bution are in reasonably good agreement with those found experimentally. It should be pointed out that the determination of the four types of glycerides does not take into account the actual position a given fatty acid occupies on the glyceride molecule, as discussed by Quimby *et al.* (20).

The percentages of solid glycerides estimated from dilatometric measurements (Table IV) show further evidence of the effect of the sodium methylate treatment on lard. The lard containing lard flakes showed little difference in content of solids above 30°C., but below that temperature the effect of the treatment was still considerable. Tallow did not show any appreciable change.

Cooling curves and micropenetration measurements (Figures 1-5) present additional evidence of change in character of lard. A slight but apparently significant change in tallow was observed in the cooling curves. Despite the apparent increase in solid glyceride content of treated lard at 30°C. or higher temperatures (Table IV), the micropenetrations were

TABLE IV

Dilatometric Data—Estimated Percentages of Solids in Lard and Tallow before and after Treatment with Sodium Methylate

Temp. °C.	Lard				Tallow	
	Untreated	Treated	Untreated + 8% lard flakes	Treated + 8% lard flakes	Untreated	Treated
10	27.0	28.7	33.6	31.9	58.0	57.1
15	24.2	21.3	31.1	27.6	56.7	55.9
20	20.4	14.2	27.7	22.7	51.6	50.0
25	14.3	12.5	22.4	19.1	43.6	43.1
30	4.2	9.5	15.1	16.4	34.6	34.7
35	3.0	6.7	14.0	14.2	26.7	26.7
40	1.6	3.4	12.0	11.6	19.1	18.4
45	0.0	2.0	7.7	6.9	9.4	8.8
50	....	....	0.2	0.2	....	....

greater at these temperatures than those for the untreated lard (Figure 3). The addition of lard flakes greatly lessened the differences in micropenetrations between the treated and untreated lard.

Cake volume tests were conducted with the lard and treated lard to which 8% lard flakes had been added. In a typical test with pound cake formulation the treated lard yielded a cake volume of 225 cc. per 100 g. of cake compared to 190 cc. per 100 g. of cake for the untreated.

Summary

Treatment of lard with sodium methylate did not affect fatty acid composition nor the usual chemical constants and melting points. The glyceride composition however was altered considerably and showed close agreement with values calculated for random distribution. This change in glyceride composition was accompanied by significant changes in physical character as shown by consistency numbers, dilatometric and micropenetration measurements, and cooling curves.

Beef tallow remained almost unaffected by the sodium methylate treatment. The glyceride composition before and after treatment as determined by Kartha's method agreed well with values calculated for random distribution. Only the cooling curves indicated any change induced by the treatment.

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[Received April 27, 1955]

An Investigation of the Oil of Laemonema Morosum Matsubara. I. Research on the Docosenol Fraction

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THE FISH *Laemonema Morosum* Matsubara is native to the Pacific ocean near the northern part of Japan and is caught by a depth drag-net at 300–350 m. below the surface in deep sea areas. The flesh of this fish is used as food, and the oil is used in the leather industry. In this investigation it was found that the oil of this fish contains a large amount of unsaponifiable matter, consisting of the esters of higher alcohols and fatty acids instead of glycerides. Except for toothed whale oil, such an animal oil has not been reported before. The main component of the unsaponifiable matter of this oil is a new alcohol, 11-docosen-1-ol. Toyama has reported (6) the existence of docosenol in the oil of a bottle nose whale, but the structure of this alcohol was not determined because its content was very small. The docosenol in whale oil is liquid at room temperature while 11-docosen-1-ol is solid, m.p. 31.5–32.1°C. In the vegetable kingdom the existence of 13-docosen-1-ol has been confirmed in the seed wax of *simmondsia californica* (1).

Experimental and Discussion

a) *Properties of the Oil of Laemonema Morosum Matsubara.* The fish used in this research were obtained at the port of Shiogama, Miyagi Prefecture in Japan, and the photographs of the fishes are shown in Figures 1 and 2.

