ature must be carefully controlled. For anything approaching precision work the temperature must be controlled, or at least known, to a few hundredths of a degree. Any temperature may be used, provided an accurate index-temperature curve is at hand. Third, for precise results each operator should calibrate his own instrument and his own technique against a pure sample. Most people will read a refractometer consistently the same, but one person may read it consistently different from another. For this reason we have preferred not to regard the above reported indices as absolute values. It is clear, however, that once the calibrations are obtained, the refractive index provides an extremely simple and direct tool. The calibration reported above may be used for many purposes where the highest precision is not required.

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Valencia Orange-Seed Oil

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Processing residues from various crops have been utilized from time to time as minor sources of oils. In Europe oils have been produced from tomato and grape seeds; raisin-seed, apricot-kernel, walnut, and avocado oils are now being manufactured and sold in this country. Expansion in the citrus industry in recent years calls attention to citrus seeds as a potential though very minor oil source. It has been estimated that the seed oil corresponding to the 1940 pack of canned orange products would amount to about 264 tons. This figure would become only 700 tons if based on the total oranges harvested but not sold as fresh fruit (11). Except for a small plant in Florida producing annually about 45 tons of grapefruit-seed oil no commercial production of citrus-seed oils has been reported thus far (13).

The work reported here was undertaken in 1941 at the Western Regional Research Laboratory in Albany, California. It had as its purposes a brief examination of some aspects of the recovery and processing of orange-seed oil and also an examination of the oil in somewhat greater detail than had been previously reported (9).

Experimental material. The seeds used were drawn from a lot of air-dry Valencia orange seeds obtained from a Southern California processing plant in the fall of 1940. They had been stored several months in burlap bags and then transferred to steel drums. The drums had been filled by strata and each layer had been lightly sprinkled with chloroform to kill insects. A grab sample showed that about half the seeds were somewhat discolored with mold.

Whole seeds contained 70.8 per cent of kernels by weight. Skin and pulp fragments reduced the proportion of kernel in the bulk sample to 62 per cent. Uncleaned air-dry seeds contained 9.2 per cent moisture and 31 per cent oil. On the dry basis the oil content of uncleaned seeds was 34.2 per cent. Dry, clean kernels contained 55 per cent of oil.

Decortication. A coffee mill equipped with granulating burrs set far apart was used to crack the hulls and loosen the kernels. Although most of the kernels were merely split in half in the process, the coffee mill produced some kernel dust which tended to cling to the hulls. Air-dry seeds and seeds that had been oven-dried to a moisture content of 1.5 per cent were decorticated in this manner. Oven drying rendered the hulls more brittle but increased kernel breakage. Hulls separated from air-dry seeds by fanning and screening were less contaminated with kernel dust after decortication than those from oven-dried seeds. Table I shows the degree of separation achieved when oven-dried seeds were decorticated.

TABLE I

Separation Accomplished by Decorticating Valencia Orange Seeds

Fraction	Weight of fraction as per cent of weight of whole seeds	Oil content of fraction in per cent	Oil in fraction as per cent of total oil in seeds
Cleaned seeds before decortication	100	35.9	100
Hulls	41.3	15.2	17.6
Kernels	58.7	50.4	82.4

Optimum moisture content for hydraulic pressing. Tests on cooked kernel meal performed under comparable conditions showed the optimum moisture content to lie between 7.5 and 8.0 per cent on the moisture-free basis, which level is within the known optimum range for most seed meals. The relationship between oil yield and moisture content is shown in Figure 1.

Oil recovery by continuous pressing. Only a few tests of continuous pressing were made. They were sufficient, however, to indicate that orange seeds would present no unusual problems in this type of process. A midget Anderson Duo Expeller was used in the tests.

