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Bazyli CZECZUGA[1]), Ryszard GUTKOWSKI[2]) and Romuald CZERPAK[2])

[1]) Department of General Biology, Medical Academy, Kilińskiego1, 15-230 Białystok
[2]) Department of Biology, Branch of Warsaw University, Lipowa 41, 15-424 Białystok, Poland

Studies on the carotenoids of the *Embryophyta*. VII. Representatives of the families *Gramineae* and *Caryophyllaceae* from King George Island (South Shetland Islands)

ABSTRACT: Carotenoids of two species of the Antarctic higher plants from King George Island were analysed. Using thin-layer and column chromatography 16 carotenoids were identified. The total carotenoid content ranged from 4.064 to 17.257 mg/g of dry weight material.

Key words: Antarctic, King George Island, higher plants, *Colobanthus, Deschampsia,* carotenoids

1. Introduction

There was rich flora in the Antarctic in the past geological ages. Fossil remnants of about 90 species of plants have been identified so far. The present Antarctic, however, is regarded as an "ice desert", in which plant life is very poor.

Plant life concentrates mainly in the Antarctic oases, i.e. on the ice-free areas, which are usually found in the coastal regions. These oases have very specific environmental conditions. The following are the most characteristic features: dry atmosphere, intense heating of the rocks due to very strong solar radiation, severe and abrupt changes of temperature (Allen, Grimshaw and Holdgate 1967). Under these specific ecological conditions the plant world is relatively poor, although a few species of fungi, lichens, mosses and ferns occur here and there (Gimingham and Smith 1970). Seed plants are represented only by two species.

The flora of King George Island, just as that of the whole mainland, is poorly developed due to shallow soils poor in assimilable components. Owing to the severe climatic conditions the phylum *Bryophyta* (30 species) and lichens (40 species) are predominant in the plant world of the Island (Gimingham and Smith 1970). Two vascular plants were identified: *Colobanthus quitensis* and *Deschampsia antarctica* (Allison and Smith 1973, Smith 1981).

The aim of this study was to make a thorough analysis of the active biological substances, such as cartoneoids, i.e. provitamins of vitamin A, found in plants growing in the specific ecological environment of the Antarctic

2. Material and methods

Colobanthus quitensis (the whole plant) and *Deschampsia antarctica* (overground parts of the plant) were collected from storm-ridges on King George Island. This region borders on Admiralty Bay, on one side, and on a fresh-water lake, on the other. The area in which the above-mentioned species of vascular plants may be found lies close to the penguin migratory routes. *Deschampsia antarctica* and *Colobanthus quitensis* grow in groups in shallow soil among the pebbles of the storm-ridges.

Carotenoid pigments were extracted in a dark room from 70 g of fresh weight material from each plant by means of 98% acetone. Saponification was made with 10% KOH in ethanol, at the temperature of about 20°C, in dark chamber, in nitrogenous atmosphere.

The thin-layer and column chromatography, described in details in earlier papers (Czeczuga 1978), was used for the dissociation of various carotenoids. A glass column (Quickfit-England), approximately 1 cm in diameter and 15—20 cm in ligth, filled with Al_2O_3 was used in the column chromatography. The extract was passed through the column and eluted with an appropriate solvent. Silica gel with various solvent combinations was used in the thin-layer chromatography, the R_f values were determined for each point.

Pigments were identified by the following methods: a) behaviour in column chromatography, b) adsorption spectra of the pigments in various solvents in a Backman spectrophotometer, Model 2400 DU, c) partition characteristic for carotenoids betwene hexane and 95% methanol, d) comparison of the R_f values in thin-layer, for identification of α-carotene, β-carotene, α-cryptoxanthin, β-cryptoxanthin, antheroxathin, lutein, zeaxanthin, and canthaxanthin; co-chromatography with standard carotenoids way used (Hoffman-La Roche a Co., Basle, Switzerland and Sigma chemical company, USA), e) the presence of allylic hydroxyl groups was determined with acid chloroform, f) the epoxide test.

