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PRENYLLIPIDS AND PIGMENTS CONTENT IN SELECTED ANTARCTIC LICHENS AND MOSSES

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ABSTRACT

The content and relative composition of tocopherols, plastochromanol, plastoquinone and pigments in fifteen Antarctic species (five mosses and ten lichens) were analyzed by HPLC. Total tocopherols in mosses ranged from 90 µg/g (*Warnstrofia sarmentosa)* to 220 µg/g (*Syntrichia magellanica*), while in lichens it ranged from 0.89 µg/g in *Caloplaca* sp. to 45 µg/g in *Placopsis contortuplicata*. With the exception of *Ochrolechia frigida*, in all other mosses and lichens species, α-tocopherol accounted for more than 90% of total tocopherols. Plastochromanol was detected in four mosses and two lichen species; the highest level was found in *Polytrichastrum alpinum* (19.1 µg/g). The highest content of plastoquinone-9 (PQ-9) in mosses was found in *Bryum pseudotriquetrum* (42.6 µg/g), whereas in lichens it was 24.5 µg/g in *Stereocaulon alpinum*, and 23.17 µg/g in *Umbilicaria antarctica*. Pigment composition in mosses was typical for higher plants. Some lichen species lacked chlorophyll *b*, violaxanthin and β-carotene. Based on these results it is suggested that tocochromanols and carotenoid pigments are involved in the protection of mosses and lichens against the oxidative stress caused by the extreme Antarctic conditions.

Keywords: Antarctica; lichens; mosses; pigments; tocopherols; plastochromanol; plastoquinone

INTRODUCTION

Antarctic, on average, is the coldest, driest and windiest continent, and it has the highest average elevation of all continents. Antarctic is considered a desert, with annual precipitation of only 200 mm along the coast and far less inland. Only cold-adapted plants and animals can survive there. Plants growth is inhibited by low temperatures, poor soil quality, prolonged drought, high solar irradiance, ultraviolet-B radiation levels, and winter darkness[1]. Flora largely consists of lichens, bryophytes, algae, and fungi, which generally occur in summer. Nowadays more than 200 species of lichens and 50 species of bryophytes are known to exist and only two species of flowering plants can be found: *Deschampsia antarctica* and *Colobanthus quitensis*[2]. Extreme Antarctic conditions increase the reactive oxygen species (ROS) formation. Thus plants and lichens contain considerable amounts of antioxidants to protect them against damage caused by oxidation in its extreme environmental conditions[3].

Tocochromanols are a group of four (α, β, g, δ) lipophilic antioxidants synthesized by all photosynthetic organisms, occurring mainly in leaves and seeds[4]. Tocochromanols contain a polar chromanol "head" and isoprenoid side chain ("tail")[5,6](Figure 1). PC is a γ-tocotrienol homologue that also shows antioxidant activity[7,8]. The only difference between them is a longer prenyl chain in the structure of PC-8 (eight isoprenoid subunits) (Fig. 1). Plastochromanol has been found in vegetable oils[9]; its richest source is *Brassica napus*, *Linum* sp. oil, and *Cannabis sativa* seeds[7,10,11], and widespread in leaves[8,12,13]. Tocochromanols are antioxidants that participate in the inhibition of membrane lipid peroxidation, scavenging ROS and free radicals[5,14]. They are also involved in plant metabolism participating in sugar export from leaves to phloem[15,16].

Tocopherol/ Tocotrienol	R1	R2
α	CH_3	CH_3
β	CH_3	H
γ	H	CH_3
δ	H	H

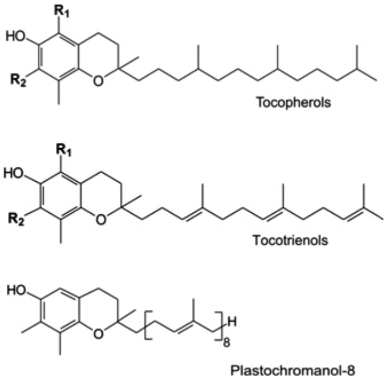

Figure 1. Chemical structure of tocochromanols.