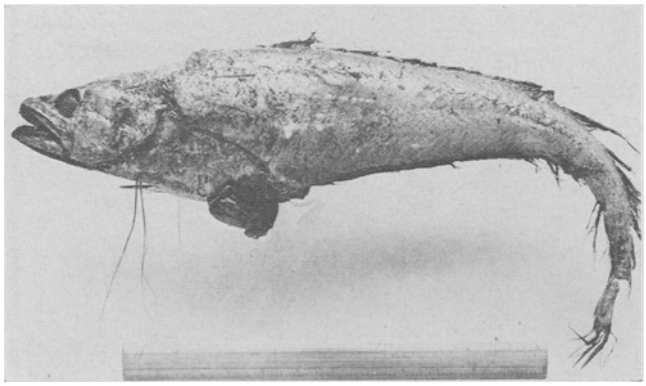

FIG. 1

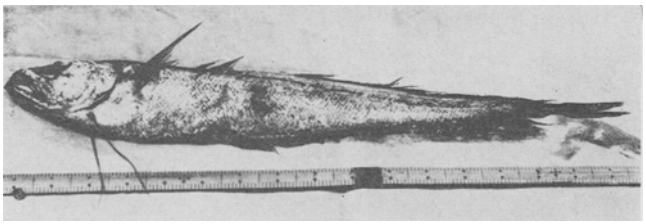

FIG. 2

The weight of each part of the fish is shown in Table I. Sample No. 1 in Table I was obtained from the fish shown in Figure 1.

The characteristics of the oils obtained from three sources are given in Table II. Sample No. 1 was a market oil of *Laemonema Morosum* Matsubara. Oil No. 2 was prepared by wet-rendering from the internal organs of the fish of Figure 2. Oils Nos. 3–5 were obtained by ether extraction from each part shown in Table I.

TABLE I

Sample No.	Length of fish (cm.)	Weight of fish (g.)	Weight of liver (g.)	Weight of internal organs except liver (g.)
1	55	857	57	37
2	46	560	71	39
3	51	472	27	16
4	51	550	37	18
5	44	362	42	19
Sum	....	2,801[a]	234[b]	129[c]

[a] Yielded 28 g. or 1.0% oil.
[b] Yielded 204 g. or 87.1% oil.
[c] Yielded 12 g. or 9.3% oil.

All samples showed a large amount of unsaponifiable matter and were different from common fish oil. Though it was a marketable oil, oil No. 1 was considered not to contain any other oil, and so we used it in the following experiments.

b) *Fractionation of the Unsaponifiable Matter.* From oil No. 1, (1,500 g.) the unsaponifiable matter (522 g.) was extracted by the usual method. This unsaponifiable matter was converted into acetate and was distilled as shown in Table III. Up to Fraction No. IV a long-necked (30 cm.) Claisen flask packed with Makmahon was used. For the other fractions a short-necked Claisen flask was used under high vacuum (0.1 mm. Hg.) in order to avoid isomerization at high temperature.

c) *Research on the Docosenol Acetate Fraction.* Fractions VIII and IX were considered to be docosenol acetate from the distillation temperature, the saponification value, and the iodine value. Research on these fractions was undertaken first because the existence of docosenol in natural oil is very rare. Fraction VIII (140 g.) was saponified and the alcohol obtained (128 g.) was fractionally crystallized from 300 ml. of methanol as shown in Table IV.

TABLE IV

Crystal No.	Cooling temp. (°C.)	Yield (g.)	Melting point (°C.)
1	0	31.1	28.0–31.7
2	−5	25.3	27.7–29.8
3	−15	29.6	28.8–29.1
Residue	....	33.8	yellow liquid at 20°C.

The crystals 1, 2, and 3 were mixed and recrystallized from methanol, acetone, and n-hexane successively. The crystals (41.5 g.) thus obtained had the following constants, m.p. 31.5–32.2°C., iodine value 78.7 (theoretical, 78.3), and acetyl value 153.0 (theoretical, 152.4). One gram of the crystals was hydrogenated over platinum black and then recrystallized from ether.

The crystals thus obtained had a melting point of 70.3–70.8°C. and were recognized as docosanol by the mixed melting point test with pure docosanol (3). Therefore the original unsaturated alcohol was docosenol. We concluded that the oil of *Laemonema Morosum* Matsubara did not contain any docosanol, partly because the iodine value of the docosenol mentioned above agreed with the theoretical value of docosenol and partly because the crystals, No. 1 in Table 5, readily dissolved in methanol.

