Investigation of Barcelona and Du Chilly Filbert Nuts.*

I. Chemical Study of Barcelona and Du Chilly Filbert Nuts and Oils

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CULTIVATED filberts are closely related to the wild hazel nut and were brought to the United States from Europe. All cultivated varieties are of the species *Corylus avellona.* In this country they are grown in a very limited area which comprises the Willamette Valley in Oregon and smaller area around Vancouver in Southern Washington. Filbert growing is a relatively new agricultural enterprise and has expanded rapidly in the past ten years. Present production is 7,000 to 8,000 tons annually, about 85% from Oregon and 15% from Washington (12).

Data on the composition of filbert oil are few and not in agreement (1, 10, 11, 13). Numerous reports on the common chemical and physical characteristics are available for European filbert nuts, but those which have been obtained in the examination of domestic oils are indeed few. No investigations of the oils from Barcelona and Du Chilly filberts from the Pacific have been made. These two varieties were introduced from Europe in 1885 by Felix Gillette and now are grown commercially in the Pacific Northwest.

This study was undertaken in the hope that the data derived from the investigation may provide accurate information on the chemical composition of Oregon-grown filberts.

Composition of the Filbert Nut

The samples used in this study were from the 1946 crop supplied by the Northwest Nut Growers Association. The shells were ground into a powder with a Wiley mill, and the nut kernels were ground by a meat grinder. The procedures used were those listed as official by the Association of Official Agricultural Chemists Manual (2).

The compositions of Barcelona and Du Chilly filberts are given in Tables I and II. For purposes of comparison, the corresponding data for European filberts from the literature are also included in the tables.

Characteristics of Filbert Oil

The filbert oil used in this study of its characteristics and fatty acid analyses was obtained from the ground nut by cold expression with a Carver hydraulic press and by solvent extraction with petroleum ether (Skellysolve F). The characteristics of the filbert oils which were determined according to A.O.A.C. methods and the estimation of the vitamins (4) are shown in Table III. Values obtained from the literature are also included.

TABLE I

Chemical Composition of Barcelona and Du Chilly Filbert Nut Shells

	Barcelona Filbert	Du Chilly Filbert	European Filbert (Literature)
	%	%	%
Moisture	7.08	7.81	
Total ash	0.997	1.297	0.82(9)
Hot water insoluble ash	0.416	0.645	
Hot water soluble ash	0.581	0.652	
Alkalinity of insoluble ash	0.87*	1.36*	
Alkalinity of soluble ash	0.34*	0.92*	
Crude protein, N × 6.25	1.35	1.70	1.19(9)
Ether extract	nil	nil	
Reducing sugars	0.98	1.15	
Sucrose	0.20	0.75	
Starch	nil	nil	
Pentosans	27.0	25.3	24.1, 28.4 (6, 9)
Crude fiber	67.8	67.7	

* The alkalinity of ash was calculated and expressed in terms of number of ml. of normal acid per 100 grams of moisture free sample.

The Fatty Acids of Filbert Oil

As a preliminary step in determining the fatty acid composition of filbert oil it was first necessary to convert the glycerides into fatty acids, separate these acids into saturated and unsaturated fractions, convert each fraction into methyl esters, and distill these esters. This was accomplished as follows: The oil was saponified with alcoholic potassium hydroxide. The soaps were extracted continuously with ether to remove the unsaponifiable matter. They were then converted into the free fatty acids by warming with dilute sulfuric acid. When the acids were completely liberated, they were removed by extraction with ether and dried under reduced pressure at 50°C. The acids were then separated into "solid" and "liquid" fatty acids by a modified Twitchell method (6). Each group of acids was converted into the methyl ester.

The methyl esters of the liquid fatty acids of filbert oil were distilled through a 48-inch glass helix

TABLE II

Chemical Composition of Barcelona and Du Chilly Filbert Nut Kernels

	Barcelona Filbert	Du Chilly Filbert	European Filbert (Literature)
	%	%	%
Moisture	3.43	3.58	
Total ash	2.53	2.69	2.7(13)
Hot water insoluble ash	1.09	1.50	
Hot water soluble ash	1.44	1.19	
Alkalinity of insoluble ash	2.02*	1.90*	
Alkalinity of soluble ash	0.78*	1.29*	
Crude protein, N × 6.25	17.1	15.6	12.7(13)
Ether extract	65.5	63.1	60.0(13)
Reducing sugars	0.12	0.18	
Sucrose	4.79	5.57	14.3(13)
Starch	3.54	4.16	(Carbohydrate)
Crude fiber	2.09	1.94	3.4(13)

* The alkalinity of ash was calculated and expressed in terms of number of ml. of normal acid per 100 grams of moisture free sample.