Because of the nutritional importance of vitamin E, literature data on content and composition of tocopherols have mainly been focused on seed oils, where its reported concentration reaches up to 2 mg/g oil[17]; in leaves it is usually significantly lower (10-50 µg/g fresh weight), between 300-500 mg/g fresh weight in oil palm[18] and a few tropical plants[19], and nearly 1 mg/g fresh weight in *Eucalyptus gunni*[20]. Concerning the composition of tocopherol homologues, γ-tocopherol prevails in seed oils, while α-tocopherol is the predominant form in leaves (>90%)[21,22]. Interestingly, tocopherol pattern is present in lettuce[17,22], young leaves of runner bean[23] and parasitic dodder shoots[22,24] where γ- or δ-tocopherol occur in the highest amounts. Significance of these differences is so far unknown.

Plastoquinone (PQ) is mainly known as a component of the electron transport chain in photosynthesis, but its reduced form (PQH_2) shows, similarly to tocopherols, antioxidant activity *in vitro*[8,25,26]. It has also been shown that PQH_2 may inhibit *in vivo*[27] membrane lipid peroxidation, and scavenge reactive oxygen species[28,29]. Numerous data also indicate the regulatory function of the PQ-pool in many physiological and molecular processes[30].

Photosynthetic organisms have developed a number of strategies to avoid damage caused by oxidative stress. One of them is the xantophyll cycle (violaxanthin cycle) in which the reversible conversion of violaxanthin to zeaxanthin via antheraxanthin occurs[31,32]. The xantophyll cycle is essential for the adaptation of all vascular plants and many algae to different light conditions.

As part of our current interest on Antarctic flora, we now report the results of a study on the prenyllipids (tocochromanols and plastoquinone) and pigments of five moss and ten lichen species growing in King George and Ardley islands. By HPLC analysis of the extracts, the relative concentrations of α-tocopherol, γ-tocopherol, δ-tocopherol, plastochromanol, oxidized and reduced forms of plastoquinone (PQ) and photosynthetic pigments were obtained.

EXPERIMENTAL

Five moss species (*Syntrichia magellanica, Polytrichastrum alpinum, Sanionia georgicouncinata, Warnstrofia sarmentosa, Bryum pseudotriquetrum*) and ten lichen species (*Turgidosculum complicatulum, Sphareophorus globorus, Placopsis contortuplicata, Caloplaca regalis, Ochronlechne frigide, Usnea aurantiaco-atra, Stereocaulon alpinum, Caloplaca coralloides, Himantornia lugubris, Ochrolechia frigida, Umbilicaria antarctica*) were collected from natural standings in the Ardley and King George Antarctic islands during the southern hemisphere summer. Mosses were identified by Professor Ryszard Ochyra from Wladyslaw Szafer Institute of Botany, Polish Academy of Sciences (Krakow, Poland), and the lichen species by Professor Maria Olech from Institute of Botany, Jagiellonian University (Krakow, Poland).

In order to perform tocopherols and pigments analysis, a sample 150-300 mg of mosses and lichens material was frozen in liquid nitrogen, crushed by

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baguette and ground in a mortar with 2 μl of cold HPLC solvent (acetonitrile/methanol/water, 72/8/1, v/v/v). The extract was transferred to an Eppendorf tube and shaked on vortex for 3 hours. After that, the extract was centrifuged (10 min) on a benchtop centrifuge (10 000 *g*) and analyzed by HPLC (100 mL, triplicate). For plastochromanol (PC) and plastoquinone (PQ) analysis the same method was applied but with a different HPLC solvent (methanol/hexane, 340/20, v/v). The HPLC measurements were performed in a 100 mL loop, Jasco PU-980 pump and a UV-VIS UV-970 detector system (255 nm for PQ and PC detection and 440 nm for pigments detection), Shimadzu RF10-AXL fluorescence detector (excitation/emission detection at 290/330 nm), Teknokroma (Barcelona, Spain), C_{18} reverse-phase column (Nucleosil 100, 250 x 4 mm, 5 mm) and isocratic solvent system - acetonitrile/methanol/water (72/8/1, v/v/v) or methanol/hexane (340/20; v/v) at the flow rate of 1.5 mL/min. PQ-9 and its reduced form was obtained and prepared as described by Kruk[33]. Tocopherol homologues of HPLC grade (≥99.5%) (Merck), PQ-9 was obtained as previously described[33], and PC was dotained according to the procedure described by Gruszka and Kruk[11].

Pigments were measured by HPLC using 100 μL loop, Agilent Technologies Series 1200 (Waldbronn, Germany) Quat Pump and DAD detector (440 nm), Tecnocroma (Barcelona, Spain) C_{18} reverse-phase column and isoctaric solvent system acetonitrile/water (78/8/1, v/v/v) at flow rate 1.5 mL/min.

