COMPONENT FATTY ACIDS OF NORTHERN ELEPHANT SEAL OIL

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The marine carnivores such as the whale and seal has generally a thick layer of fatty tissue under the skin, called as blubber, which is the source of the oil.

The seal and whale oils have been used for many purpose. A number of studies has been given to the whale family oil. While, as to the study on the component acid of the seal family oil, we can find the following reports: the common seal, *Phoca vitulina*, oil (Williams & Makhrov, 1935); Saghalien seal oil (Tsujimoto, 1916); common seal oil (Bauer & Neth, 1942); commercial Newfoundland seal oil (Burke & Jasperson, 1944); blubber and liver oils of Grey Atlantic seal, *Halichoerus grypus* and common seal (Hilditch and Pathak, 1947, 1949); milk oils of Grey Atlantic and common seals (Meara, 1952); blubber oils of leopard seal, *Hydrurga leptonyx* and crabeater seal, *Lobodon carcinophagus* (Winter and Nunn, 1950, 1953). Tsujimoto and Bauer supported the view that the seal oil and the ordinary whale oil are similiar in fatty acid composition from their works. In the elephant seal, there are two species, the northern elephant seal, *Mirounga angustirostris* and the southern elephant seal, *Mirounga leonina*.

Reviewing the works ever reported on the elephant seal oil, Winter and Nunn studied the fatty acid composition of the blubber oils from a wide range of specimens of the southern elephant seal caught at Macquarie and Heard Islands in the Antarctic (Winter & Nunn, 1950, 1953). On the other hand, the writer studied the differences in the properties of the oils contained in various blubbers and tongue of the northern elephant seal (Tsuyuki, 1957). However, there has not yet been a study of the component fatty acids of the northern elephant seal oil. So, the writer was fortunate enough to obtain the dorsal blubber oil of the northern elephant seal and examine its fatty acid composition.

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EXPERIMENT AND RESULT

The northern elephant seal, *Mirounga angustirostris* caught off the coast of Mexico in January, 1955 and died on the 7th of June, 1956 in Kyoto, Japan was used as the experimental material in the present work. This is the same as used in the previous report (Tsuyuki, 1957).

The oil contained in the dorsal blubber of the seal body was prepared by boiling the material with water and refined with a centrifugal separator.

Some properties of the obtained oil were examined in ordinary manners and iodine value was determined by the Wijs method. Saponification was continued for two hours in an atmosphere of nitrogen gas. The results obtained are shown in table 1.

TABLE 1. PROPERTIES OF OIL

Appearance (20°C.)	d_4^{15}	N_D^{30}	Acid value	Sapon. value	Iodine value	Unsapon. matter (%)
Reddish brown, semitransparent liquid	0.9224	1.4636	15.6	187.6	128.7	0.98

TABLE 2. PROPERTIES OF UNSAPONIFIABLE MATTER

Appearance (30°C.)	N_D^{40}	Melting point (°C.)	Iodine value
Yellowish brown, nontransparent solid	1.4246	28.5～32.5	99.5

Next, to some 400g. (I.V. 128.7) of the oil was added 400c.c. of absolute ethanol and further potassium hydroxide solution (KOH 176g. and H_2O 320c.o.) and heated in an atmosphere of nitrogen gas for two hours on a water bath, after which nearly 80% of alcohol was distilled off and the resulting soap solution was cooled and diluted with water. The unsaponifiable matters (Table 2) were removed from the soap solution with ether, and the 365.5g (I.V. 133.9) of the mixed fatty acids were recovered after decomposing the soap solution with 10% sulfuric acid solution. The 340g. of the mixed fatty acids thus obtained were subjected to the lead salt alcohol separation method (Twitchell, 1921), whereupon 51g. (I.V. 8.3) of solid (insoluble) fatty acids and 289g. (I.V. 155.8) of liquid (soluble) fatty acids were obtained.

