Possibilities of Peanut, Pecan and Safflower Seed Oils as Supplements for Olive Oil[1]

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The supply of olive oil from the region of the Mediterranean was threatened immediately upon the outbreak of hostilities in Europe. As the war spread, imports of olive oil decreased from the pre-war volume of approximately 100 million pounds to 15 million pounds in 1941. Imports have practically ceased and little or no receipts can be expected for the duration of the war. The decline in imports is evident from Table 1 in which imports for years 1938 and 1941 are shown. Domestic production, principally from California olives, has been increasing steadily and in 1941 amounted to approximately 10.3 million pounds. This production is, however, wholly inadequate to meet normal domestic requirements, consequently prices have increased three-fold since hostilities began in Europe and edible grade oil is now quoted at 5 to 6 dollars a gallon.

TABLE 1

Olive Oil: Imports for Consumption (1,000 Pounds)

Year	Edible	Sulphured or foots	Inedible	Total
1938	71,085	22,355	5,444	98,884
1939	62,866	28,180	11,303	102,349
1940	50,080	24,479	5,135	79,694
1941	10,119	4,026	866	15,011

Although olive oil is consumed primarily as a table oil, appreciable quantities are used industrially. Consumption of olive oil foots in the production of soaps varied from approximately 33 million pounds in 1933 to approximately 17 million pounds in 1940. The present and past status of olive oil from the industrial viewpoint was summarized in an article in *Soap and Sanitary Chemicals* (1) from which the following is quoted:

> "By far and away the most important use of olive oil foots for many years has been in the manufacture of soaps. And soaps made from olive foots have found their greatest application in the textile field. Soaps made from olive oil foots played an important part for years in many branches of the textile industry. In fact it was once said that soaps were the most important things in textiles.
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> "Olive oil soaps were used for wool throwing, for 'boiling off' or degumming silk, for silk dyeing, for dyeing cotton goods or to brighten certain colors after dyeing, for calico printing, and for many other operations in the wool, silk, and cotton industries. More recently, they also have been used extensively in the manufacture of rayons and acetates.
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> "In this last-named field, olive oil soaps are still being used as they perform much more effectively than any other product which has been developed for the purpose and are used in such relatively small quantities that their price has practically no effect on the cost of the finished material. Even if the price of olive oil foots were two or three times what it is today, soap made from it would still be used by the rayon and acetate industries."

In the fall of 1941 the Southern Regional Research Laboratory was requested to undertake the development of a suitable substitute for olive oil, especially for use in the textile industry. Efforts to develop such a substitute were directed toward the modification of cottonseed and peanut oils by appropriate chemical treatment, and toward the examinaton of several minor oils originating, or capable of being produced, in the Southern part of the United States. In the latter class are pecan oil and safflower seed oil.

Pecans are widely grown in the Southern part of the United States, production amounting to 87 million pounds in 1940, of which 62 million pounds were grown in Texas and Oklahoma and 8.5 million pounds were grown in Georgia. Of the 87 million pounds of pecans produced in 1940 approximately 67 million pounds were from seedling varieties and 20 million pounds from improved varieties. Increasing demand on the part of the consumer for improved varieties of pecans, and greater production on the part of the grower to meet these demands have made it increasingly difficult to dispose of the seedling variety of nuts and it was believed in some quarters that a portion of these seedling nuts together with broken and damaged nuts and kernels originating in shelling plants could be diverted to production of an oil capable of replacing imported olive oil. The nuts from seedling trees contain from 35 to 38 per cent of kernels and those from improved varieties contain from 45 to 55 per cent of kernels. The kernels contain from 60 to 70 per cent oil.

Safflower seed oil has been produced on an experimental scale in New Mexico for a number of years, and one cottonseed oil mill located in Deming, New Mexico, has regularly crushed this seed for the past several years.

Pecan and safflower seed oils, together with a sample of peanut oil used in the oil modification experiments, were examined and compared with a sample of high grade olive oil imported from the Mediterranean region. The chemical and physical characteristics of the four oils are reported here. Work on the modification of the domestic oils will be reported in a separate publication.