Preliminary trials showed that kernel meal did not press as well alone as when mixed with shredded hulls. Ground whole seeds appeared to press satisfactorily. Two test runs differing only in moisture content were made with a mixture comprised of 85 per cent kernel meal and 15 per cent shredded hulls. The meal was preheated to 90°-95° C. in a steam-jacketed kettle and the expeller tempering trough set to maintain a wall temperature of 110° C. throughout the runs. While

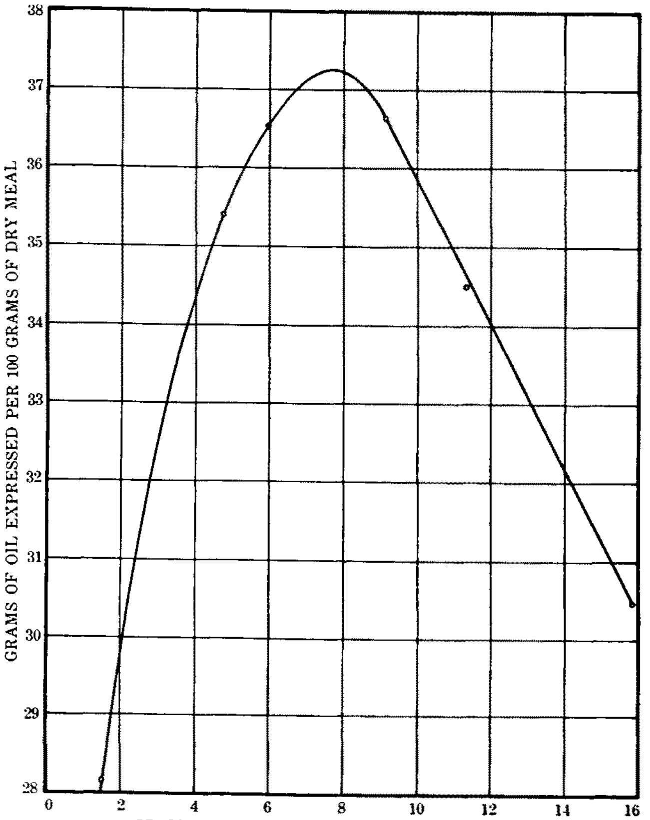

FIG. 1. Relation of moisture content of Valencia orange-seed meal to oil recovery by hydraulic expression.

the results of the tests given in Table II do not show what the optimum moisture content is for this type of oil recovery, they indicate that it is low.

TABLE II

Oil Yields by Continuous Pressing

Trial	Material	Per cent moisture	Per cent oil	
			Wet basis	Dry basis
1	Feed Cake	6.5 10.1	40.0 7.7	46.6 8.6
2	Feed Cake	4.9 7.4	44.3 6.1	46.6 6.6

This method of oil recovery is already being used on grapefruit seeds (13), and appears well suited to this type of material.

Solvent extraction. Like many other seed meats of high oil content orange-seed kernels cannot be rolled into firm flakes for solvent extraction. When this type of material is flaked or ground and then extracted the fine meal that is formed causes very poor drainage which in turn greatly increases the ratio of solvent required to meal extracted. Coarse grinding or thick flaking usually offers no advantage, since the contact time necessary to establish equilibrium is thus prolonged to the point that the process becomes impractical.

Figure 2 shows the entrainment curve for equilibrium mixtures of solvent, orange oil, and orange-kernel meal. The solvent used was petroleum ether (boiling range 26°-36° C.), and the temperature 0° C. The low temperature doubtless increased entrainment somewhat and probably accounted for the abrupt rise shown in the entrainment curve beginning at about 65 per cent oil. Although the conditions of the tests were not those to be expected in commercial practice, it is possible to illustrate the general behavior of the meal by making calculations based on the portion of the curve representing solutions containing less than 65 per cent oil.

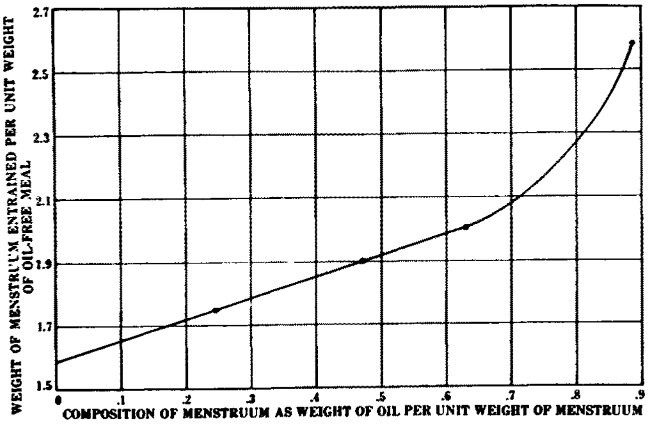

FIG. 2. Petroleum ether-oil entrainment in Valencia orange-seed kernel meal.

