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POTENTIAL NATURAL SOURCES OF TOCOPHEROLS AND TOCOTRIENOLS AND POSSIBILITIES THEIR USE IN THE FOOD INDUSTRY®

Potencjalne naturalne źródła tokoferoli i tokotrienoli oraz możliwości ich zastosowania w przemyśle spożywczym®

Tocopherols and tocotrienols are natural compounds found in oil plants. Their antioxidant properties make them interesting for food producers and consumers looking for healthy food. The aim of this study is to present the potential natural sources of tocopherols and tocotrienols, which as antioxidants are increasingly used as food additives to extend their durability, and additionally enrich the product with vitamin E. The work shows their chemical structure, methods of obtaining and legal regulations allowing tocopherols and tocotrienols for use in food processing. The current ways of using them in food production were discussed.

Key words: vitamin E, tocopherols, tocotrienols, antioxidant, food stability, food quality.

Abbreviations: α – alpha
 β – beta
 γ – gamma
 δ – delta

Tokoferole i tokotrienole to naturalne związkami występujące w roślinach oleistych. Ich właściwości przeciwutleniające sprawiają, że są interesujące dla producentów żywności i konsumentów poszukujących zdrowej żywności. Celem artykułu jest omówienie potencjalnych naturalnych źródeł tokoferoli i tokotrienoli, które jako substancje przeciwutleniające są coraz częściej wykorzystywane jako dodatki do żywności w celu przedłużenia jej trwałości, a dodatkowo wzbogacają produkt w witaminę E. W artykule przedstawiono ich strukturę chemiczną, sposoby pozyskiwania oraz regulacje prawne dopuszczające tokoferole i tokotrienole do wykorzystania w przetwórstwie żywności. Omówiono dotychczasowe sposoby ich wykorzystania w produkcji żywności.

Słowa kluczowe: witamina E, tokoferole, tokotrienole, antyoksydant, stabilność, jakość.

INTRODUCTION

The content of bioactive ingredients with documented and beneficial effects on health as well as high quality and nutritional value of foods are now becoming the main determinant of the choice of food products [29]. Consumers are looking for foods, which can improve their health and prevent diseases. Food producers focus on research into, among others, new, natural substances, which increase the nutritional value of products, extend the shelf life of foods, including natural antioxidants, which effectiveness are comparable with synthetic counterparts [35]. Thermal processing of food raw materials, time and method of storage of raw materials or finished products, type of packaging determine the durability of the product and its final quality. One of the most important mechanisms leading to lowering the nutritional value and quality of foods, shortening the shelf life of products containing fat in their composition is the

process of lipid oxidation, which causes undesirable changes in the final products. This process leads to the formation of an unpleasant taste and smell, a decrease in the nutritional quality and the safety of food products [20,22]. The main initiators of lipid oxidation are free radicals, i.e., molecules having at least one unpaired electron on the outer shell, and therefore having a high affinity, e.g. to lipids. Prevention of oxidation depends primarily on eliminating free radicals as they form and inhibit the propagation process. One of the most effective and convenient strategies for delaying or preventing lipid oxidation is the addition of antioxidants, including vitamin E [43]. Vitamin E encompasses a group of eight fat-soluble compounds – four tocopherols (α , β , γ , δ) and four tocotrienols (α , β , γ , δ) (Fig. 1.), of which the highest biological activity is shown by α -tocopherol. Biochemically, α -tocopherol acts as an antioxidant by breaking chain reaction and interfering with reactive oxygen species formed by scavenging lipid peroxy

