89 and 4.94 ppm in the spectrum of (III) show the presence of an exomethylene group in the molecule of the lactone. These signals have disappeared in the spectrum of (IV). This group is not conjugated with the lactone carbonyl: λ_{max} in the IR spectrum 1780 cm^{-1}. Consequently, the $=CH_2$ group is attached to the C_4 carbon.

The spectrum of (III) shows the protons of an angular methyl group in the form of a narrow singlet at 0.93 ppm, and of a secondary methyl group in the form of a doublet with a center at 1.16 ppm (J = 7.5 Hz). The signal of an acetyl group can be seen in the 1.98 ppm region and the signal of its geminal proton in the form of a quartet with its center at 5.38 ppm (J = 5.6 Hz). The resonance signal of the lactone proton appears in the form of a sharp doublet with its center at 4.45 ppm (J = 10 Hz), which shows the attachment of the lactone ring in the C_5-C_6 position. A secondary methyl group is attached to the C_{11} carbon and appears in the form of a doublet with a valley of half the height of the signals because of the interaction of the methyl protons on the adjacent C_6 carbon. Consequently, the most probable position for the tertiary hydroxy group is at C_{10}. The attachment of the secondary group to the C_3 atom is excluded because of the absence in the UV spectrum of oxoarsubin (V) of the characteristic maximum showing the conjugation of the C = C bond with the C = O group. Its location at C_7 is unlikely since, when the lactone was subjected to prolonged heating with a solution of alkali, followed by acidification, the lactone ring opened at the C_5-C_6 position. This group must be attached to one of the atoms C_1, C_2, or C_8.

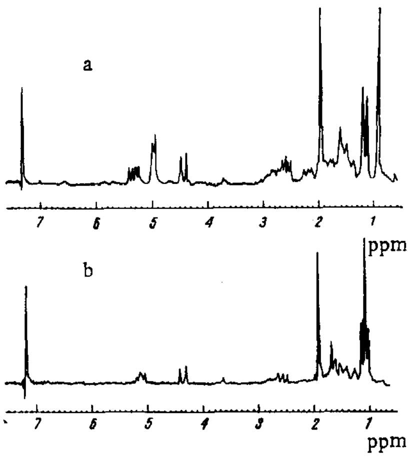

Fig. 1. NMR spectra ($CDCl_3$, 100 MHz) of arsubin acetate (a) and of dihydroarsubin acetate (b).

When dihydroarsubin (II) was dehydrogenated over selenium, a naphthalene derivative was obtained – 7-ethyl-1-methylnaphthalene, identified in the form of its picrate, mp 93-95°C.

Thus, from its type of carbon skeleton arsubin belongs to the lactones of the eudesmane series and is possibly a stereoisomer of artemin [2]. These facts permit the following partial structure to be proposed for arsubin:

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* As in Russian original; in the previous paper this was given as A. transiliensis – Translator.

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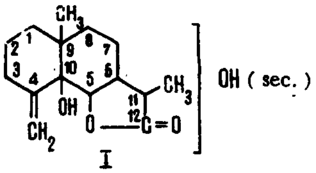

I

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrophotometer (tablets with KBr), the NMR spectra on a JNM-4H-100/100 MHz instrument in $CDCl_3$ (δ scale), and the mass spectra on an MKh-1303 instrument. The analyses of all the compounds corresponded to the calculated values.

Arsubin (I). The epigeal part of the plant (small stems and leaves) (10 kg) was steeped in hot water (85°C) for 1 h four times. The cooled aqueous infusions were extracted with chloroform five times. The solvent was distilled off under vacuum. The combined extractive substances were dissolved in ether, and after brief standing the solution deposited arsubin, $C_{15}H_{22}O_4$, mp 233-234°C (from ethanol). Yield 13.2 g.

Dihydroarsubin (II). A solution of 0.1 g of arsubin in 13 ml of ethanol with 0.03 g of platinum oxide was hydrogenated for 2.5 h. The amount of hydrogen absorbed was 10 ml, and 0.07 g of a crystalline substance with mp 238°C (from ethanol), mol. wt. 268 (mass spectrometry) was obtained.

Arsubin Acetate (III). A solution of 0.2 g of arsubin in a mixture of 2 ml of dry pyridine and 2 ml of acetic anhydride was left to stand at room temperature for 15 h. Then the solvents were driven off in vacuum. A substance was isolated with the composition $C_{17}H_{24}O_5$, mp 200°C (from ethanol), mol. wt. 308 (mass spectrometry).

Dihydroarsubin Acetate (IV). A solution of 0.1 g of dihydroarsubin in 2 ml of pyridine was treated with 1 ml of acetic anhydride. After the mixture had stood for 5 h, the solvent was driven off in vacuum and the reaction product was recrystallized from ethanol. A compound was isolated with the composition $C_{17}H_{26}O_5$, mp 187-188°C, mol. wt. 310 (mass spectrometry). IR spectrum, ν_{max}, cm^{-1}: 3490 (OH), 1780 (γ-lactone), 1735, 1265, 1223 ($OCOCH_3$).

Oxoarsubin (V). A mixture of 0.1 g of chromium trioxide and 1 ml of 90% acetic acid was added dropwise to an ice-cooled solution of 0.1 g of arsubin in 3.3 ml of 90% acetic acid. The temperature of the reaction mixture was kept at 0 to +3°C for 3 h. Then 5 ml of water was added (0°C). The reaction product was extracted with ether, and the extracts were washed with sodium bicarbonate solution and with water. After the solvent had been distilled off, a compound $C_{15}H_{20}O_4$ with mp 255°C (from ethanol) was obtained in a yield of 0.03 g. IR spectrum, ν_{max}, cm^{-1}: 3440 (OH), 1778 (γ-lactone), 1720 (C = O), 1665 (C = C).

7-Ethyl-1-methylnaphthalene. A mixture of 1.5 g of dihydroarsubin and 1.5 g of selenium was heated at 280-300°C for 7 h. From the reaction mixture petroleum ether extracted a liquid hydrocarbon which was purified by passage through a column of alumina, by boiling with metallic sodium, and by vacuum distillation. Then it was treated with a hot ethanolic solution of picric acid. Crystals deposited in the form of orange needles – 7-ethyl-1-methylnaphthalene picrate, with mp 93-95°C (from ethanol).

CONCLUSIONS

A new sesquiterpene lactone – arsubin – has been isolated from Artemisia sublessingiana. Structure (I) has been proposed for it on the basis of chemical and spectroscopic information.

LITERATURE CITED

1. V. A. Tarasov, Sh. Z. Kasymov, and G. P. Sidyakin, Khim. Prirodn. Soedin., 6, 480 (1970).
2. L. P. Tolstykh, V. I. Sheichenko, A. I. Ban'kovskii, and K. S. Rybalko, Khim. Prirodn. Soedin., 4, 384 (1968).
3. T. Karivohe, T. Fukui, and T. Omoto, J. Pharmac. Soc., Japan, 78, No. 7, 7110 (1958).
4. W. Herz, G. Hogenauer, and A. Vivar, J. Org. Chem., 29, No. 7, 1700 (1964).
5. R. I. Evstratova, V. I. Sheichenko, A. I. Ban'kovskii, and K. S. Rybalko, Khim. Prirodn. Soedin., 5, 239 (1969).