The portion of the curve dealing with menstruum containing more than 65 per cent oil was not used for calculation of quantities shown in Table III.

In Table III figures are given for two solvent extraction processes applied to orange-seed-kernel meal.

TABLE III

Countercurrent Solvent Extraction

	Batch system	Continuous system
Oil in fresh kernel meal, per cent	45.8	45.8
Fresh meal (feed), pounds	218	218
Oil in fresh meal, pounds	100	100
Fresh solvent (feed), pounds	273.4	484.4
Extract (product menstruum), pounds	185	406
Oil in extract, per cent	65	30
Oil in extract, pounds	99.4	99.4
Solvent in extract, pounds	85.6	306.6
Entrainment (menstruum leaving system adhering to exhausted solids), pounds	188.4	188.4
Solvent in entrained menstruum, pounds	187.8	187.8
Solvent-free exhausted meal, pounds	118.8	118.8
Oil in extracted meal, per cent	0.5	0.5
Oil in extracted meal, pounds	0.6	0.6
Number of percolators required	6	....
Number of equilibrium lengths required[1]	....	6

[1] Ravenscroft defines equilibrium length as a "section of the extractor length such that the wash menstruum leaving has the same concentration as the entrained menstruum leaving with the sludge." It is thus analogous to the height equivalent to a theoretical plate in fractional distillation in packed columns.

The values in the table were calculated by Ravenscroft's graphical method (15). In each instance the concentration of oil desired in the product menstruum and the efficiency of oil recovery to be attained were arbitrarily selected. These arbitrary values, together with the oil content of the original meal and the entrainment curve, formed the basis from which the other quantities were calculated. Both examples shown in the table represent countercurrent extraction, one by the batch system, the other by a continuous system such as is used in screw-feed tubular extractors.

Compared upon the basis of equal quantities of oil recovered, orange-seed meal appears to exhibit about the same solvent requirements as other high-oil-content seed meals.

Refining, bleaching, and deodorizing. When alkali-refined by the A. O. C. S. method for hydraulic-pressed cottonseed oil (1), a sample of hydraulic-pressed orange-seed oil, having a free fatty acid content of 5.9 per cent expressed as oleic acid, gave a refining loss of 15.5 per cent. The refined oil was bleached with 2 per cent of acid-activated bleaching earth (Neutrol No. 5), and 0.25 per cent of bleaching carbon (Darco S-51), and then vacuum steam distilled. The refined oil had lost most of the bitterness caused by the presence of isolimonin in the crude oil (3) and the deodorized product was quite bland and pleasant tasting. The colors for 5¼-inch columns in Lovibond units were: crude 50 yellow, 29 red; refined 50 yellow, 4.1 red; refined and bleached 35 yellow, 2.0 red; refined, bleached, and deodorized 35 yellow, 2.7 red.

Characteristics and composition of the oil. The analyses reported here were performed on a sample of hydraulic-pressed oil that contained 5.9 per cent of free fatty acid expressed as oleic. A. O. C. S. methods (1) were employed except as otherwise indicated. Unsaponifiable-free mixed acids were used as starting material for the determination of the various acids.

TABLE IV

Characteristics of Valencia Orange Seed Oil

Specific gravity, 25° C./25° C.	0.9153
Refractive index 25° C.	1.4686
Iodine value (Wijs)	101.7
Saponification value	197.5
Unsaponifiable matter, per cent	0.95
Titer of fatty acids, ° C.	35.3
I.V. unsaponifiable-free acids	105.4

Saturated acids. Solid and liquid acids were separated by the modified Twitchell method. A corrected value for the saturated acids was obtained by subtracting from the per cent of impure saturated acids the figure given by the expression:

$$\frac{\text{Iodine value of impure saturated acids} \times \text{Per cent of impure saturated acids}}{\text{Iodine value of liquid acids}}$$

described by Baughman and Jamieson (2). Duplicate determinations gave the following corrected values for the proportion of solid saturated acids in unsaponifiable-free mixed acids:

Determination No. 1	26.3%
Determination No. 2	26.3%

Determination of the individual saturated acids was made by analyzing fractions of the methyl esters of the solid acids partitioned by vacuum distillation. The solid acids used for this purpose were prepared by the same method employed in the determination of total saturated acids.

