COLOR CHANGES IN OLIVE OIL

By C. K. McWilliams

It is generally believed that the color of olive oil, which varies from yellow to green, depends principally on the characteristics of the olive and the method of production. It may not, however, be so well known that the color of the refined oil can change, depending on the composition of the oil and method of packing.

Recently this laboratory was called upon to investigate a rather unusual color change experienced by a local canner who had packed California olive oil in tin cans. At the time of packing, it was of a golden yellow color, but on opening some months later was found to have changed to a bright green. While this investigation was made primarily from a practical viewpoint of overcoming the objectionable color change, without any attempt to study the chemistry of the coloring matters involved, nevertheless, certain features of a technical nature were brought out that should prove of interest from a scientific as well as a practical standpoint.

The color of commercial olive oils appearing on the market varies from yellow through greenish yellow to green and is sometimes almost colorless. As is well known, the natural or original color of the oil at the time of production depends on a number of factors, such as the variety of olive, climatic and soil conditions under which it is grown, ripeness of the fruit, method of pressing and refining, etc. Generally the fruit is gathered just before the period of maturity which produces an oil of superior quality to that expressed from the ripe or over-ripe fruit.

In the commercial production of olive oil, the olive is generally given two or three pressings, the first pressing producing the best edible grades. After the first pressing the pulp is taken out of the press, mixed with hot water and pressed once or twice more. The oils obtained by the second or third pressing are inferior in flavor and greener in color than that of the first pressing and are generally used for lubricating or soap-making purposes. The remaining pulp, which still contains considerable amounts of oil, is sometimes treated with various solvents, by which is extracted an inferior oil usually of a bright green color due to extracted chlorophyl.

In European countries the finest qualities of olive oil are said to be produced from hand-picked fruit selected with special reference to its state of ripeness and pressed without breaking the kernels. Sometimes the olives are peeled and seeded before pressing, and this produces a particularly fine oil free from the coloring and flavoring matters associated with the skin and seeds.

In California, three pressings are usually made. The color of the oil from the first pressing varies from green to yellow, depending principally on the ripeness of the fruit, the color of each successive pressing being

greener than the one before. The oil so obtained, either by pressing or extraction, is usually turbid and is refined by washing and filtering.

While all these methods of treatment, as well as the selection of the olive and its variety, affect the original color of the oil, they are not the only influencing factors. That the color of the oil may change after production, depending on the composition and conditions of packing, will be shown later.

Although this investigation was concerned primarily with the color change occurring in the California olive oil referred to above (herein designated as Brand "A"), a large number of olive oils of both foreign and domestic origin were examined for comparative purposes.

Experiments

Table No. 1 shows the examination of the California olive oil (marked "Brand A") that turned green.

TABLE 1

BRAND "A" CALIFORNIA OLIVE OIL

Sample Can No.	Color	Odor and taste	Free fatty acids (as oleic) %
	In Cans		
1	Very light green	Normal	0.22
2	Very light green	Normal	.25
3	Light green	Normal	.33
4	Light green	Normal	.43
5	Dark green	Normal	.80
6	Dark green	Normal	.98
7	Very dark green	Normal	1.10
8	Very dark green	Normal	1.22
	In Bottles		
Bottle No.			
1	Deep yellow	Normal	0.23
2	Deep yellow	Normal	.33
3	Deep yellow	Normal	.82
4	Deep yellow	Normal	1.20

Eight cans and four bottles were examined. The color of the oil in the cans varied from light to dark green, while that in the bottles was deep yellow, although the canned and bottled oil belonged to the same lot and both were yellow when packed. The odor and taste of both the canned and bottled samples were normal and no difference could be detected in this respect. There was, however, considerable difference in the free fatty acids, and it is to be noted that the depth of the green color increased directly with the fatty acid content, indicating that the formation of green color was in some way connected with the acidity.

This green oil from the tins was transferred to bottles, stoppered and allowed to stand on the table for several months, during which time the

green color gradually reverted to yellow. This color change was evidently a reversal of the other brought about by diffused sunlight. It was later found that direct sunlight caused this reversal of color to take place much more rapidly.

In order to determine what agencies had brought about the formation of green color, yellow California olive oil was treated with the different substances that might have come in contact with it while in the tin. Table 2 shows the results of these experiments.

