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Molecules of Interest

Plastochromanol-8: Fifty years of research

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ABSTRACT

Plastochromanol-8 (PC-8) is an antioxidant that, together with tocopherols and tocotrienols, belongs to the group of tocochromanols. Plastochromanol-8 has been found to occur in several plant species, including mosses, and lichens. PC-8 is found in seeds, leaves and other organs of higher plants. In leaves, PC-8 is restricted to chloroplasts. The identification of tocopherol cyclase (VTE1) as the key enzyme in the biosynthesis of PC-8 suggests that plastoglobules are the primary site of its biosynthesis. Other enzymes related with PC-8 biosynthesis in plastoglobules include: NDC1 and the ABC1-like kinase ABC1K3. The antioxidant properties of PC-8 are similar to those of other chloroplastic antioxidants in polar solvents but considerably they are enhanced in hydrophobic environments, suggesting that the unsaturated side chain performs some quenching activity. As a result of a non-enzymatic reaction, singlet oxygen can oxidize any of the 8 double bonds in the side chain of PC-8, giving at least eight hydroxy-PC-8 isomers. This review summarizes current evidence of a widespread distribution of PC-8 in photosynthetic organisms, as well as the contribution of PC-8 to the pool of lipid-soluble antioxidants in both leaves and seeds.

1. Introduction

Plastochromanol-8 (PC-8), as a natural component of plant tissues, was discovered 50 years ago in the leaves of the rubber tree (*Hevea brasiliensis*), where its content exceeded even that of α-tocopherol and plastoquinone (Whittle et al., 1965). Spectroscopic and chromatographic properties of the compound were found to be identical to those of synthetic PC-8, a γ-tocotrienol homologue but with a longer side chain (Fig. 1). Together with tocopherols and tocotrienols, PC-8 belongs to the group of tocochromanols, all of which contain a chromanol ring that is responsible for their spectral and antioxidant properties. Further research revealed that PC-8 occurs in the leaves of other plants (Dunphy et al., 1966), as well as in rape and maize seed oils (Dunphy et al., 1966) and that of flax (Leerbeck et al., 1967). Besides the leaves, PC-8 was also found in abundant amounts in latex from *H. brasiliensis* together with PC-8 esters (Dunphy et al., 1966).

Interest in PC-8 was renewed through recent studies of *Arabidopsis* vitamin E (*vte*)-biosynthetic mutants that revealed the biosynthetic pathway of PC-8 (Fig. 1) (Szymańska and Kruk, 2008, 2010a; Zbierzak et al., 2010). Earlier studies of *Brassica napus* with overexpressed tocopherol cyclase (Kumar et al., 2005), where the PC-8 level was increased in seeds, had led to the suggestion that the enzyme might be involved in PC-8 formation from plastoquinol.

This review summarizes current evidence of a widespread distribution of PC-8 in photosynthetic organisms. Furthermore, the contribution of PC-8 to the pool of lipid-soluble antioxidants in both leaves and seeds is discussed.

2. Distribution of PC-8 in photosynthetic organisms

Together with tocopherols and tocotrienols, PC-8 belongs to the group of tocochromanols. Tocopherols are ubiquitous in all plant species and are particularly concentrated in photosynthetic tissues, while tocotrienols are only found in some plant species and are almost exclusively found in seeds and fruits, particularly in monocots (Falk and Munné-Bosch, 2010). Although our knowledge of PC-8 distribution is still limited, the data accumulated thus far suggest a widespread distribution of PC-8 in the plant kingdom. PC-8 appears not to be found in cyanobacteria that synthesize tocopherols (Kruk, unpublished).

Since its discovery in the leaves of the rubber tree (*H. brasiliensis*) (Whittle et al., 1965), PC-8 has been found in the leaves of several species belonging to unrelated families, including mosses and lichens (Tables 1 and 2). The relative abundance of PC-8 depends on several factors, including the species, subspecies, cultivar,

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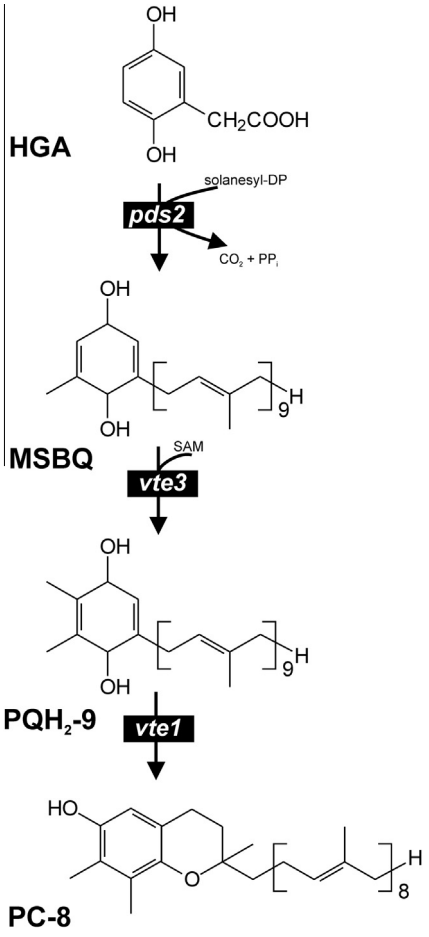

Fig. 1. Biosynthesis of plastochromanol-8 (PC-8) in plants.

Table 1
Occurrence of plastochromanol-8 (PC-8) in leaves of several higher plant species. The amounts of PC-8 are given in μg/g of dry matter (DW) and as a percentage of total tocochromanols (%, w/w). Note that PC-8 has also been detected, although not at quantifiable levels, in leaves of *Lotus japonicus*, *Nicotiana tabacum*, *Solanum lycopersicum*, *Solanum tuberosum* and *Oryza sativa* (Zbierzak et al., 2010).