The 280g. of the liquid fatty acids was then subjected to the lithium salt acetone separation method (Hilditch, 1956), when 222.4g. (I.V. 118.2) of lowly unsaturated (insoluble) fatty acids and 57.6g. (I.V. 301.3) of highly unsaturated (soluble) fatty acids were obtained.

Some characteristics of the fatty acids thus obtained were measured by the usual manner and the following results were obtained (Table 3).

Each group of the fatty acids were separately converted into methyl esters (Table 4) and fractionated as usual through Longenecker's E.H.P. column modified by the writer (Figs. 1, 2). Saponification values and iodine values of each of the subfractions of all the groups of methyl esters were determined, and the data are given in tables 5~7.

TABLE 3. PROPERTIES OF FATTY ACIDS

Kind of fatty acids	% in mixed fatty acids	Appearance (20°C.)	Refractive index	Melting point (°C.)	Iodine value	Neutral. value	Average molecular weight
Mixed fatty acids	—	Yellowish brown, nontransparent solid	1.4640 (30°C.)	27.5~29.5	133.9	198.3	282.9
Solid fatty acids	15.0	Brownish white, nontransparent solid	1.4352 (60°C.)	47.0~51.5	8.3	214.5	261.6
Lowly unsat. fatty acids	67.5	Reddish brown, transparent liquid	1.4621 (30°C.)	—	118.2	197.5	284.1
Highly unsat. fatty acids	17.5	Reddish brown, transparent liquid	1.4695 (30°C.)	—	301.3	187.1	299.9
Liquid fatty acids	85.0	Reddish brown, transparent liquid	1.4685 (30°C.)	—	155.8	195.3	287.3

TABLE 4. PROPERTIES OF METHYL ESTERS

Kind of ester	Appearance (20°C.)	Sapon. value	Iodine value
Ester of solid acids	Brownish white, nontransparent solid	205.2	6.2
Ester of lowly unsat. acids	Reddish brown, transparent liquid	188.0	113.1
Ester of highly unsat. acids	Reddish brown, transparent liquid	178.8	283.6

From the iodine value and saponification value of each ester fraction obtained by the fractional distillation, it seems that the following fatty acids are contained in the northern elephant seal oil:

Saturated fatty acids:

myristic acid $C_{14}H_{28}O_2$, palmitic acid $C_{16}H_{32}O_2$, stearic acid $C_{18}H_{36}O_2$, arachidic acid $C_{20}H_{40}O_2$, behenic acid $C_{22}H_{44}O_2$.

Unsaturated fatty acids:

mono- ethenoid C_{14} acid.
mono- and tri- ethenoid C_{16} acids.
mono-, di-, tri- and tetra- ethenoid C_{18} acids.
mono- and tetra- ethenoid C_{20} acids.
mono-, tetra- and penta- ethenoid C_{22} acaids.
mono- and penta- ethenoid C_{24} acids.

The composition of each of the ester fractions was calculated from saponification values and iodine values according to the method described by Hilditch (Hilditch, 1956). The mean unsaturation expressed as the fractional number of hydrogen atoms short of saturation, for example, −2.0 (monoethenoid), was determined by interpolation and extrapolation from the respective ester fractions in each of the groups from which the mean saponification value of each of the homologous ester groups (C_{16}, C_{18}, C_{20}, etc.) follows. The results calculated are shown in Tables 8~10.

