Changes in Olive Oil After Long Standing

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OLIVE oil, although the best known and most desirable edible oil, is, unfortunately, one of the oils most subject to oxidation and other changes which develop rancidity. The principal factor is oxygen; indeed it has been said that without oxygen there can be no rancidity. However, other factors, such as light, heat, moisture and contact with metals, serve to accelerate the oxidation. The chemical reactions involved are rather complex and some of the products formed have a very disagreeable taste or odor, while others do not seem to be responsible for the effects known under the term "rancidity."

In earlier years it was supposed that the principal changes consisted of the slow liberation of free fatty acids from the glycerol esters constituting the oil, due to a fat-splitting ferment or enzyme (olease or lipase) naturally present or formed by bacteria allowed to get in during careless manufacture; and subsequently the oxidation of the free fatty acid to oxyacids having disagreeable taste, etc. Oleic acid is the principal fatty acid (combined with glycerol as an ester and called "olein" or "triolein") in olive oil and being an "unsaturated" acid capable of uniting directly with iodine (hence the analytical item known as "Iodine absorption" or "Iodine No.") and other elements, it takes up oxygen readily. Oleic acid when fresh is white, tasteless and odorless, but quickly becomes yellow in color and acquires a rancid odor from oxidation. Thus the present commercial practice of requiring a very low content of free fatty acid in edible oil is well founded, as it stands to reason that the less free acid there is present to start with the less rancidity there will be when ageing has enabled oxidizing changes to take place. It must be remembered, however, that the proportion of free fatty acid can in time increase, due to the aforementioned ferment or enzyme naturally present and especially that formed by bacteria present as the result of careless manufacturing methods.

The per cent of free fatty acid if not a measure of rancidity, as freshly liberated oleic acid is not rancid (as said above) and, if the oil is well protected from oxidation, an oil with a 1 per cent free fatty acid content can remain "sweet" while a carelessly protected oil with only 0.5 per cent acidity may become quite objectionable. However, on general principles, the less free fatty acid there is present the better. More recently it has been determined that other compounds than the oxidized free fatty acid are formed by the combined effects of oxygen, light, moisture, etc., some of which are also disagreeable tasting and smelling substances. Various aldehydes, ketones and acids of less molecular weight than the fatty acids originally present, are formed and appear to be constant constituents of fats and fatty oils which have stood too long under unfavorable conditions and become rancid. Most of the various color-forming tests used for the detection of incipient or masked rancidity ("Kreis rancidity test," for instance) depend on the presence of several or all of these

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various constituents resulting from oxidation changes, and it is to the effect of all of them, including the oxidized free fatty acid, that the characteristic odor and taste of rancid fats and oils are due.

The development of rancidity in a carefully manufactured and properly stored olive or other edible oil is very slow, especially if the per cent of free fatty acid be low to start with. In a grocery store where turnover of stock is frequent, a good olive oil, even though stored in glass and exposed to light on a shelf, will test normal and show no very objectionable rancidity. In sealed tin cans it will keep "sweet" for a relatively long time. However, there are stores in certain sections where olive oil is infrequently asked for and a small batch of bottles may stand exposed to light for a year or so, or one or two bottles may be shoved in back of a new shipment or otherwise get displaced so as to stand many years. There is always an air space in the neck of each bottle, one-fifth of which is oxygen; moreover, there is more or less dissolved air and oxygen in the oil and for the small amount of oxidation necessary to render an oil rancid and to make it analyze abnormally in time this is sufficient.

How abnormal an old olive oil sample can analyze will be illustrated below with data on a pure oil, originally normal in every way and of very excellent quality, with a very low content of free fatty acid to start with. An oil showing less change than this particular oil would be found to analyze so abnormal as to lead to the charge of adulteration unless the official chemist studied into the matter very thoroughly.

The oil in question was one of the first commercial olive oils produced in California, being carefully pressed from selected olives grown on the Windermere Ranch of Mr. Andrew McNally at La Mirada, Cal., and sold through their Eastern office in the Rand, McNally Building in Chicago. The writer was called upon to analyze this oil in the Fall of 1906 and found it to be a pure, very high grade olive oil, testing as given below. On account of its being the first California olive oil which the writer had knowingly tested and because of the rather attractive bottle, it was allowed to stand year after year on an exhibition sample shelf to the present day (1927), being kept corked, but exposed indirect to light and room temperature meanwhile. It was analyzed a second time in 1916 and more recently in 1926 as follows:

In 1916 an official analysis would have resulted in this oil being declared "adulterated," in fact, probably at the end of five years the regular data would have been found to be suspiciously abnormal. The lowering of the iodine absorption value is due, no doubt, to the satisfaction by oxygen of the nor-

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	1906	1916	1926
Odor and taste	No rancidity	Very rancid	Extremely rancid
Kreis rancidity test	.....	Positive	Very strong
Specific gravity (15.5° C)	0.9132	0.9254	0.9383
Iodine absorption No.	83.60	75.26	68.58
Saponification No.	190.80	199.60	213.20
Acid No. (from per cent free acid)	0.96	8.04	15.68
Ester No. (Sap. No.—Acid No.)	189.84	191.56	197.52
Free fatty acids (of oleic)	0.48%	4.02	7.84%