TABLE 2

AGENCIES CAUSING COLOR CHANGE

Substances added to yellow olive oil	Color of oil after standing 10 months at room temperature	Color of oil after heating one hour at 100°C.
Flux for end seams	Yellow (no change)	Yellow (no change)
Flux for side seams	Yellow (no change)	Yellow (no change)
Glucose	Yellow (no change)	Yellow (no change)
Glycerine	Yellow (no change)	Yellow (no change)
Gelatine	Yellow (no change)	Yellow (no change)
Zinc chloride	Yellow (no change)	Yellow (no change)
Stannous chloride	Yellow (no change)	Yellow (no change)
Stannic chloride	Yellow (no change)	Yellow (no change)
Ammonium chloride	Yellow (no change)	Yellow (no change)
Hydrochloric acid	Yellow (no change)	Yellow (no change)
Ferrous chloride	Yellow (no change)	Yellow (no change)
Ferric chloride	Yellow (no change)	Yellow (no change)
Tin plate	Changed to green	Changed to green
Metallic tin (C.P.)	Changed to green	Changed to green
Metallic iron (C.P.)	Changed to green	Changed to green

For these tests, "Brand A" California olive oil from bottle No. 3 was selected because it had an average acid content. Small amounts of this oil, placed in bottles, were treated with the two fluxes used in sealing the cans, as well as separately with the ingredients composing these fluxes. Iron and tin chlorides were also tried, as these substances might be formed by action of hydrochloric acid of the flux on the metal. Tinplate itself and the two metals, iron and tin which compose tinplate, were also placed in the yellow oil. Two series of these tests were made, one of which was allowed to stand at room temperature for 10 months and the other heated for one hour at 100°C. Fortunately, those standing for 10 months were put away in a closet and protected from light as it was later found that absence of light is necessary for the formation of green color at ordinary temperatures. It is to be noted that no change occurred with either flux or with any of the substances contained in the fluxes, but only with the tinplate or chemically pure metals composing the plate. These experiments indicate that the formation of green color has been brought about by the combined action of the free fatty acids and metal of the tinplate,

presumably a reaction of the free fatty acids on the metal whereby the yellow color of the oil is reduced to green.

In order to demonstrate the effect of the acid concentration of the oil on the color change, oils of various known acidity were next treated with tinplate. For this purpose "Brand A" California olive oil from bottle No. 3 was again used. This oil was refined by the usual alkali treatment for removing free fatty acids from vegetable oils. The residual acidity of the refined oil was 0.02% oleic acid and the oil was of a deep yellow color. A portion of this refined oil was also bleached with charcoal and fuller's earth in the usual manner, by which the color was reduced to a very light yellow. The acidity was not altered by bleaching. To these two neutral oils (yellow and bleached) were added known amounts of pure fatty acids prepared from the bleached olive oil, giving a series of oils of known acidities, ranging from 0.02% up to 2%. These oils were then placed in contact with tinplate and allowed to stand at room temperature for 10 months. The results of these tests are shown in Table 3.

TABLE 3

EFFECT OF FREE FATTY ACIDS AND TINPLATE ON YELLOW OLIVE OIL

Acidity of oil (as oleic acid) %	Color change in oil originally deep yellow	Color change in oil originally light yellow
0.02	Deep yellow (no change)	Light yellow (no change)
0.10	Changed to very light green	Changed to greenish yellow
0.25	Changed to light green	Changed to greenish yellow
0.50	Changed to green	Changed to greenish yellow
1.00	Changed to dark green	Changed to greenish yellow
2.00	Changed to very dark green	Changed to greenish yellow

As indicated in the table, no change in color took place with the practically neutral oil (0.02% acidity) while the remaining oils containing free fatty acids changed to green and the depth of this green color increased directly with the acid content. In the case of the bleached oil, however, only a very slight greenish yellow developed, due to the fact that the original yellow color of the oil had been removed by bleaching. From these experiments, it is very evident that the formation of green color depends on two factors: (1) free fatty acids, (2) depth of original yellow color of the oil.

In contact with metal the fatty acids presumably react with the former, reducing the yellow color to green. If, however, the original yellow coloring matter is not present, or only present in small amount, little or no formation of green color can take place.

