THE SESQUITERPENE LACTONES OF *Stizolophus balsamita*

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We have previously isolated two sesquiterpene lactones — stizolin and stizolicin — from the epigeal part of *Stizolophus balsamita* (Lam.) Cass. ex Takht [1]. In the present paper we report the isolation from this plant of a third sesquiterpene lactone, which we have called balsamin, with the composition $C_{20}H_{26}O_6$ [mp 242-244°C (from ethanol), $[\alpha]_D^{18}$ − 45.70° (c 1.9; chloroform)], propose a structural formula for it, and supplement the structures proposed previously for stizolin and stizolicin [2, 3] by stereochemistry.

In the IR spectrum of balsamin there are absorption bands at (cm^{-1}) 3415 (OH), 1750 (γ-lactone), 1715 (OCO), and 1655 (C=C). In the UV spectrum there is an absorption maximum at 217 nm (log ε 4.24), showing the presence of conjugation.

Balsamin forms a monoacetate with the composition $C_{22}H_{28}O_7$ [mp 166-170°C (from ether)] the IR spectrum of which lacks the absorption band of a hydroxyl.

The NMR spectra of balsamin (III) and of acetylbasamin (IIIa) (Fig. 1) showed that balsamin is a germacranolide containing an epoxy group, double bonds, and a lactone ring in the same position as in stizolin (I) and stizolicin (II). Balsamin differs from stizolicin by the nature of the acyl group: In balsamin, the acyl group is a β,β-dimethylacrylic acid residue (two doublets at 1.85 and 2.06 ppm with J = 1.0 Hz, and a multiplet at 5.64 ppm).

As in stizolin, the acyl group in balsamin is located at C_6, as is shown by the coupling constant between the protons of the exocyclic methylene group. When an acyl group is present in the β position to an exocyclic methylene of a γ-lactone ring, a coupling constant between the protons of the exocyclic methylene ring greater than 0.6 Hz is observed only in germacranolides with the trans attachment of the lactone ring and the acyl group [4]. All this is clearly observed in the NMR spectra of acetylstizolin (Ia) (Fig. 2), of stizolicin (Fig. 3), and of balsamin, where $J_{13,13'}$ is 1.0, 0.85, and 1.0 Hz, respectively. If in the β position to the exocyclic methylene of a γ-lactone ring with the trans linkage of the lactone ring there is a hydroxy group in trans linkage, the distance between the signals of the protons of the exocyclic methylene will be less than 0.3 ppm and the coupling constant greater (about 2.2 Hz); on acylation, the distances between the signals will increase and the coupling constant decrease [4]. This situation is clearly realized in the case of stizolin (see Fig. 2). In the NMR spectra of all the lactones mentioned, the coupling constant between the H_8 and H_9 protons is greater (J about 9.5 Hz), which also indicates the trans position of these protons. Thus, stizolin is represented by the stereochemical structure (I) and stizolicin by (II).

The geminal proton in the NMR spectrum of balsamin is represented by a doublet at 4.56 ppm ($J_{6,7}$ = 4.0 Hz), while in the spectra of acetylstizolin and stizolicin the geminal proton is represented by multiplets at 4.50 and 4.58 ppm. Consequently, there is a substituent adjacent to the acyl group in balsamin. This substituent is a hydroxy group. A singlet at 4.40 ppm corresponds to the hemihydroxyl proton; in the NMR spectrum of acetylbalsamin (IIIa), as was to be expected, the signal of this proton is shifted downfield (5.18 ppm).

The small value of the coupling constant between the H_5 and H_6 protons (<1 Hz) in the NMR spectra of balsamin and acetylbalsamin shows that the dihedral angle between the protons approximates to 90°. It follows from a consideration of molecular models that such an orientation of the protons can exist in the case of a transoid position of the substituents at C_5 and C_6, i.e., balsamin is represented by structure (III).

