DEHYDRATED FOODS

Chemical Aspects of Dried Fruits

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Most of our knowledge of dried fruits is based on food technology rather than chemistry or any of the basic sciences, although the objectives of research on dried fruits would be furthered by a more complete knowledge of the chemistry involved. Recent work has dealt largely with improving the acceptability, stability, and utilization of dried fruit. Acceptability has been improved by raising moisture contents to higher levels, utilizing new packaging materials, pasteurization, and chemical sterilization, selecting the optimum maturity of fresh fruit before drying, and improving control of drying conditions and use of sulfur dioxide. The nature of the browning reaction in dried fruits and the role of enzymes and storage temperature have been evaluated. Dried fruits, like many other established food products, must be presented to the customer in new forms to compete successfully for the consumer dollar.

THE DRYING OF FRUIT is one of the oldest methods of food preservation known to man. The methods used for drying have been greatly modified in recent years for some fruits, but, for others, have not been appreciably changed since ancient times. Marked changes in color, flavor, and texture are characteristic of many dried fruits, compared with the fresh fruits from which they are derived. Outstanding examples of dried fruits which bear little resemblance to the original fresh fruit are raisins (from unpigmented grapes), and prunes (from plums).

No significant differences in carbohydrates, protein, fiber, and ash are noted when the variation in moisture content is taken into consideration. The differences between fresh and dried fruits lie with the minor constituents.

The changes that take place during drying are principally chemical, particularly if enzymatically induced reactions are included as chemical changes. None of the changes normally taking place during fruit drying is due to the activity of microorganisms, although, when drying conditions are unsatisfactory or unsound fresh fruit is dried, microbial activity sometimes takes place, resulting in unmarketable culls.

Changes during processing or preparation for market are relatively minor chemically and are due principally to heating, partial cooking, and adjustment of moisture content to the most desirable range. The final moisture content is determined by keeping qualities, palatability, and custom.

Often very marked chemical changes take place on prolonged storage. Except when stored at temperatures near 0° C., dried fruits are subject to considerable deterioration, due almost entirely to nonenzymatic chemical reactions.

Dried fruits vary in their gross composition and in their tendency to undergo various chemical reactions. About ten kinds of fruit are dried in significant quantities to be of commercial importance. The methods used in drying vary considerably and, to a large extent, determine the type of reactions taking place.

Maturity of Fruit

The maturity of the fruit at the time of harvest determines the types of reactions that take place during drying. Consequently, the fruits fall into three classes: (1) fruit picked green and cured before drying, (2) fruit dried immediately after harvesting, and (3) fruit partially dried before harvesting.

Pears and apples are picked green for marketing fresh, and the unmarketable portion is dried, after fruit is allowed to ripen and cure for some time. This curing helps in making a more uniform dried product. The drying of these fruits is primarily a by-product business. Kadota figs and clingstone peaches are ordinarily picked for canning only the surplus being dried.

Grapes, prunes, apricots, and freestone peaches are picked at optimum maturity and are promptly dried. Unfortunately, no lot of fruit can be picked so that all pieces are at the same stage of maturity, but salable dried fruit must have a fairly uniform appearance. The methods for drying fruits in this group have been worked out so that the variations in maturity of the fresh fruit are hardly detectable in the dried product. A number of chemical reactions are involved in processes used to produce uniform color.

Figs and dates are the best examples of fruits that are partially dried before harvesting. Figs could be picked fresh, as is the case with most of the Kadota figs, but the product is different from the other dried figs of commerce. Dates, on the other hand, are not ripe until partially dried on the tree. The process of ripening in dates is combined with all the phenomena of fruit drying, such as cell breakdown, evaporation of moisture, and permeation of tissues with a sugar sirup. Even the crystallization of sugars sometimes takes place in dates before the fruit is ready for harvest. Prunes, also, are sometimes allowed to pass the stage of optimum maturity before harvesting. Where partial tree drying takes place, the color of the product is darker but more uniform than when the fruit is harvested before drying begins.

