GUAIANOLIDES OF Saussurea amurensis

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The genus Saussurea DC. – one of the largest genera of the family Asteraceae (Compositae) – is represented in the flora of the Soviet Union by 34 species [1]. Far-Eastern saussureas, like the majority of representatives of this genus, have scarcely been studied in the chemical aspect [1, 2].

We have investigated the sesquiterpene lactones of the epigeal organs of the Amur saussurea (S. amurensis Turcz.) – one of the most widespread species in Maritime Territory and Priamur'e. This plant is used in folk medicine as a general tonic [3]. It has also been established that a tincture of the saussurea herbage possesses a high antiprotozoal activity [4, 5]; according to a preliminary evaluation, the epigeal part of the plant contains γ-lactones [6].

To isolate the lactones, the comminuted air-dry raw materials (10 kg) collected in the second half of the mass flowering phase of the plant in the environs of the village of Mukhen, Laso region, Khabarovskii krai, in August, 1984, were exhaustively extracted with ethanol. The extract was evaporated in vacuum and the residue was treated with 60% aqueous ethanol; the resulting precipitate was filtered off and the filtrate was treated with chloroform, to give 175 g of total material, part of which (90g) was chromatographed on a column of type KSK silica gel at a ratio of material to sorbent of 1:20. The fractions (550 ml) of the chromatographic separation were distributed in the following way: 1-28 (benzene); 29-56 [benzene–ethyl acetate (24:1)]; 57-102 [benzene–ethyl acetate (19:1)]; 103-135 [benzene–ethyl acetate (9:1)]; 136-151 [benzene–ethyl acetate (4:1)]; 152-200 [benzene–ethyl acetate (1:1)]; 201-231 (ethyl acetate); 232-251 (ethanol).

By rechromatographing fractions 52-64 in the way described in [7], we obtained two lactones in the form of colorless viscous oils with the compositions $C_{19}H_{24}O_5$ (I) [mass spectrum: m/z 332 (M^+), 224, 226, 197, 71] and $C_{19}H_{22}O_5$ (II) [mass spectrum: m/z 330 (M^+), 224, 226, 197, 69]. Lactones (I) and (II) were identified as aguerins A and B by a direct comparison of IR spectra [7].

Fractions 127-140 contained a lactone (III) with the composition $C_{19}H_{22}O_6$ (oil). Mass spectrum: m/z 346 (M^+), 262, 244, 226. By a comparison of spectral characteristics with those given in the literature, lactone (III) was identified as cynaropicrin, and this was confirmed by the formation of a diol with the composition $C_{16}H_{22}O_5$ (M^+ m/z 294), m.p. 156-157°C, on the hydrolysis of (III) ($MeOH-K_2CO_3$, in a current of nitrogen), which corresponded to the product of the saponification of cyanropicrin [8].

Fractions 142-146 deposited crystals of lactone (IV) with the composition $C_{15}H_{18}O_4$, mp 148-149°C (ethyl acetate), M^+ 262, which was identified by a mixed melting point and by a direct comparison of IR spectra as eleganin (8α-deacylcynaropicrin) [9].

The amounts of the lactones that had been isolated, calculated on the air-dry raw material, were (%): (I), 0.008; (II), 0.01; (III), 0.12; (IV), 0.07.

The action of the tinctures of the herbage of S. amurensis that are used in folk medicine is probably due to the class of substances investigated, since the results of recent years have shown that the sesquiterpene lactones isolated possess cytostatic, antitumoral, and antimicrobial activities [10-12].

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COUMARINS OF Physochlaina physaloides

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The air-dry roots of the plant Physochlaina physaloides (L) Don, family Solanaceae, which is used in Indo-Tibetan and traditional Mongolian medicine, that had been gathered in September, 1984, were extracted with 80% ethanol. The extract was concentrated in vacuum to small volume (1.5 liters from 10 kg of roots) and was extracted successively with hexane, chloroform, ethyl acetate, and butanol. By column chromatography on silica gel [chloroform–methanol (99:1)] the combined chloroform and ethyl acetate extracts yielded umbelliferone (I), $C_9H_6O_3$, mp 234-235°C [$\lambda_{max}^{CH_3OH}$ 256 and 325 nm] and scopoletin (II), $C_{10}H_8O_4$, mp 206-207°C [$\lambda_{max}^{CH_3OH}$ 230, 256, 298, and 343 nm] [2].

In the cold, the aqueous residue deposited a crystalline mixture of two coumarin glycosides (III and IV), which were separated by preparative chromatography on silica gel [chloroform–methanol (4:1)]. Compound (III), with the composition $C_{16}H_{18}O_9$, mp 210-211°C, and

TABLE 1. Chemical Shifts of the C Atoms of Fabriatrin (δ, ppm, relative to TMS, DMSO-d_6)

C atom	XC	C atom	XC	C atom	XC
2	160,6	9	149,0	5g	76,7
3	113,4	10	112,4	6g	68,3
4	144,3	OCH_3	56,1	1x	104,2
5	109,9	1g	99,6	2x	73,1*
6	146,1	2g	73,4*	3x	76,7
7	149,9	3g	75,5	4x	69,3
8	103,2	4g	69,6	5x	65,7

Note. g, glucose; x, xylose; *, assignment ambiguous.

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