For the purpose of confirming these findings and to ascertain whether these color changes were peculiar to California olive oil or common to olive oils in general, a considerable number of other brands of California, as well as foreign, olive oils were examined. These olive oils include

French and Italian products packed in both cans and bottles. In all cases the same brand of oil in both bottles and cans were examined, if obtainable. Table 4 shows the results of examination of several varieties of domestic and foreign oils packed in bottles.

TABLE 4

COLOR AND COLOR CHANGES OF VARIOUS BRANDS OF BOTTLED OLIVE OIL

Brand	Source	Free fatty acids as oleic acid %	Original color as recd.	Color after contact with tinplate			
				Heated at 212°F. in light	Heated at 212°F. in dark	Standing cold in light	Standing cold in dark
A	Calif.	0.33	Deep yellow	Light green	Light green	Deep yellow	Light green
A	Calif.	.80	Deep yellow	Dark green	Dark green	Deep yellow	Dark green
B	Calif.	.82	Deep yellow	Dark green	Dark green	Deep yellow	Dark green
C	Calif.	.61	Deep yellow	Medium green	Medium green	Deep yellow	Medium green
D	Calif.	1.30	Deep yellow	Dark green	Dark green	Deep yellow	Dark green
E	Calif.	2.21	Deep yellow	Dark green	Dark green	Deep yellow	Dark green
F	Calif.	0.60	Medium yellow	Medium green	Medium green	Medium yellow	Medium green
G	Calif.	2.40	Medium yellow	Medium green	Medium green	Medium yellow	Medium green
H	France	0.69	Medium yellow	Medium green	Medium green	Medium yellow	Medium green
I	France	.85	Medium yellow	Medium green	Medium green	Medium yellow	Medium green
J	France	.83	Light yellow	Light green	Light green	Light yellow	Light green
K	France	1.76	Light yellow	Light green	Light green	Light yellow	Light green

It is especially noteworthy that all of these oils, as received, were yellow in color, varying from light to deep yellow, and with considerable variation of free fatty acids among different brands. These samples were divided into four portions and placed in contact with tinplate. Two portions were allowed to remain for 10 months at room temperature (one in the light and one in the dark) and the other two portions heated one hour (one in the light and the other in the dark) at 212°F. Practically the same change took place in every case whether heated or cold, the only difference being that heat accelerated the reaction. In the case of the heated oil, light or darkness had no effect on the color change because of the rapidity of the reaction due to increased temperature. With the samples standing in the cold, however, the one in the light did not change, because of the reversible reaction due to light, preventing the formation of green color. In the

dark, a green color formed in from 2 to 10 months. In every case it was found that in a general way the depth or strength of green color depended on the depth of the original yellow color and the acidity of the oil, that is, a deep yellow oil high in fatty acids gave a deep or dark green color, while one either light yellow or low in acids gave a lighter green.

Table 5 shows the examination of various brands of foreign and domestic oils packed in tin.

TABLE 5

COLOR AND COLOR CHANGES OF VARIOUS BRANDS OF CANNED OLIVE OIL

Brand	Source	Free fatty acids as oleic acid %	Original color as recd.	Color after transferring to glass: Standing cold in light	Standing cold in dark	Standing cold with tin in light	Standing cold with tin in dark
A	Calif.	1.10	Dark green	Deep yellow	Dark green	Deep yellow	Dark green
A	Calif.	0.22	Light green	Deep yellow	Light green	Deep yellow	Light green
B	Calif.	1.27	Dark green	Deep yellow	Dark green	Deep yellow	Dark green
C	Calif.	0.70	Medium green	Deep yellow	Medium green	Deep yellow	Medium green
L	Italy	.56	Medium green	Light yellow	Medium green	Light yellow	Medium green
M	Italy	.90	Medium green	Medium yellow	Medium green	Medium yellow	Medium green
N	Italy	.97	Medium green	Medium yellow	Medium green	Medium yellow	Medium green
O	Italy	.95	Light green	Light yellow	Light green	Light yellow	Light green
P	Italy	.56	Light green	Light yellow	Light green	Light yellow	Light green
Q	Italy	.31	Light green	Light yellow	Light green	Light yellow	Light green
R	Italy	1.18	Light green	Light yellow	Light green	Light yellow	Light green
S	Italy	0.59	Light green	Light yellow	Light green	Light yellow	Light green
T	Italy	.47	Light green	Light yellow	Light green	Light yellow	Light green
U	Italy	.40	Light green	Light yellow	Light green	Light yellow	Light green

Again it is especially noteworthy that the color of these oils on opening, varied from light to dark green with considerable variation in acidity among different brands. These experiments were the reverse of those in Table 4, that is, the samples were divided into four portions, transferred to bottles and allowed to stand cold, with or without tin, in dark and light. It is to be noted that the yellow color returned by the action of light whether tin was present or not. This seems to indicate that the reversible

reaction of green to yellow through the action of light is more rapid than the formation of green color.

