THE SEPARATION OF NATURAL COMPONENTS OF FATS AND OILS BY MOLECULAR DISTILLATION[1,2]

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I. INTRODUCTION

"Molecular distillation" is the term used for the process of distilling material from a heated layer to a nearby condenser across space so highly evacuated that the mean free path of the distilling molecules is equal to or greater than the distance from the evaporating surface to the condensing surface. In practice, the distillation is usually done on thin layers of material at a pressure of about 1 micron (0.001 mm.) of mercury, and the condenser is placed about 1 cm. away from the distilling surface. When a small amount (less than 20 ml.) of material is to be distilled, a "pot" still is used (figure 1). A shallow puddle of distilland on a heated surface is located immediately below a condensing surface.

When a larger amount of material is to be distilled, a "falling-film" still is used (figure 2). The distilland flows in a thin film over a heated surface located near a condensing surface. The design most popular on both a laboratory and a commercial scale uses two vertical concentric cylinders.

[1] Presented at the Symposium on the Molecular Structure of Fats and Oils, which was held under the auspices of the Division of Biological Chemistry and the Division of Agricultural and Food Chemistry at the 101st Meeting of the American Chemical Society, St. Louis, Missouri, April 7–11, 1941.

[2] Communication No. 22 from the Laboratories of Distillation Products, Inc.

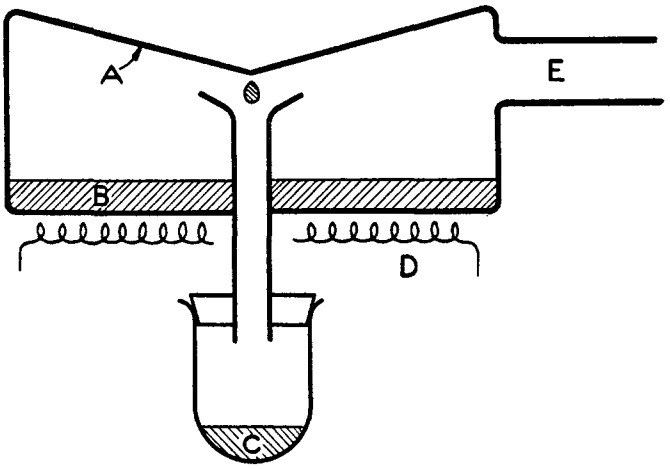

FIG. 1. Simplified diagram of a pot still. A, condensing surface; B, distilland; C, distillate; D, heating element; E, connection to vacuum pumps.

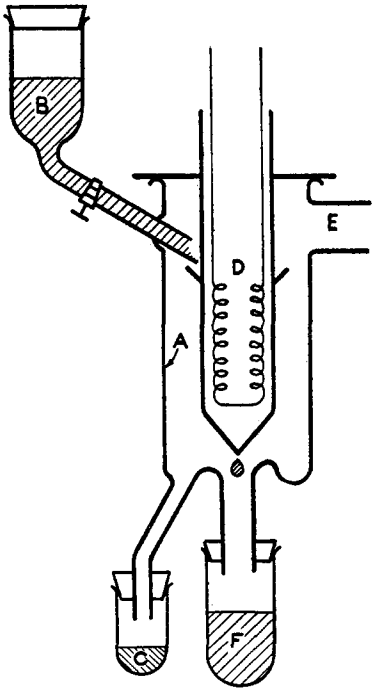

FIG. 2. Simplified diagram of a falling-film still. A, condensing surface; B, distilland; C, distillate; D, heating element; E, connection to vacuum pumps; F, undistilled residue.

The distilland flows down over the outside of the inner cylinder, and the distillate collects on and flows down the inner surface of the outer cylinder.

Readers interested in all the modifications of molecular stills described in the scientific and patent literature should refer to the bibliographies on molecular distillation compiled by Detwiler and Markley (10) and Detwiler (9), which give over two hundred references. There will appear soon in this journal a complete review (30) of the history of molecular distillation and of its scientific accomplishments. This present article is limited in scope to a discussion of the distillations that have been carried out on natural animal and vegetable oils, except for a brief mention of analytical distillations.