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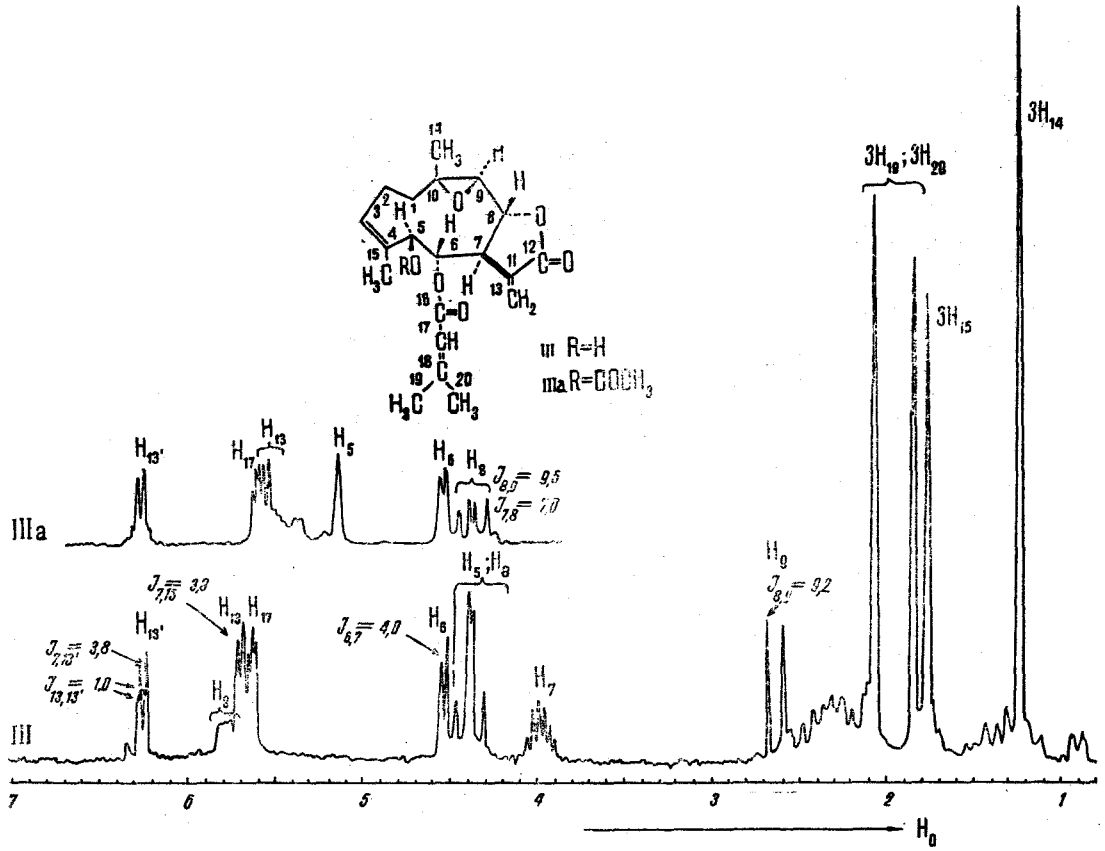

Fig. 1. NMR spectra of balsamin (III) and acetylbalsamin (IIIa).

