Grape Fruit Seed Oil

Contribution from The Oil, Fat and Wax Laboratory, Bureau of Chemistry and Soils, United States Department of Agriculture

By G. S. JAMIESON, W. F. BAUGHMAN and S. I. GERTLER

IN RECENT years the commercial canning of grape fruit has become of some importance, both in Florida and Porto Rico, and it is desirable that use be made of the quantities of seed which accumulate at the canneries. As the air dried seed usually contain thirty per cent or more of oil, the possibility of the utilization of the seed for the oil has attracted attention, but no information was available as to the character of the oil, or the purposes for which it might be used if prepared on a commercial scale. Some time ago Ralph Polk of the Polk Company, Haines City, Florida, had a quantity of the seed pressed by an Anderson oil expeller and we obtained a gallon sample of the oil for examination. When the investigation was nearly completed, we were informed by J. L. Hutton of the Oil Processes, Incorporated, Harrison, New Jersey, that they had made some experiments on the solvent extraction of the oil from Florida cannery seed and as we were interested in comparing this oil with the expressed product, a sample together with some of the extracted seed was sent to us.

Grape fruit seed and the oil, like those from other citrus fruit, have a bitter taste, and apparently no one has yet devised a feasible method for the removal of this taste from the oils, consequently, it would appear that the only market for this oil would be found among the soap manufacturers. R. S. McKinney, of this laboratory, has shown recently that a medium-hard, light-colored soap can readily be prepared by saponifying the oil with caustic soda. After the cakes had air-dried for five days, the soap was found to lather very readily.

From the analyses given below, it will be observed that the press cake and extracted meal have considerable value as feed, or as fertilizing material. Owing to the very bitter taste, however, cattle in this country will not eat the cake and meal, although the seed are said to be eaten by animals in the vicinity of the cannery in Porto Rico. In order to utilize them for feeding, the bitter taste must be considerably reduced by mixing the products with other suitable materials.

Characteristics of the Oil

THE chemical and physical characteristics are given in Table I for both the expressed and solvent extracted oils. The percentages of saturated and unsaturated acids were determined by the lead-salt ether method (J. Assoc. Offic. Agri. Chemists 1928, 11, 303), and corrections were made for the small quantity of unsaturated acids that is precipitated and weighed with the saturated acid fraction. The percentage of unsaturated acids has also been corrected for the unsaponifiable matter that remains with the unsaturated fraction. From the iodine number, it will be observed that the oil belongs to the semi-drying class, particularly so in view of the large quantity of linolic acid present as glyceride in the oil.

A sample of the oil extracted by the Oil Processes, Incorporated, was examined by H. P. Trevithick, Bureau of Chemistry of the New York Produce Exchange, with the following results: Specific gravity at 15.5°—0.9207; iodine number (Wijs)—103.3; saponification value—194.8; unsaponifiable matter—0.5; acid value—4.0, titer—36.1°; and refining loss (using 7.1 per cent of 16° Baumé caustic soda), 7.1 percent. The refined oil had a color of 90 yellow, 3 red, and 2 blue (Lovibond glasses).

For comparison, the color of the crude oils (depth of column 5.25 inches) was measured, with the following results: Expressed oil 35 y and 6.6 r, extracted oil 35 y and 6.9 r. The expressed oil was a clear, bright yellow, whereas the extracted oil was yellow with a greenish tint and when viewed by reflected light in a bottle, had a strong purple fluorescence.

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 155.2. This value was used in the calculation of the oleic and linolic acids present in the oil, with the following results:

	Unsaturated Acids	In Oil	As Glycerides
	%	%	%
Oleic acid	28.70	19.66	20.5
Linolic "	71.30	48.84	51.0

TABLE I

Chemical and Physical Characteristics.