II. AMOUNT OF SEPARATION TO BE EXPECTED

Since in molecular distillation practically all of the molecules of vapor leaving the distilling surface are caught on the condenser, there is no "fractionation" in the usual sense of the word. Burch (6) and Washburn (45) have pointed out that the rate of molecular distillation of substances may be calculated by the Langmuir (36) equation:

$$n = PA\sqrt{\frac{1}{2\pi MRT}}$$

when n = rate in moles per second,
p = vapor pressure in dynes per square centimeter,
A = area of distilling surface in square centimeters,
M = molecular weight,
R = ideal gas constant, and
T = temperature in °K.

Assuming a perfect solution of two substances, the relative enrichment of the condensate will be $(P_1/M_1) \div (P_2/M_2)$ instead of $P_1 \div P_2$, the factor for the simplest ordinary distillation. The separations will be the same as that in an ordinary distillation if $M_1 = M_2$ and may be better or worse if $M_1 \neq M_2$, depending on the magnitude of the relative enrichment ratio. The first example of the case where molecular distillation had a better degree of fractionation than ordinary distillation was reported by Brønsted and Hevesy (5). They distilled mercury containing two isotopes in a molecular pot still and found that the isotopes which had the same vapor pressure were partially separated, owing to their different molecular weights. Although substances present with other materials of similar vapor pressures and molecular weights cannot be purified with a reasonable number of distillations, it is often possible to study their distillation characteristics and even to identify them by means of the analytical distillations that are discussed in the next section.

III. STEPWISE OR ANALYTICAL DISTILLATIONS

The study of the distillation of the more volatile constituents, such as the free fatty acids or vitamins, from an animal or vegetable oil has been carried out with the use of a "cyclic" molecular still. The cyclic still is a small falling-film still equipped with two oil reservoirs and an oil-circulating pump so arranged that the oil being distilled may be passed over the evaporating surface of the still as many times as desired without requiring any interruptions, such as breaking the vacuum to recharge the still or to remove the undistilled residue. It is also equipped with a means to remove the distillate samples without breaking the vacuum.

"Analytical" distillations are carried out on the cyclic still in the following manner: The still is charged with a solvent oil that is substantially non-volatile in the temperature range to be investigated (the least volatile fraction of corn oil is often used), and dissolved in the solvent oil is a small amount of the substance to be investigated. After the vacuum has been established, the oil solution is passed over the evaporating surface at room temperature a few times to remove the traces of dissolved air and water. The temperature of the evaporation surface is then raised to a point where the substance under study just begins to distill. After all the oil has passed over the evaporating surface at this temperature, the distillate is removed, the oil is passed over the evaporating surface at a slightly higher temperature, and the distillate again is removed. This cycle of operations is repeated until ten to twenty distillate samples are obtained corresponding to a series of temperatures, which, as a rule, are separated by constant intervals of 5 or 10 degrees.

In practice, there is added to the oil solution a small amount of mixed triglycerides made from C_4 to C_{12} fatty acids (2). A fraction of this "constant yield oil" distills at each temperature to wash the distillate into the distillate receiver. Furthermore, impurities (often up to 99 per cent) in the preparation of the substance under examination act as constant yield oil and do not invalidate the distillation unless they affect the determination of the relative concentration of the substance in the distillates. The distillation requires the presence of only enough of the substance so that it may be assayed in the five or six most potent distillates.

The amounts of the substance in the distillates increase for the first few temperatures, because the vapor pressure of the substance increases with each increase in the temperature. But when the amount of the substance left in the distilland is nearly exhausted, the amounts in the distillate will become less and less until the substance is finally completely distilled. The progress of the distillation is best shown by an "elimination curve," the curve drawn through the points obtained by plotting the relative yield

of the substance in the distillates against the temperature of the distillation (figure 3). Under controlled conditions of distillation the temperature corresponding to the maximum of the elimination curve was found, by Hickman (25) on experimental grounds and by Embree (11) on theoretical grounds, to be as characteristic of the substance as a boiling point.

