[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER AND GAMBLE COMPANY]

THE COMPOSITION OF WHALE OIL

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Although little systematic study of the composition of marine animal oils has been attempted, a survey of the literature leads to the conclusion that the fatty acids of these oils are complicated mixtures of acids of various molecular weights and that the fractions of higher molecular weight contain the more highly unsaturated acids.

Bull[1] subjected to fractional distillation the methyl esters of the fatty acids of cod-liver oil and obtained fractions which showed successively higher iodine values with increasing molecular weight up to a maximum of 168.7 iodine value for a fraction of 179.0 saponification value. Higher fractions showed decreasing iodine values, the significance of which will be discussed later. The fractions of greatest weight were obtained at saponification values corresponding closely to 14, 16, 18, 20 and 22 carbon content. The most representative fractions obtained are shown in Table I. An interesting result of this investigation was the discovery of a 16-carbon analog of oleic acid in cod-liver oil, the presence of which is responsible for the rather high iodine value of the fraction distilling at 185–186°.

TABLE I

MOST REPRESENTATIVE FRACTIONS OF THE METHYL ESTERS OF COD-LIVER OIL FATTY ACIDS[1]

Boiling point °C.	Yield %	Saponification value	Approximate carbon content of fatty acid	Iodine value
161.5–163	2.00	229.5	14	9.5
185 –186	7.48	204.6	16	57.2
205 –206	17.00	188.1	18	100.6
223 –225	9.26	173.2	20	152.2
239 –240	3.52	159.8	22	130.0

Twitchell[2] studied the composition of menhaden oil by means of a method which consisted in adding the mixture to be analyzed to a much larger amount of pure fatty acid of the kind to be determined and observing the resulting depression of the melting point of the pure fatty acid. His final conclusions are summarized in Table II.

TABLE II

COMPOSITION OF MENHADEN OIL FATTY ACIDS[2]

Acid	Palmitic	Myristic	Stearic	C_{16} unsat.	C_{18} unsat.	C_{20} unsat.	C_{22} unsat.
%	22.7	9.2	1.8	none	24.9	22.2	20.2

No study of the composition of whale oil comparable with the above investigations of cod-liver oil and menhaden oil appears to have been made. Svendsen,[3] however, has investigated the composition of a sample of hydrogenated whale oil of 59.8 iodine value, to which he assigned the composition shown in Table III. Svendsen's paper is

[1] Bull, *Ber.*, **39**, 3570 (1906).

[2] Twitchell, *J. Ind. Eng. Chem.*, **6**, 564 (1914); **9**, 581 (1917).

[3] Svendsen, *Tidsskrift f. Kemi, Farm. og Terapi*, Nr., **20**, 285 (1916); *Z. angew. Chem.*, **30**, II, 95 (1917).

available to the writers only in abstract form and we are unable to state what was his method of examination.

TABLE III

COMPOSITION OF A SAMPLE OF HYDROGENATED WHALE OIL[3]

Acid	%	Acid	%	Acid	%
Myristic	10.8	Stearic	10.8	$C_{22}H_{36}O_2$[a]	8.0
Palmitic	17.9	Oleic	27.7	Behenic	2.5
Palmitoleic	10.6	Arachidic	3.4	$C_{22}H_{44}O_2$	8.8

[a] Probably this is a misprint in the abstract and should be $C_{20}H_{36}O_2$.

From the foregoing it appears probable that whale oil, although of lower average iodine value and therefore lower in its content of the highly unsaturated acids, closely resembles in its composition menhaden and cod-liver oils. However, this view is by no means confirmed in the critical review of Lewkowitsch,[4] who considered palmitic acid to be the principal solid fatty acid of whale oil and regarded the highly unsaturated acids as containing 18 carbon atoms. Also certain work of Bull[5] throws doubt upon the view that the more highly unsaturated acids of whale oil contain mainly 20 and 22 carbon atoms. Bull separated, from various marine animal oils, fractions of very high iodine value which were characterized by yielding sodium soaps soluble in anhydrous ether. Eleven samples of whale oil were examined by this method and from Bull's data on these samples we have calculated the following average values: iodine value of original oils, 112.1; yield of highly unsaturated fraction, 7.1%, iodine value of unsaturated fraction, 270.2; acid value of unsaturated fraction, 206.3. The average acid value (206.3) of the highly unsaturated fractions corresponds to an approximate carbon content of only seventeen.