Upon esterification the weight of methyl esters recovered amounted to 99.2 per cent of the theoretical yield calculated from the weight of the acids taken and their apparent equivalent weight. The esters were distilled from a 150 ml. Willstäter bulb (5) under a pressure of 1-2 mm. Thirteen distillate fractions and a residue totaling 96.3 grams were recovered from 96.7 grams of original esters. The percentages of the various saturated acids present in the mixtures were calculated from the equivalent weights and iodine values according to the method given by Hilditch (6).

The results of the saturated acid determinations, based upon the total weight of their esters recovered from the distillation and the percentage of saturated acids in the unsaponifiable-free mixed acids, are given in Table V.

TABLE V

Composition of Saturated Acids in Valencia Orange-Seed Oil

Acid	Acids as per cent of total saturated acids	Acids as per cent of mixed acids
Palmitic	78.5	20.7
Stearic	17.9	4.7
Arachidic	3.6	0.9
Total	99.9	26.3

Unsaturated acids. Qualitative tests performed by treating the unsaponifiable-free mixed acids with bromine indicated the presence of linolenic acid. When attempts were made to determine the composition of the unsaturated acids by the F.A.C. thiocyanogen procedure it was found that the quantity of linolenic acid present was too small for satisfactory estimation by that method. Results obtained by the thiocyanogen method in its present form are well known to be subject to uncertainty (7), (16), (17). This is especially true when all three of the common unsaturated acids are present in the mixture being analyzed. In the present instance variations between thiocyanogen values determined separately were in proportionate agreement with those reported by other workers (8), (10), (16), but even these small differences produced significant differences in the estimated proportion of linolenic acid and corresponding but less important variations in the values for the other two unsaturated acids. The reason for this situation is evident from the following equations which relate composition to thiocyanogen value (0.2 N solution), iodine value and percentage of saturated acids.

$$\text{Per cent oleic acid} = 1.6054\ \text{TV} - 1.2273\ \text{IV} + .6678\ (100 - \%\ \text{satd. acids})$$

$$\text{Per cent linoleic acid} = 1.3557\ \text{IV} - 3.1879\ \text{TV} + 1.6315\ (100 - \%\ \text{satd. acids})$$

$$\text{Per cent linolenic acid} = 1.5824\ \text{TV} - 0.1285\ \text{IV} - 1.2993\ (100 - \%\ \text{satd. acids})$$

In the foregoing equations TV and IV signify respectively the thiocyanogen and iodine values of the mixed acids. The thiocyanogen values of pure oleic, linoleic and linolenic acid used in deriving the equations were respectively 89.4, 96.8 and 167.5 (16), and the corresponding iodine values were 89.9, 181.0 and 273.5.

The alternative method of analysis chosen was partition of the bromides of the unsaturated acids by the Eibner and Muggenthaler procedure (12) followed by analysis to determine the bromine content of each of the separated fractions.

For the purpose of calculation it was assumed that the crystalline bromides insoluble in cold ether were comprised of linolenic hexabromide and linoleic tetrabromide only, while those insoluble in cold petroleum ether were made up of only linoleic tetrabromide and oleic dibromide, and that further quantities of these last two bromides remained in solution in the cold petroleum ether together with the saturated acids. Since the saturated acids were not removed from the unsaponifiable-free mixed acids before bromination it was necessary to use the calculated weight of the saturated acids present in each sample in estimating the weight and bromine content of the unsaturated acid bromides soluble in cold petroleum ether.