Docosenol having m.p. 31.5–32.3°C. was acetylated with acetyl chloride. The acetate (5.0 g.) obtained was oxidized with powdered potassium permanganate (10 g.) in acetone (50 ml.) as mentioned in a previous report (4). After removal of 1.44 g. of neutral

TABLE II

Sample No.	Refractive index n_D^{20}	Acid value	Sap. value	Iodine value	Unsaponifiable matter		
					Yield (%)	Sap. value of acetate	Iodine value
1	1.4712	4.2	130.6	108.4	34.9	163.4	73.9
2	1.4709	1.8	135.6	112.6	31.0	165.7	75.4
3[a]	1.4694	2.1	130.3	120.7	34.0	164.2	78.6
4[b]	1.4729	2.8	157.3	115.7	22.5	169.3	80.5
5[c]	1.4783	2.3	137.3	113.5	28.9	172.5	81.3

[a] Liver oil. [b] Oil of internal organs except liver. [c] Body oil.

TABLE III

Fraction	Distill. temp. (°C.)	Yield (g.)	Yield (%)	Sap. value	Iodine value	Appearance at 20°C.
I	124/1 mm.	2.5	0.5	173.0	19.0	yellow liquid
II	124–135/1 mm.	7.0	1.3	199.4	13.8	light yellow liquid
III	135–145/1 mm.	7.5	1.4	197.2	23.5	crystal
IV	145–154/1 mm.	29.0	5.5	189.3	21.6	crystal
V	150/0.1 mm.	18.5	3.5	169.0	61.7	light yellow liquid
VI	150–160/0.1 mm.	112.5	21.2	167.9	70.3	light yellow liquid
VII	160–164/0.1 mm.	138.0	26.1	162.8	76.7	light yellow liquid
VIII	164–166/0.1 mm.	182.0	34.4	153.7	78.7	light yellow liquid
IX	166–167/0.1 mm.	13.5	2.5	153.0	86.2	light yellow liquid
Residue	.....	14.5	2.7	154.0	.....	light yellow liquid

substances, the oxidized product (3.37 g.) was fractionally distilled as in Table V.

Fraction 2 was recrystallized from water containing acetone and crystals having an m.p. 26.5–27.1°C. and a neutralization value 302.3 (theoretical value of undecanoic acid 301.4) were obtained.

TABLE V

	Distill. temp. (°C.)	Yield (g.)	m.p. (°C.)
1	155	0.3	18.3–19.8
2	155–175	1.67	23.0–24.5
3	175–215	1.52	.....

These crystals were proven to be undecanoic acid by the mixed melting point test. Fraction 3 in Table V was saponified, and the hydroxy acid was oxidized with chromic acid in acetic acid at 40°C. for one hour. The excess of chromic acid was reduced with methanol, and the acetic acid was distilled off under diminished pressure at 40°C. The oxidation products were extracted with ether, and a white powder (0.75 g.) having an m.p. 104.5–105.1°C. was obtained.

After washing with petroleum ether, the white powder was recrystallized from hot water, yielding crystals having an m.p. 107.5–108.3°C. The crystals were mixed, in the same ratio, with nonamethylene-1.9-dicarboxylic acid (m.p. 109.0–110.0°C.), and the mixture had an m.p. 108.5–109.5°C.

Therefore it was recognized that the dicarboxylic acid was nonamethylene-1.9-dicarboxylic acid and the original docosenol was 11-docosen-1-ol. This alcohol has never been reported and corresponds to cetoleic acid ($\Delta^{11,12}$-docosenoic acid). From the data of Table III the docosenol seems to constitute about 50% of the unsaponifiable matter of this oil. It might be thought that the melting point of 11-docosenol is too high compared with cetoleic acid (m.p. 32.5–33°C.) because the melting points of higher alcohols are much lower than those of corresponding acids as shown in Table VI.

