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STABILIZATION OF LIPOIDAL SUBSTANCES

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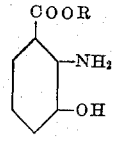
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The invention herein described may be manufactured and used by or for the Government of the United States of America for governmental purposes throughout the world without the payment to us of any royalty thereon.

This invention relates to and has among its objects the provision of novel processes for stabilizing materials which are normally subject to oxidative deterioration. Briefly described, such a result is achieved by incorporating with the material 2-amino-3-hydroxy-benzoic acid or the esters thereof. Other objects and advantages of this invention will be obvious from the description herein.

The compounds which we utilize for their antioxidant properties can be represented by the formula.



wherein R is hydrogen or an alkyl radical, as for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert. butyl, pentyl, hexyl, octyl, decyl, dodecyl, etc.

The following examples demonstrate the invention in greater detail. It is understood that these examples are submitted only by way of illustration and not limitation.

Example I

A solution was prepared containing 0.06% of carotene in mineral oil (liquid petrolatum). This solution was divided into a series of portions and a different benzoic acid derivative was dissolved in each portion at a concentration of one mole of the benzoic acid derivative for each two moles of carotene. The solutions were stored at 75° C. and measurements were made periodically to note the amount of carotene remaining in each portion. The compounds used and the results obtained are summarized in the following table:

STABILITY IMPARTED TO CAROTENE SOLUTIONS IN MINERAL OIL

Compound added	Time for disappearance of 20% of the carotene, hours
none (control)	less than 1.
2-Amino-3-hydroxy-benzoic acid	65.
Methyl ester of 2-amino-3-hydroxy-benzoic acid	70.
n-Propyl ester of 2-amino-3-hydroxy-benzoic acid	72.

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Example II

To samples of edible grade cottonseed oil and prime steam-rendered lard was added n-propyl ester of 2-amino-3-hydroxy-benzoic acid in a concentration of 0.05%. In each case the benzoic acid derivative was thoroughly stirred into the fatty material. These mixtures and samples of the untreated oil and lard (controls) were maintained at 97.7° C. while passing air therethrough at the rate of 2.33 ml./sec., these conditions providing the medium for an accelerated storage test.

The results are summarized in the following table:

Antioxidant	Substrate	Relative antioxidant activity [1]
none (control)	cottonseed oil	7.0
n-Propyl ester of 2-amino-3-hydroxy benzoic acid.	do	10.0
none (control)	lard	9.0
n-Propyl ester of 2-amino-3-hydroxy benzoic acid.	do	18.4

[1] The relative antioxidant activity is expressed as the number of hours required by one kilogram of the substrate to acquire a peroxide content of 100 milliequivalents during aeration at 97.7° C. with an air flow of 2.33 ml./sec.

The benzoic acid derivatives of this invention possess marked antioxidant properties and thus can be used to stabilize various substances which normally tend to undergo autoxidation or rancidification. Thus for example they may be incorporated with fats or oils so that these products may be stored for long periods of time without developing off-flavors or odors. In general, the compounds should be added in a concentration from about 0.001 to about 0.1%, the higher proportions in this range giving, of course, the greater protection from rancidification. In the same way the benzoic acid derivatives may be incorporated in about the same proportion with mayonnaise, salad dressings, canner or frozen meat products, sausages, cheeses, and so forth. All of these types of food products contain fats to a greater or lesser extent, hence are subject to development of off-flavors and odors by reason of rancidification of the fat content. Many other feed and food products contain lipoidal materials and are normally subject to oxidative changes on storage. A prime example in this category is alfalfa which is valued chiefly because of its carotene content. However, the usual dried alfalfa meal of commerce rapidly loses its carotene content. For example, if the meal is stored at 80° F., it will lose about two-thirds of its