Species	PC-8 (μg/g DW)	PC-8 (%)	References
Alchornea castaneaefolia	218	46	Kruk, unpublished
Amomyrtus luma	45	23	Strzałka et al., 2009
Annona cf. hypoglauca	23	47	Kruk, unpublished
Apeiba sp.	617	84	Kruk, unpublished
Araucaria araucana	132	58	Strzałka et al., 2009
Berberis buxifolia	9	3	Strzałka et al., 2009
Cecropia sp.	1783	106	Kruk, unpublished
Chusquea quila	32	25	Strzałka et al., 2009
Crathaeva benthamii	13	36	Kruk, unpublished
Crescentia amazonica	35	11	Kruk, unpublished
Erythrina fusca	220	38	Kruk, unpublished
Fuchsia magellanica	66	55	Strzałka et al., 2009
Garcinia brasiliensis	101	4	Kruk, unpublished
Hevea brasiliensis	318	225	Whittle et al., 1965
Hypopterygium arbuscula	3	9	Strzałka et al., 2009
Laetia corymbulosa	84	19	Kruk, unpublished
Macrolobium acaciifolium	41	5	Kruk, unpublished
Misodendrum linearifolium	24	12	Strzałka et al., 2009
Misodendrum punctulatum	3	0.5	Strzałka et al., 2009
Mitraria coccinea	11	17	Strzałka et al., 2009
Mutisia spinosa	3	7	Strzałka et al., 2009
Nectandra amazonum	55	5	Kruk, unpublished
Notophagus betuloides	44	42	Strzałka et al., 2009
Pouteria glomerata	20	7	Kruk, unpublished
Pseudobombax munguba	3640	182	Kruk, unpublished
Psidium acutangulum	10	9	Kruk, unpublished
Pterocarpus amazonum	36	17	Kruk, unpublished
Tabaernamontana siphilitica	276	80	Kruk, unpublished
Triplaris pyramidales	5	2	Kruk, unpublished
Vitex cymosa	55	13	Kruk, unpublished
Zygia sp.	40	8	Kruk, unpublished

Table 2
Occurrence of plastochromanol-8 (PC-8) in mosses and lichens. The amounts of PC-8 are given in absolute amounts (as μg/g DW) and as a percentage of total tocochromanols (%, w/w). All values are taken from Strzałka et al. (2011).

	PC-8 (μg/g DW)	PC-8 (%)
Bryum pseudotriquetrum	13	8
Placopsis contortuplicata	0.6	1
Polytrichastrum alpinum	19	9
Syntrichia magellanica	4	2
Usnea aurantiaco-atra	1	44
Warnstrofia sarmentosa	4	4

growth conditions and tissue. Many species have been analyzed to date and PC-8 has generally been found to be less abundant than tocopherols, with the exception of *Cecropia* sp., *Pseudobombax munguba* and *H. brasiliensis*. It is notable that the levels of PC-8 in leaves depend not only on the species but also on the leaf age or developmental stage. In *B. napus* leaves, the highest contents were found during stem formation; and in *Arabidopsis*, PC-8 levels were found to increase in young leaves under strong light conditions (Nogala-Kalucka et al., 2002; Szymańska and Kruk, 2010a). Very few studies report the distribution of PC-8 in different organs of the same species; although, PC-8 has been detected in several organs, including leaves, buds, flowers, pods and seeds of *B. napus* (Nogala-Kałucka et al., 2002). PC-8 was also detected in tomato fruit (Zbierzak et al., 2010), but the highest levels are generally found in leaves (9.5 μg/g DW) and seeds (4 μg/g DW, Table 3). PC-8 has also been detected at non-quantifiable levels in the yam tuber (*Dioscorea alata*, Cheng et al., 2007).

Seeds and seed oils are another natural source of PC-8 (Table 4); it has been detected, although not quantified, in several species (Bagci et al., 2004; Bagci and Özçelik, 2009; Velasco and Goffman, 2000). In general, the levels of PC-8 in seeds and in seed oils are similar to those in leaves. In all the seeds and seed oils analyzed, PC-8 levels are lower than those of tocopherols, although in *Linum usitatissimum* "*oleofarm*", PC-8 content is more than 50% that of tocopherol (Gruszka and Kruk, 2007). PC-8 levels in seeds or seed oils can vary within the same species, as illustrated in *B. napus, Camelia sativa, Cannabis sativa* and *L. usitatissimum*. Different experimental approaches to the growth of plants or the extraction of oil as well as the use of different subspecies could explain these differences. In *L. usitatissimum*, different subspecies display important differences in PC-8 levels, ranging from 26 μg/g of seed in *L. usitatissimum* subsp. *angustifolium* to 72 μg/g of seed in *L. usitatissimum* subsp. *usitatissimum* var *pekinense* (Velasco and Goffman, 2000).

3. Intracellular distribution and antioxidant function

Fractionation of *Polygonum* leaves indicated that PC-8 is mainly, if not exclusively, located in chloroplasts (Dunphy et al., 1966). The identification of tocopherol cyclase (VTE1) as the key enzyme in PC-8 biosynthesis suggested plastoglobules as the primary site of PC-8 formation and its localization within chloroplasts (Sattler et al., 2003; Vidi et al., 2006). As the content of plastoglobules is in equilibrium with thylakoid membranes (Austin et al., 2006), it can be assumed that PC-8 is also found in thylakoids where it fulfills an antioxidant function (Zbierzak et al., 2010). In wild-type *Arabidopsis* plants, a large fraction of plastid PC-8 was located in plastoglobules with most of the remaining fraction more