In Table II are listed the I.V. and refractivities published for the same samples; their H.V. calculated from the I.V. using relation (II). In two cases (Samples 3 and 4) the refractivities were given for 25°C.,

TABLE II

Comparison Between Actual and Calculated Refractive Indices n_D^{20} of the Samples of Methyl Esters Listed in Table I

No.	I.V.	H.V.	n_D^{20}		Deviation
			Calculated	Actual	
1	86	68	1.4515	1.4517	−0.0002
2	86	68	1.4515	1.4508	+0.0007
3	173	137	1.4615	1.4611	+0.0004
3a	173	137	1.4615	1.4613	−0.0002
3b	173	137	1.4615	1.4616	+0.0001
3c	173	137	1.4615	1.4613	−0.0002
4	260	207	1.4716	1.4726	−0.0010
4a	260	207	1.4716	1.4709	+0.0007
4b	260	207	1.4716	1.4711	+0.0005
5	319	253.5	1.4784	1.4798	−0.0014
6	445	355	1.4930	1.4930	+0.0000

and it was necessary to extrapolate for 20°C., using the known increment: 0.00038/degree (6, 10).

Table II shows moreover the values of n_D^{20} calculated by expression (I). The calculated values show little deviation from the experimental one.

There remains little doubt that the relationship expressed by relation I indicates definite structural characteristics common to all the esters examined; any material which does not follow this rule must be structurally different or must contain appreciable amounts of structurally different material. This latter type of material would be represented by points falling below the line D_1H, and these must include the points situated on the HR branch of the curve shown on Fig. 1.

The new evidence strongly supports the views expressed previously and confers an enhanced interest on the hydrogenation value/refractivity relationship of naturally occurring unsaturated fatty acids.

It is very likely that similar relationships exist between the unsaturation values and the refractive indices of other esters of the unsaturated, naturally occurring fatty acids. These would include the glycerides or mixtures of glycerides.

It is interesting to note in this connection that empirical relationships between I.V. and refractive indices have been found for samples of oils of natural origin (5), but these are not to be confused with the relationship described by the present paper. The relationship for natural oils varies with the type of oil and is only applicable within narrow limits. The presence of variable proportions of saturated constituents accounts for this behavior.

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Lye-Dipping for the Removal of Objectionable Skin Color From Various Grades of Shelled Spanish Peanuts

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MUCH interest has been shown in the production of solvent-extracted meals and light-colored proteins from peanuts (2, 3) for nutritional and industrial applications. By their presence red peanut skins discolor meals, and the pigments in such skins impart a dark brown color to protein during processing. These color difficulties may be avoided by using white-skinned peanuts (5), but their availability is limited. Light-colored proteins may be produced by controlling the pH at which they are precipitated (7), and still lighter proteins (cream color) may be produced by treating the kernels with a dilute solution of sodium hydroxide for removal of objectionable skin color (3, 4).

Pilot-plant work on peanut kernels and oil and protein losses, using the sodium hydroxide treatment on 100-g. portions of kernels, have been reported by Burnett (3). The present paper reports on the application of the sodium hydroxide treatment, commonly referred to as lye dipping, to large amounts of the three commercial grades of shelled Spanish peanuts. Data are given on oil and protein losses of these kernels after treatment, and on the protein solubility of materials from various steps involved in the preparation of solvent-extracted meal from the original shelled kernels. Information is included on the color of proteins prepared from meals produced by solvent extraction of treated kernels.

Materials

Commercial U. S. No. 1 shelled Spanish peanuts were used in an initial series of tests of several dilute sodium hydroxide treatments. Upon completion of these tests another lot of U. S. No. 1 plus lots of U. S. No. 2 and oil mill stock shelled Spanish peanuts were evaluated using a common method of lye treatment. Spanish peanuts were used in both series since this type is the most widely distributed in this country.