On the other hand, the view that the more highly unsaturated fatty acids of whale oil are of high molecular weight is partially confirmed by Tsujimoto,[6] who found in whale oil and other marine oils a highly unsaturated acid which gave an octobromide at first considered to be that of clupanodonic acid ($C_{18}H_{28}O_2$), but in a later paper[7] identified as the octo-bromide of the acid $C_{20}H_{32}O_2$.

The recent work of Brown and Beal[8] on menhaden oil, cod oil and herring oil further strengthens the general conclusion that the fatty acids of marine animal oils are complicated mixtures of various molecular weights with the unsaturation concentrated largely in the acids containing more than 18 carbon atoms.

[4] Lewkowitsch, "Chemical Technology of Oils, Fats and Waxes," MacMillan, 1914, 5th edition, Vol. II, pp. 458–9.

[5] Bull, *Chem.-Ztg.*, **23**, 1043 (1899).

[6] Tsujimoto, *J. Coll. Engineering, Imp. Univ. Tokyo*, **4**, 11 (1906); *J. Soc. Chem. Ind.*, **23**, 819 (1906).

[7] Tsujimoto, *Chem. Umschau*, **29**, 261 (1922).

[8] Brown and Beal, THIS JOURNAL, **45**, 1289 (1923).

Experimental Method

The writers have investigated the composition of whale oil by means of a combination of two methods, namely, the fractional distillation of the methyl esters of the fatty acids and the separation of solid and liquid fatty acids by the fractional precipitation of the lead salts of the solid acids from alcoholic solution.

The methyl esters which were used in the fractional distillation were prepared by saponifying the oil with a slight excess of dil. aqueous sodium hydroxide and esterifying the liberated fatty acids with methyl alcohol in the presence of dry hydrogen chloride until the free fatty acid content of the reaction mixture was reduced to less than 0.5%. The fractional distillations were carried out by means of a Vigreux distilling tower (90 cm. in length and 25 mm. in cross section) or two such towers arranged in series with an extra distillation flask at the bottom of the second tower. The pressure on the distillation system was maintained at 7 to 9 mm. by means of a Nelson pump.

The separation of solid from liquid fatty acids, both for purposes of preparing material for distillation and for purposes of chemical examination, was carried out essentially according to the method described by Twitchell.[9]

Fractional Distillation of the Esters of the Solid and of the Liquid Fatty Acids of Whale Oil

With the exception of the work recorded in Table IX, the whale oil used in these experiments was a sample obtained from fisheries operating off the west coast of the United States. No authentic information could be obtained regarding the species of whale from which this oil was derived. At the beginning of our work no other sample of whale oil was available to us. Some of the characteristics of this oil were as follows: iodine value, 121.6; average molecular weight of fatty acids, 277; percentage of solid acids (Twitchell method), 16.7; iodine value solid acids, 5.6. A sample of this oil was saponified and the solid acids precipitated as lead soap from a solution of the mixed fatty acids in 95% alcohol. (The alcohol contained methyl alcohol as denaturant, but we have found that the presence of small amounts of methyl alcohol is of no disadvantage in the Twitchell method of separating solid from liquid fatty acids.) The lead soaps thus obtained were twice recrystallized from alcoholic solution, previous investigation having shown that further recrystallization was of no advantage. The precipitated lead soaps were acidified with dil. nitric acid for the recovery of the solid fatty acids, while the combined filtrates and extracts were partially evaporated and acidified with dil. hydrochloric acid for the recovery of the liquid fatty acids, the usual precautions being taken to avoid oxidation of the fatty acids by air.

[9] Twitchell, *J. Ind. Eng. Chem.*, 13, 806 (1921).