Weather conditions during this tree-ripening period greatly affect the rate of drying and definitely limit the areas in which these fruits can be grown. Enzymatic darkening and other oxidative changes take place, with the result that the final product is very different from the fresh fruit.

Color Changes

Color changes have had the greatest influence in determining the drying procedures for each fruit.

The green color of chlorophyll is seldom present in dried fruits, and it must not be present if the fruit is to be marketable. In living tissue, chlorophyll is in equilibrium with its precursors and end products. Normally, when tissues die, brown colored compounds are formed. This is evident in fruit that is dried on the tree. In apples, the green color is avoided by curing before drying and by peeling. In sun-dried raisins, the action of sunlight in producing the characteristic dark brown color obscures or destroys the green color. In sulfured fruits, the sulfur dioxide and sunlight bleach chlorophyll and some of the other pigments. In dehydrated fruits, the chlorophyll or its brown decomposition products are masked by other fruit colors, or in sulfured dehydrated fruits, such as Kadota figs, chlorophyll is bleached by exposure to the sun for a short time before dehydrating.

The anthocyanin pigments present in fruits are generally altered to various degrees, both during and after drying. Some anthocyanin pigments, particularly those appearing as a bloom on apricots and peaches, are bleached by the sulfur dioxide treatment. Others, normally present as leuco bases in the fresh fruit, turn red on prolonged exposure to the sun. These are considered undesirable in the finished product. It is common practice to dry fruits that are subject to this red coloration by exposure to the sun for a day or two, and finish drying in stacks or in a dehydrator.

Anthocyanin pigments on unsulfured fruits generally turn brown through oxidation during drying. The purple color in the skin of prunes is largely destroyed during drying, either in the sun or in dehydrators. The purple pigment of the Black Mission fig is exceptionally resistant to change. Although these figs are tree-dried, the color is hardly affected and is very prominent in the final product. For certain purposes, it would be desirable to bleach out this color. It is apparently completely resistant to the action of sulfur dioxide, and can be bleached only with hydrogen peroxide or chlorine.

Enzymatic browning by peroxidase and other oxidative enzymes occurs in fruit drying unless measures are taken to prevent it. This reaction proceeds most rapidly on freshly cut surfaces of fruit. Commercially, all fruits that are cut or sliced preparatory to drying are treated with sulfur dioxide after cutting and before drying starts. Sliced apples are dipped in dilute sulfur dioxide solutions and most other cut fruits are exposed to the fumes of burning sulfur for several hours. This effectively prevents enzymatic darkening, partly through the reducing action of this chemical and partly because the enzymes are inactivated.

Blanching with steam or hot water also inactivates enzymes, but this is not general commercial practice. Blanching frequently results in excessive tissue breakdown and is not effective in preventing other oxidative reactions during drying.

Another case of intense enzymatic activity takes place in the preparation of sun-dried raisins. The grapes are exposed to the direct rays of the sun immediately after picking without any intermediate treatment. The green grapes turn a reddish brown, while the riper ones turn a darker brown. The final result is a fairly uniform appearing product. Drying in the shade or in a dehydrator will not produce this uniform product, nor will it develop the characteristic raisin flavor.

Nonenzymatic Browning

Changes continue to take place after the dried fruit has been packed. All dried fruits turn brown with age. Under normal marketing conditions, where the crop can be readily and promptly disposed of, no serious problem exists. For military use, where long storage periods are necessary, particularly at elevated temperatures, the darkening problem is very serious. During the past 10 years, this browning of dried fruits has been intensively studied by a number of investigators. Its exact chemical nature has not been determined, nor has a satisfactory way been found to prevent it. However, the relationships of oxygen, sulfur dioxide content, storage temperature, and moisture content to the rate of browning have been determined for some dried fruits. Dried apricots darken most readily and have been studied more than the other fruits. Much of this work on apricots was done by Stadtman (*4*).

