ALKALOIDS OF Senecio othonnae

D. S. Khalilov and M. V. Telezhenetskaya

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Otosenine, onetine, and seneciphylline have previously been isolated from Senecio othonnae collected in Western Georgia [1]. As literature information shows, this plant from the flora of Azerbaidzhan has been little studied. However, the presence of seneciphylline in it has been reported [2].

We have investigated S. othonnae from Azerbaidzhan collected on July 12, 1971 in the flowering phase. The combined alkaloids obtained by the ion-exchange method after preliminary reduction with Zn dust amounted to 0.48% on the epigeal part and 0.76% from the roots. In the determination of the N-oxides in S. othonnae it was found that they amounted to 76.4 and 67% of the total, respectively.

The crystallization of the mixture of substances isolated from acetone gave a base (I) with mp 230-231°C, $[\alpha]_D + 20.4°$ (c 2.0; chloroform), picrate with mp 245°C (decomp.). The properties of this base, and also its IR, NMR, and mass spectra coincide with the corresponding data for the alkaloid otosenine [1, 3]. A mixture of base (I) and an authentic sample of otosenine gave no depression of the melting point. Otosenine made up 63% of the total alkaloids of the epigeal part and 8.8% of those from the roots.

The acetone mother liquor after the removal of the (I) was evaporated and the residue was recrystallized from acetone–chloroform. This gave a base (II) with mp 194-196°C, $[\alpha]_D + 66.7°$ (c 0.82; chloroform), picrate with mp 223-225°C; the acetyl derivative in the form of an adduct with benzene had mp 120-129°C, after drying 176-178°C.

The IR spectrum of (II) showed absorption bands of active hydrogen at 3400-3500 cm^{-1} and of an ester group at 1740 cm^{-1}, and also a diffuse band in the 1530-1680 cm^{-1} region of a carbonyl group bound transannularly with nitrogen [3, 4].

The mass spectrum of (II) had peaks of ions with m/e 441 (M^+), 397, 354, 338, 337, 238, 168, 150, 141, 123, 122, 110, 108, 97, 96. In the NMR spectrum of (II) taken in CD_3OD there were the signals of five methyl groups (δ scale, ppm); three-proton singlets of $N-CH_3$ (2.20), $OCOCH_3$ (2.0), and $C-CH_3$ (1.57); and a six-proton signal consisting of two superposed doublets from $CH-CH_3$ groups (1.15). In addition to this, the spectrum showed the broadened signal of a vinyl proton at 6.05 ppm, and also multiplets characteristic for methylene and methine protons of otonecine esters.

The properties of the base (II) and its spectral characteristics coincide with the properties and structure of the alkaloid floridanine [3]. This is the main alkaloid of the roots (76.4% of the total), its amount in the epigeal part being 17%. Cava et al. [3] did not consider the proposed structure of floridanine as definitive, since they were unable to show it chemically, and the NMR spectrum that they recorded in trifluoroacetic acid was poorly resolved. However, as mentioned above, the spectrum of (II) taken in CD_3OD gives well-resolved signals. The singlet at 1.57 ppm for a quaternary methyl group is shifted downfield, which shows the position of the acetyl group on the same carbon atom. Furthermore, the periodic oxidation of floridanine gave us acetaldehyde, identified in the form of its dimedone derivative. This is convincing proof of the presence of two free hydroxy groups on adjacent carbon atoms. Thus, the additional results that we obtained confirm the structure of floridanine proposed previously.

This is the first time that floridanine has been isolated from the genus Senecio. Seneciphylline was not detected in the residual mother liquors.

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