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REVIEW

Carotenoid biosynthesis in diatoms

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Abstract Diatoms are ubiquitous and constitute an important group of the phytoplankton community having a major contribution to the total marine primary production. These microalgae exhibit a characteristic golden-brown colour due to a high amount of the xanthophyll fucoxanthin that plays a major role in the light-harvesting complex of photosystems. In the water column, diatoms are exposed to light intensities that vary quickly from lower to higher values. Xanthophyll cycles prevent photodestruction of the cells in excessive light intensities. In diatoms, the diadinoxanthin–diatoxanthin cycle is the most important short-term photoprotective mechanism. If the biosynthetic pathways of chloroplast pigments have been extensively studied in higher plants and green algae, the research on carotenoid biosynthesis in diatoms is still in its infancy. In this study, the data on the biosynthetic pathway of diatom carotenoids are reviewed. The early steps occur through the 2-*C*-methyl-D-erythritol 4-phosphate (MEP) pathway. Then a hypothetical pathway is suggested from dimethylallyl diphosphate (DMAPP) and isopentenyl pyrophosphate (IPP). Most of the enzymes of the pathway have not been so far isolated from diatoms, but candidate genes for each of them were identified using protein similarity searches of genomic data.

Keywords Carotenoids · Diadinoxanthin · Diatoms · Diatoxanthin · MEP pathway · Xanthophylls

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Abbreviations

Car	Carotenoid
CDMDE	4-(Cytidine 5′-diphospho)-2-*C*-methyl-D-erythritol
CEC	2-*C*-methyl-D-erythritol 2,4-cyclodiphosphate
Chl	Chlorophyll
CHYB	Nonheme β-carotene hydroxylase
CMK	4-(Cytidine 5′-diphospho)-2-*C*-methyl-D-erythritol kinase
CMS	4-Diphosphocytidyl-2-*C*-methyl-D-erythritol synthase
CRTISO	Carotenoid isomerase
CytP450	Cytochrome P450
DDE	Diadinoxanthin de-epoxidase
Ddx	Diadinoxanthin
DEP	Diatoxanthin epoxidase
DMAPP	Dimethylallyl diphosphate
DME	4-Diphosphocytidyl-2-*C*-methyl-D-erythritol 2-phosphate
DOXP	1-Deoxy-D-xylulose 5-phosphate
Dtx	Diatoxanthin
DXR	1-Deoxy-D-xylulose 5-phosphate reductoisomerase
DXS	1-Deoxy-D-xylulose 5-phosphate synthase
FCP	Fucoxanthin–chlorophyll complex
GGPP	Geranylgeranyl pyrophosphate
GGPPS	Geranylgeranyl pyrophosphate synthase
HD	(*E*)-4-hydroxy-3-methylbut-2-enyl diphosphate
HDS	(*E*)-4-hydroxy-3-methylbut-2-enyl diphosphate synthase
HDR	(*E*)-4-hydroxy-3-methylbut-2-enyl diphosphate reductase
HMED	4-Hydroxy-3-methylbut-2-enyl diphosphate
IDI	Isopentenyl diphosphate:dimethylallyl diphosphate isomerase

IPP	Isopentenyl pyrophosphate
LCYB	Lycopene β-cyclase
LCYE	Lycopene ε-cyclase
LHC	Light-harvesting complex
LTL	ε-Ring hydroxylase-like gene
LUT1	ε-Ring hydroxylase
MCS	2-*C*-methyl-D-erythritol 2,4-cyclodiphosphate synthase
MEP	2-*C*-methyl-D-erythritol 4-phosphate
MEV	Mevalonate pathway
MGDG	Monogalactosyldiacylglycerol
NDH	NADPH dehydrogenases
NPQ	Non-photochemical quenching
PDS	Phytoene desaturase
PG	Phosphatidylglycerol
PS	Photosystem
PsbS	Subunit S of the photosystem II
PSY	Phytoene synthase
SQDG	Sulfoquinovosyldiacylglycerol
VDE	Violaxanthin de-epoxidase
Vio	Violaxanthin
Z-ISO	15-*cis*-ζ-carotene isomerase
ZDS	ζ-Carotene desaturase
Zea	Zeaxanthin
ZEP	Zeaxanthin epoxidase

Introduction

Diatoms (Bacillariophyta) are the best known unicellular planktonic algae. They are ubiquitous (Morgan-Kiss et al. 2006) and constitute an important group of the phytoplankton community because this community is thought to be responsible for *c.a.* 25–40% of the total marine primary production (Nelson et al. 1995; Falkowski et al. 1998; Field et al. 1998), i.e. comparable to that to the terrestrial rain forests (Field et al. 1998; Ragueneau et al. 2000). Diatoms can even constitute the dominant group in extreme environment such as cold waters (Choi et al. 2008). The most characteristic feature of diatoms is the box-like cell wall, which consists in two valves. Although diatoms exhibit a large variety of shapes, they can be ranged in two taxonomic orders on the basis of the valve symmetry. One distinguishes the Centrales with a concentric radial symmetry and Pennales with symmetry around a line (Kooistra et al. 2003; Jeffrey and Vesk 1997; Kröger and Poulsen 2008). Fossil records indicate that centric diatoms appeared at least 180 million years ago, whereas pennate diatoms would have evolved from centric diatoms more recently (90 million years ago) (Kooistra et al. 2003).

As the diatom chloroplasts are surrounded by 4 membranes (Mereschkowsky 1905; McFadden 2001; Whatley and Whatley 1981), it is believed that diatoms have obtained their plastid from a secondary endosymbiosis between a heterotrophic eukaryote and an ancient red alga, an event that occured at least 800 million years ago (Bhattacharya and Medlin 1998; Keeling 2004; Boore 2008; Braun and Phillips 2008). During evolution of the endosymbiosis, the nuclear gene encoding plastid-localised proteins have been transferred to the host nucleus (Hackett et al. 2004) and today, the whole set of genes coding the enzymes needed for carotenoid (Car) synthesis are located in the nucleus.

