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REGULATION OF CHLOROPHYLL DEGRADATION IN PLANT TISSUES

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The purpose of the review was to analyze the basic biochemical processes leading to the chlorophyll degradation and ways to control this process in plant product storage. First of all, this is a complex of enzymatic reactions starting with the hydrolysis of chlorophyll with the formation of acyclic diterpene phytol and water-soluble chlorophyllide. An alternative primary reaction is the removal of magnesium from the chlorophyll tetrapyrrole ring to form pheophytin with the participation of Mg^{2+}-dechelatase and/or low-molecular Mg^{2+}-dechelating substances. The chlorophyll breakdown can also be caused by free radicals formed in the peroxidase-catalyzed reaction of H_2O_2 with phenolic compounds or fatty acids. The unstable product of chlorophyll peroxidation, $C13^2$–hydroxychlorophyll a decomposes to colorless low-molecular compounds. Expression of the genes of chlorophyll catabolism enzymes is controlled by phytohormones. Methods for controlling the pigment decomposition during storage of plant products are associated with the use of activators and inhibitors of chlorophyll decomposition. The best known inductor of the synthesis of catabolic enzymes is ethylene, widely used to accelerate fruit ripening. Gibberellins, cytokinins and nitric oxide, on the contrary, slow down the loss of chlorophyll.

Key words: chlorophyll, chlorophyllase, pheophytin, peroxidase, phytohormones, ethylene.

Chlorophyll (Chl) degradation is a complex process which occurs in plants at all times of their lifecycle, most actively during aging and ripening. The saturated green color associated with the presence of chlorophyll (Chl) in plant tissues is an important consumer marker for the freshness and quality of the product of leafy vegetables (spinach, parsley, and green onions), broccoli inflorescence, etc. Maturing of "green fruits" (bananas, tomatoes, citrus, etc.), on the contrary, is accompanied by a loss of Chl. Today the fruits of certain crops (e.g. bananas) are harvested before maturation, because in this state they can be transported without mechanical damage, and the ripening of the fruit can be induced as needed. The regulation methods of Chl conservation and degradation in plants are therefore an important biotechnological problem.

Annually on Earth, a huge amount of Chl is synthesized and destroyed [1, 2]. For a long time, the global phenomenon of biological breakdown of Chl remained poorly studied and was biological enigma [3]. Only in the last decades, after some intermediate products of the Chl degradation have been characterized, it has become possible to identify the enzymes participating in this process [4–6]. Now Chl catabolism can be considered a sequence of synchronized reactions deactivating Chl molecules that, after separation from photosynthetic polypeptide complexes, become photocytotoxic due to the development of the photodynamic effect [7].

Under non-optimal conditions of transportation and storage, active oxygen (ROS, reactive oxygen species) accumulates in fruit and vegetable crops causing multiple tissue damage [8, 9]. It induces antioxidant reactions that slow the aging and degradation of Chl. Hence, suppression of oxidative and activation of antioxidant reactions can be used as an effective way to preserve quality and extend the shelf life of products [10]. Maturation and associated breakdown of Chl are accelerated by the treatment of fruits with phytohormones or effectors actively interacting with them at certain temperatures. The most common way to regulate the rate of

maturation is the treatment of fruits with ethylene gas [11].

This review examines the mechanisms involved in the degradation of Chl in the aging of plant tissues and fruit ripening, as well as the factors that accelerate and slow down the processes of Chl breakdown.

Stages of chlorophyll degradation

In plant leaves, Chl degradation occurs in chloroplasts with the participation of six known Chl-catabolic enzymes and metal-chelating agents of as yet unidentified nature [12]. In functioning chloroplasts, Chl is localized almost exclusively in pigment-protein complexes of thylakoid membranes [1]. The Chl breakdown during the aging of leaves or ripening becomes possible only after removal of the pigment from the polypeptide matrix [9]. Chl degradation begins with a two-stage reduction of Chl *b* to Chl *a*, catalyzed by Chl*b*- reductase and 7-hydroxymethyl Chl*a*-reductase [13].