The temperatures of the elimination maxima and the shape of the elimination curves have been used to characterize the nature of various substances present in fish-liver oils that could not be separated in their pure states. Analytical distillations have shown (26) that vitamins A and D occur in fish-liver oils both in the free (alcohol) state and esterified with fatty acids. The shapes of the elimination curves for the vitamin

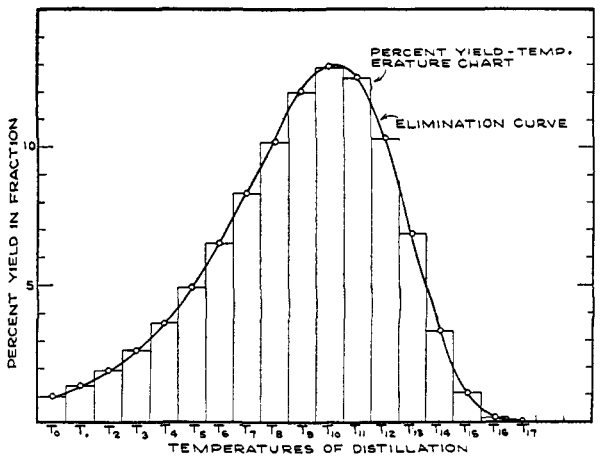

FIG. 3. Elimination curve (Embree (11))

esters show that several different fatty acids are present in the vitamin esters.

The elimination curves for a series of fatty acids were determined by Gray and Cawley (23). The curves they obtained for lauric, myristic, palmitic, and stearic acids are shown in figure 4, and those for the C_{18} acids,—stearic, oleic, linoleic, 9,11-linoleic, and α-eleostearic,—in figure 5. The overlapping of the elimination curves shows the poor separation that could be expected by a single molecular distillation of a mixture of these acids. Therefore, molecular distillation is not as suited as the conventional vacuum distillation methods for the separation and analysis of mixtures of fatty acids.

Molecular distillation will probably contribute a great deal to the study of certain specialized problems on fatty acids. A notable instance was the work done on the acids of cod-liver oil by Farmer and Van den

Heuvel (14). It had previously been thought by Webb (50) and Toyama and Tsuchiya (43) that the principal acid was "clupanodonic," a pentaene C_{22} acid. When the cod-liver oil acids were separated by molecular distillation, no clupanodonic acid was found, and the principal acid was a hexaene C_{22} acid. Ordinary methods of distillation had changed the natural hexaene acid into the artifactual clupanodonic acid.

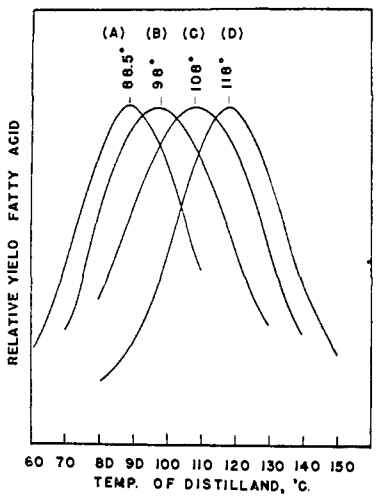

FIG. 4

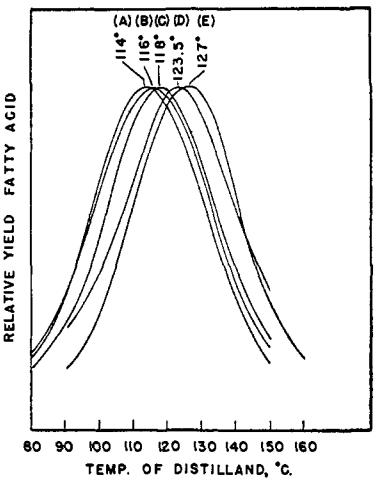

FIG. 5

FIG. 4. Elimination curves of four saturated fatty acids. A, lauric acid; B, myristic acid; C, palmitic acid; D, stearic acid. (Gray and Cawley (23)).

FIG. 5. Elimination curves of four unsaturated fatty acids and stearic acid. A, linoleic acid; B, oleic acid; C, stearic acid; D, 9,11-linoleic acid; E, α-eleostearic acid. (Gray and Cawley (23)).

IV. DISTILLATIONS OF ANIMAL AND VEGETABLE OILS

Oils (including fats) when expressed or extracted from animal and vegetable tissue usually contain the following types of materials: (*1*) phospholipids and mucilaginous matter; (*2*) free fatty acids; (*3*) substances with potent flavors and odors; (*4*) unsaponifiable matter, including sterols, vitamins, antioxidants, and other alcohols, ethers, and hydrocarbons; (*5*) triglycerides.