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TABLE I

Grading Composition of the Shelled Spanish Peanuts

Fractions	Shelled Peanut Grades			Standards for U. S. No. 1 (9)
	U. S. No. 1	U. S. No. 2	Oil Mill Stock	
	%	%	%	%
Whole	94.6	29.0	37.3	92.9
Splits	2.7	62.2	20.6	2.0
Off color	1.9	0.9	0.8	1.25
Damaged	0	2.5	11.7	0.75
Unshelled	0.6	0	0	
Foreign matter	0.2	0	1.1	0.10
Shrivels	0	4.1	20.0	2.00
Pieces	0	1.3	8.5	0
Other varieties	0	0	0	1.0

The composition of the three commercial grades[2] of kernels used in the second series of tests in this investigation is shown in Table I, in which standard requirements for U. S. No. 1 grade are also given. The lipids and nitrogen contents of these shelled peanuts are given in Table II.

TABLE II

Analyses of Shelled Spanish Peanuts, Moisture-Free Basis

Material	Lipids	Nitrogen
	%	%
U. S. No. 1	52.49	4.96
U. S. No. 2	50.29	5.10
Oil mill stock	44.26	5.15

Method of Treatment

Batches of peanut kernels were placed in baskets made from 16- by 16-mesh galvanized wire-screen cloth backed by 4- by 4-mesh galvanized hardware cloth, which was supported by an iron frame (3).

[2] Commercially shelled Spanish peanuts are usually available in three grades, U. S. No. 1, U. S. No. 2, and oil mill stock grades. Standards (9) have been set up by the Department of Agriculture for U. S. No. 1 and No. 2 peanuts, which are essentially whole and split peanut kernels, respectively. Oil mill stock consists of small kernels, shrivels, pieces, and damaged kernels rejected during grading operations. The amounts of the three commercial grades of shelled peanuts produced by conventional shelling and drying operations from a ton of peanuts depends upon the original grade of the unshelled peanuts (Farmers Stock U. S. No. 1, 2, or 3) and the moisture content of the kernel. The yield from a ton of peanuts of U. S. No. 1 shelled Spanish peanuts ranges from 1,130 to 1,480 lb.; U. S. No. 2, 130 to 350 lb.; and oil mill stock 80 to 240 lb. (6).

The basket of kernels was dipped into an agitated solution of sodium hydroxide. The basket was then drained of the lye solution and the batch washed while in the basket successively in several tanks of water; the wash water also was agitated with a stirrer. The batch was then dried at 120° to 125°F. in a tray dryer, using circulating air.

Effects of Different Concentrations and Temperatures (U. S. No. 1 Peanut Kernels)

Experiments were made on three batches, each of approximately 120 lb. of kernels from U. S. No. 1 peanut kernels, using the following conditions of dipping and alkali concentrations:

a) Dipping for 5 minutes in 0.1% sodium hydroxide solution at 125°F.

b) Dipping for 5 minutes in 0.5% sodium hydroxide solution at room temperature.

c) Dipping for 1 minute in 0.5% sodium hydroxide solution at room temperature.

All treated peanut kernels were dried to approximately 8% moisture.

The lipids and protein losses after treatment are given in Table III. The wash solutions gave the only reliable data since the losses were so low. Lipids were determined in these wash solutions by an adaptation of an acid hydrolysis method (1). The losses reported here when compared with the figures reported by Burnett (3) show that the present lipid values are the lower. His figures varied between 0.21 and 0.36% on shelled peanuts for lipids and between 0.19 and 0.32% for protein. The protein losses on Batches 1 and 3 are practically the same as those observed by Burnett. In general, the lipids and protein losses, though not high in any instance, were smaller with cold dipping than with hot dipping.

Analyses of the dried skins of the kernels before and after alkali dipping showed a loss of lipids during dipping. Whereas the average lipids content of the skins before dipping baskets 1 and 2 was 17.79%, after undergoing the lye treatment and drying, the lipids content, m.f.b., was 10.25%. The skins have a much higher moisture content than the kernels.