The solid and liquid acids were separately esterified with methyl alcohol and the methyl esters fractionally distilled, with the results shown in Tables IV and V. In Table VI the approximate composition of the methyl esters of the solid acids has been calculated on the assumption that each fraction is a mixture of the two saturated acids of even carbon content between which the average molecular weight of the fraction lies. A similar calculation is made in Table VII for the esters of the liquid fatty acids, but in this case we are not dealing even approximately with a single fatty acid for each carbon content. Consequently, for purposes of calculation, it is necessary to assume an average molecular weight for each even

TABLE IV

DISTILLATION OF METHYL ESTERS OF SOLID FATTY ACIDS OF WHALE OIL

Iodine value of fatty acids, 5.6. Average molecular weight of fatty acids, 260.0. Iodine value of 196° fraction, 13.3.

B. p. °C. (upper limit)	Weight of fraction G.	Molecular weight	B. p. °C. (upper limit)	Weight of fraction G.	Molecular weight
160	5.44	247.0	185	12.75	279.1
170	17.22	251.4	190	3.83	289.1
176	17.15	258.7	196	14.13	299.1
178	65.30	269.0	Residue[a]	8.82	...
181	32.03	272.0	Total	176.67	

[a] This residue was lost by accident. For purposes of calculation in Table VI, it is assumed to be 75% stearic acid and 25% unsaturated acid of higher molecular weight. The percentage error involved in this procedure, calculated to original oil, is very small.

TABLE V

DISTILLATION OF METHYL ESTERS OF LIQUID FATTY ACIDS OF WHALE OIL

Iodine value of methyl esters, 138.2. Average molecular weight of methyl esters, 296.0.

B. p. °C. (upper limit)	Weight of fraction	Molecular weight	Iodine value
160	6.63	249.7	43.2
165	8.30	256.1	50.0
170	13.46	266.6	78.7
175	40.49	276.9	93.8
180	40.57	291.2	95.4
185	26.68	299.1	99.6
190	76.61	301.5	101.3
200	20.02	304.3	115.7
210	14.75	313.7	175.7
220	29.01	325.9	231.9
225	18.47	340.1	228.9
255[a]	22.49	355.6	236.2
Residue	22.60	393.8	174.2
Saponifiable in residue	20.13	350.7	181.3[b]
Unsaponifiable in residue	2.47	...	...
Total	340.08		

[a] This fraction was distilled through the first of two columns and obtained from the flask at the bottom of the second column at the end of distillation.

[b] Iodine value of free fatty acid instead of ester.

carbon content. The assumed molecular weight is based on the iodine value of what appears to be the most representative fraction of the carbon content in question and is shown in the second column of Table VII.

TABLE VI

COMPOSITION OF METHYL ESTERS OF SOLID ACIDS

Estimated from Table IV

Fatty acid	Wt. G.	%
Myristic	24.0	13.6
Palmitic	120.2	68.0
Stearic	29.7	16.8
Higher acids, unsaturated	2.8	1.6

TABLE VII

COMPOSITION OF METHYL ESTERS OF LIQUID ACIDS

Estimated from Table V

Carbon content of fatty acid	Assumed av. mol. wt. (ester)	Wt.	%
14	242.0	9.3	2.7
16	268.3	52.2	15.4
18	295.7	145.3	42.7
20	320.8	68.7	20.2
22	347.5	52.6	15.4
24	375.0	9.6	2.8
Unsaponifiable	...	2.5	0.7

Fractional Distillation of the Esters of the Mixed Fatty Acids of Whale Oil

A comparison of Tables IV and V shows that the molecular weight of a liquid fraction is greater than that of the solid fraction of the same boiling point. The methyl ester of oleic acid is known to have a slightly lower boiling point than the methyl ester of stearic acid, about 2° at 15mm. pressure. From our results, it appears that increasing unsaturation lowers the boiling point of the ester. It is to be expected, therefore, that considerable quantities of the more highly unsaturated fatty acids will distil with the saturated acids of lower molecular weight, in case the methyl esters of the mixed fatty acids of whale oil are distilled. This view is confirmed by the data in Table VIII, which shows the results of the distillation of the methyl esters of the mixed fatty acids of the whale oil used in the preceding experiments. Comparing fractions of the same boiling point, we note that the esters of the solid acids show the lowest molecular weight and those of the liquid acids the highest molecular weight, while those of the mixed acids are intermediate. For instance, the average molecular weights of the solid, mixed, and liquid fractions of boiling point 185–190° are as follows: solid (Table IV) 289.1; mixed (Table VIII) 295.0; liquid (Table V) 301.5.