Molecular distillation cannot be carried out with oils that contain more than traces of phospholipids and mucilaginous matter. These materials cause excessive foaming and the deposition of carbonaceous matter on the distilling surface. The substances responsible for this trouble, however, may be satisfactorily removed by refining processes involving treatment with acid, alkali, or salt solutions (15, 44).

A. Distillation of free fatty acids from oils

Tables 1 to 6 give some of the properties of the fractions from the molecular distillation of various oils. The free fatty acids are concentrated in the first fractions in all the distillations.

B. Distillation of materials with strong flavors and odors from oils

The odoriferous and flavoring materials distill into the first fractions when the oil is molecularly distilled (27), and may therefore be removed from the bulk of the oil.

When the flavoring ingredients are valuable instead of a nuisance, removing them by molecular distillation will enable them to be recovered without the loss by hydrolysis, pyrolysis, or aqueous extraction which is inherent in the conventional steam distillation process. For example: Waterman and van Vlodrop (49), by molecular distillation, removed the first fraction from butter. This fraction, amounting to about 5 or 10 per cent of the original butter, contained all of the flavoring matter and could be used to flavor margarine or other food products.

C. Distillation of unsaponifiable matter from oils

The distillation data of various oils shown in tables 1 to 6 show that the unsaponifiable matter is concentrated in the first few fractions. The exceptions to this general rule that have been met with so far occur with oils such as dogfish-liver oil where the unsaponifiable material is partly composed of the glyceryl ethers known as batyl, selachyl, and chimyl alcohols. These diacidic alcohols occur naturally as the di-fatty acid esters, and these esters have substantially the same vapor pressures and distillation characteristics as the triglycerides (35).

Hydrocarbons. Baxter (1) found hydrocarbons with probable formulas ranging from $C_{15}H_{32}$ to $C_{19}H_{40}$ occurring in small amounts in the very first fraction of distillate from a commercial distillation of cod-liver oil. Hickman (29) found considerable quantities of sesquiterpenes and hydrocarbons from the commercial distillation of mixed vegetable oils. It seems likely that the small fractions from large commercial batches of oils will yield hydrocarbons in quantities large enough for complete characterization.

Sterols. The unsaponifiable materials from most oils are mainly sterols. Hickman and Tischer (33) have described general processes for obtaining sterols from natural oils, and Fawcett and Myles (17) have described a process for concentrating stigmasterol from soybean oil. Both processes are based on the fact that the sterols distill before the main bulk of the triglycerides. Hickman (29) points out that there is little chance of sepa-

rating the sterols from one another by a single molecular distillation because their elimination maxima are so close together.

Antioxidants (tocopherols). It was noticed by Hickman and Baxter (32) and Fawcett (16) that early fractions from the distillation of vegetable oils were considerably more stable towards oxidation than the later fractions and the original oil, and that these early fractions would confer increased stability on other oils when admixed with them. Riemenschneider *et al.* (41) confirmed this in a study of cottonseed oil. Tocopherol concentrates are now being prepared in commercial quantities by molecular distillation (29).

Vitamins. In addition to the concentration of tocopherols (vitamin E), molecular distillation has been used to prepare concentrates of other fat-soluble vitamins by the distillation of natural oils.

Vitamin A. It has been known for some time that vitamin A concentrates could be made by the molecular distillation of fish-liver oils (7, 20, 24). Vitamin A was found by Hickman (26) to be concentrated in two separate fractions during a single distillation. Experiments showed that the lower boiling fraction contained vitamin A in the alcohol form and the higher boiling fraction contained fatty acid esters of vitamin A. The bulk of the vitamin A occurs in the ester form, and, since the vitamin A esters are more stable to oxidation (42) and are generally more active biologically (13, 21, 22, 37), the preparation of vitamin A concentrates by molecular distillation on a commercial scale was both feasible and desirable. In the United States, Distillation Products, Inc., are now producing distilled vitamin A ester concentrates on a large scale. In England, the British Drug Houses, Ltd., have been distilling vitamin A alcohol from the unsaponifiable fraction of fish-liver oils on a commercial scale since 1934.