In general, the results of experiments tabulated in Tables 4 and 5 show that these color changes are common to all olive oils and bear out the conclusions drawn from the examination of green California oil, *viz.*, that yellow olive oil containing fatty acids, and in contact with tinplate, turns green at normal temperatures in absence of light, or, at increased temperature in presence of light, and that a reversal of this color change is brought about by light.

Although, theoretically, this color reversal can be repeated any number of times on the same oil, nevertheless, it was found after several reversals that the yellow-colored oil acquired a fluorescence and became cloudy, showing that other reactions were modifying the color and that there is a limit to the number of reversals.

Summary and Conclusions

The following is a summary of the conclusions and facts brought out in this investigation:

(1) That yellow olive oil packed in tin may turn green, and that this reaction is brought about by reduction of the yellow color through the action of the free fatty acids of the oil on the tinplate.

(2) That this reaction will not take place at normal temperatures in the presence of light.

(3) That the green color of olive oil, so formed, reverts to yellow by the action of light.

(4) That the formation of green color in olive oil is dependent on the acid strength of the oil and depth of the original yellow color and increases proportionately with these.

(5) That, in general, most olive oils on the market packed in tin, are of a greenish color, while the bottled product is yellow. This, of course, does not apply to fresh oil, but only that which is sufficiently old to have permitted any color change to have taken place.

(6) That it is not possible to pack olive oil in cans without development of greenish color unless the original oil is rendered neutral or bleached. As it is not practical to render the oil absolutely neutral or to bleach it, the formation of green color in tin cannot be entirely prevented in practice but may be controlled to a certain extent.

(7) That the development of excessive green color, which might be objectionable, can be prevented either by packing in cans only oil of low acidity (below 0.25%) or oil, the original color of which is light yellow. In the latter case the acidity is of little consequence as far as color is concerned.

(8) That green-colored oil in cans can be reconditioned by transferring

to bottles and exposing to light, whereby the original yellow color is restored.

CURTIS & TOMPKINS,
SAN FRANCISCO, CALIF.

STUDIES ON THE OIL AND AMMONIA CONTENT OF COTTONSEED

A Progress Report

BY A. F. SIEVERS

The work of the Bureau of Plant Industry in connection with the Basic Research Committee of the American Oil Chemists' Society and the Interstate Cottonseed Crushers' Association concerns itself with a study of the influences of soil and climate on the oil and ammonia content of cottonseed. In the report of the first season's work presented at the 1924 convention of this Society it was pointed out that such a program must extend over a number of years in order to furnish sufficient data to warrant definite conclusions. The first year's work included analysis of the seed from about 29 varieties grown at 10 different stations. From these analyses it appeared that those varieties which produced seed of either exceptionally high or low oil content in any one locality displayed the same tendency in the other localities from which seed was obtained.

During the past winter and spring the analysis of seed grown in 1924 has been proceeding along the same lines. Some new varieties have been added and a few of those included in last year's list could not be obtained this year. The stations from which samples were obtained are substantially the same as last year. The work has been unavoidably interrupted several times this winter with the result that only about two-thirds of the analyses have been completed to date. It has therefore been impossible to correlate the data and note the trend of results as was done in last year's report. It should be understood that there has in no sense been any curtailment of the work but that some of the analyses have been delayed but will probably be completed in about a month or six weeks. The ammonia determinations are being made, as last year, by the Barrow-Agee Laboratories.

It is planned to continue the program during the present growing season for the third successive year. If it is possible to complete the analyses of the samples from the coming season in sufficient time next spring it will be possible to render a report covering three years at the 1926 meeting of the Society.

BUREAU OF PLANT INDUSTRY,
U. S. DEPARTMENT OF AGRICULTURE