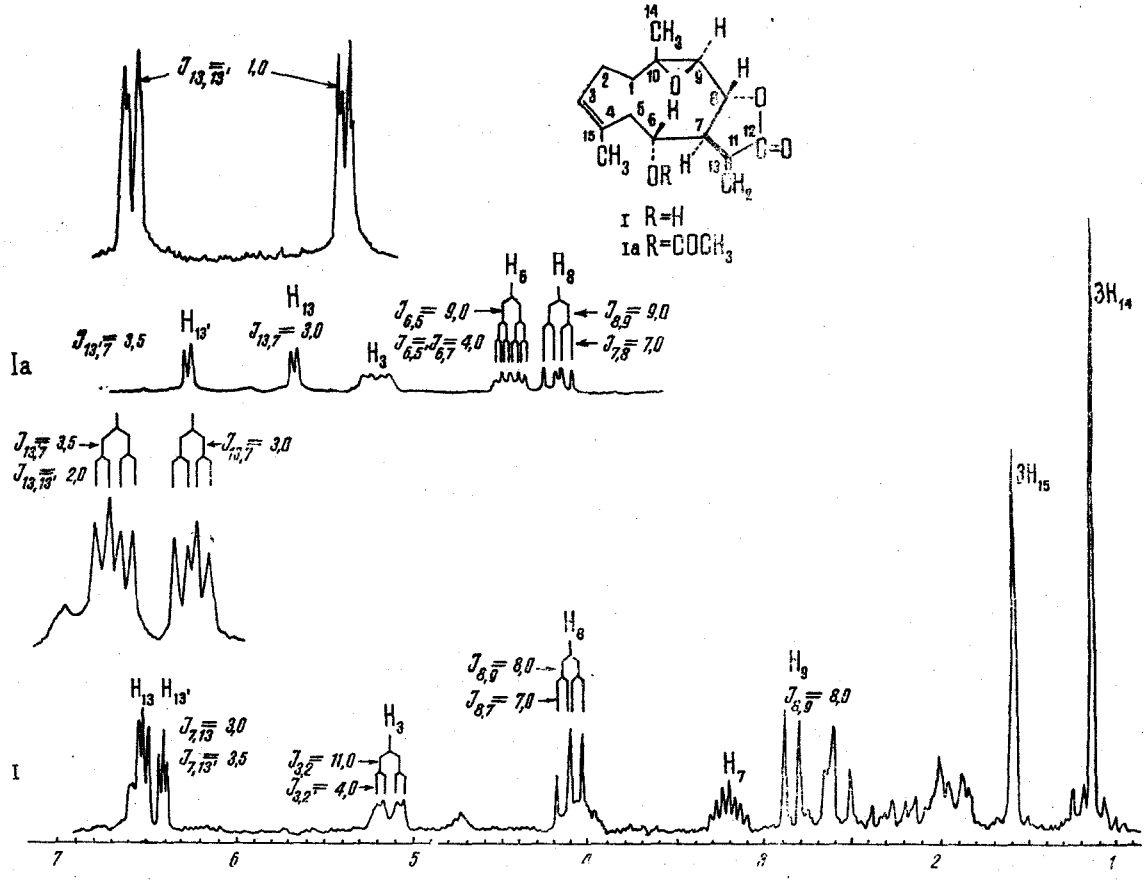

Fig. 2. NMR spectra of stizolin (I) and acetylstizolin (Ia).

