LIPOSOLUBLE PIGMENTS OF LEAF VEGETABLES.

I. PIGMENTS OF DOCK AND SPINACH

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In food technology, considerable attention is being devoted to the development of formulations and regimes for obtaining tonic chlorophyll-carotene food pastes prepared from leaf vegetable tops (dock, spinach, etc.) [1] and used for coloring and enriching with biologically valuable substances first courses, and confectionery, dairy, and diabetic products. However, there is no information in the literature on the chemical composition of the chlorophylls and carotenoids of the varieties of dock and spinach that are the most common and promising for processing.

In view of the necessity for taking the chemical composition of the raw material into account in the development of new formulations and technologies of the production of vegetable compositions, we have investigated the pigment complex of dock of the varieties Odesskii-17 (sample 1) and Shirokolistnyii (sample 2) and of spinach of the varieties Isponskii (sample 3) and Viktoriya (sample 4), grown on an experimental plot under the conditions of Odessa province and gathered at the stage of commercial ripeness. The pigments were isolated as described in [2]. An aliquot part of an extract intended for the isolation of carotenoids was freed from chlorophyll and lipids by saponification and was fractionated into carotenes and xanthophylls by using a sucrose column [3].

A second part of the extract was used for determining chlorophylls after their preliminary freeing from accompanying impurities by column chromatography on silica gel [4].

Subsequently, the pigments were separated by TLC on cellulose (Nagel) using for the xanthophylls and chlorophylls the solvent system heptane–methyl ethyl ketone (5:3) and for the carotenes hexane–acetone (96:4). The compounds were identified and determined quantitatively as described in [5, 6] (%):

Pigment	Sample 1	Sample 2	Sample 3	Sample 4
Chlorophylls and their structural analogs				
chlorophyll a	70.4	52.6	61.5	57.5
chlorophyll b	29.6	13.7	22.1	16.6
pheophytin a	--	4.2	--	--
pheophytin b	--	1.6	--	--
pheophorbide a	--	6.0	7.3	10.9
pheophorbide b	--	2.5	2.4	4.6
methylchlorophyllide a	--	4.1	--	--
methylchlorophyllide b	--	1.4	--	--
chlorophyllide a	--	9.0	4.9	7.5
chlorophyllide b	--	4.9	1.8	2.9
Total amount, mg/kg of dry mass	833	615	1320	1137

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Carotenoids				
α-carotene	1.6	--	1.4	2.2
β-carotene	32.4	39.5	28.9	31.2
lutein	25.9	43.5	49.2	50.1
zeaxanthin	4.8	--	2.0	1.2
lutein 5,6-epoxide	2.3	--	--	--
violaxanthin	19.7	12.6	12.7	11.2
neoxanthin	13.3	4.4	5.8	4.1
Total amount, mg/kg of dry mass	155	136	322	290

The total amounts of both chlorophylls and carotenoids in spinach were considerly higher (1.5-2 times) than in dock. Dock of the Shirokolistnyii variety, in contrast to Odesskii-17, contained a large amount of magnesium-free and phytol-free chlorophyll derivatives which is possibly explained by the high activity of chlorophyllase in variety and by the formation of methyl derivatives from the chlorophyllides as the result of the occurrence of methanolysis in the extraction process [6]. The low content of pheophytins or their absence in leaf vegetables is obviously connected with a low acidity of the medium.

The carotenoids were represented by 4-7 forms of pigments of which the predominating (60-80%) components were β-carotene and lutein.

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PHENOLCARBOXYLIC ACIDS AND IRIDOIDS OF Ziziphora bungeanae

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Hydroxycinnamic acids and bitter glycosides of terpene alcohols belonging to the iridoid group are frequently found in plants of the family Lamiaceae [1, 2]. In view of this, it appeared of interest to investigate Ziziphora bungeanae for the presence of these compounds.

The acids were extracted with ether from a dried methanolic extract of the ziziphora [1, 3]. The ethereal solution was treated with 2% sodium bicarbonate solution. The sodium bicarbonate solution was acidified with 10% hydrochloric acid to pH 3-4 and was again extracted with ether. The solvent was distilled off to dryness. When the residue was crystallized from a mixture of ether and ethanol (7:1), a substance with the composition $C_9H_8O_4$, M^+ 180, mp 192-193°C was obtained.

The physical constants, physicochemical properties, and IR, UV, and PMR spectra [4] of the substance isolated and of caffeic acid were identical.

After the isolation of the caffeic acid, the filtrate and the mother liquor were combined, the solvent was driven off, and the mixture was chromatographed on a column of silica

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