The primary products of Chl degradation are either water-soluble chlorophyllide (Chlide), formed upon separation of acyclic diterpene phytol from the Chl molecule, or pheophytin (Pheo) resulted from the removal of magnesium from the tetrapyrrole pigment ring. After separation of phytol and removal of magnesium, pheophorbide (Pheide) is formed (Table).

The initial and subsequent stages of Chl breakdown are catalyzed by the corresponding enzymes. One of them is chlorophyllase (Chlase) (chlorophyll chlorophyllidohydrolase 3.1.1.14), which was discovered a little over 100 years ago, the first of the known plant enzymes. In many plant species, Chlase is a constituent part of the catabolism system, and significant levels of the enzyme are maintained during the vegetation [3, 5, 14]. Chlase with a high degree of stereospecificity accelerates the cleavage of the Chl molecule into chlorophyllide carboxylic acid and phytol (Fig. 1). Suppression of Chlase activity, for example in transgenic broccoli plants (*Brassica oleracea*) with an antisense construct (*BoCLH1*) [15] resulted in a decrease in the rate of post-harvest degradation of Chl.

The water-soluble Chlide formed by Chlase is able to leave the lipid matrix of the membranes, which is a prerequisite for further Chl biodegradation.

In the intracellular matrix, Chlide becomes available for Mg^{2+}-dechelatase and then, like pheophorbide, rapidly converts to red metabolites involving Pheo oxygenase that are catalyzed by reductase to decompose into colorless linear tetrapyrroles, so-called non-fluorescent chlorophyll catabolites (NCCs) which eventually accumulate in vacuoles [16]. These reactions are believed to constitute the main pathway of Chl breakdown in chloroplasts. All but one of the by now identified NCCs are Chl *a* derivatives, and it is shown that to destroy the chlorophyll pool, Chl *b* must transform into Chl *a* [17, 18]. Therefore, in mutants with a deficiency of chlorophyll-*b*-reductase which catalyzes the first of two successive reactions of the Chl *b* reductive transformation in Chl *a*, large amounts of Chl are retained and a STAY-GREEN (SGR) phenotype is formed [19, 20].

Screening of SGR mutants in many species revealed a new SGR protein localized in chloroplasts [19], which itself is not believed to be a catabolic enzyme of the chlorophyll cycle yet participates in the Chl breakdown process, providing interaction of Chl-disrupting enzymes such as pheophytinase, Pheo *a* oxygenase and reductase of red Chl catabolites with thylakoid membranes [6].

It is assumed that the contact of the SGR protein with subunits of the light-harvesting complex of photosystem 2 (LHCII) destabilizes the Chl bond with the apoprotein, resulting in the release of Chl and facilitating its and apoproteins' degradation [19, 20]. Thus, during the active destruction of chlorophyll, the SGR protein and LHCII interact dynamically in the thylakoid membranes. A possible role of these interactions is to reduce the risk of accumulation of excited Chl and

Structural elements of chlorophyll and the primary products of its degradation

	Mg^{2+}	Phytol	Abbreviation
Chorophyll	+	+	Chl
Pheophytin	–	+	Pheo
Chlorophyllide	+	–	Chlide
Pheoforbide	–	–	Pheide