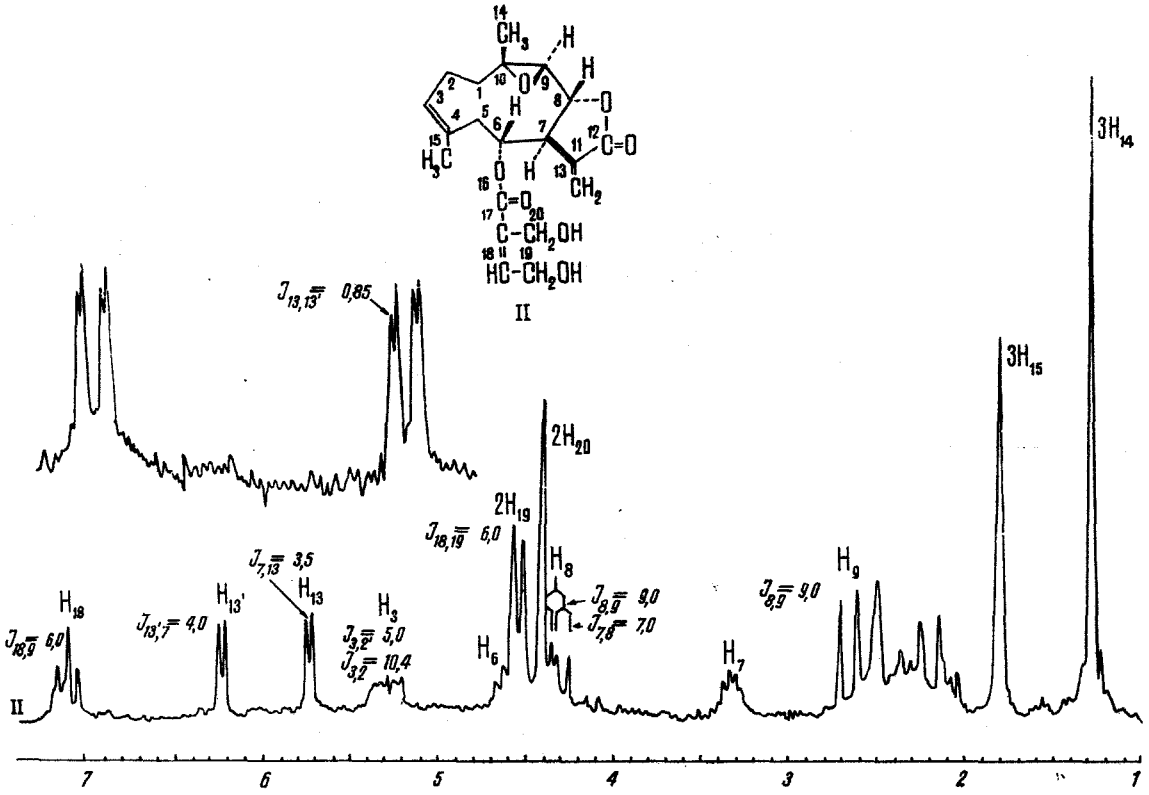

Fig. 3. NMR spectrum of stizolicin (II).

EXPERIMENTAL

The IR spectra (of mulls in paraffin oil) were taken on a UR-10 spectrophotometer, the UV spectra (of solutions in 96% ethanol) on a Hitachi EPS-3T instrument, and the NMR spectra on a Varian HA 100D instrument.

Isolation of Balsamin. After the isolation of the stizolin (from the leaves and flower heads of *Stizolophus balsamita*), 20 g of the mother resin was chromatographed on neutral alumina (activity grade IV). On elution with benzene, a crystallizing resin was obtained [one spot with R_f 0.52 in the benzene–ethanol (9:1) system] from which, on treatment with ether, colorless crystals of balsamin were obtained; after two recrystallizations from ethanol and drying in a vacuum pistol over P_2O_5, mp 242-244°C, $[\alpha]_D^{18}$ − 45.70° (c 1.9; chloroform). Yield 0.5 g or 0.005% calculated on the plant raw material.

Balsamin Acetate. A mixture of 0.3 g of balsamin, 6 ml of pyridine, and 3 ml of acetic anhydride was heated in the water bath at 60°C for 1 h. After cooling, a fivefold amount of water was added and the reaction product was extracted with chloroform. The chloroform extract was washed with 3% HCl and then with water to neutrality, and the chloroform was distilled off. From the liquid products, on the addition of ether, crystals precipitated, which were washed with ether. This gave ~0.21 g of colorless crystals with the composition $C_{22}H_{28}O_7$, mp 166-170°C.

SUMMARY

From the epigeal part of *Stizolophus balsamita* (Lam.) Cass. ex Takht. a new sesquiterpene lactone balsamin has been isolated with the composition $C_{20}H_{26}O_6$, mp 242-244°C (from ethanol), $[\alpha]_D^{17}$ − 45.70° (c 1.9; chloroform). On the basis of the IR, UV, and PMR spectra of balsamin and its acetate, a stereochemical structure has been proposed for balsamin, and the structures of stizolin and stizolicin isolated previously from the same plant have also been supplemented by stereochemistry.