The large-scale distillations of fish-liver oils have made possible the isolation of minute quantities of other substances related to vitamin A. Of these, "cyclized" vitamin A (12), which distills before and with the vitamin A alcohol, has no biological activity, but interferes with both the ultraviolet absorption method and the antimony trichloride blue-color method of assaying vitamin A.

Carotene. Waterman and van Vlodrop (49) distilled red palm oil completely and found that the carotene was not concentrated in any one fraction, but that all the distillates had substantially the same red color as the original oil. But when the combined distillates were again distilled, the carotene was concentrated in the first fractions, as it is when a solution of carotene in a bleached oil is distilled. No explanation for this effect has been given.

Vitamin D. Vitamin D also may be distilled from fish-liver oils. A small amount of vitamin D alcohol appears before the main fraction of the

fatty acid esters of vitamin D (26). Although the present type of commercial falling-film stills causes a certain amount of destruction of vitamin D by pyrolysis, new designs being developed distill vitamin D from fish-liver oils with a very good recovery (30).

Vitamin K. Vitamin K is concentrated in the first fractions from soybean oil, but less than six human daily doses can be recovered from a gallon of the crude oil (31). The availability of cheap synthetic antihemorrhagic agents has rendered such a concentrate of little commercial value.

D. Separation of the triglycerides

It has been shown above that molecular distillation gives very little separation for mixtures of fatty acids. Since natural oils are "mixtures

TABLE 1

The molecular distillation of linseed oil

Hickman (1938)

	ORIGINAL	FRACTION 1*	FRACTION 2	FRACTION 3	FRACTION 4	RESIDUE
Iodine No.	177.9	148.7	148.0	173.3	187.9	190
Saponification No.	192.5	171.3	163.1	183.3	194.2	184.1
Non-saponifiable matter	1.36	16.14	2.67	0.93	0.56	0.93
Free fatty acids as oleic acid	1.6	36.8	0.8	0.25	0.25	0.37
Unsaturated fatty acids	85.57	69.45	86.11	88.11	88.04	88.6

* The amounts of the fractions were not given in the reference. They are as follows: first fraction, 4 to 5 per cent; other fractions, 20 to 25 per cent.

of *mixed* triglycerides" (34), it is not to be expected that any great separation of the triglycerides will be obtained upon the distillation of an oil.

Linseed oil. The data for the molecular distillation of linseed oil by Hickman (28) are given in table 1. Since the original oil had an iodine value of 177.9 and the fractions had iodine values of 148 to 190, it is evident that some fractionation took place.

Castor oil. The data in table 2 give some of the properties of the fractions from the molecular distillation of castor oil (40). Since the fatty acids of this oil consist almost entirely of ricinoleic acid (34), it is not surprising that practically no fractionation was obtained. Disregarding the small first fraction, the iodine values varied only from 82.4 to 87.7 and the acetyl values from 122 to 133.5.

Corn oil. The distillation data in table 3 describe the first few fractions of corn oil distilled by Rawlings (39). The composition of the tri-

TABLE 2

The molecular distillation of castor oil

Rawlings (1941)

FRACTION*	IODINE VALUE	SAPONIFICATION VALUE	PER CENT UNSAPONIFIABLE MATTER	SAPONIFICATION VALUE OF GLYCERIDES	IODINE VALUE OF UNSAPONIFIABLE MATTER	IODINE VALUE OF GLYCERIDES	ACETYL VALUE
1	101.8	169.0	7.8	183.0	127.0	99.6	
2	87.7	182.0	0.25	182.5	182.5		122
3	85.8	182.0	Nil	182.0			124
4	85.6	181.5	Nil	181.5			125.5
5	85.2	180.5	Nil	180.5			128.5
6	85.0	181.0	Nil	181.0			131
7	82.4	180.5	Nil	180.5			133.5
Residue	82.8	180.5	Nil	180.5			127.5
Original	85.0	180.0	0.4	180.5	228.0	84.5	128.0

* The amounts of the fractions are as follows: first fraction, 4 per cent; other fractions, 12 to 15 per cent.