Mention has already been made of the fact that, in the distillation of methyl esters of cod-liver oil, Bull obtained fractions of increasing iodine

value up to a maximum, beyond which the iodine value decreased with increasing molecular weight. We believe that this is due to the greater volatility of the more highly unsaturated esters as compared with the less unsaturated of the same carbon content and do not believe that the average iodine value of the C_{22} acids of cod-liver oil is lower than that of the C_{20} acids, as might appear from a superficial examination of Bull's data.

TABLE VIII

DISTILLATION OF METHYL ESTERS OF WHALE OIL

From the United States Pacific Coast

Iodine value of oil, 121.6. Average molecular weight of fatty acids, 277.0.

B. p. °C. (upper limit)	Weight of fraction	Molecular weight	Iodine value
160	21.00	249.4	28.9
165	35.49	259.0	38.9
170	25.65	270.4	56.8
175	123.25	276.9	59.6
180	34.18	281.8	61.4
185	20.62	291.5	80.9
190	157.42	295.0	96.5
195	65.68	301.2	100.2
200	22.79	302.0	118.7
210	8.33	309.8	167.2
220	41.85	323.0	207.9
225	35.17	334.2	215.0
230	16.48	344.0	227.4
250[a]	12.85	350.9	207.6
Residue	53.00	378.1	166.9
Saponifiable in residue	47.93	342.2	184.0[b]
Unsaponifiable in residue	5.07	...	...
Total	673.76		

[a] This fraction was distilled through the first of two columns and obtained from the flask at the bottom of the second column at the end of distillation.

[b] Iodine value of free fatty acid instead of ester.

TABLE IX

DISTILLATION OF METHYL ESTERS OF WHALE OIL

From S. Shetland Islands district

Iodine value of oil, 111.3. Average molecular weight of fatty acids, 276.8.

B. p. °C. (upper limit)	Weight of fraction	Molecular weight	Iodine value
160	4.77	242.2	25.0
165	23.64	247.1	21.4
170	10.99	252.9	27.9
175	14.62	261.8	41.3
180	61.60	274.8	54.4
184	34.42	277.6	56.8
186	11.52	280.3	55.2
190	24.49	289.5	71.6
194	79.34	299.7	94.8
196	21.59	298.3	91.9
200	23.27	299.7	98.2

205	16.13	301.3	114.8
210	6.43	304.0	133.8
220	15.55	317.9	229.1
230	16.97	329.7	256.3
240[a]	20.37	348.3	277.5
Residue	19.37	403.4	166.2
Saponifiable in residue	17.06	355.3	169.8[b]
Unsaponifiable in residue	2.31	...	...
Total	405.07		

[a] This fraction was distilled through the first of two columns and obtained from the flask at the bottom of the second column at the end of distillation.

[b] Iodine value of free fatty acid instead of ester.

Table IX shows the results obtained in the distillation of the methyl ester of the mixed fatty acids of a different sample of whale oil, obtained from fisheries operating in the vicinity of the South Shetland Islands. This oil is very similar to the oil obtained from the west coast of the United States, but shows a slightly higher myristic content and a slightly lower iodine value. No attempt has been made to estimate the composition of the esters of either sample of whale oil from the data in Tables VIII and IX, because of the uncertainty incident to the distillation of mixtures containing components of such varying degrees of unsaturation.

The whale oil from the vicinity of the South Shetland Islands was derived chiefly from that species known as the blue whale, according to statements of the captain of the boat from which the oil was unloaded.