LITERATURE CITED

1. M. N. Mukhametzhanov et al., Khim. Prirodn. Soedin., 56 (1969).
2. M. N. Mukhametzhanov, V. I. Sheichenko, A. I. Ban'kovskii, and K. S. Rybalko, Khim. Prirodn. Soedin., 505 (1970).

3. M. N. Mukhametzhanov, V. I. Sheichenko, A. I. Ban'kovskii, and K. S. Rybalko, Khim. Prirodn. Soedin., 405 (1971).
4. H. Yoshioka et al., Tetrahedron, 27 (15), 3317 (1971).

TRITERPENE GLYCOSIDES OF *Scabiosa soongorica*

II. THE STRUCTURE OF SONGOROSIDES C, G, AND I

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In the roots of *Scabiosa soongorica* Schrenk, family Dipsacaceae, we have found 11 triterpene glycosides originally called scabiosides [1]. On a more careful study, it became clear that some of the substances found consisted of mixtures of two compounds. Consequently, it is more correct to consider that the roots of the Dzhungarian scabious contain not less than 17 triterpene glycosides which, in degree of increasing polarity, we have called songorosides (the name scabiosides has been used by Bukharov and Karlin [2]) A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, P, and R. The main components are the more polar (i.e., richer in sugars) glycosides — songorosides G, I, K, M, O, and R.

From the combined saponins we have so far isolated in the individual state five glycosides — songorosides C, G, I, M, and O. Below we give information on the determination of the structures of songorosides C, G, and I. All three glycosides are derivatives of oleanolic acid (I) and are not saponified by alkali, which shows the absence of acyloside chains in them.

Songoroside C is a bioside with the composition $C_{41}H_{66}O_{11}$. The acid cleavage of glycoside C yielded L-rhamnose and D-xylose. In the hydrolyzate of a permethylate of glycoside C we identified 2,4-di-O-methyl-D-xylose and 2,3,4-tri-O-methyl-L-rhamnose. Consequently, songoroside C has the structure of oleanolic acid 3-O-[O-α-L-rhamnopyranosyl-(1 → 3)-β-D-xylopyranoside] (III).

Songoroside G is a tetraoside with the composition $C_{51}H_{82}O_{19}$, and songoroside I a pentaoside with the empirical formula $C_{56}H_{90}O_{23}$. From the results of acid hydrolysis and gas—liquid chromatography of the silyl derivatives of the methyl glycosides, the sugar moieties of both glycosides consist of L-rhamnose and D-xylose, in a ratio of 1:3 for songoroside G and 1:4 for songoroside I. In the periodate oxidation of songorosides G and I, L-rhamnose and D-xylose remain unchanged.

The exhaustive methylation of songorosides G and I followed by their hydrolysis gave, qualitatively, the same set of methylated sugars, consisting of 2,3,4-tri-O-methyl-D-xylose, 2,4-di-O-methyl-D-xylose, and 2,4-di-O-methyl-L-rhamnose.

To determine the structures of songorosides G (V) and I (VI), we performed stepwise hydrolysis of the glycosides under identical conditions. Among the products of the hydrolysis of each of the glycosides we found an oleanolic acid monoside, $C_{35}H_{56}O_7$, a bioside with the composition $C_{41}H_{66}O_{11}$, and a trioside $C_{46}H_{74}O_{15}$. From the products of hydrolysis of songoroside I, in addition to the compounds mentioned, we isolated a tetraoside $C_{51}H_{82}O_{19}$, identical with songoroside G. The monosides from (V) and (VI) coincided completely in their properties and proved to be oleanolic acid 3-O-β-D-xylopyranoside (II). This compound has been described in the literature previously [3]. It was not found in plants but was described as a product of the degradation of patrinoside D from *Patrinia intermedia* Roem et Schult.

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