The oils which were examined are briefly described as follows:

The olive oil was a commercial brand imported and sold for table use. It was purchased in sealed tins on the open market, and it was found to compare favorably in organoleptic qualities with other edible olive oils.

The peanut oil was a commercial product which had been refined, bleached, and deodorized. At the time it was examined it was of good quality both as to taste and odor.

The sample of "refined" pecan oil, presumably of edible quality, was furnished to the Office of Surplus Marketing Administration by the National Pecan Growers Exchange of Albany, Georgia. According to information obtained from the National Pecan

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Growers Exchange (2) the oil was produced by expeller pressing of meats accumulated over a period of about 10 to 12 months, and included broken and damaged kernels. The crude oil was water-washed and treated with activated charcoal and settled, and the clarified supernatant oil layer was removed and shipped to New Orleans. The oil as received was not deodorized, and was not strictly fresh as was evident by the onset of incipient rancidity.

The sample of crude safflower seed oil was expeller-pressed from Russian Type No. 14 seed grown in the vicinity of Deming, New Mexico. According to information (3) supplied with the sample of oil, safflower grows well in the plains of Texas and New Mexico and yields 1,500 to 2,000 pounds of seed per acre. The seed has an oil content of 18 to 24 per cent. The crop is grown and harvested in a manner similar to spring wheat. Cottonseed oil mills can process the seed without change in equipment. Additional information relative to the production of safflower seed is available in U.S.D.A. Circular No. 366 (4).

Methods of Analysis and Calculations

Iodine number: Iodine numbers were determined by the A.O.C.S. modification of the Wijs method (5) using 100 per cent excess of reagent and a thirty-minute reaction time.

Thiocyanogen number: Thiocyanogen numbers were determined with a 0.2 N solution of thiocyanogen prepared by bromination of dry lead thiocyanate[2] suspended in a mixture of purified glacial acetic acid and carbon tetrachloride. A 100 per cent excess of reagent was used and the reaction time was 24 hours at 18° C. (6).

Saponification number: Saponification numbers were determined in alkali-resistant glassware using 0.5 N alcoholic potassium hydroxide solution and a reflux period of one hour.

Acid number: Hot neutralized ethyl alcohol was used as a solvent and the free acid of the sample was titrated with 0.1 N aqueous sodium hydroxide solution.

Acetyl number: The acetic anhydride-pyridine method of West, Hoagland, and Curtis (7) was used. The acetyl number is expressed as the number of milligrams of "acetyl" which react with one gram of the oil.

Unsaponifiable matter: The percentage of unsaponifiable matter was determined by the A.O.C.S. method (5) for normal animal and vegetable fats.

Saturated glycerides: The percentages of saturated glycerides were determined by the Bertram oxidation method as modified by Pellikan and Von Mikusch (8). The latter investigators made use of the following equation in calculating the content of higher saturated fatty acids:

$$G = \frac{100}{S}\left[W - \frac{IW}{90}\right],$$

in which W represents the weight of "saturated *fatty acids*" of iodine number I, obtained from the oxidation of S grams of *glycerides.*

For the determination of the composition of various fats and oils, especially with fats containing relatively large amounts of saturated glycerides, it is advantageous to employ an equation which yields directly a value representing either the percentage of saturated glycerides present in an oil or the percentage of saturated fatty acids existing in the mixed free fatty acids derived from the oil.

It can be shown that the weight in grams of fatty acids obtainable from one gram of glyceride is equal to 1—(0.0002261) (saponification number). Insertion of this factor in the equation of Pellikan and Von Mikusch gives rise to Equation (1) which satisfies both of the above-mentioned stipulations. Substitution of the data obtained from the Bertram oxidation in this equation leads to the evaluation of the percentage of saturated fatty acids present in a mixture of fatty acids and to a very close approximation expresses the percentage of saturated glycerides present in the original oil.

$$SG \doteq SA = \frac{100W\,(1 - \frac{I}{90})}{S\,(1 - 0.0002261SN)} \qquad (1)$$

SG = Percentage of saturated glycerides in the oil

SA = percentage of saturated acids in mixed acids

W = weight of isolated fatty acids

I = iodine number of isolated fatty acids

S = sample weight of the oil or fat

SN = saponification number of the fat or oil.

