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ISOLATION OF (—)-KAURENAL FROM THE CULTURE LIQUID OF Fusarium moniliforme

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UDC 547.597

The fungus Fusarium moniliforme Sheld. is known for its ability to produce gibberellic acid [1], and the industrial preparation of gibberellic acid is based on this [2]. The neutral substances accompanying gibberellic acid and isolatable from the culture liquid of this fungus are represented mainly by kaurane diterpenoids [3], of which only (—)-kaurene (I) participates in the biosynthesis of the gibberellins [4]. The products of its subsequent biosynthetic transformations, (—)-kaurenol (II) and (—)-kaurenal (III) [5], have not been found the culture liquid of this fungus. They have been detected in extremely small amounts in an extract of mycelium of some strains of Fusarium moniliforme [6-8]. It has been suggested [9] that they are rapidly metabolized by the fungus to highly oxygenated derivatives — the gibberellins.

In an investigation of the total metabolites of Fusarium moniliforme (strain 857, variant 919) impoverished in gibberellin A_3 and forming the wastes of the industrial product of gibberellin (fermentation based on the method of Muromtsev et al. [2]), we have isolated by the chromatography of its neutral fraction a substance with mp 113-114°C (from heptane), $[\alpha]_D^{2^1}$ -78.5° (c 2.81; chloroform), the NMR spectrum of which corresponds to that of (-)-kaurenal [10, 11], which has mp 114°C and $[\alpha]_D$ -95° [10]. The reduction of the aldehyde isolated with sodium tetrahydroborate in ethanol yielded (-)-kaurenol with mp 142-143°C (from heptane), $[\alpha]_D^{19}$ -71° (c 1.67; chloroform); literature data [10]: mp 140-141°C, $[\alpha]_D$ -82°. The amount of (-)-kaurenal in the mixture of neutral compounds studied was 0.8%, which somewhat exceeds the amount of (-)-epimanoyl oxide, a well-known metabolite of Fusarium moniliforme [3], found in the same mixture (0.5%).

The presence of a relatively large amount of (-)-kaurenal in the mixture of metabolites of Fusarium moniliforme is of definite interest if one takes into account the high efficiency of the biosynthesis of the gibberellins by this strain. As Bearder [8] has found in the mutant strain B1-41a there is a blockage at the stage of the transformation of (-)-kaurenal into (-)-kaurenic acid. Apparently, in the strain investigated, as well, there is a partial blockage of this type the presence of which in this case is shown by an accumulation of (-)-kaurenal. (-)-Kaurenal was first isolated as a natural product from two plants of the family Compositae [10, 11].

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OLEANOLIC ACID AND HEDERAGENIN FROM THE STEMS OF Cephalaria transsylvanica

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UDC 615.32

In a study of the chemical composition of the stems of *Cephalaria transsylvanica* (L.) Schrad. (family Dipsacaceae), collected in the full-flowering period in the Dzhalilabad region of the Azerbaidzhan SSR, in addition to flavonoids and other substances we detected triterpene compounds in them [1, 2].

The triterpenoids were extracted from the raw material with chloroform. The chloroform extract was concentrated, treated with activated carbon, and filtered. The presence of two triterpenoids A and B in the filtrate was established by thin-layer chromatography in various solvent systems. The separation of these triterpenoids in the individual form was performed on a column of Al_2O_3 (activity grade II) in the ethyl acetate—benzene (5:2) system.

After repeated recrystallization from methanol, triterpenoid A had mp 304-308°C, $[\alpha]_D^{20}$ +80° (c 1.0; chloroform), and B had mp 324-326°C, $[\alpha]_D^{22}$ +76° (c 1.2; chloroform).

On the basis of their physicochemical properties, IR spectral characteristics, and comparative chromatographic studies with markers, it was established that triterpenoid A was oleanolic acid and B hederagenin.

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