

6458	5	12.0	1.7	3.6
6459	5	12.0	1.7	3.6
6537	5	12.2	2.0	3.3
6552	5	12.0	3.5	3.2
6533	5	13.0	5.7	9.8
6546	5	10.4	7.5	10.1
6564	5	10.7	10.5	12.8
6567	5	12.6	14.5	18.5

From the above analyses there appears to be no appreciable increase in fatty acid where the moisture is below 10 per cent. Seed containing as much as 14 per cent in every case showed a marked increase in fatty acid while between these moisture limits lies a margin in which the fatty acid may or may not increase. A group of seed of low moisture and low fatty acid content, after several months' storage, were stored in a moist atmosphere at room temperature to ascertain if such condition would prove conducive to the production of free fatty acid. Although little increase was noted at the end of one week's storage, all samples had increased to more than 10 per cent at the end of two weeks with considerable mould.

The foregoing test was repeated excepting that at the end of 15 days' exposure to the moist atmosphere, the samples were divided in two parts, one part remaining in the moist room while the other was heated to 175° F. for 4 hours and then stored in one-gallon compression top can. The following table indicates the inhibitive action of either the heating or the dehydrating of the sample during the stage of rapid increase of the fatty acid.

TABLE IV

Sample	A	B	C	D	E	F
5865	0.5	1.4	11.4	21.0	14.7	13.6
5901	1.0	1.8	12.0	22.0	14.3	15.0
5935	2.5	3.3	8.8	17.1	8.7	10.3
6552	3.2	4.1	6.7	20.4	8.3	8.7
6427	6.8	11.7	25.4	32.6	22.9	25.7
6546	10.1	13.6	15.4	22.8	16.2	17.9

A—Free fatty acid beginning of storage.

B—Free fatty acid after 7 days' storage in moist atmosphere at room temperature.

C—Free fatty acid after 14 days' storage in moist atmosphere at room temperature.

D—Free fatty acid after 17 days' storage in moist atmosphere at room temperature.

E—Free fatty acid after 15 days' storage with subsequent heating to 175° F. for 4 hours.

F—Same as E after 40 days' total storage.

Attempting to correlate the susceptibility of seed to decompose producing free fatty acid with the germinating power of the seed, six samples were heated to 175° F. for 8 hours to completely kill the germ followed by a

two weeks' storage in the moist room to compare with the results obtained on similar seed without the pre-heating. Table V exhibits the marked difference in the two treatments.

TABLE V

Sample	Without Pre-heating		With Pre-heating	
	Original F.F.A., %	After 14 Days' Storage, %	Original F.F.A., %	After 14 Days' Storage, %
5865	0.5	11.4	6323	1.2
5901	1.0	12.0	6441	1.5
5935	2.5	8.8	6331	1.9
6552	3.2	6.7	6328	2.6
6427	6.8	25.4	6455	2.8
6546	10.1	15.4	6564	3.1
Average	4.0	13.3		2.2

It would thus appear that live seed is more resistant to the action producing free fatty acid than sterile or otherwise damaged seed.

**Conclusions**

The foregoing tests were conducted in the laboratory to observe the tendencies of seed to form free fatty acid when subjected to certain atmospheric and temperature conditions. The results of individual tests are given in all cases to elicit a discussion from others who may have conducted similar tests in hopes of arriving at more definite conclusions or to arrive at properties which may be attributed as common to all cotton seed.

The following statements are to be taken merely as tendencies and by no means as conclusive.

Cottonseed having less than 10 per cent moisture will remain stable under ordinary storage conditions.

Seed of 10 to 14 per cent moisture may or may not remain stable while seed having 14 per cent or more moisture will deteriorate in storage with a rapid increase of free fatty acid.

Deterioration of high moisture seed is inhibited either by cold storage or by heating seed to reduce moisture content.

Seed pre-heated to 175° F. to kill the germ is more sensitive than live seed to the formation of free fatty acid in moist atmosphere.

More experimental work is necessary to prove whether or not all cotton seed will increase appreciably in free fatty acid when subjected to the pre-drying treatment as prescribed by the official method of the National Cottonseed Products Association for determining this constituent.

Note: The author wishes to acknowledge his indebtedness to Mr. A. K. Schwartz for the helpful suggestions and for several of the samples used in conducting the tests.