TABLE 3

The molecular distillation of corn oil

Rawlings (1939)

CHARACTERISTIC	ORIGINAL OIL (REFINED)	FRACTION 1	FRACTION 2	FRACTION 3	FRACTION 4	RESIDUE
Per cent distilled		0.01	2.58	2.73	5.05	
Distillation temperature, °C.		180	245.	257.	280.	
Color (Evelyn L440)	1.40	Brown solid	Brown mush	1.28	1.00	0.85
Color (Evelyn L520)	0.23			0.242	0.085	0.201
Lovibond (yellow)				35.	35.	50.
Lovibond (red)				10.6	4.3	11.2
Free fatty acid (oleic), per cent	0.033	10.6	0.95	0.20	0.10	0.02
Unsaponified matter, per cent	1.6	64.2	15.0	5.0	2.7	0.8
Refractive index at 40°C	1.4678			1.4682	1.4674	1.4672
Iodine value (Wijs)	127.0	151.4	125.7	121.3	123.6	127.6
Iodine value of fatty acids		115.6	121.9			
Thiocyanogen value	79.4			74.6	76.8	80.3
Thiocyanogen value of fatty acids		79.8	77.2			
Saponification value	190.	70.	165.	184.	188.	192.
Saponification value of glycerides	193.	196.	194.	194.	193.	193.
Saturated fatty acids, per cent	7.3	(11.4)*	(14.5)			
		0.4	12.3	8.0	7.8	5.9
Oleic acid, per cent	35.4	(49.0)	(36.2)			
		17.5	30.7	31.1	33.4	36.8
Linoleic acid, per cent	54.4	(39.6)	(49.3)			
		14.2	41.8	51.6	51.8	52.2

* Values in parentheses are per cent composition of fatty acid portion.

TABLE 4

The molecular distillation of distilled soybean oil

Rawlings (1939)

CHARACTERISTIC	ORIGINAL OIL (REFINED)	FRACTION 1	FRACTION 2	FRACTION 3	FRACTION 4	FRACTION 5	FRACTION 6	FRACTION 7	RESIDUE
Per cent distilled		0.02	3.4	4.4	4.4	23.2	20.4	28.4	
Distillation temperature, °C.		170–178	255–265	265–270	275	280	295	295	
Color (Evelyn L440)	1.35	Too dark		1.28	1.28	1.10	0.33	0.40	1.28
Color (Evelyn L520)	0.716	Too dark		0.328	0.172	0.059	0.019	0.023	0.810
Lovibond (yellow)	70*			35†	35†	25†	18†	20†	95‡
Lovibond (red)	14.1*			11.2†	6.2†	3.0†	1.6†	1.7†	66‡
Free fatty acid (as oleic), per cent	0.04	5.0	0.5	0.2	0.15	0.10	0.06	0.04	0.09
Unsaponified matter, per cent	0.8	74.2	10.7	1.5	0.7	0.28			
Saponification number	193	50	175	193	193.5	193	193	194	193
Saponification number of glycerides	194	194	196	196	195	194	193	194	193
Refractive index at 40°C.	1.4682			1.4673	1.4672	1.4673	1.4676	1.4674	1.4682
Iodine value (Wijs)	134.5	150.8	131.2	127.2	127.8	129.9	131.2	132.0	137.6
Thiocyanogen value	83.7			79.7	79.2	82.3	83.0	80.6	87.1
Iodine value of fatty acids	139.2		136.3	134.7	132.8	136.8	136.8	137.0	143.2
Thiocyanogen value of fatty acids	86.8		81.3	83.1	82.8	85.8	86.3	85.8	90.1
Solid fatty acids, per cent	12.5		16.0	14.9	15.8	12.9	12.6	12.2	11.0
Unsaturated acids (by difference), per cent	87.5		84.0	85.1	84.2	87.1	87.4	87.8	89.0
Oleic acid	29.7		23.2	28.2	29.2	30.9	31.7	31.3	30.4
Linoleic acid, per cent	49.4		54.8	50.1	47.7	48.4	47.7	49.4	48.0
Linolenic acid, per cent	8.4		6.0	6.8	7.3	7.8	8.0	7.1	10.6

* 2.5-in. column.

† 5.25-in. column.

‡ 1-in. column.

glycerides was almost exactly the same in all fractions except the first, which amounted to only 0.01 per cent in weight.

