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Investigations on Carotenoids in Lichens. XIX. Carotenoids in Lichens of the Tundra of Kamchatka Region (Far East)

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With 1 Figure

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Summary

CZECZUGA B., SKIRINA I. P., MAXIMOV O. B. & STEPANENKO L. S. 1989: Investigations on carotenoids in lichens. XIX. Carotenoids in lichens of the tundra of Kamchatka region (Far East). – Phyton (Austria) 29 (1): 7–13, with 1 figure. – English with German summary.

Column and thin-layer chromatography revealed the presence of the following carotenoids in the thalli of 12 lichen species from the tundra of Kamchatka region: α-carotene, β-carotene, rubixanthin, α-cryptoxanthin, β-cryptoxanthin, zeaxanthin, lutein, lutein epoxide, canthaxanthin, astaxanthin, rhodoxanthin, neoxanthin, violaxanthin, mutatochrome, mutatoxanthin, auroxanthin, luteoxanthin, β-apo-2'-carotenal and β-citraurin. β-cryptoxanthin and lutein epoxide occurred in all species. The total content of carotenoids ranged from 11.8 *(Cladina stellaris)* to 57.7 $\mu g\ g^{-1}$ dry wt *(Alectoria ochroleuca)*.

Zusammenfassung

CZECZUGA B., SKIRINA I. F., MAXIMOV O. B. & STEPANENKO L. S. 1989. Untersuchungen über Carotinoide in Flechten. XIX. Carotinoide in Flechten der Kam-

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tschatka-Tundra. – Phyton (Austria) 29 (1): 7–13, mit 1 Figur. – Englisch mit deutscher Zusammenfassung.

In den Thalli von 12 Flechtenspezies aus der Tundra von Kamtschatka wurden mittels Säulen- und Dünnschichtchromatographie folgende Carotinoide gefunden: α- und β-Carotin, Rubixanthin, α- und β-Cryptoxanthin, Zeaxanthin, Lutein, Luteinepoxid, Canthaxanthin, Astaxanthin, Rhodoxanthin, Neoxanthin, Violaxanthin, Mutatochrom, Mutatoxanthin, Auroxanthin, Luteoxanthin, β-Apo-2'-carotenal und β-Citraurin. β-Cryptoxanthin und Luteinepoxid kamen in allen Species vor. Der Gesamtcarotingehalt lag zwischen 11,8 *(Cladina stellaris)* und 57,7 $\mu g\ g^{-1}$ dry wt *(Alectoria ochroleuca)*.

Introduction

Lichens play an important role as pionier plants in some geographical latitudes. They are of particular significance in regions with a harsh climate where they are often the only vegetation and provide the basic food for reindeer (MAGNUSSON 1952). We have studied the carotenoids in the lichens which abound in Greenland (CZECZUGA & ALSTRUP 1987), in Scandinavian Lapland (CZECZUGA 1986) and in the far north of the Soviet Union (CZECZUGA & SHCHELKUNOVA 1986). The tundra of the Far East in the Kamchatka region is also characteristic for its species climatic conditions. It was, therefore, considered that the publication of the results of the present studies would augment our knowledge of the carotenoids in lichens of the tundra in other latitudes.

Material and Methods

The investigations were carried out on the following 12 species collected in the tundra of Kamchatka region (Far East): *Nephroma arcticum* (L.) TORSS., *Cladina stellaris* (OPIS.) BRODO, *Umbilicaria muhlenbergii* (ACH.) TUCK., *Cetraria andrejevii* OXN., *Cetraria cucullata* (BELLARDI) ACH., *Cetraria delisei* (BORY) TH. FR., *Cetraria islandica* (L.) ACH., *Cetraria laevigata* RASSAD., *Cetraria nivalis* (L.) ACH., *Parmelia centrifuga* (L.) ACH., *Alectoria ochroleuca* (HOFFM.) MOSS and *Dactilina arctica* NYL. (Table 1).

