Olive Oil Foots Oleine

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In a previous article by M. F. Lauro and the writer, and published in the Journal of Oil and Fat Industries, March, 1926, the subject of olive oil foots or sulphur olive oil, its manufacture and uses was discussed.

In brief, that article shows that, after a series of first cold and then hot pressings, without the use of added water or steam, and then with either or both water and steam added, all the oil which can be removed from the olives by pressure, has been obtained. These oils, although of many different grades and qualities, can be classed in two groups, edible and commercial. They are all pure olive oils with the usual qualities or characteristics of pure olive oil. They vary chiefly in the color, odor, flavor, and free fatty acid contents.

In the crushed pulp or marque, there still remains a considerable quantity of oil, which can be removed by extraction. After drying, the pulp is extracted with some solvent, usually carbon bisulphide, whence comes the name of sulphur olive oil. The extract, after filtration, is freed from solvent by distillation with steam, and the residual oil and water allowed to settle in a tank to remove the entrained water.

This sulphur olive oil, or olive oil foots, is dark green in color, containing chlorophyll from the pulp, and is usually of heavier body, with more stearine, than the pressed oil. However, it is a pure olive oil and not a foots. The values of the constants or characteristics of this oil fall within the usual range of values for those of a pure olive oil, except that the iodine value tends towards the lower limits of those for a pure olive oil, and the specific gravity tends towards the higher limits. The iodine value may even fall below that allowed for pure olive oil, due to the fact that it contains more stearine. The titre also runs rather higher than the values usually shown by pressed oil, but if the sulphur olive oil or olive oil foots is allowed to stand in tanks in the open, it will winterize itself, giving a stearine which may run as high as 38° C. in titre with an iodine value of 50.

The name of olive oil foots is a misnomer, since the oil is a true olive oil, obtained by extraction rather than by pressing. In fact when olives are not of good quality, they may be put in with the pulp for extraction, without any preliminary pressing at all.

The manufacture of the edible olive oil is the primary purpose of the olive oil industry, with the manufacture of the commercial grades second, and the preparation of the olive oil foots a very poor third. Since the olives must be handled whenever they are ready, the pulp is often stored in heaps or piles in pits, until there is time to process it. It may happen that there will be a period of many months between the manufacture of the pressed olive oil and the time when the extraction of the pulp can take place. During this time, the pulp is subject to both fermentation and decay, causing many changes in the oil.

These changes in the oil are of two general kinds, the first the oxidation of the molecule at the double bond of the oleic acid group, and the second the formation of inner anhydrides or lactones in the carboxyl group. As a result, oxyacids, oxidized acids, hydroxy acids, anhydrides or lactones, etc., are formed.

In addition, the ferments in the pulp hydrolize the oil, causing the free fatty acid content to increase rapidly. Further these changes tend to kill the chlorophyll, turning it brown, and causing the sulphur olive oil to give a brownish soap rather than the desired green colored product. Whereas the pulp, if extracted immediately after pressing was completed, would have given a nice green oil with low acidity, of good quality, free from gums, etc., and with a low unsaponifiable content, after standing, it yields a browner oil with high free fatty acid content and high unsaponifiable matter, and containing these oxidized products. The soap from some of these oxidized acids is rather soluble in salt water, and so washes out with the "nigger," or waste lye waters. As a general result of this delay in extracting the pulp, the color of the oil and the soap is poorer, the yield of soap is lower, and the soap is not as clean and soluble as that made from good foots. It also contains some of the gummy materials present in the oil as a result of the oxidation. This soap is used in washing textiles, and the presence of these extraneous materials renders it less soluble and therefore it is less easy to rinse it from the cloth, and also tends to make the subsequent dyeing spotty.

For some years, the olive oil plants in Europe have been refining the low acid oils with caustic alkali, obtaining a rather reddish brown oil, which was sold as "recovered" olive oil. Now, however, this refined oil is bleached and deodorized, giving an oil of good color, with a smooth bland flavor. This finished oil can then be added even to edible oils with rather strong flavors, since its own flavor is "neutral" and tasteless, and thus it is sold as an edible product. As the refineries became more adept at the art of refining these sulphur olive oils, they were able to handle foots of higher and higher acidity until now oils with 25 per cent or 30 per cent free fatty acid content are refined satisfactorily.