1. Fruit stored in the presence of oxygen darkens faster than in the absence of oxygen.
2. Oxygen absorption is greater for fruit at the higher moisture levels.
3. The darkening rate is greater for lower moisture (10%) than for the higher moisture levels. This indicates that oxygen absorption has less effect on darkening than the inhibiting effect of moisture in preventing the interaction of various fruit constituents.
4. The darkening rate is directly proportional to the storage temperature. The rate doubles for approximately 5° C. increases in storage temperature.
5. The darkening rate is inversely proportional to the sulfur dioxide concentration between 1000 and 8000 p.p.m.

The formation of furfuraldehydes appears to play an important role in dried fruit darkening. Darkening was almost completely checked in apricot concentrates by continuous extraction with ethyl acetate at temperatures that would otherwise cause rapid darkening. The ethyl acetate extracts contained furfuraldehydes and possibly other unsaturated aldehydes. The brown pigment is a humanlike substance, and is probably the result of several reactions in which sugars, organic acids, and nitrogenous compounds are the principal reactants. Furfuraldehydes have been detected by their absorption spectra in all dried fruits which have started to darken or have been subjected to conditions that tend to cause darkening. Therefore, it might be assumed that the furfuraldehydes are formed from the breakdown of sugars and that they act as catalysts for the formation of other brown compounds from sugars, organic acids, and nitrogenous compounds.

Sulfur Dioxide The action of sulfur dioxide in retarding darkening seems to substantiate this theory with respect to dried fruits.

Sulfur dioxide, because of its reducing action and its enzyme-inhibiting properties, prevents enzymatic and other oxidizing reactions from taking place during the drying of fruit.

It also forms addition compounds with the aldehydes present in dried fruits. After the fruit has dried, the sulfur dioxide is almost completely in the form of the glucose addition compound. This possibly tends to prevent the breakdown of sugars to furfuraldehyde and probably also inhibits the catalytic action of the furfuraldehydes in browning by the formation of furfuraldehyde-sulfite addition compounds. All evidence points to the fact that sulfur dioxide retards the formation of the dark pigments but neither prevents their formation nor bleaches them after they have been formed.

Flavor Changes

Flavor changes in dried fruits generally closely follow color changes—fruits that undergo marked color changes during drying also show marked flavor changes. The tree-dried fruits undergo the greatest flavor changes and the sulfured fruits the least change.

Many of the flavor changes that occur during the drying of fruits are considered desirable; others are highly undesirable. Very little is known chemically about these flavor changes. O'Neal (*3*), comparing volatile reducing substances in fresh and dried prunes, found that glyoxal and acetaldehyde were present in fresh prunes at optimum maturity, but could not be detected after drying. The dried prunes, however, contained crotonaldehyde, which was not present in the fresh prunes. This formation of an unsaturated aldehyde is similar to the formation of furfuraldehydes in the first stages of deteriorative browning.

Another flavor change that sometimes occurs in dried fruit soon after drying is the development of the undesirable tobaccolike or geraniumlike off-flavor. This has been demonstrated to be caused by enzymes. Chari *et al.* (*1*) dehydrated prunes to various moisture contents, sterilized them with epoxides, and noted the development of this off-odor, particularly in fruit of higher moisture contents. To prove further that enzymes were responsible, they demonstrated that by blanching sufficiently to inactivate peroxidase and phenolase, this off-flavor formation was prevented. Normally, prunes are stored at low moisture contents before processing. This prevents the off-flavor formation. The processing prior to packing is a sufficient heat treatment to inactivate the enzymes, so that this off-flavor does not develop in packed prunes, even though the moisture content may be high.

Additional undesirable flavor changes occur in dried fruits in conjunction with the browning on storage; they are most pronounced in the latter stages of darkening as the products become inedible.

The change in texture that takes place in the drying of fruit can hardly be construed as a chemical change, but the processing methods used to attain the desired texture result in certain chemical changes. Most fresh fruits contain considerable air in the intercellular tissues, and to attain desirable translucency, this air must be substantially removed. Sulfuring, followed by sun drying, achieves this successfully for pears, apricots, and peaches. This translucency can also be attained by blanching before sulfuring and drying. Economically, the production has not proved feasible as yet.