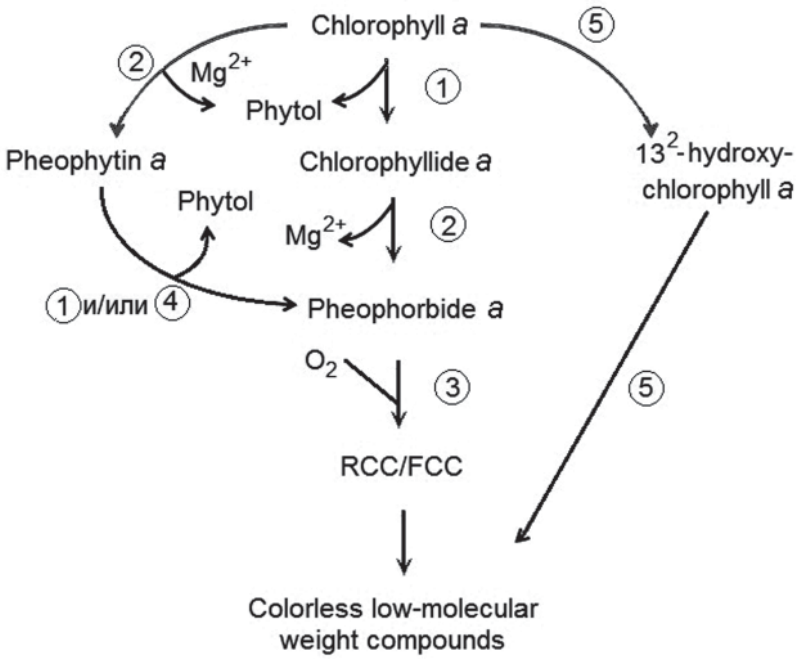

Fig. 1. **Assumed pathways of chlorophyll degradation in plant tissues:**
1 — chlorophillase, Mg-dechelatase, *2* — Pheophorbide a oxidase; *3* — pheophytinase;
4 — peroxidation of phenols; *5* — peroxidation of lipids;
RCC — red chlorophyll catabolites; FCC — fluorescent chlorophyll catabolites

the colored intermediate products of its catabolism, deactivation of which causes the formation of free radicals and the development of photodynamic effect. SGR-proteins-directed destruction of Chl prevents the accelerated cell death during the aging of the leaves. Recently, 7-hydroxymethyl chlorophyll *a*-reductase (*HCAR*) which catalyzes the second stage of the Chl *b* transformation in Chl *a* has been identified [21]. Nevertheless, the Chl breakdown pathway, in contrast to the well-studied process of its biosynthesis, still needs to be clarified.

The recent study of *Arabidopsis* leaf aging has shown that the magnesium removal from Chl occurs after the Chl hydrolysis, catalyzed not by Chlase but by another enzyme, pheophytinase [22]. At the same time, it has been proved that the Chl degradation in ripening fruits is catalyzed by Chlase hydrolyzing Chl to water-soluble Chlide and phytol [23, 24].

It is believed that Chl can also be oxidized involving peroxidase in the presence of phenolic compounds to form C13^2-hydroxy-chlorophyll *a* (C13^2-hydroxy-chl *a*). These assumptions were confirmed in experiments *in vitro* [25, 26].

Mechanisms regulating the activity of enzymes that participate in Chl catabolism have not been studied sufficiently. Chlase activity is presumed to be regulated at the level of gene expression, with ethylene being the most effective of the known inducers of biosynthesis of this enzyme *de novo* both at the mRNA and at the protein synthesis levels [11, 23, 24, 27].

Ethylene-dependent activation of chlorophyllase

Ethylene, a gaseous plant hormone, directly participates in the regulation of fruit ripening at all stages. Both endogenous and exogenous ethylene synchronizes and speeds up the biochemical reactions that occur during this process. Various proteins such as membrane receptors, protein kinases, transmembrane vectors, nuclear transcription factors are involved in the metabolism of endogenous ethylene. The biosynthesis of ethylene in plants is regulated at two stages: the first takes place during normal vegetation of plants, while the second functions by positive feedback and is responsible for the rapid stimulation of ethylene production during the maturation of climacteric fruits. The respiration of mature climacteric fruits after harvest is usually reduced to minimum values, after which there is a rapid rise to the maximum level, the so-called climacteric peak. The rate

of maturation of climacteric fruits at certain temperatures can be regulated by treatment with phytohormones or with effectors actively interacting with phytohormones. Ethylene significantly accelerates the ripening of citrus fruits, which mature very slowly if taken from the tree. The role of ethylene is to regulate a number of reactions, including changes in gene expression [28]. Then, the expression of Chlase genes is induced in the green fruit skin and the associated destruction of Chl is repeatedly accelerated [11, 29]. Similar processes occur in bananas [30]. Ethylene found widespread commercial application. Ethylene has found widespread commercial application, one of the first examples being bleaching the celery due to the accelerated loss of Chl. The treatment with ethylene leads to an increase in Chlase activity in spinach leaves and accelerates their yellowing [27].