carotene content in 24 weeks. Of course, at higher temperatures such as prevail in barns or warehouses in summer, the rate of carotene loss is greatly accelerated. By incorporating the benzoic acid derivatives with the alfalfa the rate of carotene loss will be greatly retarded. For application, the alfalfa meal may be tumbled about in a rotating drum while it is sprayed with a solution of the antioxidant dissolved in a suitable solvent such as ethanol, propanol, butanol, deodorized kerosene, 2 - methoxy - ethanol, 2-ethoxy-ethanol, and so forth. Many other forage, cereal, legume, and oilseed products are prone to rancidification on storage. A notorious example which may be mentioned is rice bran which undergoes very rapid autoxidation. Thus our invention may be utilized by the incorporation of the benzoic acid derivatives, by spraying of solutions thereof or other obvious applicative procedures, with such materials as dried grasses, rice bran, brown rice, wheat bran, wheat germ, soy beans, soybean meal, cottonseed, cotton seed meal, and so forth. If the product is intended to be used as a food, it is advisable to limit the concentration of antioxidant to about from 0.001 to about 0.1%. If the product is intended for feed or inedible purposes then the proportion of antioxidant may be increased to afford greater protection against oxidation and thus may be increased to, say 0.5% or higher, as may be necessary. Another point to be noted is that dehydrated vegetables contain small though significant amounts of fat and, particularly if their moisture content is very low, they will develop off-flavors and odors due to rancidification of their fat content. In the case of vegetables the fat particles are minute and distributed throughout the vegetable tissue and it is necessary that the antioxidant be dispersed throughout the vegetable tissue so that it will be in intimate contact with these fat particles. Such an end may be achieved in several alternative ways, as follows:

The first alternative technique is applicable at any stage prior to dehydration, the important point being that the vegetable material be treated while it is moist. In this technique, the benzoic acid derivative is dissolved in water and sprayed on the vegetable. If desired, the vegetable may be dipped into a solution of the antioxidant, although in general, spraying is preferred as it gives better control of antioxidant concentration. In the normal processing of dehydrated products, it is customary to blanch the vegetables and then subject them to sprays of water for cooling. In addition, the blanched product may be sprayed with an aqueous solution of a sulphiting agent (sulphur dioxide, sodium sulphite, sodium bisulphite, etc.) in order to minimize browning. Either the washing or sulphiting sprays can be utilized for the introduction of the antioxidant by simply dissolving the antioxidant in the liquid used for the spray. Since the antioxidants are poorly soluble in water, it is necessary to employ vigorous agitation and use an essentially saturated solution of the antioxidant. Actually, the concentration of antioxidant in the spray liquid is not critical, since the ultimate aim is to apply sufficient spray so that the vegetable contains from about 0.001 to about 0.1% of the antioxidant (on a dry basis).

In this type of procedure, thorough penetration and dispersion of the antioxidant occurs because the interstices of the tissue are filled with water, these interstices thus providing the channels through which the antioxidant solution can enter the tissue and penetrate into every portion thereof. It is further to be emphasized that at this stage of the processing the vegetable is moist and spraying with the antioxidant solution does not interfere with the orderly progress of the operations. Although we prefer to dissolve the antioxidant in the cooling water or sulphiting solution, it is evident that if desired, the vegetables may be subjected to a spray of water containing the antioxidant just for this purpose and not concerned with cooling, sulphiting, or other operation.

A second method of dispersing the benzoic acid derivatives throughout the tissue of the vegetable involves production of the dehydrated product by the conventional methods. This dehydrated product is placed in a container which also contains a pad of paper, cloth, clay, bentonite, etc., impregnated with the selected antioxidant. The container is then sealed. Upon standing, the antioxidant vaporizes and diffuses into the vegetable tissue. In this case, the penetration of the tissue involves a vapor phase system. Since the product has been dehydrated, the interstices in the tissue are filled with air and these interstices provide the channels by which the antioxidant vapors can penetrate and be distributed throughout the tissue structure. In general, the pad should contain an amount of antioxidant equal to about 0.001 to about 0.1% of the weight of the dehydrated product in the container. Naturally the higher proportions within this range will effect a greater protection against rancidity. A greater proportion of antioxidant than the stated range can be used but may impart a detectable flavor to the food product. The pad containing the antioxidant need not be in actual contact with the foodstuff since diffusion takes place in the vapor phase. Thus it may be convenient to fasten the pad on the lid of the container or enclose it in a foraminous receptacle attached to the lid. In such case when the container is opened for use there will be no danger that the pad will be consumed with the edible material.

A variant of this second technique involves mixing together the dehydrated vegetable with a dry mixture of an antioxidant and an edible powder, this latter acting merely as a diluent. The diluent may be, for example, sugar, starch, or a powdered dehydrated vegetable. For example, dehydrated diced potatoes may be agitated with a mixture of the antioxidant and powdered dehydrated potatoes. The product in any case is placed in a closed container whereupon vaporization and penetration of the antioxidant takes place as explained above. As in the case of the impregnated pad, the amount of antioxidant applied in general should be from about 0.001 to about 0.1% of the weight of the dehydrated vegetable product.