The thalli were cleaned of all organic debris, macerated placed in dark glass bottles and covered with acetone. The air above the fluid in the bottle was replaced with nitrogen, to ensure an anaerobic atmosphere. The samples were kept in a refrigerator (−4°C) until analysed by chromatography for their carotenoid content.

The carotenoid pigments were extracted with 95% acetone in a dark room. Saponification was carried out with 10% KOH in ethanol at about 20°C for 24 hours in the dark in a nitrogen atmosphere.

Column and thin-layer chromatography, described in detail in a previous paper (CZECZUGA 1980b), were used to separate various carotenoids. A glass column (Quickfit-England), approximately 1 cm in diameter and 15–20 cm in length, filled with Al_2O_3 was used in the column chromato-

Table 1

Investigated species of lichens from Kamchatka region

Familia and species	Collected from	Locality
Peltigeraceae		
Nephroma articum	Stones, Ganalski hills	Kamchatka
Cladoniaceae		
Cladina stellaris	Soil surface, Kolymske eminence	Magadanska District
Umbilicariaceae		
Umbilicaria muhlenbergii	Stones, Kolymske eminence	Magadanska District
Parmeliaceae		
Cetraria andrejevii	Soil surface, Kolymske eminence	Magadanska District
Cetraria cucullata	Soil surface, Kolymske eminence	Magadanska District
Cetraria delisei	Soil surface, Kolymske eminence	Magadanska District
Cetraria islandica	Soil surface, Kolymske eminence	Magadanska District
Cetraria laevigata	Soil surface, Kolymske eminence	Magadanska District
Cetraria nivalis	Soil surface, Kolymske eminence	Magadanska District
Parmelia centrifuga	Stones, Kolymske eminence	Magadanska District
Usneaceae		
Alectoria ochroleuca	Soil surface, Kolymske eminence	Magadanska District
Dactylina arctica	Soil surface, Kolymske eminence	Magadanska District

graphy. The extract was passed through the column and the different fractions were eluted with the solvent. Silica gel was used for thin-layer chromatography with the appropriate solvent systems, the R_f values being determined for each spot. For identification of carotenoids replicate chromatography was performed with standard carotenoids (Hoffman-La Roche & Co. Ltd., Basle, Switzerland and Sigma Chemical Company, USA).

The pigments were identified on the basis of: a) their behaviour in column chromatography, b) their absorption spectra in various solvents, recorded with a Beckman spectro-photometer model 2400 Du, c) their partition between hexane and 95% methanol, d) their R_f values in thin-layer chromatography, e) the presence of allylic hydroxyl groups, determined by the acid-chloroform test, f) the epoxide test, and g) the mass spectrum (VETTER & al. 1971).

The concentrations of carotenoid solutions were determined from the absorption spectra, on the basis of the extinction coefficient E 1% cm^{-1} at wavelength of maximal absorbance in petroleum ether or hexane (DAVIES 1976).

Results

In the thalli of 12 species of lichens belinging to five families collected from the tundra of the Far East, 19 carotenoids were identified (Table 2, Fig. 1). Most of these often been noted in various species of lichen. Some

