Phenolic antioxidants: The science of food chemistry

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The suspension of ethoxyquin as an antioxidant by the European Food Safety Authority has highlighted the need of having more safe alternatives to protect food against oxidation processes. For example, there are numerous substances of natural origin with a demonstrated antioxidant performance that are well accepted by consumers who perceive them as healthy substances (Food Chemistry 71, 2000, 229).

On the other hand, the combination of synergistic antioxidants, both natural and synthetics, becomes one of OXIRIS objectives. Such combinations are giving us very good results in food preservation, and in some cases allow us to reduce the antioxidant doses. These mixtures can slow down the oxidation process more effectively than the individual components separately.

Antioxidant activity

The food oxidation processes cause the alteration of its components (lipids, proteins, carbohydrates) and are responsible for some adverse effects on the food itself and on the health of the organisms that ingest them. This is the case of rancidity, one of the most obvious consequences of lipid oxidation and, to a large degree, responsible for bad odor and taste developed in food over time.

The oxidative processes can be accelerated or slowed down under certain physicochemical conditions. For example, some pigments such as astaxanthin, also undergo oxidative degradation (Fig. 1) that leads to reduced bioavailability, discoloration and loss of freshness (Global Perspectives on Astaxanthin: From Industrial Production to Food; Ed AP).

In the specific case of lipid degradation, it is also initiated by the action of external agents, such as free radicals, radiation, high temperatures or some metallic ions. These agents contribute to destabilizing and altering the fatty acids from which oils and fats are formed.

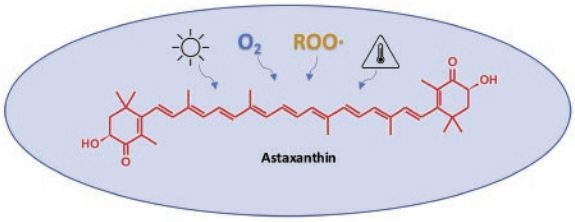

Figure 1. Oxidative degradation factors of astaxanthin.

As a result of this interaction, free radicals are formed which react with molecular oxygen, generating new free radicals and the so-called primary oxidation compounds (hydroperoxides and peroxides). These substances are unstable and decompose, releasing secondary oxidation compounds associated with the unpleasant smell (aldehydes, ketones, alcohols). The oxidative degradation of fish products is especially intense due to the high content of unsaturated fatty acids that are more sensitive to oxidation.

Because the lipid oxidative process is autocatalytic, when it starts it is not possible to stop it or repair its effects. Although it is not possible to avoid the oxidation completely, it is possible to slow it down by deactivating the oxidizing agents present in the medium.

This is the case of the primary antioxidants such as BHT, BHA, propyl gallate, carnosic acid and tocopherol. All of them are polyphenols and capable of deactivating free radicals by giving them a hydrogen atom. As a consequence, radicals are transformed into stable substances and the antioxidant into a less reactive radical that will not promote the oxidative process (Fig. 2).

Other antioxidants present different forms to protect against oxidation such as the chelators which trap metallic ions which may be present in some medium. As a result, the catalysis of the degradation processes of hydroperoxides is prevented and, therefore, the rancidity.

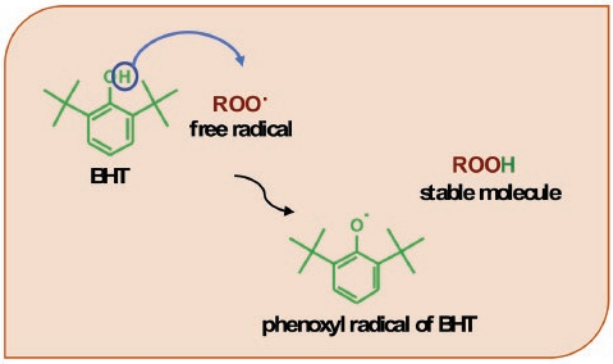

Figure 2. Representation of the inactivating process of a free radical with BHT.

Natural extracts

The botanical extracts are substances obtained from plants (roots, leaves, stems) that contain secondary metabolites with beneficial bioactive properties for organisms. Some of them can be included in the diet as a nutritional additive and/or act on the food as a technological additive.

The tocopherol extract is one of the antioxidants used by Oxiris in the NATUROL product line as it is one of the most important components in nutrition, both for its preservative capacity and its action as Vitamin E in organisms. There are four types of tocopherols in botanical resources, the so-called alpha, beta, delta, and gamma. The delta and gamma isomers (Fig. 3) have the highest antioxidant performance, and for this reason, it is advantageous to use extracts enriched in these components (Food Antioxidants CRC).

The rosemary extract is another natural product, and is present in NATUROL 25RE, which is of great interest to nutritionists due to its antioxidant properties. It contains active ingredients such as carnosic acid, carnosol and rosmanol among others (Cuvelier, Berset & Richard, 1996). The main ingredient in this extract is carnosic acid, a well-known primary antioxidant that inactivates free radicals present in the medium, and due to its high cost, it is normally used in combination with other antioxidants such as tocopherol.