# California Apricot Oil

By George S. Jamieson and Robert S. McKinney,

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**I**N view of the growing interest in the production of oil from the apricot kernels separated from the pits at the cracking plants in California, a chemical study of the oil has recently been undertaken. The more important chemical and physical characteristics, as well as the proportions of the fatty acids present in the oil as glycerides, have been determined.

As early as 1908 Frank Rabak<sup>1</sup> of the Bureau of Plant Industry, after a comprehensive investigation dealing with the possible utilization of waste fruit pits in California, called attention to apricot kernel oil, describing its chemical and physical characteristics, and pointing out its commercial possibilities. At that time the

annual accumulation of pits amounted to approximately 5,000 tons.

It is estimated that at the present time the cracking plants receive each season between 10,000 and 11,000 tons of pits from the apricot canning and drying industries. The kernels, which amount to about one-fourth the weight of the pits, usually contain from 40 to 45 per cent of oil. Although the larger portion of the kernels separated at the cracking plants is exported to Germany, Holland and Scandinavian countries, the remainder is used for the domestic production of oil, most of which is absorbed by the cosmetic industry. Before any marked increase in the local use of the kernels for the production of oil is warranted, new outlets for it must be found as the quantity taken by the cosmetic

<sup>1</sup>Peach, Apricot and Prune Kernels as By-Products of the Fruit Industry of the United States. Bul. No. 133 of the Bureau of Plant Industry, U. S. Dept. of Agriculture.

manufacturers varies little from year to year.

In many respects this oil is similar to that from cherry kernels and almonds, and it is reported to have the same excellent keeping qualities. It is a fine edible oil well suited for use in salad dressings and as a cooking oil. As in the case of cherry kernel oil, it will probably be found particularly useful for the commercial roasting of shelled nuts.

A. D. Holmes (U. S. Department of Agriculture Bulletin 781, 1919) using human subjects found that the oil was 98.4 per cent digestible as compared with 98.2 per cent for cherry kernel oil. He states that it is readily assimilated and has a nutritive value equal to that of the better known edible oils.

A laboratory experiment was made in which a pound of the crude oil was saponified in the usual manner with the calculated quantity of caustic soda. The resulting soap was poured while hot into a box frame and allowed to stand for a day. In this way a very hard, white soap was obtained, which appeared comparable to an olive oil castile soap in so far as its lathering and washing qualities are concerned.

The press cake remaining after the expression of the oil can be ground to a meal and sold as a fertilizer which has been found well adapted for use as a lawn dressing; or the meal can be moistened with water and after standing a few hours distilled with steam to recover the volatile oil (the yield of which amounts to about 1.5 per cent of the meal), which is sold as bitter almond oil. After the distillation, the residual meal is dried and sold as fertilizer; or after it has been determined to be free from hydrocyanic acid formed by the hydrolysis of the amygalin glucoside, the meal can be used as a feed for livestock. Analysis of the untreated, ground press cake showed that it contained 6.64 per cent of nitrogen (equivalent to 41.5 per cent of proteins), 2.20 per cent of phosphoric acid and 1.14 per cent of potash.

We are indebted to Sewall S. Brown and Company of Los Gatos, California, for sizable samples of kernels, meal, crude and refined oils, as well as for information concerning the domestic apricot kernel oil industry.

Table I gives the chemical and physical characteristics of the refined oil.

TABLE I

## Chemical and Physical Characteristics of Refined Apricot Kernel Oil

Specific gravity at 25/25° .....	0.9158
Refractive index at 25° .....	1.4700
Acid value .....	0.41
Iodine number (Hanus) .....	108.7
Saponification value .....	190.2
Reichert-Meissl value .....	0.2
Polenske number .....	0.1
Acetyl value (Andre-Cook) .....	4.2
Unsaponifiable matter, % .....	0.7
Saturated acids (corrected), % .....	3.57
Unsaturated acids (corrected), % .....	90.56

The crude oil gave an iodine number of 108.4 and a saponification value of 189.8. The color of this oil was read as 35 yellow and 3.3 red, and that of the refined oil as 20 yellow and 2.95 red. In each case a depth of five and a quarter inches of oil was used. The smoking point of the refined oil is 165-8°. This was determined by J. M. McCoy by his procedure<sup>2</sup>. The iodine numbers given in the literature for this oil range from 99.4 to 108, and the saponification values from 188 to 193.