It has long been known that linolenic hexabromide and linoleic tetrabromide are incompletely precipitated from their cold ether and cold petroleum ether solutions respectively, and hence analyses based on the weights of fractions separated in this way are sub-

TABLE VI

Bromide Partition of Unsaturated Acids

Bromides insoluble in cold ether				Bromides insoluble in cold petroleum ether			Bromides soluble in cold petroleum ether			Totals of individual unsaturated acids as per cent of unsaponifiable-free mixed acids		
Sample	Per cent Br in precipitate	Acids as per cent of mixed acids		Per cent Br in precipitate	Acids as per cent of mixed acids		Per cent Br in Bromides	Acids as per cent of mixed acids		Linolenic	Linoleic	Oleic
		Linolenic	Linoleic		Linoleic	Oleic		Linoleic	Oleic			
1	60.43	.63	.31[1]							.63		
2	61.08	.61	.23[1]							.61		
3	61.17	.58	.20	53.64	17.21	0.0	43.47	18.58	33.39	.58	35.99	33.39
				53.63	17.21	0.0	43.21	17.92	34.85	.58	35.33	34.85
4	66.01	.51	.00	52.68	18.19	0.89	42.89	16.83	35.37	.51	35.02	36.26
				51.26	16.63	3.02	43.33	17.92	34.14	.51	34.55	36.89
								Averages		0.58	35.22	35.35
				Averages adjusted to total 100 — % saturated acids						0.6	36.5	36.6

[1] Remainder of linoleic acid not determined. These values not included in average.
Hexabromostearic acid contains 63.26% Br.
Tetrabromostearic acid contains 53.27% Br.
Dibromostearic acid contains 36.14% Br.

ject to error. If, however, a bromine analysis is performed on each fraction, and calculations are made in the manner that has been indicated the solubility of linoleic tetrabromide introduces no error. In fact, separation of the crystalline tetrabromide could be omitted from the analysis without effect upon the results. Of course, the solubility of linolenic acid hexabromide still remains as a source of error, and as a consequence the estimated quantity of linolenic acid will be less than is actually present. Shinowara and Brown (18) reported that about 34 per cent of linolenic acid precipitated as bromide. This ratio probably varies with differing circumstances, however, and corrections based upon it would be of doubtful value. The error will be reflected as an increase in the apparent quantity of linoleic acid and a decrease in the apparent quantity of oleic acid in the sample. However, the absolute magnitudes of these errors become less as the quantity of linolenic acid present diminishes, and in view of the very small proportion of that acid in the sample it is considered unlikely that inaccuracies from this significantly affected the results for oleic and linoleic acids in this particular case.

As previously indicated, bromination was conducted according to the method of Eibner and Muggenthaler as described by Lewkowitsch (12). The hexabromide crystals were filtered from the ether solution with a sintered glass crucible. The crucible was prechilled and kept cold during the filtration. The precipitate was washed five times with 2.5 cc. of cold dry ether per gram of acid sample. The hexabromide mother liquors and washes were treated with sodium thiosulfate solution to remove excess bromine after which they were washed with water, dried with sodium sulfate, and filtered. Ether was evaporated from the filtrate and sufficient petroleum ether was added to the residue to effect solution. The solutions were cooled, allowed to stand overnight and then filtered on sintered glass to separate the crystalline precipitates. The bulk of the petroleum ether was removed from the mother liquor by evaporation. All fractions were dried by heating at 80°-85° C. for two hours before cooling and weighing.

Melts obtained by fusing the bromides with alkali hydroxide and peroxide (19) were treated with sodium bisulfite and sulfuric acid to reduce oxyhalogen acids (14), after which silver bromide was precipitated in the usual manner. The results of these analyses are summarized in Table VI.

The comparison of iodine values shown below gives an indication of the overall accuracy achieved in the analysis.

IODINE VALUE OF UNSAPONIFIABLE-FREE MIXED ACIDS

Found by direct analysis	105.4
Found by calculation from estimated composition	100.6

Summary

California Valencia orange seeds contain a fairly high percentage of oil, the recovery of which by conventional methods of pressing appears to present no unusual problems. When refined, bleached, and deodorized the oil would be quite acceptable as a food oil. It contains a very small proportion of linolenic acid but is otherwise similar to other seed oils of like iodine value.

Acknowledgment

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