Table 2

List of the carotenoids from the investigated lichen species

Carotenoid	Structure (see Fig. 1)	Semisystematic name
1. α-Carotene	A – R – B	β, ε-carotene
2. β-Carotene	B – R – B	β, β-carotene
3. Rubixanthin	C – R – E	β, ψ-carotene-3-ol
4. α-Cryptoxanthin	B – R – D	β, ε-carotene-3-ol
5. β-Cryptoxanthin	B – R – C	β, β-carotene-3-ol
6. Zeaxanthin	C – R – C	β, β-carotene-3,3'-diol
7. Lutein	C – R – D	β, ε-carotene-3,3'-diol
8. Lutein epoxide	D – R – F	5,6-epoxy-5,6-dihydro-β, ε-carotene-3,3'-diol
9. Canthaxanthin	K – R – K	β, β-carotene-4,4'-dione
10. Astaxanthin	L – R – L	3,3'-dihydroxy-β, β-carotene-4,4'-dione
11. Rhodoxanthin	M – R_3 – M	4',5'-didehydro-4',5'-retro-β, β-carotene-3,3'-dione
12. Neoxanthin	F – R_1 – G	5',6'-epoxy-6,7-didehydro-5,6,5',6'-tetrahydro-β, β-carotene-3,5,3'-triol
13. Violaxanthin	F – R – F	5,6,5',6'-diepoxy-5,6,5',6'-tetrahydro-β, β-carotene-3,3'-diol
14. Mutatochrome	B – R_1 – H	5,8-epoxy-5,8-dihydro-β, β-carotene
15. Mutatoxanthin	C – R_1 – I	5,8-epoxy-5,8-dihydro-β, β-carotene-3,3'-diol
16. Auroxanthin	I – R_2 – I	5,8,5',8'-diepoxy-5,8',5',8'-tetrahydro-β, β-carotene-3,3'-diol
17. Luteoxanthin	F – R_1 – I	5,6,5',8'-diepoxy-5,6,5',8'-tetrahydro-β, β-carotene-3,3'-diol
18. β-Apo-2-carotenal	B – R – N	3',4'-didehydro-2'-apo-β-caroten-2'-al
19. β-Citraurin	C – R_1 – O	3-hydroxy-8'-apo-β-caroten-8'-al

rarer carotenoids were, however, found in our material, that is: rubixanthin *(Cetraria laevigata)*, α-cryptoxanthin *(Alectoria ochroleuca)*, mutarochrome *(Cladina stellaris, Parmelia centrifuga)*, auroxanthin *(Nephroma arcticum)* and β-citraurin (*Cladina stellaris, Cetraria islandica,* cf: Table 3). The following carotenoids were found to predominate: β-cryptoxanthin *(Cetraria cucullata, Parmelia centrifuga)*, astaxanthin *(Cetraria laevigata, Cetraria nivalis)* and lutein epoxide (in the remaining eight species). The total carotenoid content in the thalli of the lichens species studied ranged from 11.8 *(Cladina stellaris)* to 57.7 $\mu g\ g^{-1}$ dry wt *(Alectoria ochroleuca)*.

Discussion

Of the carotenoids found in our material, rarely noted in lichens, the most worthy of note are rubixanthin, α-cryptoxanthin and β-citraurin.

