THE STRUCTURE OF THE LACTONES ARSANIN AND ARSANTIN

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Sometimes the optical-rotatory-dispersion (ORD) curves of terpenoids are compared with those of the corresponding ketosteroids, but because of the high conformational mobility of the terpenoids some of the laws established for the ketosteroids are not observed for them [1]. In particular, the acidification of methanolic solutions of 3-ketosteroids forms ketals and in a number of terpenoids the configurations of the asymmetric centers closest to the carbonyl group are changed [2]. Even more complex changes may take place, as we have found, for example, in establishing the structure of arsanin (I) and arsantin (II), new sesquiterpene lactones from Artemisia santolina Schrenk [3].

In its composition, molecular weight, and functional groups, arsanin is identical with α-tetrahydroartemisin [4]. The ORD curve of arsanin (Fig. 1), just like that of an α-tetrahydroartemisin, shows a positive Cotton effect (CE) in the 280-nm region due to an n−π* transition in the carbonyl group. But when methanolic solutions of these compounds are acidified, their ORD curves become completely different. The ORD curve of α-tetrahydroartemisin does not change on the addition of hydrochloric acid, while in the ORD curve of arsanin the CE is shifted in the long-wave direction and changes its sign (Fig. 1, curve 1a). The change of the sign and the bathochromic shift of the CE on the addition of an acid show that a double bond conjugated with the carbonyl group is formed in ring A. In the sign and position of the CE, curve 1a corresponds to the ORD curve given in the literature as characteristic for Δ^1-3-oxo compounds with a trans linkage of the A/B rings [5].

The formation of a double bond in ring A when methanolic solutions of arsanin are acidified can be explained by the loss of a molecule of water from it involving the hydroxyl at C_1 and hydrogen at C_2. This mechanism of the change in the structure of arsanin in an acid medium is confirmed by the identity of curve 1a and the ORD curve of anhydroarsanin (see Fig. 1, curve 1c), which is formed by the dehydration of (I).

Thus, the hydroxy group of arsanin is not in ring B as in tetrahydroartemisin but in ring A, at C_1. The hydrogenation of anhydroarsanin gives a compound the chemical composition and nature of the ORD of which are identical with those of α-tetrahydrosantonin [2]. Chemical transformations and the ORD characteristics confirm structure (I) for arsanin.

From the plant mentioned, a new lactone has been isolated with mp 168°C [3], which we have called arsantin (II). Arsantin has the same composition as arsanin, $C_{15}H_{22}O_4$, and the same molecular weight (266, mass spectrometry).

The IR spectrum of arsantin (Fig. 2) shows absorption bands at (cm^{-1}) 3505 (hydroxy group), 1755 (carbonyl of a γ-lactone ring), and a split maximum with $\nu_{C=O}$ 1715 and 1690 cm^{-1}. UV spectrum: λ_{max} 290 nm (log ε 1.26) – isolated carbonyl group – and 214 nm (log ε 2.36) – carbonyl of a γ-lactone.

The ORD curve of arsantin (see Fig. 1, curve 2) is similar to that of arsanin. The acidification of methanolic solutions of arsantin leads to the appearance of the same peculiar change in its ORD curve as in the case of arsanin, but it takes place considerably more slowly. While for arsanin the negative CE is clearly detectable only an hour after the addition of a drop of concentrated hydrochloric acid, in the case

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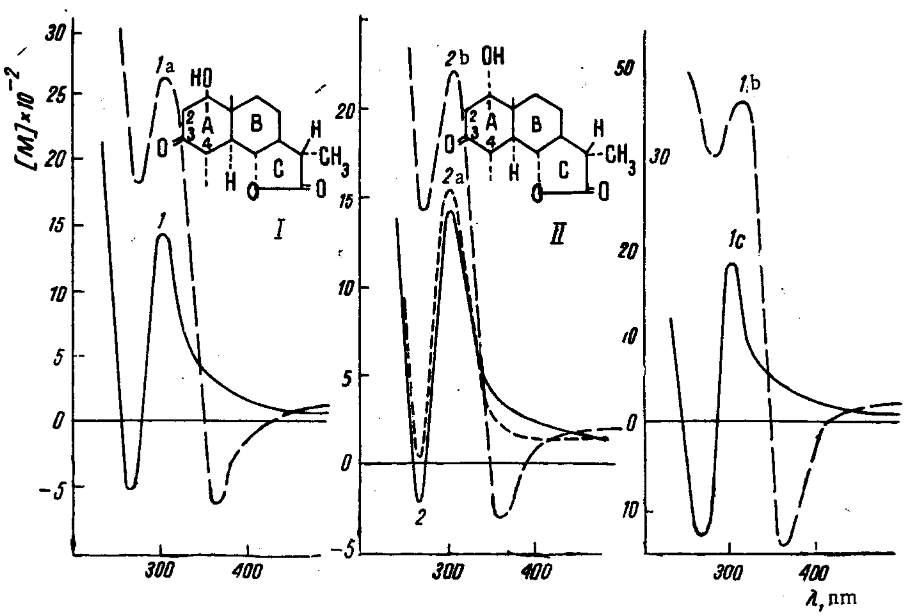

Fig. 1. ORD curves: 1) arsanin in methanol; 1a) the same 1 h after the addition of HCl; 1b) anhydroarsanin in methanol; 1c) product of the reaction of anhydroarsanin; 2) arsantin in methanol; 2a) the same 1 h after the addition of HCl; 2b) the same after a day.

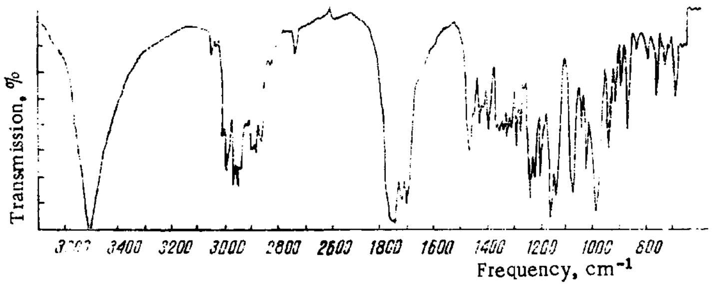

Fig. 2. IR spectrum of arsantin

of arsantin this takes a day (see Fig. 1, curve 2c). Arsantin apparently differs from arsanin only by the orientation of the OH group at C$_1$ and, consequently, structure (II) may be proposed for it. The slower rate of dehydration in the case of arsantin is probably due to the axial orientation of the OH group which on acidification changes into equatorial, after which a molecule of water is split out. In arsanin, the corresponding OH group is already equatorial, which agrees with its NMR spectrum.

EXPERIMENTAL

The isolation and chemical characterization of the compounds investigated has been described previously [3, 6]. The optical rotatory dispersions were measured on an SMU-M spectropolarimeter of the All-Union Scientific-Research Experimental Design Institute of Food Machinery. Methanol was used as the solvent. The concentrations of the solutions were 0.5-0.6 mg/ml, and the cell thickness was 0.5 dm.

SUMMARY

The structure of the sesquiterpene lactone arsanin has been confirmed and a structure has been proposed for arsantin using the method of optical rotatory dispersion.

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