Quantitative determinations of the concentrations of the carotenoid solutions were made using the quantitative absorption spectra. These determinations were base on the extinction coefficient ($E^{cm}_{1\%}$) at the wave-length of the maximum absorbance in petroleum ether or hexane (Davies 1976). The percentage content of various carotenoids and the total amount of carotenoids were determined after the Davies (1976) method.

3. Results

The average percentage content of dry weight material in the examined plants is given in Table I. Both plants, *Colobanthus quitensis* and *Deschampsia antarctica* contained the highest amount of dry mass in February.

The results from the analysis of the carotenoid content in the examined material are given in Table II and Fig. 1. Altogether 16 carotenoids were

Table I.

Average dry weight percentage share in the examined plants

Species	20 October	2 December	3 February
Colobanthus quitensis	19.3	21.4	22.2
Deschampsia antarctica	35.3	24.6	38.6

Table II.

List of carotenoids of the Antarctic plants

No	Carotenoid	Structure (see Fig. 1)	Semisystematic name
I	α–carotene	A — V — B	β, ε — carotene
II	β–carotene	A — V — B	β, β–carotene
III	ε–carotene	A — V — A	ε, ε–carotene
IV	α-cryptoxanhin	C — V — B	β, ε–caroten–3′–ol
V	β-cryptoxanhin	B — V — D	β, β–caroten–3–ol
VI	canthaxanthin	E — V — E	β, β–carotene–4,4′–dione
VII	lutein	C — V — D	β, ε–carotene–3,3′–diol
VIII	lutein epoxide	C — V — H	5,6–epoxy–5,6–dihydro–β, ε–carotene–3,3′–diol
IX	zeaxanthin	D — V — D	β, β–carotene–3,3′–diol
X	antheroxanthin	D — V — H	5,6–epoxy–5,6–dihydro–β, β–carotene–3,3′–diol
XI	adonixanthin	D — V — F	3,3′–dihydroxy–β, β–caroten–4–one
XII	α–doradexanthin	C — V — F	3,3′–dihydroxy–β, ε–caroten–4–one
XIII	violaxanthin	H — V — H	5,6,5′,6′–diepoxy–5,6,5′,6′—tetrahydro– –β, β–carotene–3,3′–diol
XIV	neoxanthin	H — W — G	5,6′–epoxy–6,7–didehydro–5,6,5′,6′–tetrahydro– –β, β–carotene–3,5,3′–triol
XV	mutatoxanthin	D — X — I	5,8–epoxy–5,8–dihydro–β, β–carotene–3,3′–diol
XVI	β–apo–2′–carotenal	B — Z	3′,4′–didehydro–2′–apo–β–caroten–2′–al