The thylakoid membranes of diatoms and the other chromist algae are usually grouped by 2 or 3 and do not form real grana stacks. So far the lipid composition of isolated thylakoids has been only established for *Cyclotella meneghiniana*. They contain the same lipid classes than higher plant thylakoids (Goss et al. 2009) but are enriched in the negatively charged lipid sulfoquinovosyldiacylglycerol (SQDG) and phosphatidylglycerol (PG) whilst the relative amount of monogalactosyldiacylglycerol (MGDG) and digalactosyldiacylglycerol are reduced. Significant amounts of phosphatidylcholine were also found (Goss et al. 2009).

Diatoms and the other chromist algae exhibit a characteristic brown colour due to the presence of high amounts of the xanthophyll fucoxanthin that masks the other Cars (e.g. β-carotene, violaxanthin (Vio), diadinoxanthin (Ddx) and diatoxanthin (Dtx) and the chlorophyllous pigments, i.e. Chl *a*, Chl c_1 and Chl c_2 (Stauber and Jeffrey 1988). The absolute and/or relative amounts of individual pigments may differ according to the taxon and its ecology (Table 1). Fucoxanthin and Ddx molecules are mostly located in the fucoxanthin-Chl *a*-Chl c2 protein-complexes (FCP) that are functionally related to the LHC of green algae and high plants. The protein moiety is coded by the family of genes *fcp* (Bhaya and Grossmann 1993; Eppard et al. 2000; Armbrust et al. 2004; Beer et al. 2006; Bowler et al. 2008; Gundermann and Büchel 2008; Hwang et al. 2008). Two different complexes namely FCPa and FCPb were isolated from *Cyclotella meneghiniana* (Büchel 2003). They slightly differ in pigment composition and

Table 1 Pigment characteristics of some diatoms under varying light conditions

Diatoms	*Phaeodactylum tricornutum*[a]		Sea ice diatoms[b]	
Light intensity (μmol m^{-2} s^{-1})	35	500	5	1000
Chl c/Chl a	0.20	0.26	21	4
Fucoxanthin/Chl a	0.66	0.58	34	11
DES	0	0.28	0	0.44

[a] Nymark et al. (2009), [b] Kashino et al. (1998). DES: De-epoxidation status (Dtx/Dtx+Ddx)

have similar absorbance and fluorescence spectra (Büchel 2003). In contrast, the oligomeric state and the polypeptide composition are different. The trimeric FCPa is composed mainly of the gene products of FCP2 and FCP6, the homologue of LI818 in diatoms whereas FCPb is a higher oligomer (hexa- or nonamer) most probably of FCP5 proteins (Beer et al. 2006). FCP have also been isolated from *P. tricornutum* (Guglielmi et al. 2005) but the correspondence with those of *Cyclotella* remains difficult (Beer et al. 2006). Regardless their origin, the pigment composition of FCP as well as the Car/Chl ratio are however greater than in LHC from higher plants, increasing the ability of diatoms and brown algae to absorb blue-green radiations that are crucial for the growth in the aquatic environment (Beer et al. 2006; Lamote et al. 2003). The details of the 3D organisation of FCP are still not complete because the atomic structure of the protein is not yet available. However, recent progresses have been recently obtained in this area using LHCII atomic structure as a model (Premvardhan et al. 2010). FCP from the centric diatom *Cyclotella meneghiniana* would contain 5–8 fucoxanthin molecules (Premvardhan et al. 2009, 2010).

The Car group is a structural diverse class of isoprenoids synthesised in all photosynthetic organisms including higher plants and algae synthesise Cars (Jeffrey and Vesk 1997; for reviews, see Lichtenthaler 1999; Britton et al. 2004). Car function as accessory molecules for light harvesting and for prevention from photo-damage and as antioxidants in the reaction centres and under stress conditions (for reviews, see DellaPenna and Pogson 2006; Lichtenthaler 2007; Li et al. 2006; Lemoine and Schoefs this issue). In addition, they are also the precursors of apoCars, which in higher plants at least are important factors for growth and may play crucial roles in the responses to biotic and abiotic stresses (Nambara and Marion-Poll 2005; Gomez-Roldan et al. 2008; Umehara et al. 2008; Seddas et al. 2009). If the biosynthetic pathways of Car pigments have been extensively studied in green algae and higher plants (reviewed by Kirby and Keasling 2009; Lemoine and Schoefs this issue), this research in diatoms is still in its infancy. In this study, the data about the biosynthetic pathway of Car in diatoms are reviewed with a special emphasis on the regulation of the xanthophyll cycles.

Carotenoid biosynthesis

The Car molecules are derived from the isoprenoid precursor molecule dimethylallyl diphosphate (DMAPP) and its isomer isopentenyl pyrophosphate (IPP). Since the pioneer experimental works in the 1990s by the team of Prof. Rohmer (Rohmer et al. 1993, 1996; for a review, see Rohmer 2010), it is currently admitted that IPP and DMAPP needed for plastidic isoprenoids, such as phytol, plastoquinone-9, isoprene, mono-, and diterpenes, and Cars are synthesised in chloroplasts using the nonmevalonate pathway or 2-*C*-methyl-D-erythritol 4-phosphate (MEP) pathway (Fig. 1) whereas the cytosolic classical acetate/mevalonate pathway (MEV) is used for the biosynthesis of sterols, sesquiterpenes, triterpenoids (for reviews, see Lichtenthaler 1999; Rohmer 2010).

The methylerythritol phosphate pathway

The division between the two pathways is not clear. For instance, Massé et al. (2004) showed that highly branched isoprenoids in the centric diatom *Rhizosolenia setigera* occurred by the MEV pathway, whereas in the pennate *Haslea ostrearia*, highly branched isoprenoids were produced principally by the MEP pathway. This suggests that, depending on the taxon, these molecules are produced by completely separated pathways. In other occasions, an exchange of intermediates can occur. For instance, Zhang et al. (2009) found that under fast growth, the MEP pathway could supply the MEV pathway with IPP and DMAPP in *Thalassiosira pseudonana*. Very interestingly, the MEP pathway is also present in apicomplexan protozoa and in most eubacteria, but it is absent from animals and fungi (Kuzuyama 2002; Bisanz et al. 2008).