As there are no published figures for the smoking points of other fats and oils which can be compared with

that given for apricot kernel oil by the McCoy method, the Bureau of Animal Industry of the Department of Agriculture has furnished the authors with the following data, which were obtained by J. M. McCoy:

Samples	Acidity as Oleic Acid %	Smoking Points ° C.	Remarks
11 of cottonseed oil.	0.11 to 0.17	160 to 195	Refined oils
4 of palm oil.....	0.23 to 0.34	155 to 178	Refined oils
2 of sunflower oil..	0.17	179 and 190	Refined oils
1 of soybean oil...	0.17	184	
2 of edible tallow..	0.5 to 0.9	140 to 156	
1 of kettle rendered beef fat .....	0.45	161°	
2 of prime steam lard .....	0.39 to 0.45	144 and 158	
4 of kettle rendered lard .....	0.17 to 0.34	161 to 176	
3 of kettle rendered leaf lard.....	0.17 to 0.34	162 to 168	
1 of refined hydrogenated lard (Clix) .....	0.11	185°	Refined by caustic soda process.
4 of refined lard...	0.23 to 0.45	150 to 160°	Not refined by caustic soda.
3 of compound (shortening) .....	0.11 to 0.23	171 to 181	Cottonseed oil and oleo stearine.

In refined oils there appears to be no relation between the quantity of free fatty acids and the smoking point, and evidently the wide range found even with samples of an oil having the same acidity is due to some unknown factor. For example, 8 samples of refined cottonseed oil with an acidity of 0.11 gave smoking points ranging from 160 to 195°; but only 2 of the samples gave values below 180°.

*Unsaturated Acids*

From the iodine number of the oil and the percentage of unsaturated acids, the iodine number of the latter was calculated to be 120.1. This value was used in the calculation of the oleic and linoleic acids in the oil with the following results:

	Unsaturated Acids %	In Oil %	As Glycerides %
Oleic Acid .....	66.93	60.61	63.34
Linoleic Acid .....	33.07	29.95	31.15

*Saturated Acids*

The saturated acids, which were separated from the saponified oil by the lead-salt ether procedure, were esterified with anhydrous ethyl alcohol in the presence of dry hydrogen chloride gas<sup>3</sup>. The esters (70.5 grams), freed from solvent and moisture, were fractionally distilled under a pressure of 3 mm. The five fractions, as well as the undistilled residue, were in turn redistilled from a 150-cc. Ladenburg fractionation flask. The resulting five fractions were analyzed, and their composition was determined as previously described<sup>4</sup>. From this analytical data, the results given in Table II were calculated.

Acids	Saturated Acids %	Acids in Oil %	Acids as Glycerides %
Palmitic .....	68.00	2.43	2.55
Stearic .....	30.58	1.09	1.14
Lignoceric .....	1.42	0.05	0.05

The acids were recovered from the ester fractions and the small undistilled residue by saponifying them with alcoholic potash and decomposing the soaps with hydrochloric acid. The acids were collected and completely separated from the potassium chloride and excess of hydrochloric acid by remelting them with hot distilled water in the usual manner. The acids obtained from the

<sup>2</sup>J. Amer. Chem. Soc. 1920, 42, 1200.

<sup>4</sup>J. Amer. Chem. Soc. 1924, 46, 775.

<sup>3</sup>Ind. Eng. Chem. Anal. Edition 1931, 3, 347.

various distilled ester fractions and the residue were fractionally crystallized from ethyl alcohol. The identity of the individual acids which were separated by this means was established in each case by their melting points and by observing whether or not these melting points were lowered when they were mixed with equal quantities of the respective acids, the composition of which had been determined by elementary analysis. In no instance was there observed any depression of the melting point.

As no myristic acid could be isolated from fraction 1, 100 grams of the unsaturated acids were esterified and fractionally distilled under diminished pressure. The acids were recovered from the first fraction and submitted to fractional crystallization from ethyl alcohol, but no myristic acid was obtained. However, a very small quantity of palmitic acid was isolated and identified.

Palmitic acid was separated from the first three saturated ester fractions, stearic acid from fractions 3 and 4, and lignoceric acid from fraction 5 and the residue.

