Review Article
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Potato and ginger peels: a potential new source of natural antioxidants

Abstract

Spoilage prevention and shelf-life extension of products will always remain an important goal to the meat industry. While the greatest emphasis is placed on the prevention of microbial spoilage, chemical deterioration, specifically oxidative spoilage, is an important consideration for fresh meats and manufactured meat products as well. In the meat industry especially fish processing, synthetic antioxidants being used for preservation of fish and fishery products. In fact many synthetic antioxidants and antimicrobials are widely used in food and beverage products today and they are safe to consume. Hence the researchers have shifted their focus towards natural antioxidants. The present short review has focus on natural antioxidant and their mode of action.

Keywords: spoilage, oxidative, fishery products, beverage products, docosahexaenoic acid, polyunsaturated, eicosapentaenoic acid, fatty acids, unsaturation

Volume 4 Issue 5 - 2017

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Received: November 15, 2016 | **Published:** July 18, 2017

Abbreviations: PUFAs, polyunsaturated fatty acids; BHA, butylated hydroxyanisole; BHT, butylated hydroxyl toluene; TBHQ, tertiary butyl hydroquinone; PG, propyl gallate; CGA, cholorogenic acid; CFA, caffeic acid; QNA, quinic acid; FIC, ferrous ion-chelating; FRP, ferric reducing power

Introduction

Food products elaborated from fatty fish have lately attracted strong interest on fish processing industry and consumers; this is mainly due to their naturally high content of essential polyunsaturated fatty acids (PUFAs) particularly eicosapentaenoic acid (20:5) and docosahexaenoic acid (22:6). These fatty acids have been shown to have potential benefits for human health.[1,2] Nevertheless, they are susceptible to oxidation to a large extent due to their high degree of unsaturation, which is associated with rancidity and loss in nutritive value of food.[3] In frozen conditions, marine fish species undergo lipid oxidation and their compounds have shown to facilitate protein denaturation (Mackie, 1993; Sikorski & Kolakowska, 1994), nutritional losses,[4,5] and loss of endogenous antioxidant systems.[6] Lipids, especially oxidized lipids, affect the hydrogen bonds and facilitate hydrophobic interactions in proteins foods. Oxidation of lipids initiates other changes in the food system which affects nutritional quality, wholesomeness, safety, color, flavor, and texture.[7] The susceptibility of meat products to oxidation and its subsequent potential hazards in humans has challenged the meat processors and technologists to come up with newer techniques to retard or inhibit oxidation, so as to preserve the quality and enhance the shelf life of such products.

Antioxidants in food may be defined as any substance which is capable of delaying, retarding or preventing the development of rancidity or other flavor deterioration in food.[8] Food antioxidants, both synthetic and natural,[9] delay the development of off-flavors by the extension of the initiation period. If antioxidants were added over the reactions leading to initiation of oxidation, it would be ineffective in retarding the rancidity development.

History

The term antioxidant (also "antioxygen") originally referred specifically to a chemical that prevented the consumption of molecular oxygen. In the 19th and early 20th century, antioxidants were the subject of extensive research in industrial processes such as the corrosion of metals, explosives, the vulcanization of rubber, and the knocking of fuels in internal combustion engines.[10]

Earlier, nutrition researchers focused on the use of antioxidants for preventing the oxidative deterioration of unsaturated fats. Antioxidants activity was measured by simply placing the fat in a closed glass container with oxygen and observing the rate of oxygen consumption. However, it was the identification of vitamins A, C, and E as antioxidants that revolutionized the field and led to the realization of the importance of antioxidants in biology. Research into how vitamin E prevents the process of lipid per oxidation led to the current understanding of antioxidants as reducing agents that break oxidative chain reactions, often by scavenging reactive oxygen species before they can cause damage to the cells.[11]