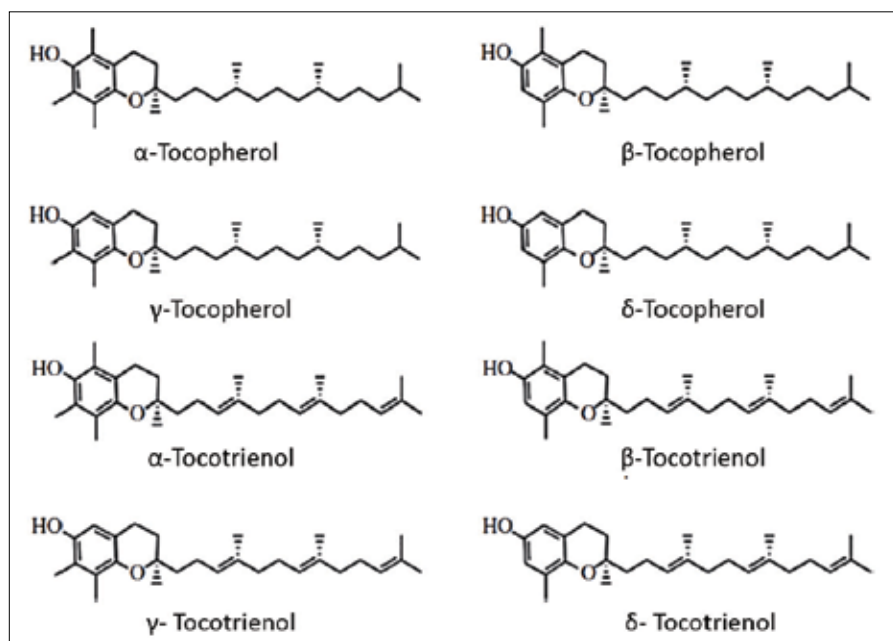


Fig. 1. Structural formulas of tocopherols and tocotrienols.

Rys.1. Wzory strukturalne tokoferoli i tokotrienoli.

Source: [37]

Źródło: [31]

radicals. During the chain-breaking reaction, α -tocopherol forms a free radical that can react quickly with another peroxide radical, thus ending two peroxidation chains [7].

VITAMIN E AS A CHEMICAL AND BIOACTIVE COMPOUND

Vitamin E was first described by Evans and Bishop in 1922, characterized as a dietary factor necessary for reproduction. Soon, vitamin E was identified as an antioxidant for polyunsaturated lipids. Subsequent studies have shown that tocopherols and tocotrienols, act as signal molecules which regulate gene expression, signal transduction and modulate cell function, regardless of antioxidant properties

[14,33]. Tocopherols and tocotrienols are amphipathic molecules containing a 6-chromanol (6-hydroxychromanol) ring and a side chain made of 3 isoprene units. In tocopherols, it is linked to the phytyl chain and in the case of tocotrienols, it is linked to the isoprenoid chain [9]. They differ in the number and location of methyl groups in chemical structures and the presence of three trans double bonds at the 3', 7', and 11' positions in the side chain of tocotrienols, which is responsible for their unsaturated nature as compared with tocopherols. Structural interrelationships are presented in Table 1 [27, 33, 41].

Tocopherols and tocotrienols are homologs to each other. α -homologs contain three methyl groups, β - and γ -homologues are mutual isomers with two methyl groups, and α -tocopherols and δ -tocotrienols are monomethyl. Synthetic α -tocopherol (all-*rac*- α -T) is a racemic mixture of individual stereoisomers. Therefore, each of the tocopherols has eight optical isomers. For α -tocopherol, these are RRR-, RSR-, RRS-, RSS-, SRR-, SSR-, SRS-, SSS-. Only RRR-tocopherols occur in nature [41].

Vitamin E is an essential nutrient, it has antioxidant properties, hence it can play an important role in maintaining good health, reducing the risk of diseases in which reactive oxygen species participate in the pathogenesis [29,38]. Deficiencies of vitamin E can cause anemia, impaired immune response, retinopathy, and neuromuscular and neurological problems. Research also points to the numerous health benefits of taking tocopherols, including the prevention of certain types of cancer, heart disease, and other conditions, and therefore it is suggested that daily vitamin E intake may be significantly higher than the presently established adequate daily intake [33].

Table 1. Structural relationship between tocopherols and tocotrienols

Tabela 1. Powiązania strukturalne między tokoferolami i tokotrienolami

Common name	Chemical name	Short	Position of the ring		
			R1	R2	R3
tocol	2-methyl-2-(4',8',12'-trimethyltridecyl)-chroman-6-ol	-	H	H	H
α -tocopherol	5,7,8-trimethyltolcol	α -T	CH ₃	CH ₃	CH ₃
β -tocopherol	5,8-dimethyltolcol	β -T	CH ₃	H	CH ₃
γ -tocopherol	7,8-dimethyltolcol	γ -T	H	CH ₃	CH ₃
δ -tocopherol	8-methyltolcol	δ -T	H	H	CH ₃
tocotrienol	2-methyl-2-(4',8',12'-trimethyltrideca-3',7',11'-trienyl) chroman-6-ol	-	H	H	H
α -tocotrienol	5,7,8-trimethyltocotrienol	α -T3	CH ₃	CH ₃	CH ₃
β -tocotrienol	5,8-dimethyltocotrienol	β -T3	CH ₃	H	CH ₃
γ -tocotrienol	7,8-dimethyltocotrienol	γ -T3	H	CH ₃	CH ₃
δ -tocotrienol	8-methyltocotrienol	δ -T3	H	H	CH ₃