Although citrus fruits are non-climacteric fruits, their maturation and Chl breakdown are stimulated by ethylene [25]. Treatment with exogenous ethylene significantly accelerates the Chl degradation in gathered fruit, in contrast to the slow yellowing of fruits remaining on the tree [31]. A direct correlation between the degradation of Chl and the expression of genes encoding Chlase in ethylene-treated fruit has been shown [11], suggesting that Chl catabolism is regulated at the level of gene expression. In protein extracts of fruits treated with ethylene, Chlases with activity increasing five times in 24 hours and 12 times 72 hours after treatment were detected [13]. Also, the expression of Chlase genes did not increase with yellowing of untreated fruit [11], which indicates other mechanisms regulating the Chl breakdown [32].

Hormonal regulation of Chl degradation in plant tissues

There are metabolic changes in the ripening fruit, including Chl degradation, biosynthesis of carotenoids and anthocyanins, transformation of starch into simple sugars, cell wall softening, ethylene receptor degradation, etc. When the green photosynthetic tissue of citrus and bananas ripens and ages, chloroplasts lose Chl becoming carotenoid-rich chromoplasts (Fig. 2) [33]. This process is partially reversible, depends on external factors, and is controlled by hormones and metabolites. It is known that an increase in the content of sugars in tissues leads to suppression of the Chl synthesis [34, 35].

Phytohormones such as indole-3-acetic acid (IAA) and kinetin inhibit the loss of chlorophyll during aging of wheat chloroplasts *in vivo* and *in vitro*. Gibberellic acid (GA) stimulates the pigment degradation in plant leaves, while at the same time it suppresses the breakdown of chlorophyll in isolated chloroplasts. The fluctuating optimal concentration of the hormone upon suppression of chlorophyll degradation suggests a change in the endogenous hormonal pool involved in the regulation of the chloroplast aging *in vivo* and *in vitro*. The slowing chlorophyll breakdown by kinetin, IAA and GA in the *in vitro* aging of chloroplasts indicates the direct action of the substances on chloroplasts, preventing the yellowing of aging leaves [36].

Gibberellins (GA^3) and cytokinins (N^6-benzyl adenine) which slowed the loss of Chl, also suppressed the ethylene-induced increase in Chlase activity [11, 13]. The correlation between the expression of genes encoding Chlase and the rate of Chl breakdown is noted in ethylene-treated citrus fruits [11].

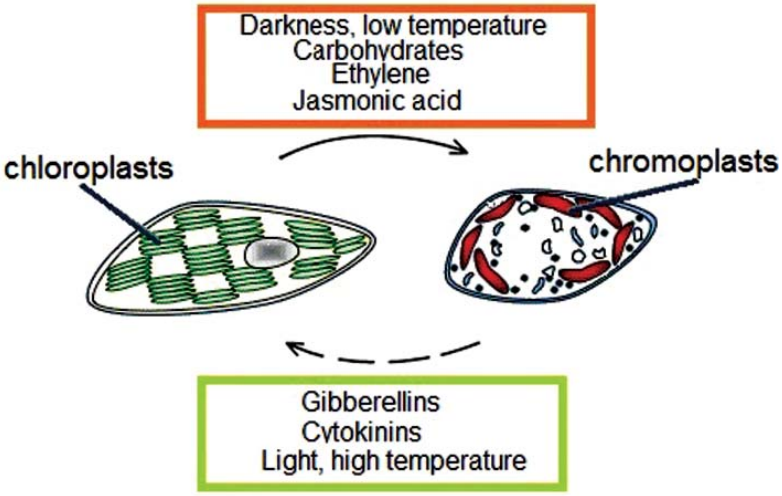

Fig. 2. **Effect of various factors on chlorophyll and chloroplast degradation and chromoplast formation**

As determined by the method of confocal spectroscopy, Chl degradation in lemon skin cells treated with ethylene did not occur synchronously. While the Chl content in some cells fell sharply in 24 hours after treatment with ethylene, in other cells it did not change. It was proved that this effect is associated with the appearance and accumulation of Chlase in certain cells under the action of ethylene [23].