The MEP pathway (Fig. 1) starts with the condensation of pyruvate and glyceraldehyde 3-phosphate, yielding 1-deoxy-D-xylulose 5-phosphate (DOXP). The reaction is catalysed by (DXS). The second step involves a reductive isomerization by the 1-deoxy-D-xylulose 5-phosphate reductoisomerase (DXR) that yields MEP. In the next step, a cytidyl moiety is introduced by the 4-diphosphocytidyl-2-*C*-methyl-D-erythritol synthase (CMS) to produce 4-(cytidine 5'-diphospho)-2-*C*-methyl-D-erythritol (CDMDE). In the next step, this intermediate is phosphorylated by a 4-(cytidine 5′-diphospho)-2-*C*-methyl-D-erythritol kinase (CMK) to yield 2-*C*-methyl-D-erythritol 2,4-cyclodiphosphate (CEC). Then the cytidyl group is lost during the catalysis of the 2-*C*-methyl-D-erythritol 2,4-cyclodiphosphate synthase (MCS). IPP and DMAPP are formed through the catalytic action of the (*E*)-4-hydroxy-3-methylbut-2-enyl diphosphate (HD) synthase (HDS) and HD reductase (HDR) (Fig. 1). DMAPP can be isomerised by the isopentenyl diphosphate:dimethylallyl diphosphate isomerase (IDI) (Fig. 2). The condensation of IPP molecules by the geranylgeranyl pyrophosphate (GGPP) synthase (GGPPS) results in the formation of GGPP. To our knowledge, none of these enzymes has been so far isolated from diatoms, but candidate genes for each of them were identified using protein similarity searches of genomic data from the diatoms *T. pseudonana, Phaeodactylum*

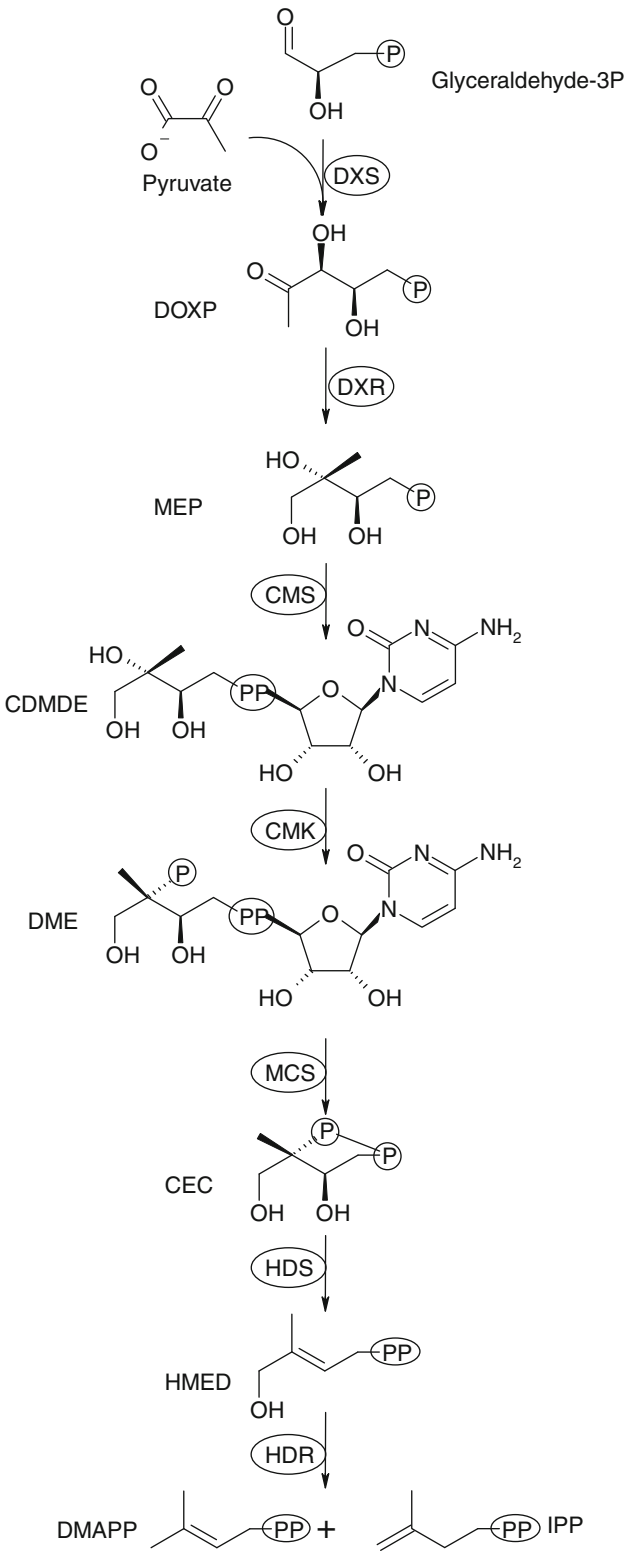

Fig. 1 The early steps of the carotenoid pathway in diatoms, i.e. the MEP pathway, from glyceraldehyde-3-phosphate to DMAPP and IPP. The enzyme names are encircled. One enzyme can be encoded by several genes

tricornutum and *Aureococcus anaphagefferens* (Frommholt et al. 2008).

The HDS protein can be divided in three domains denoted as A-, B-, and C-domains. If the A- and C-domains are commonly found in HDS from both nonphotosynthetic and photosynthetic organisms displaying the MEP pathway, the B-domain was not conserved in the former type of organisms, suggesting a regulatory role in the Car pathway (Frommholt et al. 2008).