Finally, it is worth highlighting gallic acid, a polyphenol from the family of hydrolyzable tannins, which is found in many foods and has a remarkable antioxidant capacity. Gallic acid is also the precursor of other important preservatives such as propyl gallate used in IONOL Pet Food.

The botanical extracts are excellent allies, for the food sector challenges. To get the most out of these substances it is important to know their origin, composition, antioxidant performance and their stability in different conditions as well as their safety in organisms.

Synergistic effect

It is expected that when ingredient mixtures are added to food, the effects of the ingredients are the sum of the parts. However, sometimes non-additive effects can be observed, such as a synergistic effect, by which the activity of at least one of the ingredients is enhanced, or an antagonistic effect, which results in a worse performance of at least one of the components. These effects have a direct impact on the efficiency of antioxidants.

For instance, the extracts E1 and E4 (Fig. 4) present the same content of carnosic acid, but the performance measured by Rancimat is completely different, possibly due to the effect of other components.

In the specific case of antioxidants, the synergy that is detected in certain combinations, such as BHT-BHA, tocopherol-ascorbic acid, tocopherol-rosemary extract or BHT-citric acid, is a particularity of great interest in the preparation of formulas.

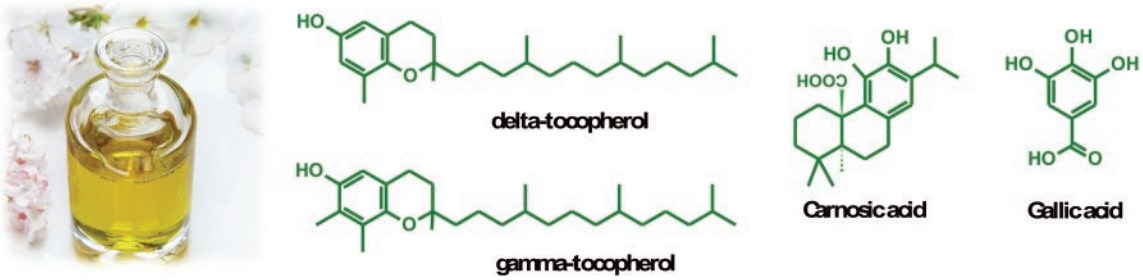

Figure 3. Molecular structure of natural primary phenolic antioxidants: tocopherol, carnosic acid gallic acid.

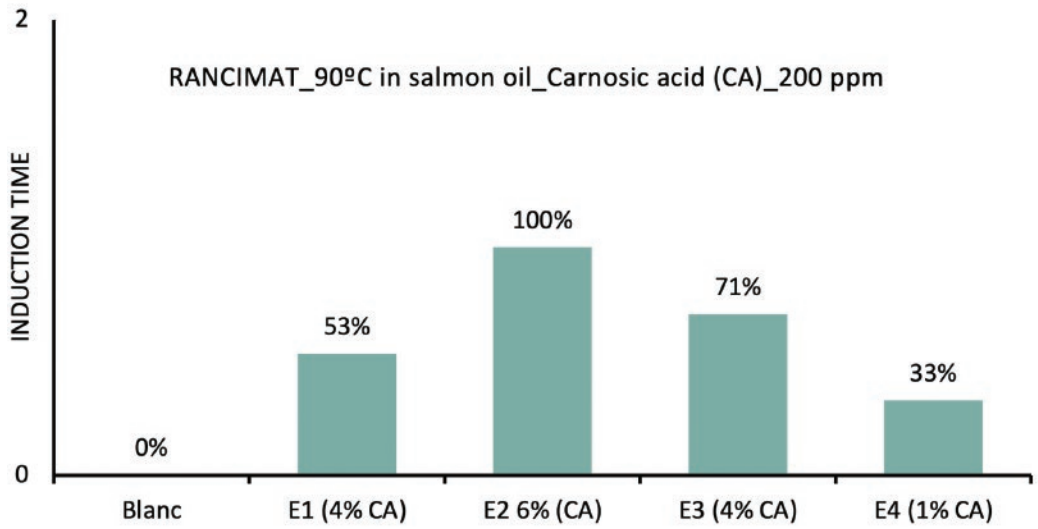

Figure 4. Comparative study of the antioxidant activity (Rancimat) of different rosemary extracts.

The mechanism by which this synergistic effect occurs is different in each mix and is not always easy to determine and quantify. One of the most common is the regeneration of the primary antioxidant by the synergist and the consequent extension of its life span.

For example, carnosic acid, one of the active components of rosemary extract, regenerates the tocopherol used during the process by giving it a hydrogen atom (Fig. 5), allowing tocopherol to be available to inactivate more radicals (Advances in Food and Nutrition Research, 42, Ed AP).