In applying the benzoic acid derivatives of this invention it is often advantageous to use them in conjunction with an antioxidant synergist, that is, a substance which itself has no antioxidant properties but which gives an increased effect when added to the antioxidant. In this category may be mentioned citric acid, phosphoric acid, phospholipids such as cephalin and lecithin, ethylene diamine tetraacetic acid and its salts such as the tetra sodium salt, and so forth. In treating vegetables, the vegetable tissue while moist may be sprayed with an aqueous solution of citric acid or other antioxidant-synergist and then dehydrated. After dehydration the benzoic acid derivative may be applied to the product by

either of the vapor transference methods previously mentioned. This technique has the advantage that the citric acid which is virtually nonvolatile is applied by liquid phase treatment whereas the benzoic acid derivatives which are volatile to a sufficient extent are applied by the vapor phase. The antioxidants of this invention may thus be applied to vegetables of every type as the leafy vegetables such as spinach, cabbage, kale, etc.; the legumes such as beans and peas; the root crops, such as turnips, rutabagas, beets, carrots, potatoes, sweet potatoes, onions, etc.

The compounds of this invention may be prepared by several methods of synthesis. We prefer to use the technique outlined as follows: A 3-alkoxy benzoic acid, such as 3-methoxy benzoic acid, is first nitrated by reaction with concentrated nitric acid or a mixture of conc. nitric and sulphuric acids. The reaction product is then subjected to a purification treatment, as by extraction with hot alcohol, to isolate the desired 2-nitro derivative. The isolated product is then reduced as by treatment with hydrogen in the presence of a hydrogenation catalyst thus to prepare the 2-amino-3-alkoxy benzoic acid. This compound is then dealkylated as by reaction with hydriodic acid and red phosphorus to produce 2-amino-3-hydroxy benzoic acid. The esters of this acid may be prepared by refluxing the appropriate alcohol with the acid in the presence of anhydrous hydrogen chloride. The following examples illustrate preferred modes of synthesis:

Example III

3-methoxybenzoic acid (310 g.) was nitrated in 20-gram portions by mixing each portion with 80 ml. nitric acid (d=1.4) in a 500-ml. Erlenmeyer to about 55°. The temperature was maintained at this point by cooling, since a vigorous exothermic reaction ensued. After the reaction had subsided and after 3 hours' standing, the solid which separated was filtered off, washed, and dried. From 310 g. of methoxy benzoic acid was obtained 270 g. of nitro compounds. This mixture was dissolved in 810 g. of 95% ethanol at the boiling point. The solid which separated was filtered off, and washed with 100 ml. hot ethanol, to remove the unwanted soluble 4-nitro compound from the desired 2-nitro derivative. The total yield of 2-nitro isomer was 57 grams.

The nitro compound was catalytically reduced by hydrogen in the presence of 1 gram of 5% palladium on charcoal, at 27° C. and 40 lbs. per sq. in. hydrogen pressure. The product, 2-amino-3-methoxybenzoic acid, obtained in quantitative yield, was demethylated quantitatively by treating one part with 10 parts hydriodic and 0.2 part red phosphorus.

Example IV

A sample of 2-amino-3-hydroxy-benzoic acid was dissolved in anhydrous n-propanol, the solution was saturated with anhydrous hydrogen chloride, then refluxed for an hour. The product, the n-propyl ester of 2-amino-3-hydroxy benzoic was obtained as the hydrochloride thereof by evaporation of excess n-propanol and hydrogen chloride.

Having thus described our invention, we claim:

1. A process of stabilizing a carotene-containing substance which is normally subject to oxidative deterioration which comprises adding thereto an antioxidant selected from the group consisting of 2-amino-3-hydroxy-benzoic acid and the esters thereof.

2. The process of claim 1 wherein the antioxidant is 2-amino-3-hydroxy benzoic acid.

3. The process of claim 1 wherein the antioxidant is an alkyl ester of 2-amino-3-hydroxy-benzoic acid.

4. A composition of matter stabilized against oxidative deterioration and comprising a carotene-containing substance which is normally subject to oxidative deterioration and an antioxidant selected from the group consisting of 2-amino-3-hydroxy benzoic acid and the esters thereof.

5. The composition of matter of claim 4 wherein the antioxidant is 2-amino-3-hydroxy benzoic acid.

6. The composition of matter of claim 4 wherein the antioxidant is an alkyl ester of 2-amino-3-hydroxy benzoic acid.

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