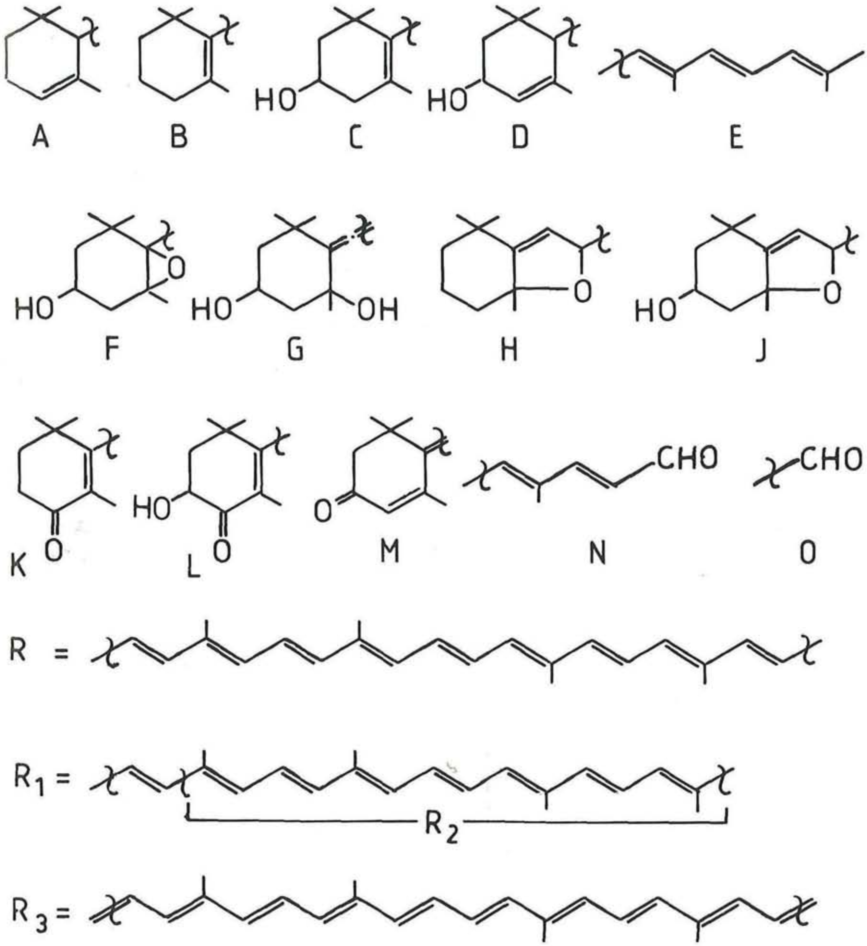

Fig. 1. Structural features of carotenoids

Rubixanthin is a derivative of γ-carotene has been quite frequently reported in various species of fungi (CZECZUGA 1978, 1979). It has also been found, though only sporadically, in higher plants, particularly in the petals of some plants (Goodwin 1980), and in algae (WETTERN & WEBER 1979). In the lichen, rubixanthin has been noted in, among others, the *Ramalina forinaceae* thalli (CZECZUGA 1980 a). The derivative of α-carotene, α-cryptoxanthin is sometimes encountered in the plant world in both algae and higher plants. In fungi (GOODWIN 1980), α-cryptoxanthin has not as yet been reported so that it can be assumed that in lichens it is formed by the alga component. This carotenoid has been found in the thalli of some lichen species from various

Table 3

Carotenoid distribution in lichens from Kamchatka region

Familia and species	Carotenoid (see Table 2)	Major carotenoid (%)	Total content ($\mu g\ g^{-1}$ dry wt)
Peltigeraceae			
Nephroma articum	1, 2, 5, 8, 12, 13, 15, 16	8 (41.6)	25.8
Cladoniaceae			
Cladina stellaris	1, 2, 5, 8, 12, 14, 18, 19	8 (43.3)	11.8
Umbilicariaceae			
Umbilicaria muhlenbergii	2, 5, 7, 8, 10, 12, 15, 17	8 (32.4)	18.1
Parmeliaceae			
Cetraria andrejevii	5, 8, 9, 10, 12, 15	8 (42.0)	20.2
Cetraria cucullata	5, 8, 12, 13	5 (46.5)	12.4
Cetraria delisei	5, 8, 11, 12, 15, 17, 18	8 (42.6)	13.9
Cetraria islandica	5, 6, 8, 13, 15, 19	8 (43.0)	30.1
Cetraria laevigata	3, 5, 8, 10, 13	10 (73.7)	40.2
Cetraria nivalis	5, 6, 8, 9, 10, 11, 15, 17	10 (40.3)	37.6
Parmelia centrifuga	5, 6, 8, 9, 14, 15	5 (56.9)	43.3
Usneaceae			
Alectoria ochroleuca	4, 5, 6, 8, 9, 10, 15	8 (65.2)	57.7
Dactilina arctica	5, 7, 8, 10, 12, 15	8 (79.4)	55.1

families which were collected from Northern Siberia in the Taimyra region (CZECZUGA & SHCHELKUNOVA 1986). As regards β-citraurin, this carotenoid belongs to the apocarotenal group which are formed as a result of the natural degradation of carotenoids. It is thought that β-citraurin is formed as a result of the degradation of zeaxanthin. It is one of the carotenoids which have to date been regarded as characteristic of ripe fruits, particularly the citrus fruits (GOODWIN 1980).

In the lichens, however, it has been found in only a few species from the mountains of Japan (CZECZUGA & YOSHIDA 1988). Its presence has also been reported in the mosses of the Antarctic region (CZECZUGA & al. 1982).

The present studies show that the thalli of the lichen species investigated have a slightly higher total carotenoid content.

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Recensiones

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