Another plant growth regulator, jasmonate (JA) and its derivatives can influence the aging of leaves and the degradation of Chl. For example, methyl-JA accelerated the aging of oak leaves and caused the Chl breakdown in barley leaves [37]. It is also noted that the Chl degradation in arabidopsis leaves treated with methyl-JA is controlled by the *AtCLH1* gene [38].

Thus, phytohormones act in different ways: ethylene increases the expression and activity of Chlase, and accelerates the Chl degradation, while cytokinins and gibberellins are aging antagonists which prevent the pigment loss and may even stimulate its accumulation.

Metal-dechelating substances

In plant products, Chl degradation determines the color change from green to yellow or gray-brown. This transition is associated with the breakdown of the green pigment Chl and the accumulation of dark olive pheophytin formed when the Chl molecule looses magnesium, for example in the treatment of the Chl solution with a weak acid. The *in vivo* dissolution of the bond of the central magnesium ion (Mg^{2+}) with the tetrapyrrole ring in Chl is still not clearly understood. In studying the dechelatation of Chl, two ways of Mg^{2+} removal were identified in *Chenopodium album* [39] and *Fragaria x ananassa* [40]. According to data obtained by Suzuki et al. [12, 39], Mg^{2+} is removed from the Chl molecule in the first stage of its breakdown, by heat-stable low-molecular compounds (molecular mass < 400 Da), called metal-dechelating substances, of unknown molecular nature. The molecular weight of such compounds isolated from strawberries was 2180 Da [40]. This component is assumed to be either a small peptide or an organic molecule acting as a chelating agent for divalent cations. However, it is still not known whether these Mg^{2+} chelating agents function by themselves or are cofactors of Mg^{2+}-dechelatase. Studies of inhibition have shown that metal-dechelating agents can contain active SH-groups, indicating a possible protein nature [40]. The assumption that these compounds are simply prosthetic groups of Mg-dechelating proteins [41] has been experimentally disproved [12]. The second type of Mg-dechelating activity is associated with thermolabile Mg-releasing proteins (MRPs) [39]. MRP activity was demonstrated only using an artificial substrate of chlorophyllin (Chl, hydrolysed in an alkaline medium). It has been suggested that de-chelation *in vivo* occurs with the participation of MRP [42]. Considering the fact that, at least in some systems, Mg-de-chelating occurs before phytol separation from the Chl molecule [43], it is possible that Chlide is not a natural substrate for metal-dechelating substances.

Degradation of Chl in peroxidation

It was shown that solutions of isolated Chl and leaf homogenates decolorize *in vitro* in the presence of peroxidase and phenolic compounds isolated from plant tissues [2]. In the presence of a peroxidase system, the Chl-Chlide and Pheo derivatives are also degraded, and notably, ascorbate effectively inhibites the oxidation of Chl and its derivatives [27].

In the case of peroxidation of Chl *a* in the presence of H_2O_2 and flavonoids, $C13^2$-hydroxychlorophyll *a*, the oxidized form of Chl is formed as the primary intermediate (Fig. 3). In the aging leaves of barley (*Hordem vulgare* L.) and beans (*Phaseolus vulgaris* L.), the level of $C13^2$-hydroxychlorophyll *a* increases in parallel with the decrease in Chl *a* content [10]. Many plant phenols present in chloroplasts [44, 45], such as *n*-coumaric acid, apigenin, and naringin, which have a hydroxyl group in the para position in the benzene ring, may serve as the electron donors in the peroxidation of Chl. As a result of peroxidation, phenoxyl radicals attacking Chl *a* are formed, which ultimately leads to the formation of colorless low-molecular derivatives. It was possible to isolate from the chloroplasts of broccoli inflorescences the cationic isoperoxidase (molecular weight 34 kDa) [46], the gene expression of which increases with aging and yellowing of the inflorescences. Its activity, which is suppressed by kinetin treatment, was also detected in chloroplasts of barley leaves, suggesting the involvement of this enzyme in the oxidative degradation of Chl *a*. With the participation of cationic isoperoxylase, OH-lactone-Chl *a* is also formed as an intermediate during the Chl *a* peroxidation [47].