Source: [41]

Źródło: [41]

Vitamin E is widely distributed in nature, but can only be synthesized by photosynthetic eukaryotes and other photosynthetic organisms such as cyanobacteria. Plants accumulate tocopherols available in seeds, fruits or young tissues undergoing active cell division [2]. Due to their amphipathic properties, they join in the phospholipid bilayer of cell membranes, with a chromanol ring directed towards the water compartment, with a side chain embedded in non-polar space [6]. In this way, vitamin E protects membrane lipids, photosynthesis apparatus and plant seeds against oxidative stress [24]. Vitamin E in plant products occurs mainly in non-esterified form. Its content varies depending on the species, variety, stage of ripeness, season, time and method of harvesting as well as processing and storage time [31].

Tocopherols and tocotrienols occur naturally in vegetable oils, sprouts and cereals, nuts and almonds. Tocopherol is found in almond, walnut, sunflower, rapeseed, and olive oil. The best sources of tocotrienols are palm oil and rice bran oil; other sources are grape seed oil, hazelnuts, oats, corn, olive oil, sea buckthorn berries, rye, linseed, and sunflower oil (Tab. 2.). Research indicates that one of the best sources of both tocopherols and tocotrienols are palm fruits, rice grains and annatto seeds from the fruit of the Achiote tree (*Bixa orellana*) [29,33].

USE OF VITAMIN E IN THE FOOD INDUSTRY

Vitamin E in fortified foods, but also in dietary supplements, is often the esterified form of α -tocopherol, the most common esters being acetate and succinate. Esterified forms of vitamin E are more resistant to oxidation as they have a longer shelf life. A small number of studies focus on other esters, such as α -tocopheryl nicotinate, which is an ester of vitamin E and niacin and is not yet well understood [7]. Some studies suggest that the potency of antioxidants may vary between natural or synthetic sources of tocopherols [2]. Due to their antioxidant activity, tocopherols play

a major role in protecting mono- and polyunsaturated fatty acids (PUFAs) from oxidation [33]. Natural tocopherols (E306) and synthetic α -, γ - and δ -tocopherols (E307, E308 and E309, respectively) are used as antioxidants in food to inhibit lipid peroxidation. They are used individually or in combination, according to Regulation (EC) No 1333/2008 on food additives and subsequent amendments according to Regulation (EU) 2018/1497. So far, no Acceptable Daily Intake (ADI) has been established, but the Upper Intake Level (UL) is set at 300 mg vitamin E per day according to EFSA or 1000 mg according to the Institute of Medicine. However, the ADI for α -tocopherol established by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) was determined to be 0.15-2.0 mg α -tocopherol/kg body weight/day [9,12,32]. No oral toxicity was observed in tocopherols. Additionally, EFSA has approved the health claim for vitamin E. Food industry may use the "vitamin E sources" claim on their products when the food contains 1.8 mg of vitamin E per 100 g or 100 ml or a single serving of food or drink [22]. The Food and Drug Administration (FDA) in the United States has granted the status of tocopherols and tocotrienols generally recognized as safe (GRAS), with an approved dose of 40 mg tocopherol per 1 kg food [10]. The Supplements Working Group of Main Sanitary Inspectorate in Poland had established maximum acceptable level of vitamin E in supplements at 250 mg/day [17].

METHODS OF EXTRATIONS OF VITAMIN E

Initially, the main commercial sources of vitamin E used as a food additive were vegetable oils, however soybean oil and wheat germ oil contain too little of it. Soon, vitamin E extraction from fatty acid distillates from vegetable oils began, which proved to be cheaper and with higher content of vitamin E. Currently, almost all producers obtain vitamin E from distillates, although new raw materials appeared, from which they tried to obtain it – palm leaves, bananas, pineapples, sugar cane, rice, wheat, barley, corn, rye, rice bran [31].