Mechanism of action of antioxidants

Antioxidants can inhibit or retard oxidation either by scavenging the free radicals that initiate oxidation or by breaking the oxidative chain reaction. Those that scavenge the free radicals are described as primary antioxidants or chain breaking antioxidants (AH). They scavenge the free radicals ($ROO^\cdot$, $RO^\cdot$) as shown in equations 1 and 2 below, and disrupt the propagation step thereby forming an antioxidant radical of such a low reactivity that will lead to no further reaction with the lipids. The resultant antioxidant radical may react either with the hydroperoxide or another antioxidant radical forming a non-radical product. The overall mechanism[12] of primary antioxidants is shown below:

$$ROO^\cdot + AH \rightarrow ROOH + A^\cdot \quad (1)$$

$$RO^\cdot + AH \rightarrow ROH + A^\cdot \quad (2)$$

$$A^\cdot + ROO^\cdot \rightarrow ROOA \quad (3)$$

$$A^\cdot + A^\cdot \rightarrow \text{non-radical products} \quad (4)$$

The primary antioxidants include the phenolic compounds such as BHT, BHA, α-tocopherol and other compounds including gallates, nordihydroguairetic acid, flavonoids, aromatic amines, etc.

The secondary antioxidants or preventive inhibitors retard the oxidation by deactivating the active species and possible precursors of free radicals by preventive mechanisms viz, binding of metal ions, scavenging of oxygen (equation 7), converting hydroperoxides to non-radical species (equation 6), deactivating singlet oxygen (equation 9), and thereby suppress the generation of free radicals and reduce the rate of oxidation. The possible reactions involved are given below:

$$A^{\cdot} + RH \rightarrow AH + R^{\cdot} \quad (5)$$

$$AH + ROOH \rightarrow A^{\cdot} + RO^{\cdot} + H_2O \quad (6)$$

$$AH + O_2 \rightarrow A^{\cdot} + H_2O^{\cdot} \quad (7)$$

$$ROOA \rightarrow AO^{\cdot} + RO^{\cdot} \quad (8)$$

$$A^{\cdot} + O_2 \rightarrow AOO^{\cdot} \quad (9)$$

Some of secondary antioxidants include peroxide decomposers such as thioethers, methionine, and thio-dipropionic acid and its esters, metal chelaters like transferrin and albumin that bind iron and copper respectively, glutathione peroxidase, catechins, theaflavins, etc.

Synergistic effect

The cooperative effect of the inhibitors during oxidation, which results by their reinforcing each other, is known as synergism.[12] It was reported that when chain-breaking antioxidants are used together with preventive inhibitors, viz., hydroperoxide decomposers, metal chelaters and singlet oxygen quenchers, they generally exhibited significant synergism. But the mode of action of most of those synergists was in different ways. For example, ascorbic acid can act as synergist with tocopherols by regenerating or restoring their antioxidant properties.[13] Ascorbic acid and its esterified derivatives may also function as oxygen scavengers.

Ascorbic acid has been demonstrated to be an effective radical scavenger of superoxide, hydrogen peroxide, hydrochlorite, hydroxyl radical, peroxyl radical and singlet oxygen. Likewise, citric acid also imparts synergistic effect through metal chelation.[14] Other polyvalent acids such as tartaric malic, gluconic, oxalic, succinic and hydroxyl glutaric acids, sodium triphosphate and pyrophosphate and phytic acid were reported to exhibit synergistic effect in lipid oxidation.[15]

Selection of antioxidant

Various antioxidants exhibit substantial differences in effectiveness when used with different types of oils or fat-containing foods, and when used under different handling and processing conditions. These differences have been attributed to their molecular structure. The factors to be considered while selecting an antioxidant for food application include exhibition of effective inhibitory action on oxidation and harmful physiological effects, ease of incorporation into food. After it should not undergo any change when heated or impart any foreign flavor, odor or color even on long continued storage and should be available in abundance and economical.[16] The problem of selecting the best antioxidant is also further complicated, by the difficulty of predicting how the added antioxidant will interact with pro-oxidants and antioxidants already present in the food item.[17]