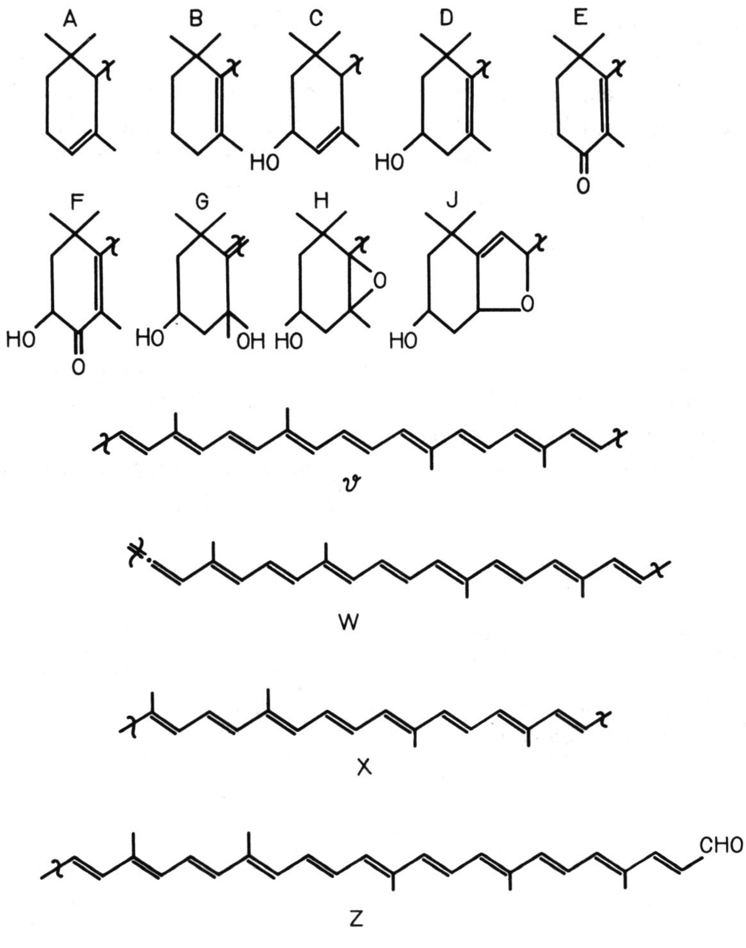

Fig. 1. Structural features of carotenoids from higher plants King George Island (Antarctic) (Antarctic)

identified. Some of them, such as: α-, β-carotene, α-, β-cryptoxanthin, lutein epoxide, zeaxanthin, antheroxanthin, and neoxanthin, were present in the material from both plant species throughout the three-months period of the investigations (Table III). The presence of carotenoids, such as: ε-carotene, α-cryptoxanthin, canthaxanthin, antheroxanthin, adonixanthin, α-doradexanthin and β-apo-2'-carotenal, in the examined material are particularly worth mentioning. The total content of carotenoids in the dry weight material ranged from 4.829 to 9.763 mg/g for *Colobanthus quitensis* and from 4.064 to 17. 257 mg/g for *Deschampsia antarctica.*

Table III.

Carotenoid content (%) in the Antarctic plants

Carotenoid	*Colobanthus quitensis*			*Deschampsia antarctica*		
Dates	20 Oct.	2 Dec.	3 Feb.	21 Oct.	29 Nov.	3 Feb.
α — carotene		22.2			16.8	24.6
β — carotene	15.3		14.9		14.7	11.2
ε — carotene		18.7				
α — cryptoxanthin			7.4			2.0
β — cryptoxanthin	5.7				9.1	6.5
canthaxanthin				8.4		
lutein	9.5	11.0	trace	35.2	10.1	2.8
lutein epoxide	23.1			27.4	18.6	34.2
zeaxanthin	27.1	15.8	31.7	26.9	18.5	8.7
antheroxanthin	8.9	32.3			7.1	5.2
adonixanthin	10.4					
α — doradexanthin			25.8			
violaxanthin					1.4	
neoxanthin			7.4			4.8
mutatoxanthin			12.6			
β — apo-2′ — carotenal				2.0		
Total content mg/g dry weight	9.763	4.829	6.838	4.064	9.048	17.257

4. Discussion

Some of carotenoids mentioned above are not commonly found in the higher plants and therefore they require careful consideration.

As regards ε-carotene it has been found mainly in some species of algae (Czeczuga 1979), whereas in the higher plants it is detected for the first time in these studies.

As regards α-cryptoxanthin, a derivative of α-carotene, for the first time described in the higher plants as physoxanthin (Bodea et al. 1978), it was found in the flowers, seeds and fruits of some species of the higher plants (Goodwin 1980).

As regards canthaxanthin in the lower plants it was found in algae (Czeczuga 1979), in fungi (Czeczuga 1978) and in the mushroom *Cantharellus cinnabarinus,* for the first time described by Haxo (1950). In the higher plants canthaxanthin was found rather infrequently (Czeczuga 1978). It was detected recently in the oak-galls (Czeczuga 1981a).