Phenoxyl free radicals are also involved in the oxidation of carotenoids and fatty acids. On the other hand, Chl oxidase and lipoxygenases catalyzing the addition of

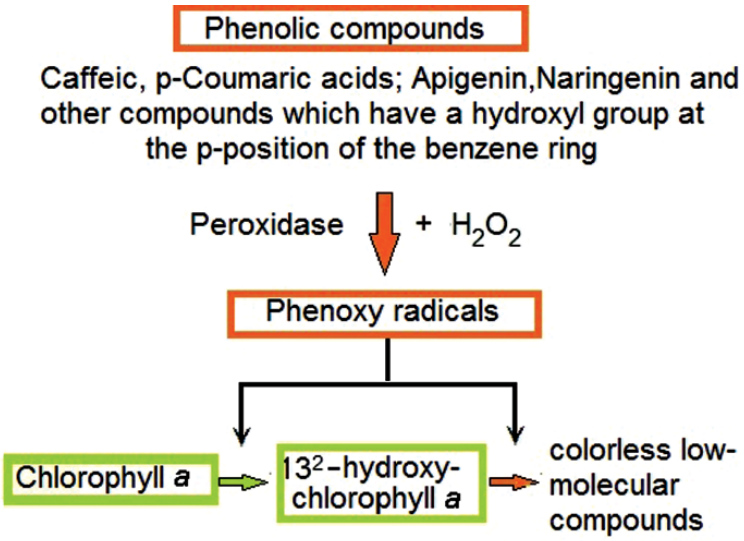

Fig. 3. **Chlorophyll breakdown induced by peroxidation**

oxygen to polyunsaturated fatty acids may be involved in the oxidative degradation of Chl. The destruction of Chl in the broccoli inflorescences is prevented by the treatment with hot water or steam. The same effect was observed when green citrus and leafy vegetables were sluiced with scalded water [10]. It was shown that the slowing down of Chl degradation in these cases is associated not only with suppression of gene expression and inactivation of enzymes participating in the Chl expansion [48], but also with higher content of hydrogen peroxide, as well as the concentration and activity of antioxidant enzymes. According to Gómez et al. [49], the concentration of hydrogen peroxide in mitochondria during thermal processing of spinach leaves increased simultaneously with the ratio of the reduced and oxidized forms of ascorbate and glutathione while Chl degradation was inhibited. An increase in the concentration of reducing agents involved in the deactivation of ROS, such as ascorbate and the components of the ascorbate-glutathione cycle contributes to slowing the aging of the fruit.

The data accumulated to date confirm the important role of peroxidation in the destruction of Chl in the aging of plant tissues.

The slowing down catabolism of Chl degradation in plant tissues is achieved with various methods of physical processing, such as high or low temperature, UV irradiation or chemical treatment, for example, processing with ethanol fumes after harvest [10, 50]. Chl breaks down in the post-harvest heat treatment of mango, papaya and citrus, traditionally used for pest and pathogen control [50]. Treatment with hot water or hot air prevents yellowing of broccoli [51], as well as leafy vegetables [49].

A number of studies have established that UV radiation, especially short-wave (UV-C), suppresses the yellowing of green vegetables during storage. UV-C inhibits the activity and gene expression of Mg-dechelating agents and enzymes that regulate the Chl degradation, such as Chlase, pheophytinase and peroxidase [40, 52]. This leads to a slowing of yellowing of the inflorescences upon aging.

The degradation of Chl in the broccoli inflorescences is blocked if they are placed in sealed bags. Their storage at 22 °C partially suppresses the expression of the genes of pheophorbidoxidase and other genes associated with Chl catabolism. Two Chlase-encoding genes, *AtCLH1* and *AtCLH2*, were found in *Arabidopsis*. The level of *AtCLH1* mRNA increases under the influence of jasmonic acid [37], when injured or attacked by pathogens [38], and decreases when stored in the dark [53] (Fig. 2). The *AtCLH2* mRNA content remains unchanged under these conditions, but its expression correlates with the level of ozone [54].