Dried figs are given their translucent appearance by subjecting them to a high temperature in retorts for a short period of time. This makes the skins tender, but results in some caramelization, and somewhat changes the flavor.

Pears are sometimes dried like apples in the form of rings or slices, but the product has a tough and undesirable texture. The usual product is sulfured for prolonged periods and is then sun-dried to obtain the almost glassy appearance typical of the commercial product.

Another texture factor that has an important relationship to chemical changes is moisture content. The lower the moisture content, the tougher the texture. Conversely, up to a certain point, the higher the moisture content, the more appetizing and edible the fruit is. Unfortunately, there is a critical moisture content for each dried fruit, above which it is subject to spoilage by microorganisms. This critical moisture content, for some fruits, is below the desirable edibility point. Within certain limits, dried fruit is less subject to storage browning at higher moisture levels.

Enzymatic browning, like microbial spoilage, is also more likely to occur at the higher moisture levels. Consequently, considerable attention has been directed toward the successful processing of dried fruits at higher moisture levels.

Sulfured dried fruits are fairly resistant to microbial spoilage because of the preservative action of sulfur dioxide. Although sulfur dioxide prevents or retards practically all undesirable changes in dried fruits, it is not accepted for use in all dried fruit products.

Moisture content is not readily controlled to precise levels in sun drying or in the dehydrator because of the variations in drying rate of individual pieces. Consequently, fruit is ordinarily dried to a low, safe level below that intended for marketing, and prior to packaging, the moisture level is brought up to the desired level. Prunes, figs, and dates are unsulfured fruits and, until recently, have been packed below 23% moisture. At this point they do not ferment or mold, but have too tough a texture to be directly consumed. The development of the technique of epoxide sterilization, by Mrak *et al.* (*5*), has made it possible to pack these fruits at moisture levels up to 30% or more, greatly improving their texture and acceptability. The epoxides used are ethylene and propylene oxide, added to the fruit at the time of packaging. These epoxides are volatile and are hydrolyzed to the corresponding glycols within a few days after application. Consequently, the treatment is a sterilization rather than a preservative treatment. No detectable changes have been noted in the treated fruit.

Raisins are packed at about 18% moisture, at which point they are fairly soft and can be directly consumed. This 18% is well below the point at which microbial spoilage could occur. Recent investigations by Mrak (*2*) have demonstrated that raisins are more palatable when they contain approximately 30% moisture. It is not easy to attain this moisture level without altering the texture and flavor, but it has been accomplished by exposing the berries to high humidity at temperatures below 165° F. At higher temperatures, a cooked or caramelized flavor is produced. This product shows promise, but the problems of commercial production and the prevention of excessive stickiness are still to be solved. Chemical sterilization by means of expoxides can be used on these high-moisture raisins to prevent microbial spoilage.

Another physical property that has caused trouble on dried fruits is the tendency of the sugars to crystallize on long storage as dextrose crystals, either as a fine powdery surface deposit, or as large granular internal crystals. The powdery surface sugaring frequently looks like mold growth and has often been mistaken for it. This sugaring can be successfully prevented at the time of packing by heating the dried fruit after packaging to 130° F. and then cooling. This dissolves all the crystalline dextrose present on the fruit and the package protects the fruit from seeding by air-borne particles of dextrose. By this treatment, sugaring can be prevented for a year or more; without it, some dried fruits may sugar within a week or two.

Much of the recent research on the browning reaction and deterioration problems has been instigated and sponsored by the Army in the hope of producing less perishable products. Industrial research is directed more to the production of new products that are palatable and acceptable to the consumer. The chemical nature of reactions peculiar to dried fruits has not been studied intensively as yet. However, more is known on how to avoid undesired changes than is being applied commercially. More improvements have been made in the preparation of dried fruits in the past 25 years than during all the previous centuries.

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Received for review April 7, 1953. Accepted May 20, 1953. Presented before the Division of Agricultural and Food Chemistry, Symposium on Dehydrated Foods, at the 123rd Meeting of the American Chemical Society, *Los Angeles, Calif.*