The second carotenoid in the group of ketocarotenoids, i.e. adonixanthin, was detected for the first time in the petals of *Adonis annua* (Egger 1965) and then it was found in other species of the genus *Adonis* (Neamtu, Tamas and Bodea 1966, Neamtu and Bodea 1968, Czygan 1969).

As regards α-doradexanthin, i.e. epimere fitschiellaxanthihn, (Goodwin

1980) it was described in the alga *Fitschiella tuberosa* (Dersh 1960, Weber 1975, Buchecker Eugster and Weber 1978), and goldfish (Katarzyna, Yokoyama and Chichester 1970). Later on it turned out that α-doradexanthin was very common in the animal world (Czeczuga 1980, 1981b).

As regards antheroxanthin it is a carotenoid which derives from zeaxanthin and belongs to the group of epoxide carotenoids and as a greater part of them occurs usually in autumn (Simpson and Chichester 1981). In the higher plants antheroxanthin has been found so far in pollen, flowers and fruits of some plants.

The β-apo-2'-carotenal, just as other carotenoids from the group of apocarotenals, originates in results of the natural degradation of β-carotene (Simpson et al. 1976). It occurs most frequently in autumn, or under similar meteorological conditions. In the higher plants apo-carotenals have been found so far in citrus fruits (Thommen 1961, 1962, Yokoyama and White 1966, Valadon and Mummery 1978), and in grass and lucerne (Thommen and Wiss 1963). Carotenoids from the group of apo-carotenals were found also in several species of the Antarctic mosses (Czeczuga, Gutkowski and Czerpak 1982).

The results of the investigations show that total carotenoid content in the material from *Colobanthus quitensis* was highest during the Antartcic springtime (October) and the lowest in the summer (December). In the case of the second species under examination — *Deschampsia antarctica* the situation was reversed, the lowest carotenoid content was recorded in springtime and the highest in summer (February):

5. Резюме

Применяя колонную и тонкослойную хроматографию, авторы исследовали присутствие некоторых каротиноидов у двух видов сосудистых растений (*Colobanthus quitensis* и *Deschampsia antarctica*) с острова Кинг Джордж (Антарктика).

Исследования установили присутствие следующих каротиноидов:

— в *Colobanthus quitensis:* α-, β-, ε-каротина, α-, β-криптоксантина, лютеина, эпоксидной формы лютеина, зеаксантина, антероксантина, адониксантина, α-дорадексантина, неоксантина, а также мутатоксантина;

— в *Deschampsia antarctica:* α-, β-каротина, α-, β-криптоксантина, кантаксантина, лютеина, эпоксидной формы лютеина, зеаксантина, антероксантина, вполяксантина, неоксантина, а также β-апо-2′-каротеналя.

Общее содержание каротиноидов изменялось с 4.829 до 9.763 у *Colobanthus quitensis* и с 4.064 до 17.257 мг/г сухого веса у *Deschampsia antarctica.*

6. Streszczenie

Autorzy stosując metodę chromatografii kolumnowej i cienkowarstwowej badali występowanie poszczególnych karotenoidów u dwóch roślin wyższych (*Colobanthus quitensis* i *Deschampsia antarctica*) z Wyspy Króla Jerzego (Antarktyka).

Badania wykazały obecność następujących karotenoidów:

— u *Colobanthus quitenesis:* α-, β, ε-karotenu, α-, β-kryptoksantyny, luteiny, epoksydowej formy luteiny, zeaksantyny, anteroksantyny, adoniksantyny, α-doradeksantyny, neoksantyny i mutatoksantyny;

— u *Deschampsia antarctica:* α-, β-karotenu, α-, β-kryptoksantyny, kantaksantyny, luteiny, epoksydowej formy luteiny, zeaksantyny, anteroksantyny, violaksantyny, neoksantyny i β — apo — 2' — karotenalu.

Ogólna zawartość karotenoidów wahała się od 4,829 do 9,763 u *Colobanthus quitensis* i od 4, 064 do 17,257 mg/g suchej masy u *Deschampsia antarctica.*

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