Unsaturated glycerides: The total amount of unsaturated glycerides existing in an oil may be computed with the aid of Equation (2).

$$UG = 100.0 - (SG + UN) \qquad (2)$$

UG = percentage of unsaturated glyceride

UN = percentage of unsaponifiable matter.

Equations relating to the various unsaturated acids present were established on the basis of triglycerides from the data in Table 2. The theoretical thiocyanogen values, although not employed in the derivations, are included for comparative purposes since equations involving these figures have been used by certain other investigators.

TABLE 2

Iodine and Thiocyanogen Numbers of Unsaturated Acids and Glycerides

Lipid	Theoretical iodine number	Theoretical thiocyanogen number	Thiocyanogen number used
	(Calculated)	(Calculated)	(Empirical)
Oleic acid	89.87	89.87	89.4[1]
Linoleic acid	181.04	90.52	96.8[1]
Linolenic acid	273.51	182.34	167.5[1]
Triolein	86.01	86.01	85.56[2]
Trilinolein	173.20	86.60	92.60[2]
Trilinolenin	261.59	174.70	160.20[2]

[1] From data of Riemenschneider *et al.* (9).

[2] Calculated from data of Riemenschneider *et al.*

The thiocyanogen numbers for the free fatty acids appearing under the heading "Thiocyanogen number used" of Table 2 are those compiled and recommended by Riemenschneider *et al.* (9) for 0.2 N thiocyanogen solutions. These values were used in the calculation of "thiocyanogen numbers used" for the glycerides.

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[2] The lead thiocyanate employed was a product of Merck & Co., Inc., prepared especially for thiocyanogen number determinations.

For fats and oils containing normal oleic and linoleic acids and no more highly unsaturated acid the following equations are applicable:

$$\text{Percentage of triolein} = 2.5268\ \text{TN} - 1.3509\ \text{IN} \qquad (3)$$

$$\text{Percentage of trilinolein} = 1.2482\ \text{IN} - 1.2548\ \text{TN} \qquad (4)$$

For those glycerides which contain linolenic acid in addition to oleic and linoleic acids the following equations are applicable:

$$\text{Percentage of triolein} = 1.6767\ \text{TN} - 1.2823\ \text{IN} + 0.66835\ \text{UG} \qquad (5)$$

$$\text{Percentage of trilinolein} = 1.4158\ \text{IN} - 3.3306\ \text{TN} + 1.6318\ \text{UG} \qquad (6)$$

$$\text{Percentage of trilinolenin} = 1.6539\ \text{TN} - 0.13356\ \text{IN} - 1.3002\ \text{UG} \qquad (7)$$

IN = Wijs iodine number of the oil
TN = thiocyanogen number of the oil, (0.2N solution)
UG = unsaturated glyceride per cent, Equation 2.

The use of Equations (3) and (4) affords an independent check on the accuracy of the analysis of certain oils since the total amount of unsaturated glycerides can be computed by two independent methods.

Refractive index: Refractive indices were determined at 25° C. by means of an Abbe type refractometer.

Color: The Lovibond color readings were determined according to the A.O.C.S. method (5).

Absorption spectra: The spectral transmittance curves for the various oils were obtained by use of a Coleman spectrophotometer, Model 10 S, employing a slit width of 5 Mu. The wave length scale of the instrument had previously been checked against a didymium filter. A cell having a width corresponding to an oil thickness of one centimeter between the faces was used. A matched cell containing carbon tetrachloride was employed as a reference.

Smoke, flash, and fire points: These determinations were carried out in accordance with the Cleveland open cup procedure as described in the A.O.C.S. methods (5).

Results and Discussion

The results of the oil analyses are recorded in Table 3 and the compositions of the oils calculated from these data are recorded in Table 4. The total percentage of unsaturated glycerides was calculated by means of Equation (2). The percentages of component acids of the unsaturated fatty acid fractions of olive, peanut, and pecan oils were calculated by means of Equations (3) and (4) and are expressed as triglycerides; those of safflower seed oil, with Equations (5), (6), and (7).