Fractional Distillation of the Methyl Esters of Hydrogenated Whale Oil

In order to avoid the uncertainty of a fractional distillation in which acids are present of the same carbon content, but of various degrees of unsaturation, a sample of the whale oil from the United States Pacific Coast was hydrogenated to an iodine value of 3.5 and the methyl esters were prepared and distilled as before. Although the oil contains a small amount of unsaturated material, the fatty acids present may be assumed to be myristic, palmitic, stearic, arachidic, behenic and lignoceric. The results of the fractional distillation are shown in Table X and the calculation of the composition of these esters is shown in Table XI.

Discussion of Results

Certain conclusions may be drawn immediately from inspection of Tables IV to XI. Any one of the fractional distillations is sufficient to justify the conclusion that the fatty acids of whale oil are of widely varying molecular weights, the carbon content ranging from 14 to 22, with indications of the presence of a small amount of fatty acid of still higher molecular weight. On account of the low iodine value of all fractions of mean molecular weight lower than C_{16}, even in the case of the distillation of the esters of the liquid acids, it appears that the C_{14} fraction consists almost

entirely of myristic acid. The C_{16} fraction, on the other hand, appears to be a mixture of palmitic and an oleic acid analog (palmitoleic), similar to that found by Bull in cod-liver oil. The C_{18} acids consist chiefly of oleic, with only a small amount of stearic and little if any acid more unsaturated than oleic. The more highly unsaturated acids of whale oil are almost wholly of the C_{20} and C_{22} series, while the saturated acids, arachidic and lignoceric, are absent or present only in traces.

TABLE X

DISTILLATION OF METHYL ESTERS OF HYDROGENATED WHALE OIL

Iodine value of hydrogenated oil, 3.5. Average molecular weight of fatty acids, 285.5.

B. p. °C. (upper limit)	Weight of fraction	Molecular weight	Iodine value
165	3.29	251.2	...
170	14.03	254.0	...
175	7.17	267.8	...
180	40.75	273.6	...
185	25.22	281.6	...
190	45.80	297.5	...
195	7.64	301.3	...
200	15.98	303.1	...
210	11.57	308.8	...
230	22.00	327.0	...
240	15.17	342.8	4.5
250	4.67	354.7	4.5
Residue	11.80	420.0	20.6
Saponifiable in residue	10.19	362.5	17.5[a]
Unsaponifiable in residue	1.61	...	...
Total	225.09		

[a] Iodine value of free fatty acid instead of ester.

TABLE XI

COMPOSITION OF METHYL ESTERS OF HYDROGENATED WHALE OIL

Estimated from Table X

Fatty acid	Wt.	%	Fatty acid	Wt.	%
Myristic	10.3	4.6	Behenic	21.7	9.7
Palmitic	64.2	28.5	Lignoceric	3.4	1.5
Stearic	88.2	39.2	Unsaponifiable	1.6	0.7
Arachidic	35.7	15.9			

Certain difficulties should be pointed out before we attempt a quantitative estimate of the composition of the fatty acids of the whale oil studied. In addition to inherent difficulties in the fractional distillation of esters of varying degrees of unsaturation, the esters of the unsaturated acids of whale oil are not entirely stable during distillation. The iodine value decreases during distillation, while the apparent molecular weight increases. The iodine values and the molecular weights of the esters described in Tables V, VIII and IX are shown below, both as observed or calculated before distillation and as estimated from the separate fractions after distillation:

TABLE XII

IODINE VALUES AND MOLECULAR WEIGHTS OF ESTERS

Esters of	Iodine value Before	Iodine value After	Mean molecular weight Before	Mean molecular weight After
Liquid acids (Table V)	138	132	296	305
Mixed acids (Table VIII)	121	107	291	297
Mixed acids (Table IX)	111	101	291	292