* The data in this paper are taken from a thesis presented by Sheng Chung Fang to the Faculty of the Graduate School of Oregon State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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TABLE III

Physical and Chemical Constants of Filbert Nut Oils Obtained by Expression and by Extraction

	Barcelona		Du Chilly		European **
	Expression	Extraction	Expression	Extraction	
Specific gravity 25°/4°	0.9102-0.9120[25]†	0.9114	0.9102-0.9123[25]	0.9116	0.914-0.917 (15.5°C.)
Refractive index 20°C.	1.4694-1.4700[25]	1.4698	1.4698-1.4702[25]	1.4700	1.4698
Viscosity 25°C. centipoise	59.1	53.6	58.2	53.0	.....
Optical rotation	Inactive	Inactive	Inactive	Inactive	.....
Titer test, °C.	8.5	.....	7.7	.....	.....
Iodine number (Hanus)	93.0- 96.7[25]	95.4	95.2- 98.5[25]	97.5	83-90
Thiocyanogen number	79.67	79.54	79.93	79.97	82.09
Saponification number	188.1-193.1[25]	186.8	188.1-194.2[25]	187.2	187-197
Soluble acid, %	Nil	.....	Nil	.....	.....
Insoluble acid, %	94.74	.....	95.31	.....	94.9-95.5
Saturated acid, %	5.5	.....	4.1	.....	4.9
Unsaturated acid, %	89.7	.....	90.7	.....	91.0
Unsaponifiable matter, %	0.40	.....	0.35	.....	0.35-0.55
Free fatty acid (oleic), %	0.12	0.44	0.10	0.43	0.15
Acetyl value	6.3	.....	3.7	.....	3.2
Carotene, γ/1 gm.	0.32-0.47[2]	0.32-0.45[6]	0.51-0.55[3]	0.34-0.53[6]	.....
Vitamin A	None	None	None	None	.....
Hexabromide test	Negative	.....	Negative	.....	Negative
Oleic acid glycerides, %*	76.83	74.87	72.72	72.50	91.98
Linoleic acid glycerides, %*	15.60	17.85	19.98	20.24	3.00
Saturated acid glycerides, %	7.17	6.88	6.95	6.91	5.10

* Calculated from iodine and thiocyanogen values. ** From literature (1, 3, 10, 11).
† Superscripts indicate the number of samples analyzed.

packed column with a partial take-off distilling head. For the solid acid, a smaller column was used. Distillations were performed at 2 mm. Hg. pressure. The iodine value, thiocyanogen value, and saponification equivalent determinations were made on each fraction. From these data the fatty acid compositions of both Barcelona and Du Chilly filbert oils were calculated. The distillation data are given in Tables IV and V. The fatty acid composition of these two oils are summarized in Table VI. The corresponding data for European filberts from the literature are also included.

Calculations

The data revealed that the iodine and thiocyanogen values are different in both solid and liquid fractions. Therefore it is believed that both monoethenoid and diethenoid acids must be present in each fraction. It is assumed that any one distillation fraction contains not more than four esters. In the case of the liquid acid fraction palmitic acid is the only saturated acid

TABLE IV

Complete Fractionation Data for the Component Fatty Acids of Barcelona Filbert Oil

In this analysis, the esters of the "solid" and of the "liquid" acids were distilled through the electrically heated and glass helix packed columns. The original oil had saponification number 188.1, iodine number 93.2, and thiocyanogen number 79.67, the mixed acids yield 35.75% "solid" and 64.25% "liquid" acids.