TABLE 5. FRACTIONAL DISTILLATION OF METHYL ESTERS OF SOLID FATTY ACIDS

Fraction	Yield		Appearance (10°C.)	B.P. °C./3.5mmHg	Sapon. value	Iodine value
	Wt.(g.)	%				
S- 1	1.83	6.2		~150	223.6	0.6
S- 2	1.41	4.8	White, nontransparent solid	150~153	220.1	1.9
S- 3	1.88	6.3	White, nontransparent solid	153~156	218.8	2.4
S- 4	1.97	6.7	White, nontransparent solid	156~159	215.3	2.6
S- 5	2.01	6.8	White, nontransparent solid	159~159	214.5	3.2
S- 6	2.38	8.0	White, nontransparent solid	159~160	212.2	3.4
S- 7	2.13	7.2	White, nontransparent solid	160~161	210.3	3.7
S- 8	1.93	6.5	White, nontransparent solid	161~163	207.1	3.8
S- 9	1.96	6.6	White, nontransparent solid	163~165	204.6	4.0
S-10	2.11	7.1	White, nontransparent solid	165~167	202.8	5.1
S-11	2.23	7.5	White, nontransparent solid	167~173	199.7	7.7
S-12	2.09	7.1	White, nontronsparent solid	173~179	196.8	8.0
S-13	2.01	6.8	White, nontransparent solid	179~188	190.7	11.5
S-14	1.50	5.1	White, nontransparent solid	188~195	186.8	12.5
S-15	1.36	4.6	Light yellowish white, semitransparent solid	195~200	184.4	16.3
S-16	0.80	2.7	Yellowish brown, nontransparent solid	Residue	171.5	30.0
Total	29.60	100.0	—	—	—	—

TABLE 6. FRACTIONAL DISTILLATION OF METHYL ESTERS OF LOWLY UNSATURATED FATTY ACIDS

Fraction	Yield		Appearance (10°C.)	B.P. °C/2mmHg	Sapon. value	Iodine value
	Wt.(g.)	%				
LU- 1	9.88	8.2	Yellow, transparent liquid	~150	214.6	38.6
LU- 2	7.20	6.0	Yellow, transparent liquid	150~155	209.4	49.3
LU- 3	8.62	7.2	Yellow, transparent liquid	155~157	200.4	73.7
LU- 4	6.88	5.8	Yellow, transparent liquid	157~160	194.7	84.2
LU- 5	5.96	5.0	Light yellow, transparent liquid	160~161	192.5	91.9
LU- 6	5.64	4.7	Light yellow, transparent liquid	161~163	190.9	93.7

TABLE 6 (Continued)

Fraction	Yield Wt.(g.)	Yield %	Appearance (10°C)	B.P.°C/2mmHg	Sapon. value	Iodine value
LU- 7	7.80	6.5	Light yellow, transparent liquid	163～165	188.6	97.9
LU- 8	8.90	7.4	Light yellow, transparent liquid	165～167	186.3	99.8
LU- 9	8.86	7.3	Light yellow, transparent liquid	167～168	185.1	106.3
LU-10	7.16	6.0	Light yellow, transparent liquid	168～169	184.2	110.1
LU-11	6.38	5.3	Light yellow, transparent liquid	169～171	183.6	114.5
LU-12	5.08	4.2	Light yellow, transparent liquid	171～172	183.2	122.6
LU-13	7.18	6.0	Light yellow, transparent liquid	172～176	180.1	127.5
LU-14	7.34	6.1	Light yellow, transparent liquid	176～183	175.4	172.0
LU-15	7.02	5.9	Light yellow, transparent liquid	183～185	172.5	214.9
LU-16	4.70	3.9	Yellow, transparent liquid	185～193	164.9	246.4
LU-17	5.40	4.5	Reddish brown, nontransparent solid	Residue	164.0	177.8
Total	120.00	100.0	—	—	—	—