	Expressed Oil	Extracted Oil
Specific gravity 25/25°	0.9170	—
Refractive Index at 25°	1.4700	1.4596
Acid value	2.5	3.3
Iodine number (Hanus)	106.3	100.4
Saponification value	194.1	194.3
Acetyl value	7.7	—
Unsaponifiable matter %	0.7	0.7
Saturated acids (corrected) %	26.60	27.63
Unsaturated acids (corrected) %	68.50	67.77
Iodine number of unsaturated acids	146.2	—

Saturated Acids

THE saturated acids which were separated from the oil by the lead-salt ether procedure were esterified with absolute methyl alcohol, dry hydrogen chloride gas being used (*Jour. Amer. Chem. Soc.* 1920, 42, 1200), and the resulting esters were fractionally distilled under diminished pressure. The data for the distillations are given in Table II. The preliminary distillation was made from a 500 cc. Claissen flask, giving five fractions and a residue, which were refractionated in the order indicated in the table from a 150 cc. Ladenburg fractionation flask.

TABLE II

103.2 grams of esters taken for distillation.

Preliminary distillation under 2 mm. pressure—

	Fraction	Temperature °C	Weight Grams
	A	160-5	14.80
	B	166-8	22.30
	C	169-70	27.65
	D	180-190	22.00
	E	191-200	19.20
	Residue		2.15
Final distillation under 2 mm. pressure—			
A + B added	1	160-5	10.30
C added	2	166-70	22.00
	3	172-4	21.95
D + E added	4	175-8	23.30
Res. added	5	180-8	17.20
	6	190-200	12.10
	Residue		1.29

TABLE III

Results of Analyses of Fractions From Distillation of Methyl Esters.

Fractions	Iodine Nos.	Sapon. Values	Esters Unsat. acids %	Mean Mol. Wt. of Esters of Sat. Acids	Palmitic Acid Grams	Stearic Acid Grams	Lignoceric acid Grams
1...	1.28	206.3	1.58	271.6	9.182	0.448	—
2...	1.65	204.3	1.20	274.5	17.462	3.081	—
3...	1.84	203.9	1.77	274.8	17.096	3.353	—
4...	2.61	203.7	2.46	275.0	16.746	4.824	—
5...	4.48	200.5	4.35	279.2	10.514	5.144	—
6...	9.63	189.6	8.52	295.9	0.486	9.985	—
Residue						0.150	0.600
Total					71.486	26.995	0.600

The iodine numbers and the saponification values of these six fractions were determined, and are recorded in Table III. The small final residue was saponified with alcoholic potash, and the fatty acids were liberated with hydrochloric acid, collected, dried and subjected to fractional crystallization from alcohol. Finally, 0.150 grams of stearic acid melting at 68-69°, and 0.600 grams of lignoceric acid melting at 80° were obtained. In addition to these acids, the residue as usual contained some decomposition products and unsaturated esters.

The mean molecular weights given in the table indicate what acids may be present in each fraction. In order to prove that these indications are correct, the free fatty acids were recovered from portions of several of the ester fractions in the usual manner after saponification with alcohol potash, and submitted to fractional crystallization from alcohol. Their identity was established by the melting points and by observing whether or not they were lowered when the substances were mixed with equal quantities of the respective acids, the purity of which had been established by analysis

The deductions drawn from the molecular weights of the saturated acids were confirmed as follows: Fractional crystallization of the acids from fraction 1, in which 10 crops of crystals were obtained, gave no evidence of the presence of myristic acid, which fact was confirmed by the mean molecular weight of the saturated acids. Palmitic acid, $C_{16}H_{32}O_2$, melting at 63° was isolated in quantity from fractions 1, 2, 4 and 5; stearic acid, $C_{18}H_{36}O_2$, melting at 68-9° was separated from fractions 2, 5 and 6; lignoceric acid, $C_{24}H_{48}O_2$, melting at 80° was found only in the residue.

The quantities of saturated acids in the fractions were calculated from the mean molecular weight of their esters and the theoretical molecular weight of the two esters in each fraction, the results of which are given in Table III.

In Table IV the percentage composition of the saturated acids is given in column 2. These values calculated to the basis of the original oil are given in column 3. In column 4, are the equivalent percentages of the glycerides.

TABLE IV

Grape Fruit Seed Oil Saturated Acids.