The lycopene synthesis

Phytoene synthase (PSY), condensing two GGPP molecules, is responsible for the first committed step of the Car biosynthetic pathway (Sandmann 2002) (Fig. 2). PSY is usually considered as the enzyme performing the rate-limiting entry reaction into the biosynthetic pathway (Lindgren et al. 2003; Chen et al. 2007; Li et al. 2008). Coesel et al. (2008) found one and two candidate(s) PSY-encoding gene(s) in the *P. tricornutum* and *T. pseudonana* genome, respectively (Table 2). A recent phylogenetic analysis of the *PSY* genes identified in the algae genomes revealed that an ancient gene duplication have created two PSY classes of proteins (Tran et al. 2009). All the PSY sequences identified so far belongs to the class I of PSY whilst the class II enzymes would have been lost during evolution (Tran et al. 2009). The PSY product, namely 15-*cis*-phytoene is converted to lycopene through a rather complicated set of four desaturation reactions (for a review, see Sandmann 2009). In higher plants, these steps are coupled to an electron transport chain involving plastoquinone (Meyer et al. 1992; Norris et al. 1995; Breitenbach et al. 1999). In photosynthetic cells, two enzymes are involved in lycopene production. The first two desaturation reactions are catalysed by phytoene desaturase (PDS), possibly a flavoenzyme (*Capsicum annuum*: Huguenez et al. 1992). The reaction consists in the introduction of a *trans*-double bound at the 11 and 11′ positions, along a *cis*-double bond at the 9 and 9′ positions, resulting in the formation of 9, 15, 9′-tri-*cis*-ζ-carotene (Fig. 2). This product is isomerised at the 15′-*cis*-double bound by 15-*cis*-ζ-carotene isomerase (Z-ISO) (Li et al. 2007) to form the 9,9′-di-*cis*-ζ-carotene. The 15′-*cis*-isomerisation could be mediated by light, but photons are probably not sufficient (Chen et al. 2010). 9,9′-di-*cis*-ζ-carotene that is in turn, the substrate ζ-carotene desaturase (ZDS). ZDS introduces *cis*-double bounds at the 7 and 7′ positions leading to the formation of poly-*cis* lycopene or pro-lycopene (Beyer et al. 1989; Matthews et al. 2003; Breitenbach and Sandmann 2005) (Fig. 2). In most organisms, PDS is encoded by a single gene but the

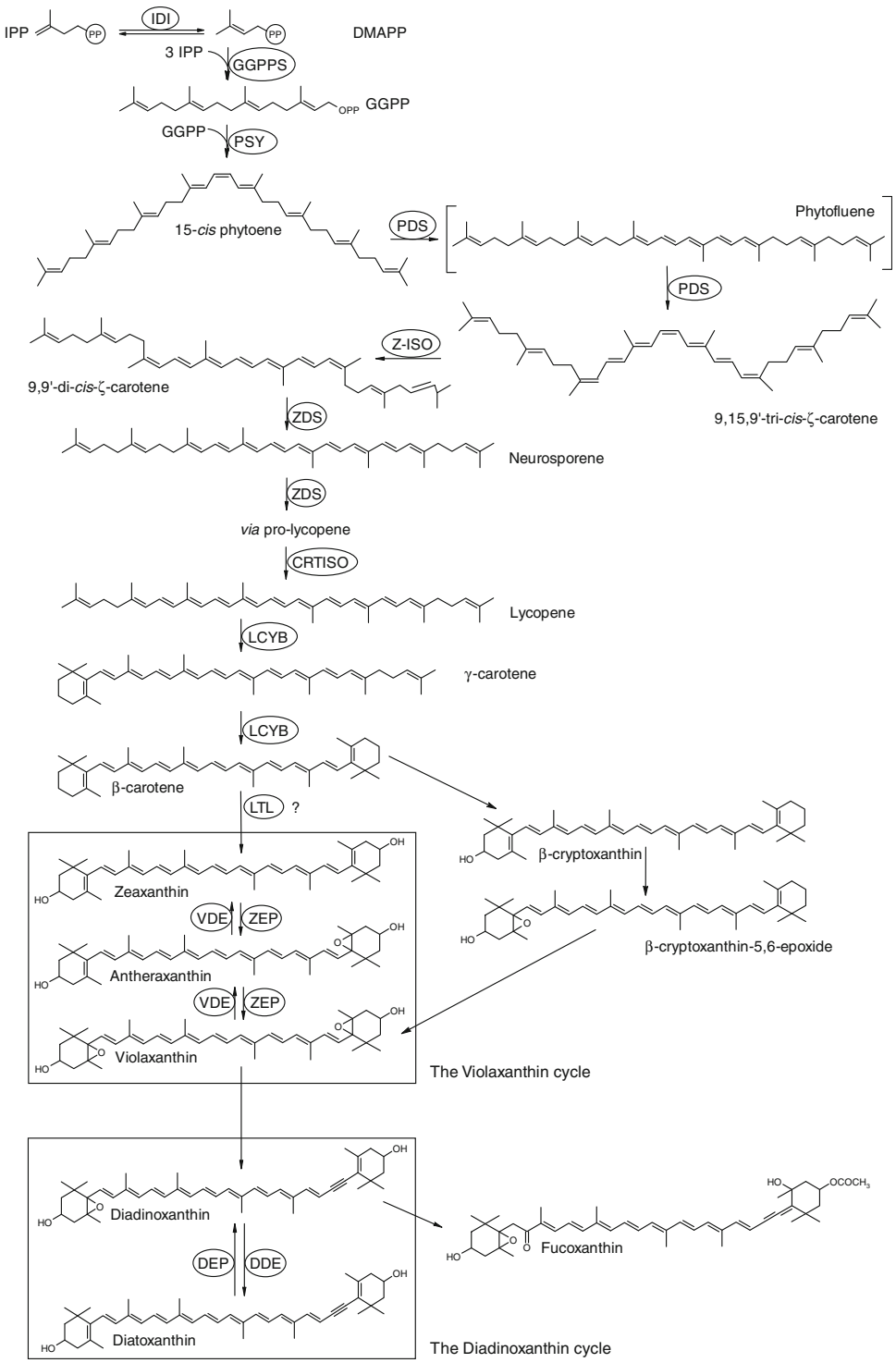

Fig. 2 Hypothetic carotenoid pathway in diatoms, from IPP and DMAPP. The enzyme names are encircled. One enzyme can have several genes. When there is no enzyme name for a reaction, the enzyme name is unknown