TABLE 7. FRACTIONAL DISTILLATION OF METHYL ESTERS OF HIGHLY UNSATURATED FATTY ACIDS

Fraction	Yield Wt.(g.)	Yield %	Appearance (10°C.)	B.P. °C./1mmHg	Sapon. value	Iodine value
HU- 1	2.24	4.4	Yellowish orange, transparent liquid	～163	219.8	181.6
HU- 2	2.73	5.4	Yellowish orange, transparent liquid	163～169	212.8	190.4
HU- 3	2.91	5.8	Yellowish orange, transparent liquid	169～176	198.5	194.7
HU- 4	3.64	7.2	Yellowish orange, transparent liquid	176～184	188.0	216.0
HU- 5	4.19	8.3	Yellowish orange, transparent liquid	184～185	186.5	300.5
HU- 6	4.66	9.2	Yellowish orange, transparent liquid	185～188	183.3	310.7
HU- 7	5.23	10.4	Yellowish orange, transparent liquid	188～190	179.8	319.3
HU- 8	4.85	9.6	Yellowish orange, transparent liquid	190～194	175.1	330.2
HU- 9	5.07	10.1	Dark yellowish orange, transparent liquid	194～196	168.5	334.3
HU-10	4.50	8.9	Reddish brown, transparent liquid	196～197	164.8	358.0
HU-11	5.57	11.0	Reddish brown, transparent liquid	197～198	163.5	340.3
HU-12	4.90	9.7	Reddish brown, transparent liquid	Residue	156.4	175.0
Total	50.50	100.0	—	—	—	—

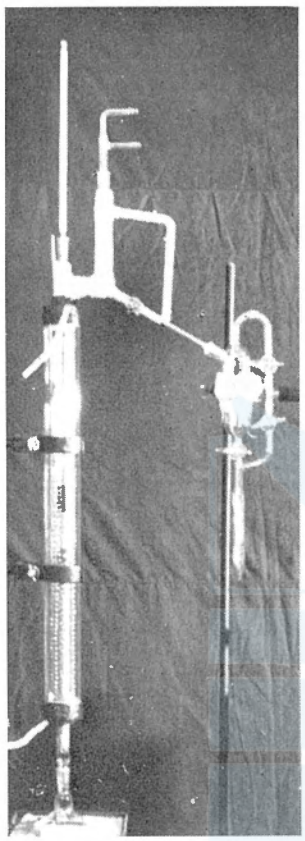

Fig. 1. E.H.P. Column modified by the writer column: 65 c.m.

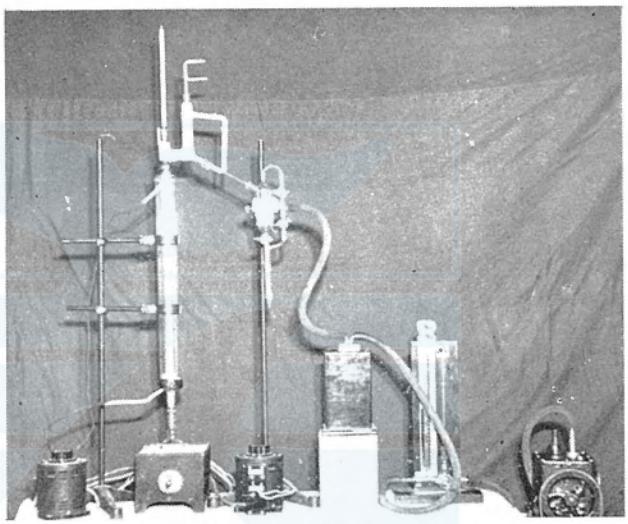

Fig. 2. Fractional distillation apparatus.

According to the results obtaind, it is noticed that the total saturated fatty acid content is 20.37% (myristic acid $C_{13}H_{27}COOH$: 3.5%, palmitic acid $C_{15}H_{31}COOH$: 12.82%, stearic acid $C_{17}H_{35}COOH$: 3.61%, arachidic acid $C_{19}H_{39}COOH$: 0.41%, behenic acid $C_{21}H_{43}COOH$ 0.01%) of the total. The unsaturated counterpart is 79.63% (C_{14} acids : 0.96%, C_{16} acids : 10.2%, C_{18} acids : 33.22%, C_{20} acids : 24.57%, C_{22} scids : 10.27%, C_{24} acids : 0.59%) of the total. In this case, the degree of unsaturation are as follows ; The C_{14} series : $-2.0H$, C_{16} series : $-2.5H$, C_{18} series : $-3.0H$, C_{20} series : $-4.4H$, C_{22} series : $-7.1H$, C_{24} series : $-6.6H$ (Fig. 3).