Table 2. Total tocopherols (T) and tocotrienols (T3) content in selected food oils (mg/100g)

Tabela 2. Całkowita zawartość tokoferoli (T) i tokotrienoli (T3) w wybranych olejach spożywczych (mg / 100 g)

Products	α -T	β -T	γ -T	δ -T	α -T3	β -T3	γ -T3	δ -T3
Barley	14.2-20.1	0.6-1.9	3.5-15.1	0.9-4.6	46.5-76.1	nd-12.4	8.5-18.6	0.5-2.6
Coconut	0.2-1.8	tr-0.25	tr-0.12	nd-0.39	1.1-3.0	nd-0.17	0.33-0.64	nd-0.1
Corn	18.0-25.7	0.5-1.1	44.0-75.2	2.20-3.25	0.94-1.50	nd	1.30-2.00	nd-0.26
Cottonseed	30.5-57.3	0.04-0.30	10.5-31.7	tr	nr	nr	nr	nr
Olive	11.9-17.0	nd-0.27	0.89-1.34	nd-tr	nd-tr	nd	nd	nd-tr
Palm	6.05-42.0	nd-0.42	tr-0.02	nd-0.02	5.70-26.0	nr-0.82	11.3-36.0	3.33-8.00
Peanut	8.86-30.4	nd-0.38	3.50-19.2	0.85-3.10	nd	nd	nd	nd
Sunflower	32.7-59.0	tr-2.40	1.40-4.50	0.27-0.50	0.11	nd	tr	tr
Rapeseed	18.9-24.0	nd-tr	37.0-51.0	0.98-1.90	nd	nd	nd	nd
Soybean	9.53-12.0	1.00-1.31	61.0-69.9	23.9-26.0	nd	nd	nd	nd
Wheat germ	15.1-19.2	31.2-65.0	tr-52.3	nd-0.55	2.5-3.6	nd-8.2	nd-1.85	nd-0.24

nd: not detected; nr: not reported; tr: trace; T: tocopherols, T3: tocotrienols

Source: Own study based on [33]

Źródło: Opracowanie własne na podstawie [33]

The distillate is a mixture of acylglycerols, free fatty acids, tocopherols and stanols, hydrocarbons and other substances that affect the organoleptic characteristics of vegetable oils. It is produced as waste from the deodorization process, i.e. the removal of undesirable substances from the raw material. The content of vitamin E in distillates is dependent on oil, from which it has been produced; most content is observed, among others, in oil from corn, sunflower, peanuts, rapeseed and cottonseed [1, 31, 36].

Many researchers have developed various methods and techniques for extracting, analyzing, identifying, purifying and quantifying tocopherols from various sources. However, scientists are still looking for a method of obtaining vitamin E which would be efficient, economical, and would lead to obtaining vitamin E concentrate, or individual isoforms, with the desired degree of purity and in the largest amount possible. Determination of tocopherols in plant products combines classical techniques with physico-chemical methods and is based on such processes as esterification, saponification, liquid-liquid extraction, crystallization, distillation, enzymatic methods, ion exchange, chromatographic methods and their combinations (Fig. 2.) [7,25]. Due to the low concentration of vitamin E isoforms in food, an effective method of pre-treatment of samples is extremely important [25]. Sample preparation protocols vary at homogenization and extraction stages. Most methods include the saponification of samples [21]. However, studies have shown that the process of saponification of samples reduced the content of individual

forms of vitamin E, which leads to a decrease in the content of overall vitamin E [7]. Similarly, the method of mechanical pressing, frequently used during extraction, have been shown to reduce the overall content of vitamin E in the tested samples compared to extraction with organic solvents [20]. Direct extraction methods are also widely used, differing in the choice of solvents, e.g. hexane, petroleum ether, pentane and in extraction procedures [29,31]. Other methods involve liquid-liquid extraction without saponification or solvent extraction after saponification. High-performance liquid chromatography (HPLC) is used in various combinations, using both the normal and reverse phases. HPLC uses UV (ultraviolet) diode, fluorescence, ELSD (evaporative light scattering detection), electrochemical and amperometric detection. In some studies [13], normal phase adsorption chromatography shows an advantage over other methods because they indicate that there is a complete separation of isomers. The use of fluorescence is described as more sensitive and selective than UV, and ELSD (evaporative light scattering detector) is used to analyze several compounds simultaneously [9,40]. Lu and Yang [25] proposed ultrasonic dispersion micro-extraction in the solid phase using multi-walled carbon nanotubes - the authors recommended the method as fast and simple, reproducible, and with lower usage of organic solvents. Rapid progress in vitamin E extraction and homologation separation technologies may lead to the development of the most cost-effective method for producing vitamin E of the highest quality and biological activity for producers, which will be used in food processing and other industries [31].