TABLE III

Lipids and Protein Losses of U. S. No. 1 Peanut Kernels After Treatment

Batch Nos.	Peanut Wt.	Peanut Treatment					Losses			
		Tank No.	Time	Temp.	NaOH[a] or H_2O	H_2O Gained % Original Peanuts	Lipids		Protein[c] % Peanut Wt.	Nitrogen[d]
							Peanut Wt.	Lipids[b]		
	lb.		*min.*	°F.			%	%		%
1[e]	119.0	1	5	72	0.5% NaOH		0.02	0.04	0.10	0.33
		2	5	72	H_2O		.....	.....	0.05	0.16
		3	5	72	H_2O		.....	.....	0.01	0.04
		4	5	72	H_2O		.....	.....	0.01	0.02
					Totals	38.7			0.17	0.55
2[e]	119.0	1	5	125	0.1% NaOH		0.03	0.07	0.09	0.28
		2	5	72	H_2O		.....	.....	0.09	0.30
		3	5	72	H_2O		.....	.....	0.05	0.16
		4	5	72	H_2O		.....	.....	0.04	0.14
					Totals	44.9			0.27	0.88
3[e]	120.2	1	1	72	0.5% NaOH		0.02	0.05	0.04	0.12
		2	5	72	H_2O		.....	.....	0.09	0.30
		3	5	72	H_2O		.....	.....	0.03	0.10
		4	5	72	H_2O		.....	.....	0.03	0.09
					Totals	37.0			0.19	0.61

[a] Ratio of solution to kernels in all cases was approximately 15 to 1 in in NaOH dip and first washing and 11 to 1 in other washings.

[b] Per cent lipids $= \frac{\text{Lipids loss}}{\text{Lipids in original kernels}} \times 100.$

[c] Protein $= 6.25 \times$ nitrogen.

[d] Per cent nitrogen $= \frac{\text{Nitrogen loss}}{\text{Nitrogen in original kernels}} \times 100.$

[e] Fresh liquids were used in all dippings and two washings were carried on in Tank 4.

Preparation of proteins. The treated peanut kernels from Batches 1, 2, and 3 (Table III) were cracked and flaked and then solvent-extracted (8) with commercial hexane at an average temperature of 64°F. The solvent extracted meal was air-dried and then oven-dried at 125°F. for six hours. Table IV shows

TABLE IV

Analyses at Various Steps of Processing

Description (Batch 3)	Analyses			N Solution at pH 8
	H_2O	Lipids	Nitrogen	
	%	%	%	%
Original peanuts	6.54	46.09	4.95	92.8
Flaked, dipped peanuts before extraction	7.45	46.35	4.86	92.2
Solvent extracted flakes after oven drying at 125°F.	5.49	0.60	10.28	91.0

analyses of materials from Batch 3 at various steps of processing. Protein solubility of the extracted products, in every case over 90%, determined with sodium hydroxide solution at pH 8 and at room temperature, showed practically no change from the protein solubility of the unextracted treated kernels.

Proteins from the three batches of the alkali-dipped solvent-extracted meals were made in the pilot plant (2) at room temperature by peptizing meal at pH 7.5 with sodium hydroxide and precipitating protein from clarified solutions at pH 4.5 using sulfur dioxide, then drying in an air-circulating oven at 120°F. Visual examination showed the proteins to be a light cream color; no other evaluation of color is reported.

Results Using Three Commercial Grades

The significant result for the initial experiments (Table III) was that in general the lipids and protein losses were smaller with cold than with hot dipping. The cold dipping as applied by Burnett was used with the three commercial grades as follows:

Fifty-pound batches of shelled peanuts from U. S. No. 2 and oil mill stock grades and a 40-pound batch of U. S. No. 1 shelled peanuts were dipped for 5 minutes in a 0.5% sodium hydroxide solution at 84°F., washed 3 times with water at 80°F., and oven-dried at 120°F. to approximately 4.5% moisture. The lipids and protein losses are given in Table V.