As a natural result of this process, the supply of low acidity olive oil foots has markedly decreased, and the general average of the shipments of the oil to this country have shown a considerably higher free fatty acid content. Also there have been less of the choice oils available, while the general average of the shipments have shown a tendency toward a standard or uniform grade.

Since there has been such an increase in the refining of the sulphur olive oils, there has been a greater quantity of the soapstock to be handled. At first this was either made into green Castile soap, or else acidulated and the resulting acids added to the foots or sulphur oil. It is now being marketed as olive oil foots oleine, a product which is simply acidulated olive oil foots soapstock. As the soapstock contained some neutral oil, which had been entrained in the settling of the soapstock, the oleine is not all free fatty acids, but contains about 60 per cent to 70 per cent of acids, the balance being the neutral oil or glcerides. The fact must therefore be recognized that while there is some glycerine in this material, the amount is probably too small to pay for recovery even in times when the value of the glycerine is more normal than it is today. The total amount of the glycerine present is only 3 per cent to 4 per cent.

Typical analyses of this oleine as compared with typical tests of Spanish olive oil foots are as follows; for comparison, also, the result of testing a sample of an unusually choice grade of foots from Tunis is also appended.

	Spanish Oil	Tunis Oil	Oleine
Specific gravity at 15.5° C.....	0.916	0.9158	0.9214
Iodine value (Wijs).....	78.8	83.5	80.7
Saponification value	189	189	187.8
Free fatty acids (Oleic).....	40%	20%	61.1%
Titre	21°C.	21°C.	18.2°C.
Soap color test.....Prime Green		P. Green	P. Green
Saturated acids (crude).....	1.45%	1.68%	4.04%
Saturated acids (corrected)....	1.36%	1.58%	3.72%
Liquid fatty acids (calc).....	93.74%	93.52%	91.47%
Iodine value (saturated acids)..	6.17	5.66	7.55
Iodine value (liquid acids calc)	88.2	93.1	88
Unsaponifiable matter	2.0%	2.0%	1.49%
Oxidized acids	6.86%	1.43%	4.05%
Iodine value (oxidized acids)..	51	61	46.9
Iodine value (total acids free from oxidized acids).....	83	..	88.1
Saponification value (ditto)...	200	..	208
"Oxyacids"	2.5%	..	1.85%

The "oxyacids" are those constituents, such as lactones or inner anhydrides, which are not soluble in petroleum ether. They are determined by dissolving the original oil, freed from moisture and insoluble matter, in petroleum ether, and allowing the solution to stand for 24 to 48 hours. The insoluble portion is filtered off on tared extraction thimbles, the beaker and thimble washed free of oil with petroleum ether, and then dried and weighed. The beaker always retains some of the insoluble matter. Some samples of olive oil foots or sulphur oil gave "oxyacids" values of 2.53 per cent, 2.12 per cent, and 3.10 per cent. The Oleine samples gave values such as 1.85 per cent and 1.76 per cent.

The "oxidized acids" are those portions of the total fatty acids which are not soluble in petroleum ether. They are developed in the oil by oxidation at the double bond, the extent of the oxidation depending upon the length of time that the pulp has been exposed to fermentation and oxidation. These compounds are brownish in appearance, are soluble in alcohol, ethyl ether or mixtures of the two, and are characterized by low iodine values. Samples obtained from olive oil foots gave iodine values of 32.4, 39.2, 51, 61, 40.8. Those from oleine gave values of 46.9, 44.0, and 54.2. Such saponification values as we determined seem to run rather low, namely 160 on one, and 180 on another.