Soybean oil. The data for the almost complete distillation of soybean oil (39) are given in table 4. The lack of separation of the constituent triglycerides is shown by the fact that the iodine values for the fatty acids in the fractions range only from 132.6 to 143.2.

Cottonseed oil. Table 5 shows the data for the distillation of cottonseed oil by Riemenschneider, Swift, and Sando (41). The separation of the

TABLE 5

The molecular distillation of cottonseed oil

Riemenschneider, Swift, and Sando (1940)

FRACTION NO.	WEIGHT	SAPONIFICATION EQUIVALENT*	FATTY ACID AS OLEIC	REFRACTIVE INDEX AT 40°C.	UNSAPONIFIABLE	IODINE NUMBER	THIOCYANOGEN NUMBER	COMPOSITION		
								Linoleic acid	Oleic acid	Saturated acids
	grams		*per cent*					*per cent*	*per cent*	*per cent*
1	88.0	280.2	0.38	1.4660	5.83	100.6	57.3	50.0	16.2	33.8
2	93.7	284.0	0.14	1.4634	0.60	100.0	58.4	48.0	19.5	32.5
3	93.0	284.3	0.13	1.4635	0.34	101.2	59.3	48.3	20.1	31.6
4	89.0	285.2	0.11	1.4638	0.25	103.0	60.3	49.3	20.4	30.3
5	87.7	285.4	0.09	1.4639	0.23	103.4	60.6	49.4	20.7	29.9
6	93.5	284.1	0.07	1.4639	0.16	103.9	60.7	49.8	20.4	29.8
7	90.5	284.6	0.06	1.4641	0.16	106.1	61.3	51.7	19.1	29.2
8	89.5	285.0	0.05	1.4642	0.13	106.1	61.9	51.0	20.6	28.4
9	90.0	284.7	0.05	1.4644	0.14	107.9	62.2	52.7	19.2	28.1
10	93.0	284.0	0.06	1.4645	0.17	109.3	63.5	52.8	20.6	26.6
11	91.0	286.3	0.06	1.4646	0.13	110.3	63.9	53.5	20.4	26.1
12	92.0	286.6	0.05	1.4648	0.09	111.9	65.2	53.9	21.5	24.6
13	89.0	286.6	0.05	1.4650	0.07	114.4	66.3	55.5	21.2	23.3
14	87.5	287.3	0.06	1.4654	0.11	116.6	67.9	56.2	22.3	21.5
15	85.5	290.1	0.06	1.4661	0.13	120.9	70.2	58.5	22.7	18.8
Residue	43.4	290.0	0.09	1.4706	0.68	118.9	67.2	59.6	18.0	22.4
Original oil	1417.0	285.8	0.10	1.4645	0.49	108.3	62.3	53.1	18.9	28.0

* Corrected for unsaponifiable material.

triglycerides is somewhat better than that in the case of soybean oil, but even so the iodine values of the fractions range only from 100 to 120.9.

Menhaden oil. The distillation data for menhaden oil shown in table 6 were obtained by Cawley, Barnitz, and Jackson (8). Since there are present in fish oils considerable amounts of each of the fatty acids from C_{14} to C_{22}, it would be expected that some degree of fractionation of the fish-oil triglycerides could be obtained. The fact that the iodine values of the distillates ranged from 142.5 to 244 shows that this is indeed the case. The molecular distillation of fish-liver oils may prove to be of

considerable value for the determination of the triglyceride structure of these extremely complex materials.

TABLE 6

Molecular distillation of menhaden oil

Cawley, Barnitz, and Jackson (1941)

	ORIGINAL OIL	FRACTION* 1	FRACTION 2	FRACTION 3	FRACTION 4	FRACTION 5
Acid value	1.45	7.14	0.09	0.05	0.08	0.20
Iodine value	183.	142.5	157.5	173.5	202.5	244.
Saponification value	180.3	181.9	184.6	181.6	176.2	171.3
Refractive index, $n_D^{25°}$	1.4794	1.4744	1.4758	1.4779	1.4818	1.4876
Mean unsaturation (double bonds per triglyceride molecule)	6.73	5.19	5.66	6.34	7.63	9.45

* Each fraction amounted to 20 per cent of the original oil in weight.