diatom genomes contain a pair of *PDS* genes (*T. pseudonana, P. tricornutum*: Coesel et al. 2008; *A. anaphagefferens*: Frommholt et al. 2008). Only one ZDS-encoding gene was found by Coesel et al. (2008) in the genomes of *T. pseudonana* and *P. tricornutum* (Table 2). Interestingly, three genes belonging to the amine oxidase family, sharing homology with cyanobacterial ZDS sequences, were identified by Coesel et al. (2008). Their participation to the Car biosynthesis is so far unknown. This pathway significantly differs from that found in bacteria that use a single enzyme, namely CRTI, with an FAD cofactor serving as hydrogen acceptor to catalyse the isomerisation and the 4 desaturation reactions (Linden et al. 1991; Fraser et al. 1992).

Table 2 Gene occurence in 5 diatoms

Gene	Taxon				
	Thalassiosira pseudonana	*Phaeodactylum tricornutum*	*Aureococcus anaphagefferens*	*Cyclotella menghiniara*	*Prymnesium parvum*
DXS	+F	+F	+F		
DXR	+F	+F	+F		
CMS	+F	+F	+F		
CMK	+F	+F	+F		
MCS	+F	+F	+F		
HDS	+(1) F	+(1) F	+(1) F		
HDR	+(1) F	+(1) F	+(1) F		
IDI	+(2) F	+(2) F	+F		
GGPPS	+F	+F	+F		
PSY	+C, F	+C, F	+F		
PDS	+(2) C, F	+(2) C, F	+(2) F		
Z-ISO	+Z				
ZDS	+(1) C, F	+(1) C, F	+F		
CRTISO	+(6) C, −F	+(6) C, −F	−F		
LCYB	+C, F	+C, F	+ F		
LTL	+(2) C	+(2) C			
CHYB	−C, F	−C, F	−F		
Cyt P450 carotene hydroxylase	−C, F	−C, F	−F		
VDE	+(1) C, F, M	+(1) C, F	+(1) F		
VDE-like	+(1) C, M	+(2) C			
DDE	+Ga	+J, Ga		+Gb, Ga	+Ga
ZEP	+(2) F, M	+(3) C, F	+(3) F		
DEP	+A	+B			

When the number of genes has been identified, it is indicated between brackets. A: Armbrust et al. (2004), B: Bowler et al. (2008), C: Coesel et al. (2008), F: Frommolt et al. (2008), Ga: Goss et al. (2005a), Gb: Goss et al. (2005b), J: Jakob et al. (2001), M: Montsant et al. (2007), Z: Chen et al. (2010)

Z-ISO would belong to a class of oxidoreductases that display an intramolecular oxidoreductase activity and transpose carbon double bonds. The enzyme is predicted to have transmembraneous segments. *Z-ISO* appeared to have evolved from an ancestor *NnrU* gene, ubiquitous in denitrifying bacteria (Chen et al. 2010). So far, a single copy of Z-ISO has been found in the genome of autotrophs (Ishikawa et al. 2009), including the diatoms *P. tricornutum* and *T. pseudonana* (Chen et al. 2010). The level of *Z-ISO* gene transcription is predicted to be highly correlated with the productions of the mRNAs corresponding to the other Car biosynthetic genes (Chen et al. 2010).

Car isomerase (CRTISO) isomerises the *cis*-double bonds at the 7, 9 and 7′, 9′ positions (no action at the 15 and 15′ positions could be observed) of pro-*cis*-lycopene to all-*trans*-lycopene (Giuliano et al. 2002; Isaacson et al. 2004), the substrate of lycopene β-cyclase (LCYB) (Fig. 2). During evolution, the plant CRTISO enzymes retained the isomerase activity of the bacterial CRTI enzyme (Sandmann 2009). The genomes of *P. tricornutum* and *T. pseudonana* both contain six putative genes exhibiting similarity with the *CRTISO* gene (Coesel et al. 2008) but they were not found by Frommholt et al. (2008).

The xanthophyll formation

LCYB catalyses the formation of the β-ionone rings at both ends of the all-*trans*-lycopene molecule yielding the formation of β-carotene (Fig. 2). One gene with similarity to *LCYB* was found in both the *P. tricornutum* and *T. pseudonana* genomes by Coesel et al. (2008) (Table 2). In higher plants, lycopene is converted to α-carotene through the catalytic action of lycopene ε-cyclase (LCYE). No sequence showing similarities with the *LCYE* gene was found in diatoms (Coesel et al. 2008), explaining why α-carotene and its derivative are not found in Bacillariophyta.