A similar regeneration process appears to occur between BHT and BHA, the main ingredients of the IONOL 175 product line. In this case, the BHT, on supplying a hydrogen atom to the phenoxy radical of BHA, allows the life span of the BHA to be extended.

When BHT/BHA mixtures of different proportions are evaluated, the synergistic effect can be detected because the performance of these mixtures is greater than the sum of the parts of each component. For example, the BHT (11%)/BHA (11%) mixture presents a higher performance as an antioxidant than the sum of their contributions obtained separately (Fig. 6). These experimental results, along with the costs and the client's needs, should be considered to define the composition of the best mixture.

The incorporation of other synergists, such as citric acid, a well-known chelating agent, improves the

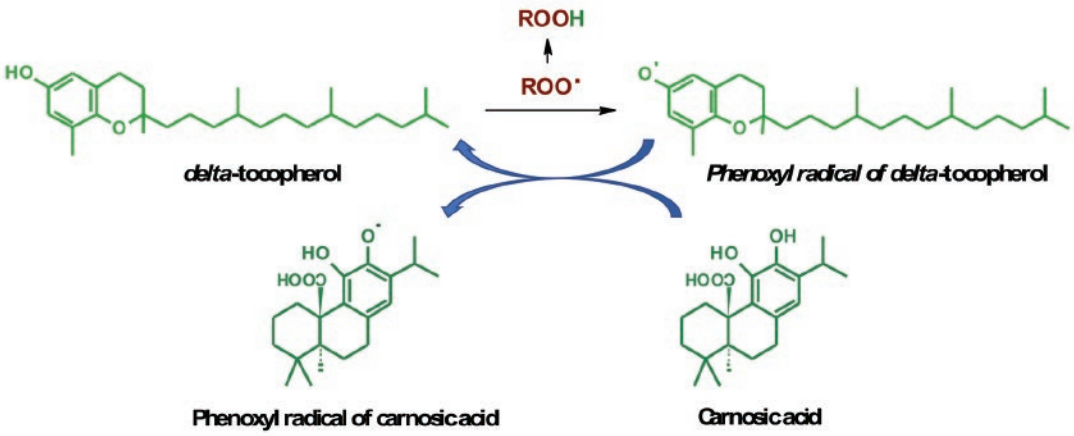

Figure 5. Representation of the regeneration process of tocopherol with carnosic acid.

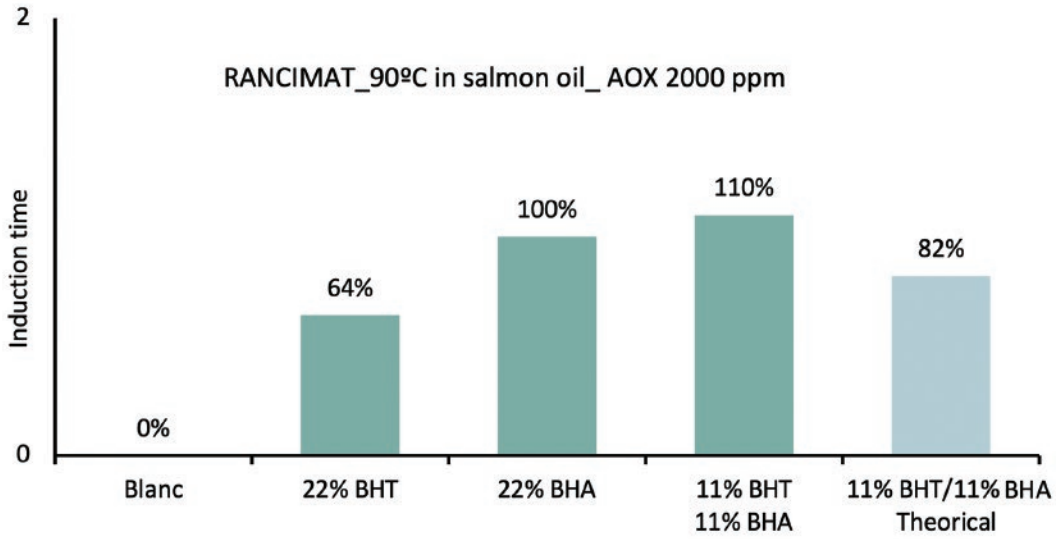

Figure 6. Comparison of the antioxidant activity of BHT/BHA mixtures.

performance of the primary antioxidant without increasing the dose is another example of how to combine antioxidants.

Conclusions

Therefore, a deep knowledge of the mechanism of action of antioxidants allows to Oxiris for, firstly, the selection of the most suitable antioxidants; secondly, the combinations which best meet the needs of the customer in the most efficient way taking advantage of their synergy; and finally, the reduction of adverse health effects by incorporating natural ingredients and improving the performances by adding synergistic substances.

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