It is apparent that large amounts of the unsaturated C_{18} acids, unsaturated C_{20} acids, palmitic acid, unsaturated C_{22} acids and unsaturated C_{16} acids are contained in the northern elephant seal oil.

TABLE 8. CALCULATED COMPOSITION OF ESTER-FRACTIONS OF SOLID FATTY ACIDS

Fraction	Saturated					Unsaturated					Tatal solid acids
	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{14} (−2.0H)	C_{16} (−2.0H)	C_{18} (−2.0H)	C_{20} (−2.0H)	C_{22} (−2.0H)	
S- 1	1.23	0.59	—	—	—	—	0.01	—	—	—	1.83
S- 2	0.73	0.66	—	—	—	0.01	0.01	—	—	—	1.41
S- 3	0.86	0.97	—	—	—	0.02	0.03	—	—	—	1.88
S- 4	0.62	1.29	—	—	—	0.01	0.05	—	—	—	1.97
S- 5	0.57	1.38	—	—	—	0.02	0.04	—	—	—	2.01
S- 6	0.45	1.85	—	—	—	0.01	0.07	—	—	—	2.38
S- 7	0.24	1.81	—	—	—	trace	0.08	—	—	—	2.13
S- 8	—	1.81	0.04	—	—	—	0.07	0.01	—	—	1.93
S- 9	—	1.60	0.28	—	—	—	0.07	0.01	—	—	1.96
S-10	—	1.51	0.48	—	—	—	0.08	0.04	—	—	2.11
S-11	—	1.27	0.85	—	—	—	0.10	0.01	—	—	2.23
S-12	—	0.86	1.04	—	—	—	0.07	0.12	—	—	2.09
S-13	—	0.24	1.50	—	—	—	0.02	0.25	—	—	2.01
S-14	—	—	1.18	0.09	—	—	—	0.19	0.04	—	1.50
S-15	—	—	0.85	0.24	—	—	—	0.19	0.08	—	1.36
S-16	—	—	—	0.48	0.01	—	—	—	0.28	0.03	0.80
Weight(g.)	4.70	15.84	6.22	0.81	0.01	0.07	0.70	0.82	0.40	0.03	29.60g.
Percentages (in total acids)	2.38	8.03	3.15	0.41	0.01	0.03	0.35	0.42	0.20	0.02	15.00%

TABLE 9. CALCULATED COMPOSITION OF ESTER-FRACTIONS OF LOWLY UNSATURATED FATTY ACIDS

Fraction	Saturated			Unsaturated					Total lowly unsat acids
	C_{14}	C_{16}	C_{18}	C_{14} (−2.0H)	C_{16} (−2.0H)	C_{18} (−2.7H)	C_{20} (−3.3H)	C_{22} (−6.2H)	
LU- 1	1.76	4.18	—	0.91	3.03	—	—	—	9.88
LU- 2	0.27	3.17	—	0.06	3.70	—	—	—	7.20
LU- 3	—	1.05	0.60	—	3.95	3.02	—	—	8.62
LU- 4	—	0.11	0.22	—	1.82	4.73	—	—	6.88
LU- 5	—	—	trace	—	0.83	5.13	—	—	5.96
LU- 6	—	—	—	—	0.45	5.19	—	—	5.64
LU- 7	—	—	—	—	—	7.42	0.38	—	7.80
LU- 8	—	—	—	—	—	7.30	1.60	—	8.90
LU- 9	—	—	—	—	—	6.45	2.41	—	8.86
LU-10	—	—	—	—	—	4.78	2.38	—	7.16
LU-11	—	—	—	—	—	4.01	2.37	—	6.38
LU-12	—	—	—	—	—	0.68	4.40	—	5.08
LU-13	—	—	—	—	—	2.87	4.31	—	7.18
LU-14	—	—	—	—	—	0.55	6.79	—	7.34
LU-15	—	—	—	—	—	—	5.87	1.15	7.02
LU-16	—	—	—	—	—	—	1.21	3.49	4.70
LU-17	—	—	—	—	—	—	1.38	4.02	5.40
Weight(g.)	2.03	8.51	0.82	0.97	13.78	52.13	33.10	8.66	120.00g.
Percentages (in total acids)	1.14	4.79	0.46	0.54	7.75	29.33	18.62	4.87	67.50%