RESULTS AND DISCUSSION

Table 1 presents the content of α-, γ- and d-tocopherol, plastochromanol and plastoquinone (both oxidized and reduced) content of the five different Antarctic moss species.

Table 1. Tocopherols, plastochromanol and plastoquinone content of selected Antarctic mosses. *N* = 3 ± SE. (α-T, α-tocopherol; γ-Toc, γ-tocopherol; δ-Toc, δ-tocopherol; Toc, tocopherols; PC, plastochromanol; DW, dry weight).

Species	δ-Toc [μg/g DW]	γ-Toc [μg/g DW]	α-Toc [μg/g DW]	PC [μg/g DW]	PQH_2 [μg/g DW]	PQ [μg/g DW]
Syntrichia magellanica	0.0	3.2 ±0.65	217.0 ± 28	3.6 ± 1.0	18.2 ± 2.30	4.8 ± 0.90
Polytrichastrum alpinum	0.0	2.2 ± 0.60	199.6 ± 12	19.1 ± 0.85	0.0	16.2 ± 1.30
Sanionia georgicouncinata	1.2 ± 0.1	6.4 ± 0.55	212.2 ± 6.5	0.0	10.7 ± 1.70	18.1 ± 2.40
Warnstrofia sarmentosa	0.0	1.2 ± 0.05	88.4 ± 5.8	3.8 ± 0.8	0.0	9.5 ± 1.40
Bryum pseudotriquetrum	0.0	4.2 ± 0.56	157.4 ± 16	12.7 ± 2.20	26.7 ± 2.80	15.9 ± 1.80

Content of α-tocopherol ranged between 88.4 μg/g in *Warnstrofia sarmentosa* and 217 μg/g in *Syntrichia magellanica*. In all examined species the content of α-homologue was fairly high in comparison to higher plants. The typical content of tocopherols in mature leaves of higher plant is in the range of 30 – 50 μg/g[17, 22]. Thus, in the case of examined mosses the amount of tocopherols was about 4-fold higher. Such high levels of tocopherols have been reported for autumn tree leaves[22], Patagonian plants[12] and a few tropical plants[19]. The increased level of these compounds is connected with stress circumstances. In the case of Antarctic mosses oxidative stress is caused by low temperature, lack or excess of sunlight and lack of accessible water. It has been reported that chilling and drought stress enhance superoxide production[34]. Asada[35] showed that superoxide dismutase, which is responsible for scavenging of superoxide is inactivated by low temperature. In such situations, tocopherols might take over the role of dismutase. It was also established that α-tocopherol is engaged in chilling stress response, while γ-tocopherol plays a role in drought stress[23]. γ-Tocopherol was present in all analyzed species, being its content relatively low (between 1.2 and 6.4 μg/g). δ-Tocopherol was present only in *Sanionia georgicouncinata* (1.2 μg/g). With the exception of *Sanionia georgicouncinata*, the remaining species contain plastochromanol, a homologue of γ-tocotrienol. The highest content of plastochromanol was found in *Polytrichastrum alpinum* (19.1 μg/g) and *Bryum pseudotriquetrum* (12.7 μg/g). PC has antioxidant properties[7], and its occurrence in the Antarctic mosses might be connected with ROS protection. Plastoquinone (oxidized) content varied between 4.8 and 18.1 μg/g. The plastoquinol (PQH_2) content was higher than PQ, but PQH_2 was not present in *Polytrichastrum alpinum*, and *Warnstrofia sarmentosa*. The total value of PQ was the highest in *Bryum pseudotriquetrum* (42.6 μg/g) and the lowest in *Warnstrofia sarmentosa* (9.5 μg/g) (Table 1). PQ-9 levels were not as high as previously reported for Patagonian plants[12]. The selected mosses are shown in Figure 2.