Data show that protein and lipids losses increased

TABLE V

Lipids and Protein Losses of Shelled Peanuts After Treatment

Peanut Grades	U. S. No. 1	U. S. No. 2	Oil Mill Stock
Wt. of peanut kernels, lb.	40	50	50
Moisture, %	7.37	7.42	8.51
Temperature of NaOH solution, °F.	84	84	84
Times washed with H_2O	3	3	3
Temperature of wash water, °F.	80	80	80
Moisture absorbed, % original wt.	36.8	36.2	49.3
Dipping losses			
Lipids, % peanut weight			
NaOH	0.06	0.36	0.78
Wash	0.07	0.43	0.46
Total	0.13	0.79	1.24
Lipids, % lipids			
NaOH	0.12	0.78	1.94
Wash	0.14	0.92	1.14
Total	0.26	1.70	3.08
Protein, % peanut weight			
NaOH	0.16	0.20	0.81
Wash	0.37	0.86	1.18
Total	0.53	1.06	1.99
Protein, % protein			
NaOH	0.55	0.68	2.76
Wash	1.27	2.91	4.00
Total	1.82	3.59	6.76
Drying time, hrs.	23.83	23.58	23.83
Drying temperature, °F.	120	120	120
Moisture after drying, %	4.35	4.57	4.86

with lowering of grade. Lipids losses increased from 0.13 to 1.24% and protein losses increased from 0.53 to 1.99% by kernel weight. Lipids and protein losses were rather high on U. S. No. 2 and oil mill stock materials. A large portion of the losses was in the washings. Oil mill stock kernels absorbed more moisture than other grades of shelled peanuts.

To check the effect of damaged and shriveled peanut kernels, small amounts of 100% shrivels and 100% damaged kernels (visibly decayed) were hand-separated from the oil mill stock grade and treated with 0.5% sodium hydroxide solution.

Preparation and color of proteins. Portions of 500 to 1,000 g. of alkali-treated kernels from the various grades and the hand-separated lots were flaked and solvent-extracted for oil removal in large Soxhlets using commercial hexane and were air-dried.

Proteins were prepared in the laboratory from the solvent-extracted meals, using the same chemical conditions as those used in preparing proteins in the pilot plant; i.e., peptization at pH 7.5 using sodium hydroxide, precipitation at pH 4.5 using sulfur dioxide, and drying of the protein at 120°F. in an air circulating oven. The dried proteins prepared from meals produced from U. S. No. 1 and U. S. No. 2 kernels had a creamy color with no discernible differences between them. The protein prepared from meal produced from 100% damaged kernels had a brown color while that from the shrivels and oil mill stock grade gave an amber and tan color, respectively, showing that damaged kernels cause discoloration in protein. Analyses for extractable skin pigments by a colorimetric method being developed at the Southern Regional Research Laboratory indicated that the dark color of protein prepared from damaged kernels is not due to extractable skin pigments but rather to other constituents.

Use of the Treatment

These studies were part of extensive pilot-plant applications of Burnett's alkali treatment for objectionable peanut skin color removal at the Southern Regional Research Laboratory. Over eight tons of shelled peanuts have been so treated. Six tons of the treated kernels were extracted with commercial hexane in a continuous extraction pilot plant (10), and approximately two tons were solvent-extracted in the batch-extraction pilot plant (8). The meal products were used in a wide variety of industrial and nutritional investigations.

Summary

Experimental data have been obtained on the lipids and protein losses in the lye treatment of the various grades of shelled Spanish peanuts. It has been shown a) that lipid and protein losses on U. S. No. 1 shelled peanuts are lower for the cold than for the hot treatment though both are of a low level; b) that these losses in the cold treatment increased with the use of lower grade shelled peanuts, U. S. No. 2 and oil mill stock; c) that protein solubility of peanut kernels was negligibly affected by lye solution treatment, drying at 125°F., cold solvent extraction with hexane, air-drying, and oven-drying at 125°F.; and d) that damaged peanut kernels imparted color to protein.