A. Fractional Distillation of Methyl Esters of the "Solid" Acids
(66.98 grams distilled through helix packed column)

No.	Grams	Temperature of			S. E.	I. V.	SCN	Calculated Weight of Ester Fraction					
								Saturated			Unsaturated		
		Still °C.	Column °C.	Head °C.				C_{16}	C_{18}	C_{20}	Oleic	Linoleic	C_{20}
BS1	2.00	202-207	145-155	135-140	283.3	48.45	40.57	0.58	0.39	.....	0.92	0.11	.....
BS2	3.34	207-208	145-149	140-145	293.3	67.98	59.35	0.34	0.60	.....	2.16	0.24	.....
BS3	6.41	208-208	159-163	145-150	296.5	79.11	69.87	.....	0.95	0.09	4.82	0.55	.....
BS4	13.00	208-209	163-167	150-152	297.5	83.72	74.06	.....	1.02	0.54	10.34	1.18	.....
BS5	21.93	209-215	167-167	152-153	301.9	88.53	78.33	.....	.....	1.58	14.25	1.62	4.46
BS6	13.86	215-215	167-167	153-154	302.3	90.57	80.68	.....	.....	.....	9.37	1.06	3.43
BS7	3.77	215-220	167-196	154-155	302.8	90.17	80.52	.....	.....	.....	2.50	0.28	0.99
BS8	2.67	Residue	.....	.....	305.1	76.30	57.06	.....	.....	0.44	1.58	0.18	0.47
	66.98	Weight of Me esters, gm.						0.92	2.96	2.65	45.94	5.22	9.35
		Me esters %						1.37	4.42	3.96	68.57	7.79	13.96

B. Fractional Distillation of Methyl Esters of the "Liquid" Acids
(128.72 grams distilled through helix packed column)

No.	Grams	Temperature of			S. E.	I. V.	SCN	Calculated Weight of Ester Fraction				
								Saturated	Unsaturated			
		Still °C.	Column °C.	Head °C.				C_{16}	Oleic	Linoleic	C_{20}	C_{22}
BL1	1.64	221-224	211-212	109-115	299.8	93.93	75.53	0.16	0.71	0.35	0.42	.....
BL2	3.43	224-234	212-216	149-153	299.0	94.95	76.37	0.30	1.65	0.73	0.75	.....
BL3	8.57	234-237	216-216	153-156	297.1	95.85	77.23	0.82	4.59	1.85	1.31	.....
BL4	8.14	237-237	216-217	156-161	298.6	97.50	78.54	0.55	4.34	1.79	1.46	.....
BL5	31.12	237-238	217-218	161-162	300.8	100.24	80.79	1.16	15.72	7.02	7.22	.....
BL6	39.70	238-238	218-229	162-163	301.3	101.67	82.77	0.58	21.57	8.70	8.85	.....
BL7	7.01	238-241	229-232	163-.....†	303.1	102.42	83.51	0.02	3.51	1.54	1.94	.....
BL8	29.17	.....*	.....*	.....	.....	.....	.....	.....	.....	.....	.....	.....
BL81	4.48	229-229	185-190	157-163	302.8	102.29	83.57	0.01	2.32	0.97	1.18	.....
BL82	7.53	229-229	185-185	163-170	302.3	102.62	83.67	0.03	3.98	1.66	1.87	.....
BL83	12.64	229-239	185-199	170-173	305.4	101.69	83.52	.....	5.55	2.65	4.44	.....
BL84	4.52	Residue	.....	.....	321.7	97.90	56.74	.....	.....	1.00	2.71	0.81
	128.72	Weight of Me esters, gm.						3.63	63.94	28.26	32.15	0.81
		Me esters %						2.82	49.67	21.95	24.98	0.63

* Refractionation. † Falling.

TABLE V

Complete Fractionation Data for the Component Fatty Acids of Du Chilly Filbert Oil

In this analysis, the esters of the "solid" acids and of the "liquid" acids were distilled through the electrically heated and glass helix packed columns.

The original oil has saponification number 188.2, iodine number 97.2, and thiocyanogen number 79.93, the mixed acids yield 63.03% "solid" acids and 36.62% "liquid" acids.

A. Fractional Distillation of Methyl Esters of the "Solid" Acids
(120.8 grams distilled through helix packed column)

No.	Grams	Temperature of			S. E.	I. V.	SCN	Calculated Weight of Ester Fraction					
								Saturated			Unsaturated		
		Still °C.	Column °C.	Head °C.				C_{16}	C_{18}	C_{20}	Oleic	Linoleic	C_{20}
DS1	2.60	225-227	205-206	80-82	291.6	78.2	69.87	0.08	0.36	.....	1.90	0.26	.....
DS2	2.31	227-235	206-214	82-124	298.9	77.2	69.19	.....	0.17	0.25	1.67	0.22	.....
DS3	25.54	235-238	214-214	124-126	298.4	82.3	73.54	.....	0.94	2.36	19.61	2.63	.....
DS4	42.93	238-270	214-217	126-128	299.2	87.2	78.72	.....	.....	2.91	34.20	3.24	2.58
DS5	8.99	270-273	217-221	128-132	300.2	89.7	80.70	.....	.....	0.26	6.72	0.76	1.25
DS6	9.25	273-284	221-225	132-134	301.1	90.8	81.15	.....	.....	0.07	7.38	0.84	2.03
DS7	1.67	284-	225-232	Falling	.....	.....	.....	.....	.....	.....	.....	.....	.....
DS8	28.10	Residue	.....	.....	301.9	90.8	78.25	.....	.....	.....	19.33	2.20	6.57
	120.8	Weight of Me esters, gm.						0.08	1.47	5.85	90.81	10.15	12.43
		Me esters %						0.07	1.22	4.84	75.17	8.40	10.29