TABLE 7

Vacuum distillation of babassu nut oil

Bömer and Hüttig (1938)

	ORIGINAL OIL	FRACTION 1	FRACTION 2	RESIDUE
Per cent cut		5.2	77.2	17.0
Temperature, °C		To 150	150–295	
Melting point, °C	25	25.5	26.8	17.0
Saponification value	251.1	(Mainly free	256.0*	222.8*
Iodine value	15.6	fatty acids)	8.8*	44.7*

* Of triglycerides.

TABLE 8

Vacuum distillation of coconut oil

Bömer and Baumann (1920)

	ORIGINAL OIL	DISTILLATE	RESIDUE
Per cent cut		87.7	12.3
Temperature, °C		250–285	
Melting point, °C	26.8	25.0	32.5
Saponification value	259.7	263.7	228.5
Iodine value	4.6	1.85	23.5

Coconut and babassu oil. The fats from the nuts of the *Palmae* have considerable amounts of each of the fatty acids containing from eight to eighteen carbon atoms. Bömer and Hüttig (4) were able partially to

distill babassu nut oil, and Bömer and Baumann (3) were able partially to distill coconut oil in a high-vacuum (not a molecular) still. The distillation data are given in tables 7 and 8. Waterman and Rijks (48) were able to distill coconut oil completely in an improved high-vacuum still to obtain the fractions described in table 9. These distillations show that the glycerides of the saturated fatty acids of low molecular weight distill first, and that the glycerides containing oleic acid distill last.

TABLE 9

Vacuum distillation of coconut oil

Waterman and Rijks (1926)

	ORIGINAL OIL	FRACTION 1	FRACTION 2	FRACTION 3	FRACTION 4
Per cent cut		30.0	17.5	27.5	21.5
Temperature of distillation, °C.		206–223	223–229	229–231	231–254
Acid value	0.945	1.4	0.9	0.9	0.27
Saponification value	256.	280.	274.	262.	237.
Iodine number	8.2	2.4	1.5	4.3	23.3

E. Conclusions

The distillation data given for the vegetable oils show that molecular distillation will remove the free fatty acids and the unsaponifiable constituents of the oil with considerable efficiency. This method of concentration is of especial value when the substance studied may be altered by saponification. Such substances are vitamin K, sterol esters, and possibly others. The present types of molecular stills will be of little value for the separation of the triglycerides of vegetable oils.

The molecular distillation of fish-liver oils for the concentration of the unsaponifiable constituents has proved to be of great value, because vitamins A and D are recovered in their natural esterified state. Furthermore, the separation of the triglycerides of fish oils by molecular distillation takes place to an extent great enough to be of scientific interest.

Since so few oils have been carefully examined by molecular distillation, the above statements may have to be modified. Many laboratories interested in the study of oils have only recently acquired molecular stills, and it is expected that much new information will soon be available on this subject. Furthermore, the scientific and commercial rewards for devising equipment which will better separate the triglycerides may lead to the development of molecular stills or combinations of stills which will have considerably enhanced powers.

V. THE MOLECULAR DISTILLATION OF BODIED OILS

Although the constituents of heat-bodied oils can scarcely be considered, to be "natural components" of oils, the work on the molecular distillation of such heat-bodied oils should be mentioned in this article. Waterman and Oosterhof (46) found that stand oil with a viscosity of 55 poises gave 32 per cent of a distillate which had poor drying qualities and deposited stearin on standing. Its molecular weight was 757, showing that it consisted of unpolymerized glycerides. The undistillable residue (68 per cent) had a viscosity of 379 poises and a molecular weight of 3463. It remained clear on standing and had *better* drying qualities than the original stand oil.

Apparently, when an oil is heat-bodied, the triglycerides containing the reactive unsaturated fatty acids are linked together through condensation of these acids. The triglycerides containing saturated fatty acids and unreactive unsaturated fatty acids do not polymerize and may therefore be distilled from the mixture. Processes for the removal of these unreactive (and hence undesirable in a drying oil) triglycerides from bodied linseed and Chinawood oils have been described by Oosterhof, van Vlodrop, and Waterman (38).

Fawcett and Walker (18, 19) have found that good drying oils may be made in a similar manner by distilling the unpolymerized glycerides from bodied fish oils.

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