THE DISCOLORATION OF CANNED CRANBERRIES

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INTRODUCTION

Cranberry sauce preserved in tin cans sometimes becomes much discolored so that when the cans are opened the natural red color is found to have changed to a dirty brown, or black, which makes the sauce unappetizing in appearance. The causes of this discoloration have been under investigation at this experiment station.

A possible chemical cause of the change in color is the action of soluble aluminum, iron, or tin on the coloring matter of the cranberries, since compounds of these metals have long been used by dyers to modify their colors. In canning cranberries, the fruit is cooked in aluminum kettles and preserved in tin cans which are made of thin sheet iron coated with tin. The cans employed in the commercial preserving of cranberries are enameled; that is, the sheets of tin are coated with lacquer before cutting and bending them into cans.

PRELIMINARY EXPERIMENTS

Preliminary experiments with some cranberry sauce that had been prepared in glass were made by spreading the sauce in a glass dish and adding to the surface of the sauce a variety of soluble compounds of aluminum and of iron.

Aluminum compounds produced no perceptible color changes. Ferric chloride, ferric ammonium sulphate, and ferric ammonium citrate, when added to the sauce either in crystals or in drops, quickly darkened the red sauce in a widening area about the spots of application.

The best sauce obtained from tin cans showed a faint brown streak down the side where it was in contact with the seam of the can and also around the top. It was easy to observe the appearance of the sauce because it could usually be removed from the can as a cylinder of firm jelly. The most reasonable explanation of this discoloration appeared to be that in bending and cutting the sheet of tin, the lacquer and the tin coatings were slightly broken, thus exposing sufficient iron to the sauce to change its color.

Tannin had been noted as present in the cranberry in another investigation. The skins of the berries had been extracted with ordinary ether, which contained a little alcohol and water. The extract consisted of wax and resin, but darkened upon application of iron salts. When this reaction occurred, the extract was washed with hot water. The washings turned green on the addition of ferric

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chloride and ferric acetate but did not indicate sufficient tannin present to produce the discoloration observed in the canned fruit. It was considered advisable to isolate the pigment of the cranberry and to study its behavior toward the soluble compounds of aluminum, tin, and iron. Willstaetter and his students have studied the pigments occurring in many of the flowers and fruits, and their published papers have been compiled by Perkin and Everest. Among the pigments described was the one occurring in the European cranberry, Vaccinium vitis idaea. Willstaetter's method was followed in most of its details in extracting and purifying the pigment contained in our American cranberry, Vaccinium macrocarpum.

The coloring matter of the cranberry is confined almost wholly to the skin of the fruit, but when the skin is crushed or cooked some of the pigment diffuses throughout the pulp, coloring the mass.

**EXPERIMENTAL PROCEDURE**

Following Willstaetter's procedure, the cranberries were crushed and pressed to remove as much juice and pulp as possible. The moist residue, consisting mainly of skins, was placed in large glass flasks, and enough glacial acetic acid was added to cover the mass. The flasks were allowed to stand about one week, and their contents then filtered through glass wool. Owing to the presence of gelatinous matter it was almost impossible to filter the extract through paper or linen.

The residues were extracted a second and third time in a similar manner. The amount of pigment in the third extraction was slight, although the skins remained red in color. A further extraction with alcohol also failed to remove more than enough to color the solution.

The acid extract, which was brilliant red in color, was poured into two and one-half times its volume of ether, shaken repeatedly, and allowed to stand 24 to 48 hours. The pigment settled as a heavy, oily liquid from the first extraction but as a sticky, waxy mass from the third. The acid-ether liquid was slightly colored and was decanted carefully from the pigment. The ether and acetic acid were recovered by distillation and used for further extractions.

The pigment was purified after the method followed with the European cranberry, picric acid being employed first and finally hydrochloric acid to form crystalline compounds. The final crystals obtained with alcoholic hydrochloric acid were scalelike, lustrous, dark red, and almost black in some lights.