These changes during distillation are serious only in the case of the unsaturated acids. In attempting an estimate of the composition of the fatty acids of whale oil, it would appear logical to give greatest weight to the results obtained by distillation of the esters of the solid acids[10] and of the hydrogenated fatty acids. This has, in fact, been done in the estimates given below. Another difficulty, however, arises in connection with the hydrogenation of whale oil, namely, a considerable increase in the mean molecular weight as estimated from the saponification value of the oil or the acid value of the free fatty acids. Table VIII shows the apparent molecular weight of the fatty acids of the raw whale oil to be 277. Complete hydrogenation should theoretically increase this value to only 279.7, but this whale oil, hydrogenated at 217°C. to 3.5 iodine value, gave fatty acids having a mean molecular weight of 285.5. This abnormal increase in apparent molecular weight, which is contrary to previous statements in the literature,[11] will be made the subject of further investigation by the authors. The observation itself has been repeatedly confirmed in the case of the whale oil in question. The increase in molecular weight is not accompanied by any increase in the unsaponifiable content of the hardened oil, as was at first suspected. Preliminary observations lead us to believe that the increase is greater at high temperature of hydrogenation, such as 217°, but is quite marked at relatively low temperature, such as 140°. Also it may be noted that the abnormal increase in mean molecular weight is gradual over the whole course of hydrogenation and not confined to oil which is almost completely hydrogenated.

In spite of the above described limitations of our experimental methods, the data in Tables IV to XI throw considerably more light on the com-

TABLE XIII

APPROXIMATE COMPOSITION OF FATTY ACIDS OF WHALE OIL

		%			%
C_{14}	Myristic	4.5	C_{20}	Unsaturated	16
C_{16}	Palmitic	11.5	C_{22}	Unsaturated	10
	Palmitoleic	17.0	C_{24}	Unsaturated	1.5
C_{18}	Stearic	2.5		Unsaponifiable	0.7
	Unsaturated (nearly all oleic)	36.5			

[10] Allowance must be made for the fact that the method of separation allows the myristic acid to be divided about equally between solid and liquid fatty acids.

[11] Compare Ellis, "Hydrogenation of Oils," D. Van Nostrand Co., 1919, 2nd ed., p. 282.

position of whale oil than previous investigations. In Table XIII we have attempted to summarize the main points of our data in the form of an estimate of the percentage composition of the fatty acids of the sample of whale oil studied (from the west coast of the United States).

Summary

The composition of whale oil has been studied by fractionally distilling the methyl esters of the solid, liquid and mixed fatty acids of the oil and also the methyl esters of the fatty acids of the hydrogenated oil. Whale oil, like other marine animal oils, contains a complicated mixture of fatty acids of carbon content varying from 14 to 22, probably with a small amount of C_{24} acids. The highly unsaturated acids are chiefly those containing 20 and 22 carbon atoms. The percentage composition of the fatty acids has been approximately estimated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE MECHANISM OF THE HOFMANN REARRANGEMENT OF METHYL ANILINE HYDROCHLORIDE[1]

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Introduction

The Hofmann rearrangement consists in the change of methyl aniline hydrochloride to *p*-toluidine hydrochloride under the influence of heat. Hofmann[3] suggested as a possible mechanism that methyl chloride was dissociated and then added again, the reaction going through the formation of dimethyl aniline. Then the methyl chloride acted on the dimethyl-aniline giving dimethyltoluidines, -xylidines, -cumidines, etc. Some of these products were isolated. In the case of trimethylphenylammonium iodide he states that the methyl groups "wander" from the aminic nitrogen to the carbon ring, giving rise to a series of quaternary, tertiary, secondary and primary amines.

Work of a more recent date makes it possible to predict as to the correctness of Hofmann's views. Chattaway[4] found that disubstitution of acyl groups upon the amino nitrogen was necessary to produce substances

[1] From a thesis presented by J. W. Howard in partial fulfilment of the requirements for the degree of Doctor of Philosophy, at the University of Illinois, June, 1915.

[2] The experimental work of this paper was performed by J. W. Howard in collaboration with C. G. Derick. The original thesis manuscript was revised and condensed for publication by J. W. Howard.

[3] Hofmann, *Ber.*, **4**, 742 (1871).

[4] Chattaway, *J. Chem. Soc.*, **75**, 1046 (1899); **77**, 134, 789, 797 (1900); **85**, 386, 589, 1187 (1904).