These oxidized acids are determined in the following manner: 5 grams of the oil are saponified with alcoholic potash in the usual manner, and then freed from alcohol by evaporation. The soap is taken up in hot water, washed into a separatory funnel, acidulated with hydrochloric acid, and cooled. The fatty acids are taken up in 100 cc. of petroleum ether by vigorous shaking. The oxidized acids appear as brown clots in the ether layer, or adhering to the sides of the funnel. The petroleum ether layer is filtered through a filter paper into a tared beaker, and the aqueous solution extracted with several portions more of the petroleum ether. All of these washes are filtered into the same beaker. The filter paper also is washed free from fat with petroleum ether. This combined extract is then evaporated to dryness, and weighed to determine the total fatty acids freed from oxidized acids.

The aqueous layer is drawn off from the separatory funnel and the acids adhering to the glass allowed to dry. Alcohol, ethyl ether, or a mixture of the two, is then used to dissolve the fat, the solution being filtered through the same filter paper into a second beaker (tared). The funnel and paper are washed clean with the solvent, the extract evaporated to dryness, and weighed as oxidized acids.

The content of oxidized acids in oleine is quite low, probably due to the fact that the foots which are suitable for refining are of low acidity, and have been made from fresh pulp. On three samples, we obtained results of 4.05 per cent, 5.03 per cent, and 3.53 per cent. On sulphur olive oil, however, values were given ranging from 1.43 per cent on a very choice sample to 12.56 per cent, the actual values being 10.49 per cent, 7.07 per cent, 6.86 per cent, 1.43 per cent, 7.11 per cent, 12.56 per cent, and 6.08 per cent. These same samples gave value for the total fatty acids (freed from oxidized acids) ranging from 80 per cent for the sample showing 12.56 per cent of oxidized acids, to 91.25 per cent for the sample with 1.43 per cent of oxidized acids.

Oxyacids and oxidized acids are two very different groups of fats, although they are the product of the same process of fermentation and decomposition of the pulp. This is proved by the fact that after the oxyacids were removed from several samples, they gave practically the same amounts of oxidized acids, as the original samples had shown. Thus the sample with 12.56 per cent oxidized acids, was tested for oxyacids and gave 2.58 per cent. After removing these, the oil then showed 12.2 per cent of oxidized acids. Similarly, the sample showing 6.08 per cent of oxidized acids originally, still showed 5.75 per cent after removing 2.12 per cent of oxyacids. The samples of oleine behaved in a like manner.

The unsaponifiable fat of oleine is also lower than that of most sulphur olive oil. The oleine samples contained 1.49 per cent, 1.21 per cent and 1.00 per cent, but very few foots samples run as low as that and most of them have 2.00 per cent or more, sometimes as much as 3.00 per cent.

Artificial color was present in some of the oleine samples and not in others, and similarly was present in some of the foots samples.

The percentage of solid or saturated acids was lower in both the olive oil foots and the oleine, than that contained in many olive oils. Thus a Spanish olive oil had 6.96 per cent, but the olive oil foots had less than 2 per cent on two samples, the oleine about 4 per cent. Of course, samples of olive oil foots which have a high percentage of stearine would also have a high solid acid content.

In general then, the analysis of oleine is comparable to that of the choicer grades of olive oil foots or sulphur olive oil from which it is made, except that the gravity seems to run high. Oleine makes a good soap with a satisfactory yield, and a soap which should be satisfactory for practically all the purposes for which an olive oil foots soap could be used. Although the amount of glycerine in oleine is negligible, 3 per cent to 4 per cent, the amount in most olive oil foots samples does not run much higher. Since the acidity of many foots is as high as 50 per cent, these samples cannot contain more than 5 per cent to 6 per cent of glycerine.

M. Lauro Honored

The Brooklyn Law School has honored one of our members, Mr. M. Lauro, of the New York Produce Exchange laboratories, by conferring upon him a degree of L.L.B. Mr. Lauro, was graduated from Yale in 1913 with a degree of Ph.B., received his Master's degree from a Brooklyn Polytechnic Institute in 1928. He has for many years been one of the outstanding members of Society and it gives his many friends and associates great pleasure that he has received this distinction.