The crystals were readily soluble in methyl and ethyl alcohols but, unlike the pigment described by Willstaetter, they were only slightly soluble in water. It was also noticed that no successive crop of crystals from alcoholic solutions would redissolve completely in a fresh lot of alcohol, but would leave a slight precipitate, black in color and insoluble in methyl or ethyl alcohol, water, and acetic or hydrochloric acids. After the insoluble residue had been moistened with concentrated hydrochloric acid and ethyl alcohol had been added, a slight solubility colored the alcohol.

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Willstaetter obtained 1.6 gms. idaein chloride from 10.7 kgm. of cranberry skins, which would be equivalent to 40 kgm. of berries, calculated from other data given by him.

The writer used one-half barrel of Early Black cranberries, a highly colored American variety. Rejecting unsound fruit, approximately 22 kgm. of berries were used. The resultant masses of crystalline chloride of the pigment, when collected together, amounted to 2.1 gm. A half barrel of MacFarlin cranberries yielded much less in volume of crystals, but no weight records were taken. Early Black cranberries produce a much darker cooked product than other common varieties, due undoubtedly to the larger content of coloring matter in the berries.

A solution of 13 mg. of the hydrochloride dissolved in 15 c. c. of water and 3 drops of concentrated HCl, was prepared and used in the following tests. To 3 c. c. of color solution was added 3 c. c. of standard iron solution containing 0.3 mg. Fe. After several hours the color had become pale and a fine, granular, dark precipitate was noted. Minute crystals of ferric ammonium sulphate were added to 2 c. c. of the color solution, which was quickly decolorized with the formation of a fine, granular, dark precipitate. To a third portion of the color solution a small scale of ferric ammonium citrate was added, which slowly decolorized the solution with the formation of the dark precipitate. Aluminum salts showed no noticeable effects.

A methyl alcohol solution of the hydrochloride crystals was prepared, sufficient pigment being used to give a brilliant, clear, red color. Portions of about 3 c. c. each were used for tests with the different salts. Aluminum nitrate and ammonium aluminum sulphate caused little, if any, change in the solution. Stannous chloride produced a purplish tint. The iron salts darkened the solution and formed dark precipitates.

The contents of one can of cranberry sauce was much darkened, black particles were observed in the syrup, and the red color was nearly faded out. Several scratches which showed in the lacquer in the interior of the can appeared to be corroded. A weighed quantity of the darkened sauce (50 gm.) was dried and ashed. For comparison an equal amount of Early Black variety cranberry sauce, cooked and preserved in glass, was also ashed. The comparison of these two lots was made colorimetrically. By ordinary analytical methods cranberries normally contain no more than a trace of iron. The discolored product from the corroded can contained between six and seven times as much iron as the sauce from glass.

Some fresh acetic acid extract of the cranberry pigment was prepared from freshly crushed fruit. The pigment was precipitated by ether and redissolved in a little acetic acid. This acid solution was diluted with water to a clear, transparent, red tint and divided into two portions. To one portion a small coil of iron piano wire was added and to the other a small fragment of aluminum foil. The vessels containing these two portions, covered from dust, were allowed to stand for observation.

The solution with the aluminum foil was unaffected throughout the observation, which continued for two weeks.
The solution containing the iron wire began in the course of hours to produce a precipitate which steadily increased in amount, while the tint became progressively paler.

At the end of 72 hours the precipitate was collected by filtering through two filters of ash-free paper 4 1/2 cm. in diameter. The filters were repeatedly washed with hot water and were finally separated and dried. The inner filter contained all the precipitate. Each paper was incinerated in a clean porcelain crucible. The paper with the precipitate yielded an ash stained with iron, which on solution gave a bright color reaction for that metal. The other filter gave but a trace of ash and a very faint color reaction for iron. The evidence was positive that the precipitate contained iron and that the filter did not adsorb the iron from the solution.

SUMMARY

The discoloration of canned cranberry sauce is due to the formation of soluble iron from the inner surface of the can and to the reaction of the iron with the coloring matter and, to a less extent, with the tannin in the fruit.