TABLE 3

Analysis of Oils

	Virgin olive oil 0-112	Edible peanut oil 0-50	Edible pecan oil 0-92	Crude safflower seed oil 0-45
Iodine number	87.0	97.7	104.5	146.5
Thiocyanogen number	78.5	69.7	84.0	86.4
Saponification number	190.4	191.2	192.8	189.9
Acid number	4.15	0.23	1.10	1.66
Acetyl number	4.3	2.5	3.6	1.1
Unsaponifiable matter, per cent	0.90	0.38	0.42	0.96
Saturated glycerides, per cent	7.9	18.4	4.0	6.8
Refractive index, N_D^{25}	1.4672	1.4690	1.4704	1.4747
Color (5¼" cell)	35Y/2.7R [1]	70Y/4.3R	35Y/8.1R	35Y/6.0R [2]
Smoke point, °F	280	388	335	318
Flash point, °F	550	628	600	602
Fire point, °F	670	685	680	682

[1] A perfect match was impossible because of the green color of the oil.
[2] A 1-inch cell was used for this crude oil.

TABLE 4

Composition of Oils

Constituent	Virgin olive oil	Edible peanut oil	Edible pecan oil	Crude safflower seed oil
	Per cent	*Per cent*	*Per cent*	*Per cent*
Unsaponifiable matter	0.9	0.4	0.4	1.0
Saturated glycerides	7.9	21.0 [1]	4.0	6.8
Unsaturated glycerides	91.2	78.6	95.6	92.2
as triolein	80.9	44.1	70.9	18.6
as trilinolein	10.1	34.5	25.2	70.1
as trilinolenin	0	0	0	3.4

[1] Computed, see text.

Application of the iodine and thiocyanogen numbers to Equations (3) and (4) indicated the presence in peanut oil of 21.0 per cent of saturated glycerides. However, the result of the Bertram oxidation indicated the presence of only 18.4 per cent of saturated glycerides. Since several determinations of the iodine and thiocyanogen numbers of the peanut oil by three analysts gave substantially the same values it was concluded that possibly the Bertram oxidation method gave abnormally low results in this particular case.

A determination of the saturated glycerides was made by means of the lead salt-alcohol separation (6). This method indicated the presence of 19.5 per cent of saturated glycerides, which is approximately one per cent higher than that obtained by the Bertram oxidation method. The analyses of numerous samples of soybean oil by the lead salt-alcohol method, which were made at the U. S. Regional Soybean Laboratory, yielded invariably values for saturated acids which were approximately two per cent lower than the value obtained by the Bertram oxidation method on the same sample. It is probable, therefore, that the value of 19.5 per cent obtained with the lead salt-alcohol method in the case of peanut oil is also somewhat low, and that the value of 21 per cent obtained by the use of the iodine and thiocyanogen numbers is more nearly correct. Presuming for the present that the analogy between soybean and peanut oils is justifiable, it may be concluded that the modified Bertram oxidation is not applicable to peanut oils. It is quite probable that the presence of the long chain arachidic acid in peanut oil may be responsible for the observed deviation. The effect of the presence of this more insoluble acid in the course of the Bertram oxidation is being investigated in this laboratory.

Of the four oils examined pecan oil was found to contain the smallest amount of saturated glycerides (4.0 per cent); olive and safflower seed oils contained intermediate and about equal amounts (7.9 and 6.8 per cent, respectively); while the peanut oil contained the largest amount (21.0 per cent) of such glycerides. The olive and pecan oils possessed a very high content of oleic glycerides (80.9 and 70.9 per cent, respectively); peanut oil was appreciably lower (44.1 per cent) and safflower seed oil was quite low (18.6 per cent). On the other hand, the peanut and pecan oils were not greatly different in their content of linoleic glycerides (34.5 and 25.2 per cent, respectively); the olive oil contained very little linoleic glyceride (9.8 per cent), while the amount present in safflower seed oil was quite large (70.1 per cent). Safflower seed oil was the only one of the four oils which appeared to contain linolenic glycerides and the percentage was quite low.