TABLE 10. CALCULATED COMPOSITION OF ESTER-FRACTIONS OF HIGHLY UNSATURATED FATTY ACIDS

Fraction	Unsaturated						Total highly unsat acids
	C_{14} (−2.0H)	C_{16} (−4.4H)	C_{18} (−6.0H)	C_{20} (−8.1H)	C_{22} (−7.9H)	C_{24} (−6.6H)	
HU- 1	0.87	1.37	—	—	—	—	2.24
HU- 2	0.27	2.46	—	—	—	—	2.73
HU- 3	—	1.72	1.19	—	—	—	2.91
HU- 4	—	—	2.96	0.68	—	—	3.64
HU- 5	—	—	2.68	1.51	—	—	4.19
HU- 6	—	—	2.03	2.63	—	—	4.66
HU- 7	—	—	1.14	4.09	—	—	5.23
HU- 8	—	—	—	4.42	0.44	—	4.86
HU- 9	—	—	—	2.20	2.87	—	5.07
HU-10	—	—	—	0.66	3.84	—	4.50
HU-11	—	—	—	0.39	5.18	—	5.57
HU-12	—	—	—	—	3.20	1.70	4.90
Weight(g.)	1.14	5.55	10.00	16.58	15.53	1.70	50.50g.
Percentages (in total acids)	0.39	1.92	3.47	5.75	5.38	0.59	17.50%

TABLE 11. CALCULATED COMPOSITION OF TOTAL ACIDS

Acid	Sloid (15.00%)	Lowly unsaturated (67.50%)	Highly unsaturated (17.50%)	Total (100.00%)
Saturated:				
Myristic	2.38	1.14	—	3.52
Palmitic	8.03	4.79	—	12.82
Stearic	3.15	0.46	—	3.61
Arachidic	0.41	—	—	0.41
Behenic	0.01	—	—	0.01
				(Total sat.) 20.37%
Unsaturated:				
C_{14}	0.03 (−2.0H)	0.54 (−2.0H)	0.39 (−2.0H)	0.96 (−2.0H)
C_{16}	0.35 (−2.0H)	7.75 (−2.0H)	1.92 (−4.4H)	10.02 (−2.5H)
C_{18}	0.42 (−2.0H)	29.33 (−2.7H)	3.47 (−6.0H)	33.22 (−3.0H)
C_{20}	0.20 (−2.0H)	18.62 (−3.3H)	5.75 (−8.1H)	24.57 (−4.4H)
C_{22}	0.02 (−2.0H)	4.87 (−6.2H)	5.38 (−7.9H)	10.27 (−7.1H)
C_{24}	—	—	0.59 (−6.6H)	0.59 (−6.6H)
				(Total unsat.) 79.63%

The component fatty acids in the ester fractions are given in Table 11 along with the composition of the original oil built up from these figures.

