FATTY ACID COMPOSITION OF A BIOLOGICALLY ACTIVE COMPLEX FROM Nostoc muscorum

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There are statements in the literature that extracts of green and blue-green algae [1] exhibit antibiotic properties. It is assumed that such properties of preparations from green algae are due to the presence of chlorophyllides [2] and fatty acids [3] in the cells. It has also been established that algae, including blue-green algae, exhibit a favorable influence on various higher plants: they increase the germinating capacity of cotton seeds, increase the lengths of their shoots, and accelerate the opening of the bolls, and they increase the yield of rice [4, 5]. However, there is no information on the isolation and identification of substances possessing growth-stimulating activity. We have isolated a biologically active complex from the biomass of the cyanobacterium Nostoc muscorum and have studied its lipid composition.

The algae were cultivated in Takha's medium [6] at a temperature of 30-32°C. The sum of the biologically active compounds was isolated by the method of [7], their yield amounting to 0.1-0.12% of the dry biomass. According to the results of laboratory investigations, this complex possesses a growth-stimulating action on the cotton plant [8]. From the results of chemical analysis, the main components of the complex were carbohydrates (70%), proteins (15%), nucleic acids, and lipids.

The lipid fraction was isolated from the comminuted complex by extraction with chloroform–methanol (2:1), its yield being 4.5% of the mass of the complex. By comparison with model samples, in the total lipids of the complex by TLC (Silufol and silica gel L 5/40 μm, Chemapol, Czechoslovakia), mainly free fatty acids (FFAs) and traces of triacylglycerols were detected. The solvent systems were: heptane–methyl ethyl ketone–acetic acid (43:7:0.5) and chloroform–methanol–ammonia (65:35:5); revealing agents: iodine vapor and the Vaskovskii [Vaskovsky] reagent. There were no phospholipids in the complex. The absence of the native classes of lipids is explained by their destruction on the isolation (with 1 and 2 N perchloric acid) and purification of the complex [7].

The FFAs were methylated with diazomethane and the methyl esters were analyzed by GLC. The FAMEs were chromatographed on a Chrom-4 instrument with a flame-ionization detector in a column (3 mm × 2.5 m) filled with 17% of PEGS on Celite-545, with helium as the carrier gas. On GLC the following fatty acids were identified (wt.%): 10:0–1.7; 12:0–2.8; 14:0–9.5; 15:0–2.7; 16:0–27.0; 16:1–3.5; 18:0–17.2; 18:1–33.8; 18.2–1.8 Σ_s – 60.9; Σ_u – 39.1.

As can be seen from the figures given, the fatty acid component of the lipids of the Nostoc muscorum complex is represented mainly by the 16:0, 18:0, and 18:1 acids, and the biological activity of this complex is apparently not due to the fatty acid components.

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A NEW DIHYDROFUROCOUMARIN FROM Smyrniopsis aucheri

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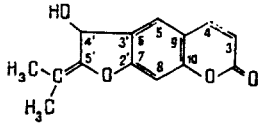
The roots of the Smyrniopsis aucheri Boiss. (smyrniopsis) collected in the flowering and fruit-bearing phase close to the village of Kuku in the Shakhbuz region of the Nachikhevan ASSR have been investigated. Thin-layer chromatography on Silufol showed that an ethanolic extract of the roots contained not less than 12 coumarin compounds. Five coumarins have previously been extracted from a plant of this species and characterized [1-3].

From an ethanolic extract, by chromatography on a column of silica gel, we isolated another seven coumarin compounds. On the basis of a study of their UV, IR, NMR, and mass spectra and physicochemical characteristics we have established the structure of one of them, which we have called nachsmyrin (I), $C_{14}H_{12}O_4$, M^+ 244, mp 135-136°C. The presence in the UV spectrum of absorption maxima at 220, 225, 247, 253, and 303 nm (log ε 3.99, 3.96, 4.17, 4.20, and 3.86, respectively) showed that the substance was a 7-O-substituted coumarin.

In the IR spectrum, absorption bands were observed at (cm^{-1}) 3500 (OH), 1730 (C=O), 1620, 1585, and 1455 (aromatic ring), which are characteristic for dihydrocoumarin derivatives [4]. The mass spectrum of the subtances contained the peaks of ions with m/z 244 (M^+), 227 (M^+–OH), 201 ($M^+ - =C\begin{matrix}CH_2\\CH_3\end{matrix}$) 198 ($M^+ - 2CH_3$, –O) 187, 158, 155, 131, 101. In the NMR spectrum (100 MHz, $CDCl_3$) of nachsmyrin signals were observed from two methyl groups at a double bond, 1.68 (6H, s, $2CH_3$); of a gem-hydroxylic, 2.93 (1H, s), and from the aromatic protons of a coumarin nucleus: 6.18 (1H, d, J = 10 Hz, H-3); 6.77 (1H, s, H-8); 7.19 (1H, s, H-5) and 7.61 (1H, d, J = 10 Hz, H-4).

When (I) was acetylated with acetic anhydride in pyridine, a monoacetate $C_{16}H_{14}O_5$, M^+ 286, mp. 121-122°C, was obtained, as was confirmed by a pronounced decrease in the absorption band of a hydroxy group in the IR spectrum, by the presence of a three-proton singlet at 2.02 ppm, and by a paramagnetic shift of the signal of the gem-hydroxylic proton in the NMR spectrum. The mass spectrum of the monoacetate contained the peaks of ions with m/z 286 (M^+) and 244 ($M^+ - 42$).

On the basis of the facts given above, and in the light of the biogenesis of similar coumarins in smyrniopsis, it may be concluded that nachsmyrin has the following structural formula



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A study of the structures of the other coumarins that we isolated from this plant is continuing.

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