Types of Antioxidants

Antioxidants have been used extensively as additives to prevent or retard the oxidative deterioration of fats and oils and in food processing. The synthetic antioxidants are phenolic compounds such as butylated hydroxyanisole (BHA), butylated hydroxyl toluene (BHT), tertiary butyl hydroquinone (TBHQ) and esters of gallic acid, propylgallate (PG). These four major synthetic antioxidants in use are subjected to a 'good manufacturing practice' limit of 0.02% of the fat or oil content of the food.[18] Some antioxidants are used in combination with resulting synergistic effects, such as BHA and BHT[19,20] or BHA and PG.[21]

The growing consumer demand for food devoid of synthetic antioxidants has focused efforts on the discovery of new natural preservatives.[22] Also, recently there has been a decline on the use of synthetic antioxidants due to their reported ability to promote carcinogenesis such as BHA, in food.[19] The Natural antioxidants have been preferred worldwide for the past 15-20years, because of the trend to avoid or minimize the use of synthetic food additives. The interest in natural antioxidants continues to grow because they are presumed to be safe since they occur in foods and have been used for centuries.[14] Furthermore, evidence is accumulating that natural antioxidants in foods may have clear benefits because they have anticarcinogenic effects and inhibit biologically harmful oxidation reactions in the body.[18] Extensively studied sources of natural antioxidants are fruits and vegetables, spices, seeds, cereals, berries, wine, tea, onion bulbs, olive oil and aromatic plants. Attempts are also made to identify and evaluate antioxidants in agricultural by-products, ethnic and traditional products, herbal teas, cold pressed seed oils, exudates resins, hydrolysis products, not evaluated fruits and edible leaves and other raw materials rich in antioxidant phenols that have nutritional importance and/or the potential for applications in the promotion of health and prevention against damages caused by radicals.[23]

Potato

Potato (*Solanun tuberosum*), besides carbohydrate supply, is a good source of vitamins, minerals, and trace elements important to human health. Perhaps best known of these is the high content of vitamin C, especially when compared to the complete lack of this vitamin in rice and wheat.[1] Potato is also rich in B vitamins, including thiamin (B1), riboflavin (B2), pyridoxine (B5), and nicotinic acid (B6). Since the B vitamins are water soluble, some of 13 them may be leached out during boiling.[24]

Antioxidant behavior has been well documented for flavonoids, and other related polyphenols. The activity of these compounds is dependent on whether or not a transition metal is available and the number and position of hydroxide substitutions on the heterocyclic rings.[25] Depending on the structure, they are able to act as antioxidants in a wide range of chemical oxidation systems. This activity is due to the ease with which a hydrogen atom from an aromatic hydroxyl group can be donated to a free radical and the ability of an aromatic compound to support an unpaired electron due to delocalization around the π-electron system.[26] From a biological standpoint, this is important because antioxidant compounds can protect cellular systems from the potentially harmful effects of processes that cause excessive oxidation. They can interrupt free radical chain reactions and scavenge free radicals.[27]

Potatoes are rich in antioxidants such as polyphenols (1226 to 4405mg/kg), ascorbic acid (170-990mg/kg), carotenoids (as high as 4mg/kg), and alpha-tocopherol (0.5-2.8mg/kg).[28] Potatoes have been reported to be a rich source of polyphenols like L-tyrosine, chlorogenic acid, caffeic acid, scopolin, and cryptochlorogenic acid. Yamamoto et al.[29] reported the caffeic acid level in potato tubers as high as 0.2 to 3.2mg/kg, with the skin containing double these amounts.[28,29] Other identified polyphenols in potato include neochlorogenic acid (7mg/kg), p-coumaric acid (4mg/kg), sinapic acid (3mg/kg), 3,4-dicaffeoyl-quinic acid, ferulic acid amides, and glycosides of delphinidin, quercetin, and petunidin.[28]

The processing of these tuberous roots in to various products includes cleaning, peeling and spotting. These steps are very critical to the manufacture of high quality products. The peelings are usually discarded. Recently, potato peels have found an alternative usage as a source of dietary fiber in foods such as bread. Potato peel contains many phenolic compounds, some in free form and some bound. The largest portion consists of Cholorogenic acid (CGA), a derivative of caffeic acid (CFA) and Quinic acid (QNA).[30,31] Singh et al.[32] demonstrated that the aqueous extract of potato peel contains a number of antioxidant compounds viz., chlorogenic acid, gallic acid, caffeic acid which can effectively scavenge various reactive oxygen species/free radicals under in vitro conditions and attributed the broad range of antioxidant activity of peel extracts to multiple mechanism.