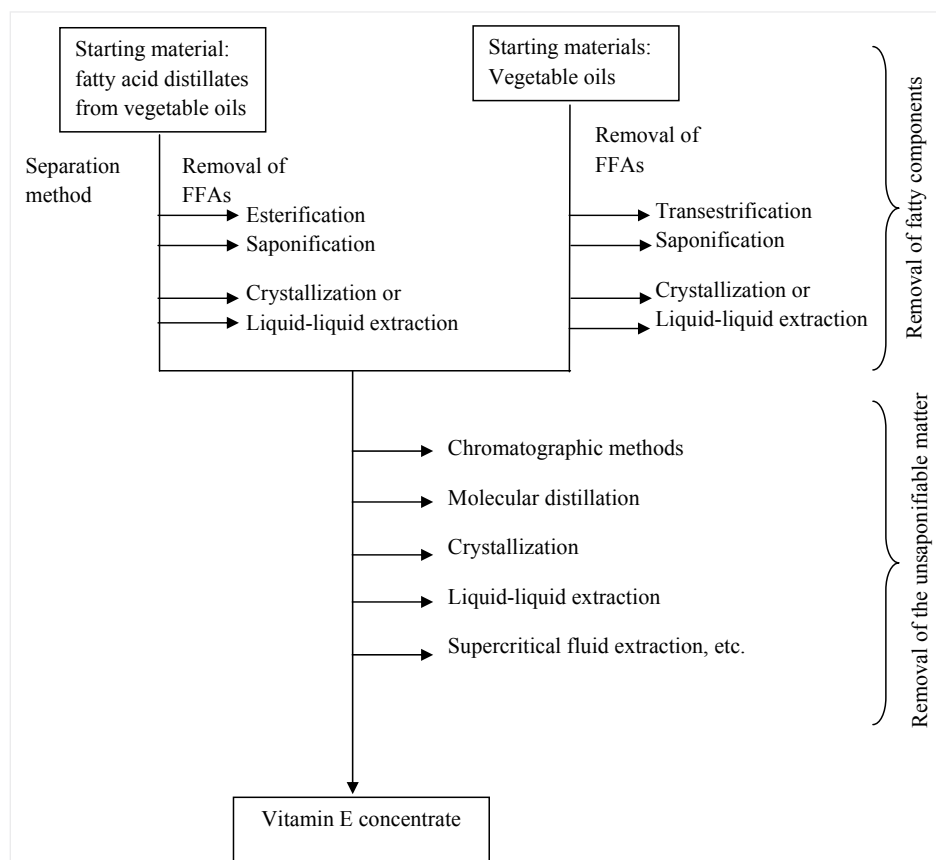


Fig. 2. Sample procedures for obtaining vitamin E.
Rys. 2. Przykładowe metody uzyskiwania witaminy E.

Source: [31]

Źródło: [31]

PRACTICAL USE OF VITAMIN E IN FOOD PROCESSING

The most common and easiest way to use vitamin E is to add it to food products as an antioxidant, in order to increase the stability of fatty acids, reduce food biochemical changes, e.g. a mixture of tocopherols obtained from soybean oil processing is often used to stabilize oxidation-sensitive lipid dietary supplements, such as fish oil. Also, oils rich in tocopherols, such as from oat, barley or wheat germ, can be mixed with other oils to stabilize them [42].

Tocopherols as antioxidants are also used to extend the shelf life of confectionery fat, lard, margarine, mixtures, drinks and infant formulas, which at the same time enriches these products with vitamin E [19, 39, 43]. Economos and co-workers [8] proposed fortifying orange juice with, among others, vitamin E, which could be a new source of fat-soluble vitamins in populations with insufficient consumption of this vitamin.

An example of a food which can be fortified with vitamin E is food consumed by the crew during missions on a spacecraft. Simons and co-workers [34] evaluated the stability and content of vitamins, sensory acceptance and color variation of fortified space food over the course of two years. It was noted that enriching food with antioxidant vitamins reduces the rate of color degradation of stored products. Vitamin E proved to be stable at different storage temperatures and did not affect the organoleptic quality.

Since tocopherols have an antioxidant effect on lipid compounds, they are at the same time most frequently used in products which are most exposed to such reactions, i.e. in meat and meat products [16]. Bolger and his team [4] evaluated the effect of increasing the tocopherol content on physical and sensory quality in poultry sausages. They studied the stability of α -tocopherol during storage, cooking, frying, and grilling. α -tocopherol was added at a concentration of 200 mg/kg of product (the amount considered necessary to reduce lipid oxidation and exceeding the amount needed to meet the requirements of the EFSA health claim). It has been found that it is possible to produce sausages enriched with sufficient α -tocopherol to meet EFSA's nutritional and health requirements without adversely affecting the quality or shelf life of the sausages. During storage or thermal treatment of the product, no significant loss of α -tocopherol was observed. Similarly, the addition of tocopherols to fish, poultry, and red meat lowered the oxidation level of fat contained in meat [33].