The next step of the pathway involves β-carotene hydroxylation. The β-carotene hydroxylases characterised

so far range in two classes, i.e. the nonheme di-iron hydroxylases and the cytochrome P450 monooxygenases (for a review, see Martín et al. 2008). These enzymes present different hydroxylation mechanisms (for reviews, see Cunningham and Gantt 1998; Tian and DellaPenna 2004). No full sequence for either types of enzymes were found in diatoms (Coesel et al. 2008; Frommholt et al. 2008) suggesting that zeaxanthin (Zea) formation requires another type of enzyme. Despite the fact that diatoms do not synthesise α-carotene (Strain et al. 1944: for a review, see Jeffrey and Vesk 1997), two genes with similarity to *LUT1,* denoted *LUT-like* (*LTL)* were found in the genomes of both diatoms *T. pseudonana* and *P. tricornutum* (Coesel et al. 2008) (Fig. 2). LUT1 proteins catalyse the hydroxylation of α-carotene to lutein in the angiosperm *Arabidopsis thaliana* (Tian et al. 2004; Kim and DellaPenna 2006). The deduced amino acid sequences of the diatom *LTL* all contain a putative signal peptide and, therefore, may be targeted to the plastid. As LTL protein showed a weak ability to hydroxylate the β-rings of β-carotene (Tian et al. 2004; Tian and DellaPenna 2004; Kim and DellaPenna 2006), the involvement of LTL should be experimentally proven. The replacement of the usual nonheme di-iron β-carotene hydroxylase by another P450-dependent monooxygenase in diatoms would even constitute an advantage (one Fe atom left) because in diatoms, and other algae as well, the amount of available iron strongly influences the photosynthetic activity, algal physiology and growth (Tsuda et al. 2003; Doan et al. 2003; Behrenfeld et al. 2006; Boyd et al. 2007).

ZEP (Zea epoxidase) catalyses the transformation of Zea to Vio, which in turn is used to synthesise Ddx and fucoxanthin, the major xanthophyll molecules of the light-harvesting complexes (Goericke and Welschmeyer 1992; Lohr and Wilhelm 1999, 2001). The transformation of Vio to Ddx would occur through neoxanthin formation (Swift and Milborrow 1981). No gene candidate coding for the enzymes involved in this step has been identified so far in diatoms.

Several copies of the putative ZEP genes have been identified in diatoms (Frommholt et al. 2008; Coesel et al. 2008) (Table 2). ZEP belongs to the lipocalin family of proteins that are characterised by a similar tertiary structure and similar functions (Grzyb et al. 2006). These enzymes are supposed to contain 8 antiparallel β-sheets and three highly conserved short consensus repeat motifs (Flower et al. 2000). The motif I is composed of the first of the eight β-sheets and a short fragment of the preceding α-helix. The motif II is composed of the loop between β-sheets number 6 and number 7 and parts of the end of β-sheet number 6 and the beginning of β-sheets number 7. The motif III is composed of the end of β-sheet number 8 and part of the C-terminal α-helix, including the loop between both fragments. These lipocalin motifs are framed by a C-terminal cysteine-enriched domain and an N-terminal glutamic acid-enriched domain. The 3D structure of lipocalins is characterised by the deep conic hollow, formed by the β-sheets. It is necessary for the binding of the substrate (Newcomer et al. 1984; Holden et al. 1987). The comparison of the deduced amino acid sequences corresponding to the three *ZEP* gene candidates identified in *P. tricornutum* revealed that the lipocalin motif I is larger in ZEP1 and ZEP2 than in ZEP3 whilst the forkhead domain of the C-terminal domain is either absent or replaced. Interestingly, ZEP3 of *P. tricornutum* would possess a transmembrane region (Coesel et al. 2008). In addition to be a member of the lipocalin family, ZEP belongs to the FAD-dependent mono-oxygenases (Coesel et al. 2008).

ZEP is localised in the stromal side of the thylakoids (Bouvier et al. 1996). From the functional point of view, it is important to note that the ZEP activity is inhibited by a strong pH gradient (Goss et al. 2006).

An alternative pathway to the Vio formation through Zea epoxidation, involving β-cryptoxanthin and β-cryptoxanthin-epoxide as intermediates, has been proposed on the basis of kinetics of pigment synthesis in *P. tricornutum* and *Cyclotella meneghiniana* (Lohr and Wilhelm 2001).

Several xanthophyll cycles are operating in diatoms

Photosynthetic organisms can experience large modification in their light environment. For instance, light could be a limiting factor for the diatoms that reside deeply in the water column whereas those close to the water surface might be exposed to irradiances that can be 10- to 20-fold higher than the one needed for photosynthesis (van de Poll et al. 2005). As high-light conditions negatively affect photosynthesis, productivity, viability and growth can be impaired. Therefore, the photosynthetic organisms have developed strategies to optimise light harvesting whilst minimising photoinhibitory damages due to the excess income of energy (Foyer et al. 1994; Park et al. 2010). These strategies range in two categories, namely photoadaptation (long-term evolutionary-based mechanisms) and photoacclimation. These short-term responses aim to reduce the photosynthetic capacity through a reduction of the size of the LHC (Perry et al. 1981), rapid structural modifications within the LHCII (Horton et al. 1996; Bassi and Caffarri 2000), the enhancement of reaction centre repairing processes, modification of the PSI/PSII stoichiometry and the establishment of nonphotochemical energy dissipation pathways, the so-called nonphotochemical quenching (NPQ). NPQ activation is controlled by the trans-thylakoidal proton gradient and the xanthophyll cycles (for a review, see Müller et al. 2001). A xanthophyll