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Determination of Moisture and Oil in Sesame Seed

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THOUGH sesame is one of the oldest cultivated oilseed crops, no systematic investigation of analytical methods for the determination of moisture and volatile matter and of the oil content of the seed has been reported. Recent interest in the domestic production of sesame has made it desirable that such methods be developed for use in agronomic investigations and to provide a basis for adoption of methods for future needs in marketing and processing.

Sesame seed are small and have tough seed coats. The high oil content makes it impossible to prepare samples of them for analysis by grinding in most mills. However, the Henry nut slicer[2] was found satisfactory for the purpose, provided the blade is changed as soon as it becomes dulled.

Samples and Their Preparation

The variety and origin of five lots of sesame seed used are given in Table I. The last four are those used as sources of sesame oil in previously reported investigations (2, 5).

TABLE I

Description of Sesame Seed

No.	Variety	Crop year	Where grown	Weight per 1,000 seeds
				grams
1	Unknown	1946	Kansas	2.645
2	SO-4	.....	Nicaragua	3.065
3	Nebraska 1025-3	1948	Nebraska	2.880
4	Clemson 4520	1948	South Carolina	2.765
5	Clemson 4522	1948	South Carolina	3.160

The seed were allowed to come to moisture equilibrium at a constant relative humidity of 65% and a temperature of 70°F. A portion of each lot was prepared for analysis with the Henry nut slicer under the same atmospheric conditions and allowed to equilibrate further for several days.

Determination of Moisture and Volatile Matter

Curves for the loss on drying vs. time were prepared from data obtained on these samples by heating 5-gram samples contained in the official A.O.C.S. moisture dishes at 101°C. and 130°C. in a forced-draft oven. The oven was equipped with a torsion balance sensitive to 5 mg. and a mechanism by which the samples could be weighed at selected time intervals without removing them from the oven. Handling of the samples and adjustment of the oven were exactly as described previously for investigations on the determination of moisture in peanuts (3) and cottonseed (4).

The curves for the loss during oven-drying for the Nicaraguan seed (No. 2) for temperatures of 101°C. and 130°C. are shown graphically in Figure 1. The

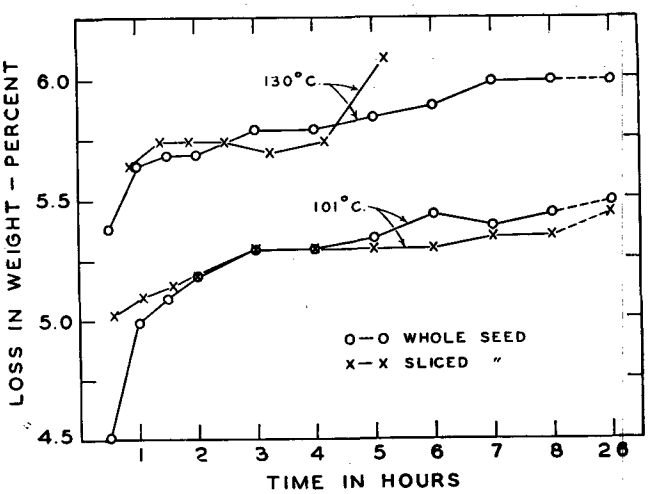

FIG. 1. Curves showing the loss in weight on oven-drying whole and sliced sesame seed.

individual points shown are averages of duplicate analyses generally agreeing within 0.1%. The curves for the other lots of the sesame seed were so similar to the ones shown that those in Figure 1 may be considered typical for all of the samples investigated.

In order to evaluate the degree of dehydration obtained under the specified drying conditions for different periods of heating, the residual moisture in the oven-dried samples was determined by the Karl Fischer volumetric method as described previously (4). The values obtained, together with those obtained by the oven-loss-in-weight methods, are shown in Table II.

Values obtained for residual moisture in samples dried at 101°C. for 4, 5, and 6 hours are essentially constant and show that complete removal of moisture was not accomplished under these conditions of heating a 5-gm. sample. These values are lower than those obtained by heating the samples at 130°C. for shorter periods. The sum of the values for residual moisture and for oven loss in weight for heating at

[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

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