Ginger Rhizomes

Ginger rhizomes (*Zingiber officinale Roscoe*) are used as spices in tropical areas. Ginger is one of the most widely used herbs and food flavoring agent. Its nutraceutical properties have been interesting in food processing and pharmaceutical industries. The volatile essential oils contributing to the characteristic flavor of ginger, varies from 1.0-3.0%. While the oleoresin, responsible to the pungent flavor of ginger, varies from 4.0-7.5% and ginger also possesses substantial antioxidant activity.[33] Reports say that the rhizome of ginger contains curcumin in addition to a dozen of phenolic compounds known as gingerols and diarylheptanoids. Fresh ginger rhizome contains gingerol but after drying it is converted into zingerone. All these compounds have antioxidant and anti-inflammatory effect and can prevent the growth of cancer.[34,35] Ginger has the strongest antioxidant level among all herbs.[35] Anon[36] suggested that the presence of 12 different Phytochemicals make the ginger one of the most potent food sources of antioxidant. Chan et al.[37] reported that leaves and rhizomes of ginger species have both very good antioxidant and tyrosinase inhibiting properties.

It is reported that natural source of antioxidants viz., beet, mint and ginger showed good antioxidant level[38] after their fortification either alone or in combination in sandesh and the antioxidant level was comparable with the synthetic antioxidant fortified sandesh. Among the natural sources, ginger in combination with mint represented excellent results. Lee et al.[39] showed that antioxidant effectiveness dependent on the kinds of preparation, pH and concentrations. It was further demonstrated that the ginger rhizome contained a potent antioxidant activity against heme-catalyzed lipid oxidation. Considering the food application ginger rhizome extract demonstrated the best protection against lipid oxidation among all treatments in beef patties stored at refrigerated temperature[40,41] and carp fillets at 5°C for 16days.

Preparation of antioxidant extracts

Dry potato peel and ginger rhizome is ground in a mixer grinder and passed through a 60 mesh screen.[40] One hundred gram of ground material is defatted by shaking three times with four volumes of petroleum ether in a rotary shaker. The residue obtained after filtration is dried overnight under a hood until all traces of petroleum ether is removed. The dried residue is extracted three times with four volumes 90% ethanol by shaking and filtered. The combined filtrates is concentrated in a rot vapor and placed under a hood to remove the residual ethanol. The obtained aqueous extract is frozen overnight and freeze dried at -60°C. The obtained freeze dried extract is stored in air-tight container at 5°C and used as natural antioxidant. The activity of the extracted antioxidant[42,43] can be determined by following methods viz., Total polyphenolic content, DPPH radical scavenging activity, Ferrous ion-chelating (FIC) ability and Ferric reducing power (FRP) and so on.

Conclusion

Lipid oxidation rending to rancidity is the most important problem for safeguarding this food during storage and processing. The process of stabilization itself is not well established, and the approach based on the addition of new bioactive compounds (i.e., antioxidants of plant origin) to marine oils is emerging as one of the most promising technologies. Plant extracts having antioxidant, antimicrobial and flavor properties have been proposed for inhibiting rancidity in fish oils and frozen fish muscle.[42] The natural extracts acts as a substitute for synthetic antioxidants and antimicrobial compounds because of its deleterious effects on consumers' health. In addition, the by-products of the horticultural crops such as potato peelings, grape and papaya seeds can be effectively used a promising natural antioxidant and antimicrobial agents on commercial scale and benefit the fish processing industry. However, the optimized use of natural antioxidants in food is still in its infancy and needs a lot of research and development.

Acknowledgements

None.

Conflict of interest

The author declares no conflict of interest.

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