cycle consists in the forward conversion of epoxidised Cars to de-epoxidised ones (for reviews, see Gilmore 1997; Moulin et al. 2010). The major xanthophyll cycle in diatoms involves the forward conversion of Ddx to Dtx (Fig. 2; Stransky and Hager 1970a, b; for a review, see Wilhelm et al. 2006). This cycle is the most important short-term photoprotective mechanism. Lohr and Wilhelm (1999) have shown that besides the Ddx cycle, some diatoms may also display the Vio cycle, leading to Zea *via* antheraxanthin (Fig. 2), even if the pool size of pigments concerned with the Vio cycle is rather low. The Vio cycle is the major xanthophyll cycle in green algae and land plants (Havaux and Niyogi 1999; Han et al. 2009; for reviews see Müller et al. 2001; Moulin et al. 2010). When the light stress disappears, the de-epoxidation reactions are reversed and the nonphotochemical quenching (NPQ) relaxes to its minimum, i.e. mostly zero (Quick and Stitt 1989; Walters and Horton 1991). In higher plants or in diatoms whilst in higher plants, the lumen acidification activates the de-epoxidising enzyme (Arsalane et al. 1994; Hager and Holocher 1994) that replaces the epoxidised xanthophylls by the de-epoxidised ones (Morosinotto et al. 2003). In diatoms, the trans-thylakoidal proton gradient is not sufficient to induce the NPQ (Lavaud et al. 2002b) but regulates it (Lavaud and Kroth 2006). In addition, a chlororespiratory pH gradient activates the Dtx cycle in the dark in *P. tricornutum* (Jakob et al. 1999, 2001) but not in *Cyclotella meneghiniana* (Grouneva et al. 2009). According to these authors, this difference would reside in the use of difference NADPH dehydrogenases (NDH) and in the capacity to flow the electron to PSI. *P. tricornutum* would use a proton-pumping NDH and would be unable to flow the electrons provided by this enzyme to PSI whereas *Cyclotella meneghiniana* would use an NDH such as the NHD2-type of NDH that is not coupled to proton translocation (Peltier and Cournac 2002) and would flow the electrons to PSI. In *P. tricornutum,* the Dtx molecules formed seemed not to confer a photoprotective advantage to the algae (Jakob et al. 1999).

In higher plants, two nonexclusive models have been proposed for NPQ. Briefly, either the de-epoxidised xanthophylls would directly take part in the quenching through a charge-transfer mechanism (Holt et al. 2005) in the minor LHC complexes associated with PSII (Ahn et al. 2008; Avenson et al. 2008, 2009) or would act as an allosteric regulator (Crouchman et al. 2006; for reviews, see Horton et al. 2008; Moulin et al. 2010) triggering a conformational change (Horton et al. 1991) in the peripheral PSII antenna (Pascal et al. 2005). In higher plants, a key factor involved in both mechanisms is the protein PsbS, a small LHC-like protein (Li et al. 2000), the level of which is correlated with the extent of NPQ (Li et al. 2002). PsbS would serve as a "sensor" for the lumen pH change (Li et al. 2004; Kiss et al. 2008; Horton et al. 2008). So far, no match for a PsbS ortholog has been reported in the diatom genome of *P. tricornutum* and *T. pseudonana* (Armbrust et al. 2004; Maheswari et al. 2005; Bowler et al. 2008). As the expression of *LI818* genes (synonymouns *LHCx, fcp6*) is highly upregulated under a high-light stress in green algae (Gagne and Guertin 1992; Savard et al. 1996; Yamano et al. 2008) and in diatoms (Beer et al. 2006; Nymark et al. 2009; Park et al. 2010), Zhu and Green (2008) have proposed that the corresponding protein, a unique member of the family of the light-harvesting complex proteins, plays the same role than PsbS. Actually, several *LI818* homologous genes have been found through phylogenetic analysis in *T. pseudonana, P. tricornutum* and *Chaetoceros cryptica* (Zhu and Green 2008; Park et al. 2010). Nymark et al. (2009) recorded a specific increase of *LHCX2 and* LHCX3 genes in within 30 min of a high-light irradiation. Interestingly, the amount of Dtx correlates with the amount of FCP6 proteins (Beer et al. 2006; Gundermann and Büchel 2008) and with the Chl fluorescence yield in trimeric FCPa (Gundermann and Büchel 2008). Surprisingly, only a pH dependence of the Chl fluorescence yield of FCPa is detected when the proteins are aggregated. This pH dependence takes place at pH values which would be expected in the thylakoid lumen under illumination and which activate the DDE (Gundermann and Büchel 2008). Regardless how the de-epoxidised xanthophylls act in the NPQ, diatoms exhibit a much larger capacity to dissipate excess absorbed light energy than green plants because their NPQ level can be as much as five times the levels registered for higher plants (Bertrand et al. 2001; Ruban et al. 2004; Grouneva et al. 2008). This higher capacity is linked to the fact that the epoxidation is inhibited by strong pH gradients (Mewes and Richter 2002; Goss et al. 2006). Interestingly, the epoxidation is also inhibited in the dark period that follows an illumination period. This is probably due to the shortage in NADPH, a cosubstrate of DEP (diatoxanthin epoxidase) (Mewes and Richter 2002; Goss et al. 2006).

The enzymes of the violaxanthin cycle of diatoms

Several copies of the putative VDE (Vio de-epoxidase) genes have been identified in diatoms (Montsant et al. 2007; Frommholt et al. 2008; Coesel et al. 2008) (Table 2). Interestingly, in *P. tricornutum* and *A. anophagefferens* but not in *T. pseudonana,* the VDE genes present a syntenic arrangement with one of the ZEP paralogs, suggesting a coregulation of the gene expressions (Frommholt et al. 2008). The enzymes corresponding to the adjacent genes might be involved specifically in the xanthophyll cycle (see below) whereas the other *ZEP* genes could code for the enzymes involved in the biosynthetic pathway (Frommholt

et al. 2008) (Fig. 2). This hypothesis is waiting for experimental arguments that could come from the determination of the enzyme localisations.

Like ZEP, VDE belongs to the lipocalin family of proteins (Ganfornina et al. 2000; Salier 2000; Charron et al. 2005; for a review, see Grzyb et al. 2006). The comparison of the VDE deduced sequences from diatoms and plants revealed that the two proteins differ and that the C-terminal domain is the less conserved (Coesel et al. 2008). This difference is likely affecting the binding of VDE to the thylakoid membrane (Jakob et al. 2001; Grouneva et al. 2006) because partial protonation of this domain would increase the binding (Hager and Holocher 1994; Bugos and Yamamoto 1996) (see also later). VDE is a soluble protein located in the thylakoid lumen and exhibiting an in vivo pH optimum between 5.0 and 5.2 (Hager 1969; Pfündel et al. 1994). In vitro enzyme assays revealed that VDE from the green alga *Mantoniella squamata* (Prasinophyceae) can use Ddx as a substrate but with a significant reduced efficiency compared to Vio (Goss 2003) whereas with the VDE purified from lettuce, the de-epoxidation rate of Ddx is two times faster than with Vio (Yamamoto and Higashi 1978).