Kaufmann and Fiedler (10) reported the presence of appreciable quantities of linolenic acid in safflower seed oil whereas Jamieson and Gertler (11) reported the presence of only a trace of linolenic acid in this oil. Other analyses reported since 1926 do not indicate the presence of linolenic acid in safflower oil.

Reference to the literature indicates that four analyses of pecan oil have been reported previously. Deiler and Fraps (12) concluded that the oil contained 76 per cent of oleic acid and 24 per cent of linoleic acid as glycerides, and that saturated acids were not present. Jamieson and Gertler (13) and Boone (14) employing the method of lead salt-ether separation, found 4 to 5 per cent of saturated glycerides and approximately 80 per cent of oleic acid and 16 per cent of linoleic acid as glycerides. More recently Whitehead and Warshaw (15) employed thiocyanogen and iodine numbers in order to calculate the percentage of composition of pecan oil. These investigators reported the presence of 64.1 per cent of oleic acid and 23.6 per cent of linoleic acid in this oil. The saturated acids were not experimentally determined, but when calculated by difference were found to be 8.0 per cent.

In the present analysis the Bertram oxidation and iodine-thiocyanogen techniques were applied to this oil and gave approximately the same percentage of linoleic glycerides as previously reported, but a somewhat smaller percentage of saturated glycerides with a correspondingly higher percentage of oleic glycerides.

The spectral transmittance curves and the Lovibond color values are recorded in Figure 1. Within the region of the visible spectrum the oils exhibit transmittances characteristic of their origin and degree of refinement; crude safflower seed oil being least transmittant and completely refined peanut oil being the most transmittant. Olive oil exhibits a strong absorption in the region of 670 mu which is characteristic of chlorophyll and the low Lovibond red value results from the masking effect of this pigment.

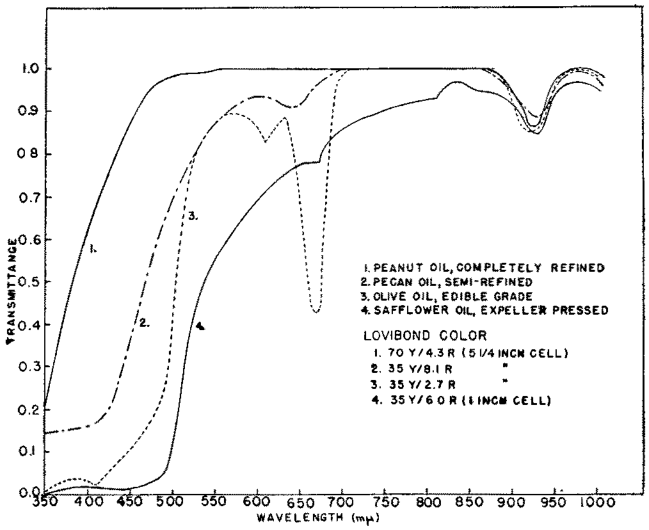

FIG. 1.

The absorption shown by all of these oils in the region of 900 to 950 mu was also observed with tripalmitin, pelargonic acid, oleic acid, and refined mineral oil. It was not observed with carbon disulfide, chloroform, and carbon tetrachloride. The absorption does not appear to be due to the presence of a specific minor component of the oil but rather to some fundamental characteristic of glycerides.

Inspection of Tables 3 and 4 indicates that none of the oils examined simulate olive oil either in composition or in properties. Pecan oil approaches olive oil in its composition more than does peanut or safflower seed oil. Even though pecan oil differs from olive oil chemically, Whitehead and Warshaw (15) state that pecan oil is of high quality and is comparable with olive oil in edible properties. Sims (16) reports that pecan oil can be used advantageously for cooking purposes in substitution for other oils.

With regard to its smoke point pecan oil appears superior to olive oil. However, the lower smoke point of the olive oil may be a peculiarity of the particular sample examined, since it contained about 2 per cent of free fatty acids. Of the four oils examined peanut oil was found to have the highest smoke point; however, it was the only one which was completely refined. Owing to the lower content of saturated and oleic acids present in pecan oil, it should be entirely feasible to produce from it, by means of controlled hydrogenation, a modified oil whose composition is quite similar to that of olive oil. Without modification pecan oil, as judged by its composition, should yield on sulfation a product which would compare favorably with sulfated olive oils.