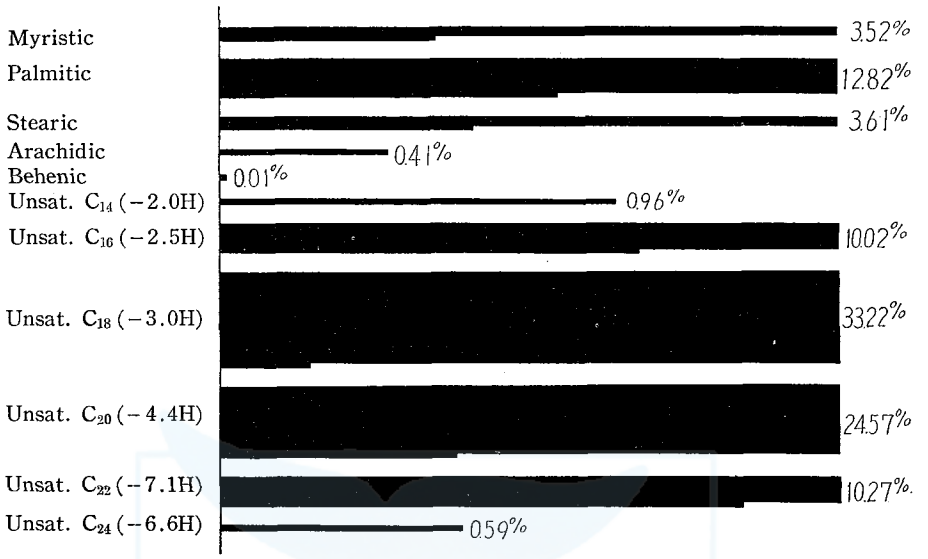

Fig. 3. Calculated composition of total acids in northern elephant seal oil.

DISCUSSION

According to the results reported by Burke & Jasperson (1944), Hildtich & Pathak (1947, 1949), Winter & Nunn (1950, 1953), the main portions of the fatty acid composition (percentages of weight) of the Newfoundland seal oil, Grey Atlantic seal oil and Antarctic elephant seal, *Mirounga leonina*, oil show the following ranges:

	North Atlantic seals	Antarctic seals
Total saturated	16 – 23	13 – 20
Palmitic	9 – 17	7 – 12
Unsaturated C_{16}	15 – 49(−2.1 to −2.2H)	8 – 16(−2.0 to −2.2H)
Unsat. C_{18}	16 – 37(−2.3 to −2.7H)	33 – 45(−2.1 to −2.7H)
Unsat. C_{20}	11 – 19(−5.7 to −7.2H)	13 – 28(−2.8 to −6.7H)
Unsat. C_{22}	5 – 18(−10.1 to −11.1H)	7 – 15(−4.9 to −10.5H)

by Hilditch (1956)

On the other hand, the component acids of the northern elephant seal, *Mirounga angustirostris*, oil studied by the writer show the following tendency:

The chief component acids belong to the unsaturated C_{18} series(33.22%; mainly oleic with some polyethenoid), the next prominent are those of the unsaturated C_{20} series (24.57%; mainly mono-ethenoid), palmitic acid (12.82%), the unsaturated C_{22} series (10.27%; mainly tetra-ethenoid) and the unsaturated C_{16} series (10.02%; mainly mono-ethenoid), whilst the saturated acids such as myristic, stearic, arachidic, behenic, and the

unsaturated C_{14}, C_{24} series are present in somewhat lower proportions.

Therefore, the composition of the northern elephant seal, *Mirounga angustirostris*, oil is on the whole similar to that of the Antarctic elephant seal, *Mirounga leonina*, oil and north Atlantic seal oil

SUMMARY

The fatty acid composition of the northern elephant seal, *Mirounga angustirostris*, oil was studied by the fractional distillation through Longenecker's E.H.P. column modified by the writer. The analysis in the present work was based on lithium and lead salt separations of the mixed fatty acids. According to the results obtained, the component acids are as follows:

The total saturated fatty acids content is 20.3% (myristic 3.52%, palmitic 12.82%, stearic 3.61%, arachidic 0.41% and behenic 0.01%) of the total. While, the total unsaturated acids content is 79.63% (C_{14} acids 0.96%, C_{16} acids 10.02%, C_{18} acids 33.22%, C_{20} acids 24.57%, C_{22} acids 10.27%, C_{24} acids 0.59%) of the total with the degree of unsaturation having $-2.0H$ in C_{14} acids, $-2.5H$ in C_{16} scids, $-3.0H$ in C_{18} acids, $-4.4H$ in C_{20} acids, $-7.1H$ in C_{21} acids and $-6.6H$ in C_{24} acids.

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