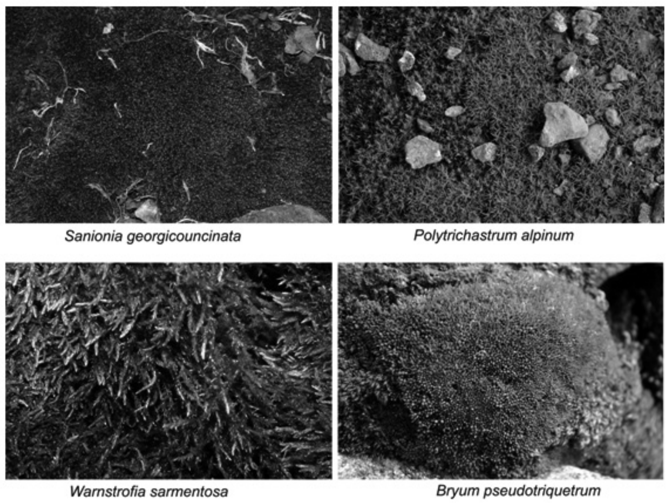


Figure 2. Selected mosses from King George Island (Antarctica).

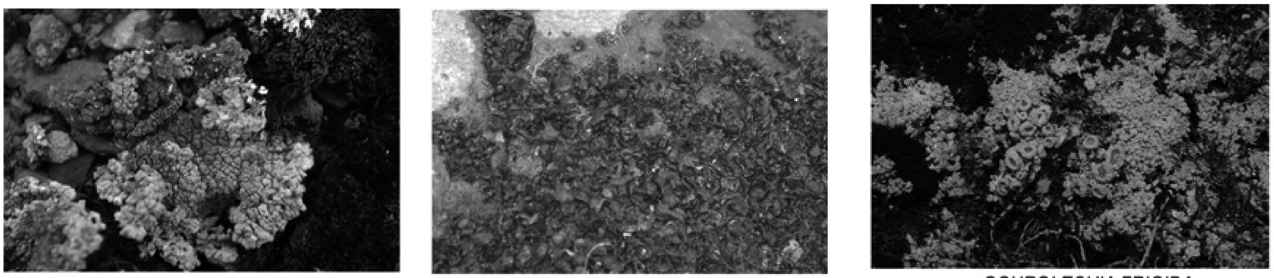
Lichens, a dominant life form throughout Antarctic are a good source of natural bioactive compounds which are related to their adaptability to extreme conditions. Table 2 presents the relative concentrations of γ-tocopherol, α-tocopherol, plastochromanol and oxidized and reduced PQ found in ten selected Antarctic lichen species. In all species α-tocopherol was present, with the highest content in *Placopsis contortuplicata* (40.4 μg/g) and *Turgidosculum complicatulum* (34.65 μg/g) (Table 2).

Caloplaca sp. and *Himantornia lugubris* had the lowest α-tocopherol content. γ-Tocopherol was present in three species (*Sphareophorus globorus, Placopsis contortuplicata* and *Ochrolechia frigida*). δ-Tocopherol was not detected in any of the lichens analyzed. Plastochromanol was present in *Placopsis contortuplicata* and *Usnea aurantiaco-atra,* but its content was very low (0.6 and 0.98 μg/g, respectively) (Table 2). The total plastoquinone content was the highest in *Stereocaulon alpinum, Himantornia lugubris* and *Umbilicaria antarctica.* In *Sphareophorus globorus* and *Himantornia lugubris* plastoquinone occurred only in a reduced state, whereas in *Placopsis contortuplicata, Caloplaca regalis, Caloplaca* sp. only in the oxidized state; the remaining analyzed species had both PQ forms (Table 2).

Table 2. Tocopherols, plastochromanol and plastoquinone content of selected Antarctic lichens. $N = 3 \pm$ SE. (α-T, α-tocopherol; γ-T, γ-tocopherol; Tocs, tocopherols; PC, plastochromanol; DW, dry weight).

Species	γ-Toc [μg/g DW]	α-Toc [μg/g DW]	PC [μg/g DW]	PQH_2 [μg/g DW]	PQ [μg/g DW]
Turgidosculum complicatulum	0.0	34.65 ± 0.67	0.0	13.26 ± 1.2	4.22 ± 0.1
Sphareophorus globorus	0.33 ± 0.05	1.9 ± 0.3	0.0	4.03 ± 0.8	0.0
Placopsis contortuplicata	5.15 ± 0.67	40.4 ± 4.82	0.6 ± 0.004	0.0	1.2 ± 0.25
Caloplaca regalis	0.0	5.44 ± 6.1	0.0	0.0	8.06 ± 2.1
Stereocaulon alpinum	0.0	7.86 ± 2.1	0.0	8.74 ± 0.9	15.75 ± 1.1
Caloplaca sp.	0.0	0.89 ± 0.03	0.0	0.0	2.34 ± 0.8
Usnea aurantiaco-atra	0.0	2.19 ± 0.8	0.98 ± 0.04	12.02 ± 3.2	0.76 ± 0.56
Himantornia lugubris	0.0	0.93 ± 0.06	0.0	24 ± 2.9	0.0
Ochrolechia frigida	21.12 ± 3.7	19.6 ± 3.3	0.0	7.25	2.15 ± 0.07
Umbilicaria antarctica	0.0	3.96 ± 1.0	0.0	21.27 ± 4.7	1.9 ± 0.6