B. Fractional Distillation of Methyl Esters of the "Liquid" Acids
(37.60 grams distilled through the helix packed column)

No.	Grams	Temperature of			S. E.	I. V.	SCN	Calculated Weight of Ester Fraction			
								Saturated	Unsaturated		
		Still °C.	Column °C.	Head °C.				C_{16}	Oleic	Linoleic	C_{20}
DL1	9.86	200-210	170-190	156-158	298.9	104.0	80.42	0.47	5.00	2.70	1.69
DL2	10.70	210-215	190-190	157-158	301.5	110.3	86.57	.....	5.09	3.25	2.35
DL3	7.99	215-215	190-197	158-159	302.6	111.9	86.84	.....	3.60	2.57	1.82
DL4	7.24	215-225	197-225	Falling	302.6	110.3	86.87	.....	4.05	1.55	1.64
DL5	1.81	Residue	.....	.....	318.6	86.3	69.06	.....	0.18	0.14	1.49
	37.60	Weight of Me esters, gm.						0.47	17.92	10.21	8.99
		Me esters %						1.25	47.66	27.15	23.91

assumed to be present. The composition of fractions was calculated directly from the saponification equivalent, iodine and thiocyanogen values by using the following equations:

$$a + b + c + d = w \quad (1)$$
$$a/E_a + b/E_b + c/E_c + d/E_d = w/E_w \quad (2)$$
$$aI_a + bI_b + cI_c + dI_d = wI_w \quad (3)$$
$$aT_a + bT_b + cT_c + dT_d = wT_w \quad (4)$$

Where a, b, c, and d were respective weights of the component esters in a fraction of weight w, E_a, E_b, E_c, and E_d are the corresponding theoretical molecular weights and E_w the observed saponification equivalent of the fraction; I_a, I_b, I_c, T_a, T_b, and T_c are the corresponding theoretical iodine and thiocyanogen values and I_w and T_w are the observed iodine and thiocyanogen values.

Sample Calculation—Fraction DS1 [Table V(A), 2.69 gm., S. E, 291.6, I. V. 78.2, SCN value 69.9 containing methyl ester of palmitic, stearic, and unsaturated acids].

If a, b, c, and d represent the palmitic, stearic, oleic, and linoleic esters, the equations are:

$$a + b + c + d = 2.60 \quad (1)$$
$$a/270 + b/298 + c/296.3 + d/294.3 = 2.60/291.6 \quad (2)$$
$$85.6c + 172.4d = 78.2 \times 2.60 \quad (3)$$
$$85.6c + 86.2d = 69.9 \times 2.60 \quad (4)$$

From the above four equations, a, b, c, and d may be calculated.

All other fractions were calculated in a similar manner. If a negative value results, the next higher acid in the series is then tried on the combination of the ester present until a positive value is first obtained.

The sitosterol was isolated and purified according to the procedure of Morrow (8). The acetyl derivative was prepared by acetylating the pure sitosterol with acetic anhydride and recrystallized from hot absolute alcohol after distilling off the excess of acetic anhydride under reduced pressure. Data are given in Table VII.

TABLE VI

Fatty Acid Composition of Barcelona and Du Chilly Filbert Oil

Acid	Barcelona			Du Chilly			European Varieties	
	Solid Acid Fraction 35.61%	Liquid Acid Fraction 63.99%	Total	Solid Acid Fraction 63.03%	Liquid Acid Fraction 36.62%	Total	Literature (11)	Value (3)
	%	%	%	%	%	%	%	%
Saturated								
Myristic	.....		.....	.....	.....	.....	0.22	8.4
Palmitic	0.49	1.80	2.29	0.04	0.46	0.50	3.21	.....
Stearic	1.57	0.00	1.57	0.77	0.00	0.77	1.66	.....
Arachidic	1.41	0.00	1.41	3.05	0.00	3.05	.....	.....
Unsaturated								
Oleic	24.42	31.78	56.20	47.38	17.45	64.83	88.10	82.0
Linoleic	2.77	14.05	16.82	5.29	9.94	15.23	2.87	10.0
C_{20} mono-ethenoid	4.97	15.98	20.95	6.49	8.76	15.25	.....	.....
C_{22} mono-ethenoid	0.00	0.40	0.40	.....	.....	0.00	.....	.....
Unsaponifiable matter	.....	.....	0.40	.....	.....	0.35	0.55	.....