The acids isolated from the fractions in each case confirmed the deductions previously made from the mean molecular weights of the saturated acid esters.

The composition of the oil in terms of glycerides is given in Table III.

Glycerides of	Per Cent
Oleic acid .....	63.3
Linoleic acid .....	31.2
Palmitic acid .....	2.6
Stearic acid .....	1.1
Lignoceric acid .....	.05

#### Summary

The characteristics and the percentages of the fatty acids present in apricot kernel oil as glycerides have been determined. The oil studied was found to contain about 90.6 per cent of unsaturated acids consisting of a mixture of oleic and linoleic acids. The saturated acids amounted to about 3.6 per cent and were composed almost entirely of palmitic and stearic acids.

Mention is made of the utilization of the press cake for the recovery of volatile oil, for fertilizer, and as a feed for livestock. An analysis of the press cake is given. A table of the smoking points for various fats and oils by the J. M. McCoy procedure is given for comparison with that of apricot kernel oil.

In addition to the established use of the oil by cosmetic manufacturers, other possible outlets include its use as a salad and cooking oil, for the roasting of shelled nuts, and for the manufacture of soap.

## Selenium: The New Catalyst in Kjeldahl Digestions

By M. F. Lauro

Ammonia determinations are everyday occurrences in the laboratory of the oil chemist, since he must analyze not only the oil content of seed and nut, but also the cake and meal left from their expression or extraction, in order to ascertain their commercial value as feed and fertilizer. Hence, an article on this subject should not be out of place in the program before the American Oil Chemists' Society.

It is common knowledge that concentrated sulphuric acid will break down the complicated structure of both animal and vegetable proteins into the simpler ammonia compound, which the chemists can more readily act upon and determine, recalculating to the original protein, than attempt to separate the protein as such or obtain by other means. Considerable charring takes place in the process of conversion to simpler forms necessitating the addition of more acid and a prolonged period of digestion before final clearance to a colorless solution. The sulphates of either soda or potash are added with the idea of so raising the boiling point as to keep the mixture liquid and prevent undue loss of acid, and thereby, with a minimum amount of acid, hasten the process to its conclusion. To still further accelerate the reaction, small amounts of either mercury or copper are used. They act catalytically and cut down the time to a matter of hours where it took practically all day in the original Kjeldahl process.

Copper was always popular with cereal chemists, because of its convenience, cheapness and the fact that it indicated by change of color the excess of lye necessary to add for the next step of distilling the ammonia from the ammonium sulphate formed in digestion. Mercury became the favorite of the oil chemist, as he dealt with a greater variety of mixed materials, more complex in nature and in addition containing greater oil content. With these substances it was found in general that the mercury compounds gave more concordant and slightly higher results. The chief objections to mercury lay in the need for its precipitation with sodium or potassium sulphide before distillation, and in the occasional low

results from prolonged digestion and consequent decrease in sulphuric acid, whereby a very stable amino-derivative of mercury is formed. Whenever this is suspected the addition of a little more acid and further digestion will break it up, otherwise precipitation with sulphide and subsequent distilling will not give all of the ammonia.

There has been no change in the method for a great many years. Improvement has proceeded rather along the line of standardizing the procedure, in developing new types of flasks and apparatus and in the change from gas to electric heater. This has helped cut down the time appreciably, so that, in general, it may be safe to say that flour may be digested completely in about an hour's time, cottonseed meal in about two hours, and other material such as meat and fish scrap in from two to three hours.

The need for more rapid digestions, however, never abated. The time factor is a most important one not only in commercial laboratories but in control mill work. Research to cut down the time still further, was therefore never wanting.

The prevailing idea favored the noble metals as catalysts, in spite of their cost. Hence the search for a new catalyst was almost exclusively restricted to them. Most of the author's previous attempts, except for nickel, lay in that special class of elements.

But logic sometimes plays peculiar tricks. Your true scientist reasons out a conclusion by *a priori* thinking; the inventor usually achieves his result by hit and miss method with, however, a one-tracked idea. Quite often what happens is, that in working out a problem logically, we may stumble on a discovery collaterally. Others then call this a stroke of luck, but is it? It would seem to me that such an apparent accident is actually created out of circumstances as a by-product of research, which but for that research would possibly never have happened.

So it was with this new catalyst, selenium. It may be said that I stumbled upon it, when as a matter of fact,