The presence of tocopherols, PC and PQH_2 in selected Antarctic lichens might be connected with its antioxidant functions. Bhattarai at al[36] showed that methanol-water extracts of few Antarctic lichen species exhibited strong antioxidant action. The highest level of antioxidants was present in *Stereocaulon alpinum* from King George Island, while the stronger antioxidant activity was found in the extracts of *Streocaulon alpinum*, *Caloplaca regalis* and *Caloplaca* sp.[36]. On the other hand, Luo et at[37] showed that acetone extracts from Antarctic lichen species had higher antioxidant properties than methanol extracts. *Caloplaca regalis* contains bioactive compounds, which have immunomodulatory effect on the macrophages *in vitro*[38]. *Umbilicaria antarctica* was found to be the lichen species with potent antioxidative capacity[37]. Furthermore, Paudel et al[39] showed that extracts from Antarctic lichens have strong antibacterial potential against human pathogenic bacteria. Our data confirm these reports and indicate that tocochromanols and PQH_2 from lichen extracts are involved in antioxidant action. Antarctic lichens and their bioactive compounds can be used as novel biosources of natural antioxidants. In traditional medicine some lichen species has been widely used for treating many diseases. Many literature data report that bioactive substances from Antarctic species show inhibitory effect on cell proliferation[40], antibacterial properties[41], antiviral, antifungal and anti-inflammatory effects[42]. Figure 3 show the Antarctic lichens with the highest tocochromanol content.



PLACOPSIS CONTORTUPLICATA   TURGIDOSCULUM COMPLICATUM   OCHROLECHIA FRIGIDA

Figure 3. Lichen species with the highest tocochromanols content.

Table 3. Percentage content of photosynthetic pigments in selected Antarctic mosses. $N = 3 \pm$ SE; (Neo, Neoxanthin; Viol, Violaxanthin; EpL, Lutein Epoxide; Ant, Anteraxanthin; Lut, Lutein; Zea, Zeaxanthin; Chl a, Chlorophyll a; Chl b, Chlorophyll b; Car, b-Carotene)

Species	**Pigments [%]**								
	Neo	**Viol**	**EpL**	**Ant**	**Lut**	**Zea**	**Chl *b***	**Chl *a***	**Car**
Syntrichia magellanica	8.4 ± 1.0	8.9 ± 0.04	0.0	1.0 ± 0.01	20.06 ± 2.1	0.57 ± 0.003	20.08 ± 3.7	37.05 ± 5.9	3.83 ± 0.07
Polytrichastrum alpinum	6.73 ± 1.4	10.7 ± 0.6	0.0	0.76 ± 0.02	22.33 ± 4.9	0.32 ± 0.01	18.36 ± 3.3	37.24 ± 7.5	3.56 ± 0.5
Sanionia georgicouncinata	7.58 ± 1.1	11.36 ± 2.2	0.03 ± 0.002	0.4 ± 0.001	22.14 ± 2.7	0.73 ± 0.01	19.88 ± 2.1	33.28 ± 4.8	4.6 ± 0.86
Warnstrofia armentosa	7.78 ± 1.0	8.17 ± 2.2	0.09 ± 0.005	0.25 ± 0.004	22.8 ± 1.7	0.38 ± 0.003	20.5 ± 4.2	35.0 ± 5.7	5.02 ± 0.95
Bryum pseudotriquetrum	7.25 ± 2.4	9.2 ± 3.8	0.25 ± 0.09	0.53 ± 0.078	22.65 ± 4.9	0.7 ± 0.03	17.74 ± 3.7	36.53 ± 7.8	5.15 ± 1.6

The percentage content of photosynthetic pigments in analyzed mosses was typical for higher plants (Table 3). Chlorophyll a, b and lutein were the predominant pigments in all examined moss species. Lutein epoxide, which is typical for shaded leaves[43] was found in three species: *Sanionia georgicouncinata, Warnstrofia sarmentosa* and *Bryum pseudotriquetrum*. Chlorophyll *a*, lutein, neoxanthin, zeaxanthin and antheraxanthin were found in all lichens (Table 4).