The green color and quality of some vegetables (spinach, lettuce, green peas, broccoli, etc.) is well preserved when frozen. However, during storage a significant amount of Chl still degrades with the participation of catabolic enzymes including chlorophyllase, and also as a result of oxidative degradation involving lipoxygenase, peroxidase, phenol peroxidase [20].

Recently, molecular genetic approaches have been actively developed to reduce the rate or degree of fruit ripening, softening and aging by regulating the activity of enzymes that destroy the structural components of membranes, cell walls, and control the metabolism of pigments. The available data reliably show that the enzymatic system of Chl degradation in the post-harvest period can be blocked when processing or storing plant products under extreme conditions.

The "green seed problem"

The influence of unfavorable weather factors (drought, high and low temperatures, early winter, etc.) causes inhibition of the natural process of Chl degradation in vegetating plants too [55, 56]. Slowed Chl breakdown in ripening seeds of oilseeds (such as soybean and rapeseed) leads to a significant increase in the residual Chl content in mature seeds, which is an economically significant problem for vegetable oil producers. If the percent of green seeds in the crop exceeds 9%, the whole batch is rejected, and the producers face huge losses [57].

In addition to the climate, other factors or deviations from the technology in the period before and after harvest, such as the use of desiccants or premature harvesting followed by drying at high temperatures, lead to the retention of chlorophyll in soybean seeds [57]. In addition to these environmental factors, various soybean varieties differently conserve Chl and generate green seeds under stress.

So far, the influence of growing conditions and drying processes on the conservation of green pigments in soybean and rapeseed seeds has not been sufficiently understood. In the early stages of seed development, photosynthesis is transferred from the leaves to the walls of the pod for the synthesis of lipids and other reserve substances in seeds during the conversion of sugars to fatty acids. This is the main metabolic pathway in which about 60% of the incoming carbon is transformed and stored as oil [58]. Developing rape embryos are able to maintain a significant rate of photosynthesis, directly related to the biosynthesis of fatty acids. As the seeds mature, the rate of lipid synthesis decreases, the need for photosynthesis decreases, and the chloroplasts break down, and the seeds do not have Chl by the time of the harvest. However, if in the early stages of development the plants were subjected to freezing, the degradation of Chl in the seeds could be disturbed increasing the green seed ratio, which largely depreciates the yield [59].

The oil obtained from seeds with a high Chl content rapidly becomes oxidized and rancid. This happens because Chl and its derivatives in the light induce the formation of free radicals sensitizing the photooxidation of oil components, primarily α-linolenic acid, causing deteriorating oil quality, shorter storage times, and necessitating additional cleaning costs.

The existing methods for removal of Chl and its derivatives from rapeseed oil can be divided into three main groups: physico-chemical, enzymatic and genetic. After standard desalination, clarification and deodorization procedures, the content of Chl and its derivatives in oil is significantly reduced. The enzymatic approach is related to the use of Chlase for the Chl degradation in the oil purification process. Chlase appeared promising in extensive studies of the Chl breakdown process in oil [60, 61], but further optimization of the process conditions is required [62].

A cardinal approach to solving the problem of "green seed" can be genetic modifications of oilseeds, leading to a decrease in the residual Chl content in rapeseed, soybean, etc. This problem can be solved by inactivating chlorophyll-producing enzymes, suppressing the synthesis of pigment-binding proteins or overexpression of chlorophyll-degrading enzymes. One of the first steps in this direction was the creation of the *Lhcb*-antisense construct to inhibit the synthesis of light-harvesting protein PSII [63]. Transgenic *B. napus* plants with Chl synthesis altered by antisense construction in the glutamate 1-semialdehyde aminotransferase gene revealed a decreased Chl content in mature seeds which proved to be completely viable [64]. Genetically modified plants with overexpression of Chlase contained 15–20% less Chl than wild species, which was not accompanied by changes in the synthesis of aminolevulinic acid. In this regard, it is very promising to obtain transgenic plants with overexpression of genes of Chl catabolism, in particular, regulating Chlase biosynthesis.