It turns out that the stage of breeding is important for the content of vitamin E in a meat product. Research proves that the way animals are fed and the use of feed with higher vitamin E content affect later meat quality [23]. The meat of rabbits, which were fed with different contents of vitamin E during breeding was examined. The content of vitamin E in meat increased with the increase of vitamin addition in feeding. During storage, a slower meat lipid oxidation rate was noted. Additionally, lower cholesterol content was found in the meat of rabbits that received 100 mg of vitamin E / kg feed compared to animals fed with a lower content of vitamin E. The assessment of individual sensory quality characteristics of meat (smell, taste, juiciness, tenderness) varied depending on the amount of vitamin E administered in the feed [23].

In recent years, the antioxidant properties of tocopherols have also been used in the production of "active" food packaging. Antioxidant films, packaging made of several layers, i.e. high-density layers and low-density layers, containing α -tocopherol as a natural antioxidant, are becoming popular [30]. It was found that the addition of an industrial mixture of natural antioxidants containing the highest concentration of tocopherols (90.2%) to the packaging was the most effective in extending the shelf life of salmon and reduced the lipid oxidation in meat to 70%. This suggests that it is possible to use active antioxidant films to extend the shelf life of high-fat products [3,5,15]. The Otero-Pazos and co-workers' study [28] evaluated the possibility of using biodegradable films for coating food with the addition of α -tocopherol as an active antioxidant in food packaging. Those films maintained antioxidant activity for over 20 days. Similarly, biodegradable

polyester-based films containing α -tocopherol showed antioxidant activity [26]. Other raw materials for producing "new" packaging are biopolymers - biodegradable, releasing natural α -tocopherol. In other studies, α -tocopherol was encapsulated in three different matrices (whey protein isolate WPI, soy protein isolate SPI and zein), which were then used as a food packaging on a thermoplastic wheat gluten film to form a double layer film. α -tocopherol was comparably stable in all films produced [11]. The new trend is called "active packaging" or "active package" [18].

SUMMARY

Tocopherols and tocotrienols are substances widely disseminated in nature. They exhibit antioxidant activity by eliminating free radicals. They can easily be obtained from available plant tissues and oil plants are their main source. Tocopherols and tocotrienols are generally recognized as safe and can be applied in food processing. Moreover, manufacturers can use health claims on the labels of products, which are vitamin E sources. Recently, food producers have become interested in new, natural ways to extend the shelf life of food products. As a result of this interest, many concepts arise for the use of vitamin E in animal breeding, in the processing of food raw materials, and in packaging materials used for food storage. These techniques are designed to preserve the flavor and odor sought by the consumer, adequate nutritional quality and food safety. Besides the use of natural vitamin E as a food additive, innovative packaging, called "active packaging" or biodegradable films for coating food products with the addition of antioxidants that release vitamin E into foods and prevent food quality changes, are created.

PODSUMOWANIE

Tokoferole i tokotrienole są substancjami szeroko rozpowszechnionymi w przyrodzie. Wykazują aktywność przeciwutleniającą poprzez eliminację wolnych rodników. Można je łatwo uzyskać z dostępnych tkanek roślinnych, a rośliny oleiste są ich głównym źródłem. Tokoferole i tokotrienole są ogólnie uznawane za bezpieczne i mogą być stosowane w przetwórstwie spożywczym. Ponadto producenci mogą stosować oświadczenia zdrowotne na etykietach produktów, które są źródłami witaminy E. Niedawno producenci żywności zainteresowali się nowymi, naturalnymi sposobami przedłużenia okresu przydatności produktów spożywczych. W wyniku tego zainteresowania powstaje wiele koncepcji zastosowania witaminy E w hodowli zwierząt, w przetwarzaniu surowców żywnościowych oraz w materiałach opakowaniowych używanych do przechowywania żywności. Techniki te zostały zaprojektowane w celu zachowania smaku i zapachu poszukiwanego przez konsumenta, odpowiedniej jakości odżywczej i bezpieczeństwa żywności. Oprócz zastosowania naturalnej witaminy E jako dodatku do żywności, powstają innowacyjne opakowania, zwane „aktywnymi opakowaniami” lub biodegradowalne folie do powlekania produktów spożywczych z dodatkiem przeciwutleniaczy, które uwalniają witaminę E do żywności i zapobiegają zmianom jakości żywności.

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