Homologous sequences to *VDE* genes were found in the genome database of two diatoms, *T. pseudonana* and *P. tricornutum*, and were named VDE-like because they are distantly related to the plant VDE (Montsant et al. 2007; Coesel et al. 2008). VDE-like could be located differently than the VDE protein because the C-terminal region, which could be important for binding the protein to the thylakoid membrane, is uncharged (Coesel et al. 2008). Coesel et al. (2008) have proposed that a VDE-like enzyme could be implicated in the Ddx cycle of these diatoms whereas Frommholt et al. (2008) found this possibility unlikely. In the same way, the *ZEP* gene product is implicated in the reverse reaction. As mentioned earlier, diatoms are not capable to synthesise lutein and therefore, the lutein-epoxide cycle (for a review, see Moulin et al. 2010) is not operating in these organisms.

The enzymes of the diadinoxanthin cycle

The de-epoxidation occurs at the thylakoid side exposed to the lumen whereas the epoxidation of Dtx occurs at the thylakoids exposed to the stroma (Hager 1969; Müller et al. 2001). The Ddx de-epoxidation reaction is faster than the Vio de-epoxidation in higher plants when exposed at illuminations of similar intensities and durations (Färber and Jahns 1998). Similarly to VDE, DDE (Ddx de-epoxidase) is localised in the thylakoid lumen and is activated upon its acidification but its pH optimum is shifted by at least 0.7 unit towards higher pH values, i.e. DDE is activated at almost neutral lumen pH (Jakob et al. 2001; Grouneva et al. 2006). An alternative explanation could be that the access to Ddx is facilitated by the fact that thylakoids are loosely appressed in diatoms (Pyszniak and Gibbs 1992; Bedoshvili et al. 2009). The affinity (K_M) of DDE for the co-substrate ascorbate is 3–4 times higher than in the case of VDE (Grouneva et al. 2006). The DEP, which catalyses the back conversion of Dtx to Ddx is almost inhibited under high light conditions (Mewes and Richter 2002) and in darkness, probably because of a shortage in NADPH (Goss et al. 2006). The reaction is however not influenced by the pH (Lavaud et al. 2002a). The reaction is inhibited by cadmium (Bertrand et al. 2001; for reviews see Bertrand and Poirier 2005; Poirier et al. 2008).

Regulation of the carotenoid biosynthesis pathway

The Car amount can be modified according to the environment. For instance, in the psychrophilic diatom *Chaetoceros neogracile*, the relative amount of Ddx and Dtx are immediately adjusted to the change in the light intensity whilst FCP transcripts are also quantitatively and qualitatively modified (Park et al. 2010). A correlation between the Dtx content and the number of PCP6 protein in the trimeric FCPa has been reported (Beer et al. 2006). How the regulation network controlling Car biosynthesis in diatoms is still in its infancy. Only a few factors such as nutrient deficiencies (Allen et al. 2008) and light quality (Coesel et al. 2008) and quantity (Lavaud et al. 2002a) have been studied. For instance using *P. tricornutum*, Coesel et al. (2008) have shown that light, especially blue light and in a lesser extent red light, controls the expression of several genes of the Car pathway, including *PSY* and *PDS* (Coesel et al. 2008).

Interestingly, *ZEP3* gene is specifically upregulated at the beginning of high-light stress (1st 30 min at 550 µmol m^{-2} s^{-1}). *ZEP1* and *ZEP3* show little or no variations during the intermediate phase. Only *ZEP1* was moderately increased during the late phase of the acclimation (Nymark et al. 2009).

Pigment analysis of isolated FCP revealed that not all Ddx molecules are bound to FCP proteins, suggesting that Ddx is, as reported for Zea (Gruszecki and Strzalka 1991), partially dissolved in the lipid phase of the thylakoïds (Guglielmi et al. 2005; Beer et al. 2006; Gundermann and Büchel 2008). Indeed, the solubilisation of the Ddx or Vio in the thylakoid membrane constitutes a crucial point for the activity of de-epoxidase enzymes (Latowski et al. 2002; Goss et al. 2005b, 2007). As Ddx is more soluble in MGDG than Vio, the MGDG concentration required for optimal DDE activity is significantly lower than for VDE (Goss et al. 2005b, 2007). However, being solubilised is not a selfsufficient condition because the de-epoxidising enzyme has to bind the membrane to process the

solubilised pigment molecules. On the other hand, it has been observed in vitro that MGDG allows the formation of inverted hexagonal structures (H_{II} phases), that in turn, promotes Ddx de-epoxidation in vitro (Goss et al. 2005b, 2007). Therefore, it is assumed that H_{II} phases favor the binding of DDE to the thylakoid membranes after its activation (Goss et al. 2009). The addition of PG, SQDG, digalactosyldiacylglycerol or PC completely suppresses the de-epoxidation in in vitro tests (Goss et al. 2005b, 2009), probably because their presence does not allow the formation of the H_{II} phases or/and creating charge repulsion between the protein and the insertion site (Goss et al. 2009). Thus, the thylakoids should contain domains from which SQDG are excluded. How this is achieved remains unclear. Goss et al. (2009) suggested that the preferential binding of lipids such as MGDG by abundant proteins such FCP may be part of the process.

Conclusions

The biosynthetic pathway used to synthesise Car is now quite well established in higher plants whilst many information are missing in diatoms. The sequencing of several genomes of diatoms allowed the search for the sequences homologous of those identified in higher plants. Using in silico analyses, several missing steps of the biosynthetic pathway have been identified and are waiting for experimental proofs. The pathway leading to the specific xanthophyll remains completely unknown. The regulation of the different steps of the pathway remains very unclear and much have to be done to understand the regulatory circuit affecting the transcriptional, post-transcriptional steps and also the enzymatic activities.

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