Acids	Grams	Percent	Acids in Oil Percent	Glycerides in Oil Percent
Palmitic	71.486	72.15	19.19	20.1
Stearic	26.995	27.25	7.25	7.6
Lignoceric	.600	0.60	0.16	.1
			26.60	27.8

A sample of the extracted grape fruit seed was examined by G. L. Bidwell and M. R. Coe, Cattle Food Unit, Food, Drug and Insecticide Administration, with the following results:

	Percent
Moisture	9.7
Ash	3.8
Ether Extract	4.3
Protein	21.4
Crude fiber	22.0
Nitrogen Free Extract	38.8

Summary

THE characteristics of both the expressed and extracted grapefruit seed oils have been determined. The samples of this semi-drying oil (iodine numbers 100-106) contained from 26.6 to 27.6 percent of saturated acids. Upon saponification with caustic soda, the oil gave a medium-hard soap, which after air-drying for five days was found to lather freely.

The extracted seed were found to contain 21.4 percent of protein, 38.8 percent of nitrogen free extract, and 22 percent of crude fiber, a composition which indicates considerable feeding value, but owing to the bitter taste it would be necessary to add other feeding materials that would render the mixture palatable to stock.

The composition of the expressed oil has been determined with the following results:

Glycerides of	Percent
Oleic acid	20.5
Linolic acid	51.0
Palmitic acid	20.1
Stearic acid	7.6
Lignoceric acid	0.1
Unsaponifiable acid	0.7

South African Whaling

THERE are two companies in Durban, Union of South Africa, engaged in whaling—The Union Whaling Co., Ltd., and The Premier Whaling Co., Ltd. Together they employ about 510 seamen and 15 whalers. The total number of whales taken during the 1928 and 1929 seasons were respectively 1,194 and 1,797. Of the sperm species 541 were taken in 1928 and 841 in 1929. There were of fin whales taken, 429 and 637 respectively for the two seasons. Other varieties included small numbers of hump, blue and sei whales.

Production of Whale Products.

1928	Long tons	Value
Whale oil	8,552	$992,570
Fertilizer	4,454	161.396
TOTAL VALUE		$1,153,966
1929		
Whale oil	12,111	$1,275,733
Fertilizer	6,468	246,045
TOTAL VALUE		$1,521,778

In 1928, the sperm oil production of Durban was exported to Europe, and about one-half of the whale fertilizer was shipped to the United States. In 1929 nearly all the sperm oil, and about one-half of the whale oil and guano was exported, all the oil being shipped to Europe. The whale oil is produced in two grades; sperm oil, and whale or train oil obtained from the other species of whales. The entire output of sperm oil and whale oil from Durban is usually disposed of in the United Kingdom and Europe at very fair prices.

During 1929, prices dropped considerably, and towards the end of the year, £16 ($77.86) per long ton, F.O.B. Durban, in drums of 90 gallons, for sperm oil was quoted, with a correspondingly low quotation for whale oil.

Exports of Whale oil—1928.
Union of South Africa.

	Gallons	Value
United Kingdom	554,958	$213,283
Holland	1,647,688	841,836
France	18,147	5,347
Germany	2,310,294	1,210,994
Portuguese East Africa	1,315	987
Total	4,542,402	$2,272,447

The exports of whale oil and whale fertilizer through the Port of Durban approximate half of the total exports of the Union.

Consular Report from Durban

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An extensive advertising campaign is being launched by the Marine Products Corporation of Seattle for its new salmon oil and salmon meal products, made from fish waste, heads, scales, and other discarded portions of salmon at canneries in Alaska and Seattle, for the use of livestock. Poultry, cattle and swine are given the new products from the waste, as a part of corrective and health-giving diets for livestock.

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The Kansas State Grain Inspection Department is doubling the capacity of its protein laboratory at Hutchinson, Kansas. Additional new equipment manufactured by the Laboratory Construction Company of Kansas City, Missouri, is being installed and upon completion the State laboratory at Hutchinson will be the largest protein laboratory in the World. The Laboratory Construction Company has just finished manufacturing a large capacity of nitrogen apparatus and laboratory equipment tables for the Omaha Grain Exchange at Omaha, Nebraska and complete nitrogen equipment for the Sao Paulo, Brazil laboratory of the Corn Products Refining Company of Chicago.