TABLE VII

Elementary Composition of Sitosterol and Its Derivative From Filbert Oils

	(Chloroform Solution)	Melting Point °C.	C		H	
			Theory	Found	Theory	Found
			%	%	%	%
Barcelona sitosterol[1]	−25.6°	136-8	83.87	83.86	11.99	12.25
Du Chilly sitosterol[1]	−35.2°	135-7	83.87	83.95	11.99	12.09
Barcelona acetyl sitosterol[2]	.....	118	81.25	81.27	11.29	11.32
Du Chilly acetyl sitosterol[2]	.....	116-118	81.25	81.45	11.29	11.35

[1] Calculated as $C_{27}H_{46}O$.
[2] Calculated as $C_{29}H_{48}O_2$.

Discussion

In comparing the results obtained in this laboratory with those from the studies of Bertram (3) and Schuette and Chang (11), Barcelona and Du Chilly filberts are shown to contain slightly more oil than the European varieties. Other values except the iodine absorption value agree quite well with those European varieties reported in the literature. There are some variations in percentage of fatty acids in European oils as compared to those of Barcelona and Du Chilly filberts. Arachidic acid and C_{20-22} monoethenoid acids were found for the first time in Barcelona and Du Chilly filbert oils.

Bertram, in the separation of solid acids by the Twitchell method (3), reported that the solid acids had high iodine value and gave no explanation for this abnormal behavior. Similar results were observed in this study on both Barcelona and Du Chilly filbert oils. Fractional distillation of methyl esters of both fatty acids fractions revealed that this abnormal behavior probably was due to a high content of C_{20} monoethenoid acid. No attempt has been made to isolate and identify this acid.

The oils obtained by extraction gave a darker color and more free fatty acids than those obtained by cold expression. The amount of crude carotene in the samples obtained by these two different methods has shown no significant differences. It is then presumable that the darker color in extracted oil is due to other coloring matters.

The sitosterol of both oils possessed properties similar to those obtained from other vegetable oils.

Summary

Barcelona and Du Chilly filbert nuts have been analyzed for their principal constituents. The characteristics of the oils obtained by solvent extraction and by cold expression have been determined and their fatty acid composition has been ascertained. Most of the chemical and physical characteristics of the oils as determined in this laboratory agree well with values previously reported by other investigators on European varieties. However, our study of the oil components shows a considerable difference in fatty acid composition.

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The Stability of Sodium Stearate Gels[1]

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ONE of the methods used to estimate the stability of lubricating greases is a determination of the rate of expression and total quantity of syneretic fluid. Most properly formulated greases undergo syneresis quite slowly, hence various accelerated tests have been devised in an attempt to determine the syneresis within a few minutes to a day (4, 5). The present paper reports the results of pressure stability experiments on systems containing less than 40% sodium stearate and less than 10% water, undertaken with the hope that some correlation could be found between phase behavior (1, 2) and the ability of the gel to retain liquid.

Materials and Apparatus

The sodium stearate and cetane used in this study have been previously described (1, 7). The syneresis press is shown in Figure 1. A synopsis of the technique of operation follows.[2] The sample for the syneresis press consisted of a sandwich of the "molded" soap gel between two mats of filter paper. Each mat contained seven to ten sheets of filter paper and was weighed to a tenth of a milligram. Between weighing the first and second mat, the sample of the soap gel was put on top of the first and weighed. This sandwich was transferred to the base of the press, and the top was bolted on. The press was then placed in a constant temperature bath (± 0.2° C.). Fifteen minutes, which had been shown to be sufficient, were allowed to elapse in order to obtain temperature equilibrium, and then the valve was turned so as to lower the plunger onto the sample. Ordinarily a five-pound plunger was used although a few experiments were carried out at higher pressures. After the elapse of a measured time interval, the plunger was raised, the press removed from the bath, cooled, and dismantled. The cake was readily and cleanly removed from the

[1] This paper was presented in part before the Division of Colloid Chemistry at the 110th meeting of the American Chemical Society in Chicago, Ill., in 1946.

[2] Complete details of the procedure are given by T. M. Doscher, Doctoral Dissertation, University of Southern California, 1946.