Table 4. Percentage content of photosynthetic pigments in selected Antarctic lichens. *N* = 3 ± SE. (Neo, Neoxanthin; Viol, Violaxanthin; EpL, Lutein Epoxide; Ant, Anteraxanthin; Lut, Lutein; Zea, Zeaxanthin; Chl a, Chlorophyll a; Chl b, Chlorophyll b; Car, b-Carotene).

Species	Pigments [%]							
	Neo	Viol	Ant	Lut	Zea	Chl β	Chl α	Car
Turgidosculum complicatulum	16.24 ± 2.3	7.47± 0.57	2.17 ± 0.06	18.76 ±2.2	2.82 ± 0.7	15.52 ± 2.4	33.66± 9.7	3.36± 0.8
Sphareophorus globorus	16.11 ± 1.7	-	23.94± 5.9	46.24± 11	5.14± 0.87	-	8.57± 1.1	-
Placopsis contortuplicata	7.51± 1.5	4.32± 0.97	3.5 ± 0.65	34.15 ± 7.1	6.08± 0.24	9.22± 1.5	28.1± 5.2	7.12± 1.1
Caloplaca regalis	15.34± 1.2	14.77± 0.9	4.5± 0.34	39.4± 3.6	1.18± 0.08	5.41± 0.78	17.36± 2.1	2.04± 0.2
Stereocaulon alpinum	23.34± 2.5	-	7.06± 0.86	50.05± 7.3	12.45± 1.8	-	7.10± 0.7	-
Caloplaca sp	14.73± 3.4	12.95± 2.7	5.15± 0.52	37.84± 6.6	1.44± 0.08	7.53± 1.0	19.35± 3.2	1.01± 0.06
Usnea aurantiaco-atra	20.2± 4.8	-	24.7± 3.9	41.174.4	8.53± 0.67	-	5.40± 1.2	-
Himantornia lugubris	20.38±5.8	-	12.03 ± 2.9	46.08± 9.3	6.54 ± 0.56	-	12.74 ± 1.8	2.23 ± 0.05
Ochrolechia frigida	21.8± 5.7	-	10.93 ± 2.8	56.57± 9.1	2.52± 0.03	5.72 ± 0.9	2.46± 0.04	-
Umbilicaria antarctica	20.87 ± 2.8	-	16.9 ± 1.5	45.2± 7.2	12.63 ± 1.2	-	4.3± 1.8	-

Apart of pigments, which play a crucial role in photosynthetic electron flow, zeaxanthin and lutein are known to have strong antioxidant properties[44, 45]. Another protective mechanism is based on the acidification of thylakoid lumen and the activation of enzyme violxanthin de-epoxidase, which catalyzes violaxanthin conversion to zeaxanthin via antheraxanthin[31, 32]. The xanthophyll cycle pigments were present in all moss species (Table 3).

In the case of lichens only four analyzed species (*Turgidosculum complicatulum*, *Placopsis contortuplicata, Caloplaca regalis, Caloplaca* sp.) contained the xantophyll cycle pigments (Table 4). The remaining lichens had no violaxanthin. Furthermore, in most species lack of violaxanthin was connected with the lack of β-carotene and chlorophyll *b* (Table 4). Interestingly, lichens where violaxanthin was not present had high level of antheraxanthin (Table 4). This result might suggest that antheraxanthin compensates the lack of violaxanthin in protecting these species against oxidative stress.

In conclusion, this first report on lipophilic antioxidants in selected Antarctic moss and lichen species shows, as expected, significant variations in relative composition among genera. However, the observed enhancement of α-tocopherol concentration in mosses and the high levels of the pigments lutein and neoxanthin detected in lichens, could be associated to adaptation to oxidative stress predominating in the site of collection. Further studies would be necessary in order to corroborate this matter.

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Abbreviations: Ant, anteraxanthin; Car, beta-carotene; Chl, chlorophyll; DW, dry weight; Epl, lutein epoxides; Lut, lutein; Neo, neoxanthin, plastochromanol; PQ, plastoquinone; PQH2, reduced plastoquinone; TOC, tocopherols; Viol, violaxanthin; Zea, zeaxanthin.

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