Possibilities of the Commercial Production of Pecan Oil

The annual average price to the grower of seedling pecan nuts has varied between 4.3 and 11.1 cents per pound during the 10-year period 1931 to 1940, and the price of improved varieties has varied from 10.9 to 15.7 cents per pound during this period. The average annual price during this 10-year period for seedling and improved varieties was 6.9 and 13.1 cents, respectively. Except for culls and broken meats from the shelling plants it is unlikely that any improved varieties would be diverted to oil production. Using the average annual price of 6.9 cents a pound to the grower, a ton of seedling nuts would cost $138.00 a ton at the grove or $140 to $142 delivered to the shelling or crushing plant.

If the seedling nuts were crushed for oil as received, grading could be dispensed with but the nuts would have to be cleaned, shelled, and at least a partial separation of hulls and kernels would have to be made prior to crushing. The shelling operation is expensive where whole meats are desired for the edible nut trade but for crushing purposes a large percentage of broken meats would not be objectionable if the meats were crushed as produced. Also, because of the high oil content of the meats it would be necessary to leave a considerable portion of the shell with the meats if the oil is expressed by the expeller method. The exact amount of shell which would have to be retained with the meats is not known from actual experiment. On a basis of 40 per cent kernels containing 65 per cent oil it would probably be necessary to leave a minimum of 200 pounds of shells with the meats for each ton of seedling nuts processed for oil. In other words, instead of obtaining 800 pounds of pure meats the cracking and separating operations would have to be carried out to produce approximately 1,000 pounds of mixed meats and shells per ton of nuts processed.

Cracking and separation could therefore be operated mechanically and much more cheaply than is the case where hand-picked meats are required for the edible nut trade. No exact figures are obtainable relative to the cost of these operations and estimates received from shellers ranged from $20 to $60 a ton of nuts handled.

Adding the widely differing costs for shelling and separating, mentioned above, to the cost of the nuts delivered to the shelling plant or oil mill, the price of one ton of seedling nuts would be increased to $160 to $200 per ton prior to crushing.

Assuming a yield of 40 per cent of kernels and a yield of 60 per cent of oil, which is liberal for seedling varieties, one ton of nuts could yield about 800 pounds of pure kernels or 480 pounds of oil. Under present prevailing prices for comparable edible oils, the oil, if of prime grade, would be worth 12 to 15 cents a pound f.o.b. mill, or $57 to $72 on the basis of 480 pounds of oil per ton of nuts. No estimate can be made of the value of the press cake since the large amount of residual shells necessary to permit expressing of the oil would necessarily affect its feeding value. The meal would, however, have some value as fertilizer or as fuel under the boilers.

If the cost per ton of seedling pecans delivered, cleaned, shelled, and with the meats separated ready for pressing, but without adding the cost of crushing, is estimated at $160 to $200 per ton it is obvious that the production of pecan oil would not be economical. In fact, in order to be profitable under the conditions set forth above, the oil would have to sell for 35 to 40 cents per pound or more, or about 3 times the price of edible oils other than olive oil. If the most unlikely assumption is made that the oil could be marketed at the present price of domestically produced edible olive oil, namely $5.00 to $5.30 per gallon, f.o.b. New York, pecans could be profitably crushed for oil.

Summary

Samples of completely refined peanut oil, semi-refined pecan oil, imported edible grade olive oil and crude safflower seed oil have been examined for composition, spectral transmittance and other properties. Compositions were determined by means of the modified Bertram oxidation method and application of the iodine-thiocyanogen number technique.

None of the oils examined simulate olive oil in composition. Peanut and pecan oils appear capable of modification to produce a product chemically similar to olive oil and for certain purposes can replace olive oil without modification.

The production of pecan oil under present market conditions with regard to prices for edible oils and seedling pecan nuts does not appear to be very attractive unless the costs of processing pecans for oil can be greatly reduced.

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