Therefore it can be concluded that Chl degradation enzymes are potentially important for agriculture and the food industry, since the possibility of regulating Chl catabolism in plant products can provide significant benefits. Deceleration of Chl breakdown prolongs the functional activity of the photosynthetic apparatus of the leaves, which can increase the productivity of crop production. On the contrary, aging, associated with the accelerated

catabolism, contributes to the maturation of the crop. The "green seed problem" is an important example of the cost-effectiveness of measures aimed at the timely removal of Chl during the ripening of the oilseed crops. An actively cultivated oilseed crop is rapeseed (*Brassica napus* L.), widely used in animal husbandry, food industry, and also for the production of biodiesel fuel. Ukraine is a very large producer of rapeseed, accounting in 2008–2009 for more than 20% of its total world export.

Thus, regulating the ripening of fruits and seeds associated with the acceleration/deceleration of Chl degradation is an economically important problem.

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РЕГУЛЮВАННЯ РОЗПАДУ ХЛОРОФІЛУ У РОСЛИННИХ ТКАНИНАХ

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Метою огляду було проаналізувати основні біохімічні процеси, що призводять до розкладання хлорофілу, і способи контролю цього процесу під час зберігання рослинних продуктів. Передусім це комплекс ензиматичних реакцій, що починаються з гідролізу хлорофілу з утворенням нециклічного дитерпену фітолу і водорозчинного хлорофіліду. Альтернативною первинною реакцією є видалення магнію з тетрапірольного кільця хлорофілу з утворенням феофітину за участю Mg^{2+}-дехелатази та/або низькомолекулярних Mg^{2+}-дехелатуючих речовин. Руйнування хлорофілу відбувається також за атаки вільними радикалами, що утворюються в каталізованій пероксидазою реакції H_2O_2 з фенольними сполуками або жирними кислотами. Нестійкий продукт пероксидного окиснення хлорофілу *a* — $C13^2$–гідроксихлорофіл — розпадається з утворенням низькомолекулярних незабарвлених сполук. Експресія генів ензимів катаболізму хлорофілу контролюється фітогормонами. Способи контролю розпаду пігменту під час зберігання рослинних продуктів пов'язані з використанням активаторів та інгібіторів розпаду хлорофілу. Кращим з відомих індукторів синтезу катаболічних ензимів є етилен, який широко використовують у практиці для прискорення дозрівання плодів. Гібереліни, цитокініни та оксид азоту, навпаки, уповільнюють втрату хлорофілу.

Ключові слова: хлорофіл, хлорофіллаза, феофітин, пероксидаза, фітогормони, етилен.

РЕГУЛЯЦИЯ РАСПАДА ХЛОРОФИЛЛА В РАСТИТЕЛЬНЫХ ТКАНЯХ

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Целью обзора было проанализировать основные биохимические процессы, приводящие к разложению хлорофилла, и способы контроля этого процесса при хранении растительных продуктов. В первую очередь это комплекс энзиматических реакций, начинающихся с гидролиза хлорофилла с образованием нециклического дитерпена фитола и водорастворимого хлорофиллида. Альтернативной первичной реакцией является удаление магния из тетрапиррольного кольца хлорофилла с образованием феофитина при участии Mg^{2+}-дехелатазы и/или низкомолекулярных Mg^{2+}-дехелатирующих веществ. Разрушение хлорофилла происходит также при атаке свободными радикалами, образующимися в катализируемой пероксидазой реакции H_2O_2 с фенольными соединениями или жирными кислотами. Неустойчивый продукт пероксидного окисления хлорофилла *a* — $C13^2$ –гидроксихлорофилл распадается с образованием низкомолекулярных неокрашенных соединений. Экспрессия генов энзимов катаболизма хлорофилла контролируется фитогормонами. Способы контроля распада пигмента при хранении растительных продуктов связаны с использованием активаторов и ингибиторов распада хлорофилла. Лучшим из известных индукторов синтеза катаболитических энзимов является этилен, который широко используют в практике для ускорения созревания плодов. Гиббереллины, цитокинины и оксид азота, напротив, замедляют потерю хлорофилла.

Ключевые слова: хлорофилл, хлорофиллаза, феофитин, пероксидаза, фитогормоны, этилен.