TABLE VI

Alcohols	m.p. (°C.)	Acids	m.p.
Oleyl	2	oleic	13 or 16
Elaidyl	36–37	elaidic	51.5
Behenyl	70.6	behenic	79.95
Erucyl	34.4–35.5(5) 33.2–33.7(3)	erucic	33.5
Brassidyl (3)	53.0–53.5	brassidic	59.9
11-docosenol	31.7–32.3	cetoleic	32.5–33

The 11-docosenol (I) having the m.p. 31.2–32.0°C. was fractionated by the urea adduct method as follows. One part of docosenol, one part of urea, and six parts of methanol were mixed and warmed to 70°C. for 10 min. and then cooled to 10°C. The results are summarized in Figure 3.

In this experiment no substance having a higher melting point was separated. The 11-docosenol (I) (3 g.) was converted to the *trans* isomer at 30–35°C. with mercury (0.06 g.) and nitric acid (d 1.42, 0.22 g.) according to the method of H. N. Griffith and T. P. Hilditch (2).

The *trans*-11-docosenol obtained showed an m.p. 52.4–52.8°C. after recrystallizing three times from ethyl alcohol.

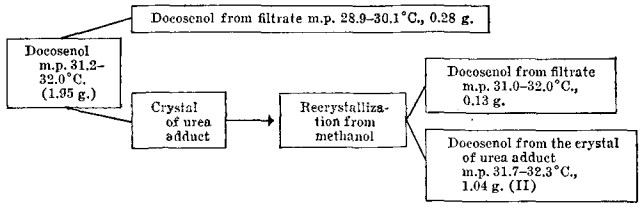

FIG. 3

The infrared spectra have been obtained on this *trans*-11-docosenol and 11-docosenol (II) in Figure 3. The measurements were made in carbon disulfide, 10% solution, 0.1-mm. thickness, with a Perkin-Elmer Model 21 Infrared Spectrophotometer. The results are presented in Figure 4. From a comparison of the

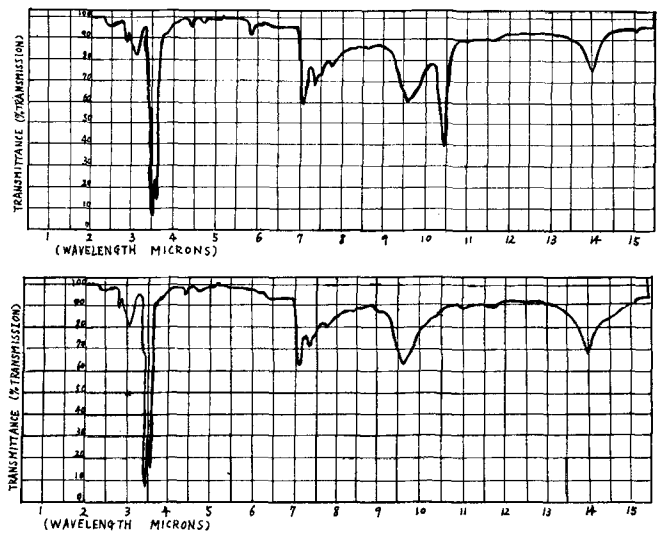

FIG. 4. Infrared spectra of trans-11-docosenol (upper figure) and 11-docosenol (II) in Figure 3 (lower figure).

absorption at 10.4 μ it was recognized that the 11-docosen-1-ol (II) did not contain any *trans* isomer which had been isomerized during the preparation of this alcohol.

Summary

It has been shown that the oil of *Laemonema Morosum* Matsubara, a deep sea fish, contains a large amount (31–34%) of unsaponifiable matter. The main component (*ca.* 50%) of which is 11-docosen-1-ol, has an m.p. 31.7–32.3°C. This alcohol has not been previously reported in the literature. From this alcohol *trans*-11-docosen-1-ol having m.p. 52.4–52.8° C. was prepared. The infrared spectra of these two alcohols are given.

Acknowledgment

The fishes and the oil used in this investigation were obtained through Yuji Suzuki, president of the Nihon Vitamin Company, and Toshiomi Nagata, manager of the Shiogama factory of the Nihon Vitamin Company. M. Matsubara, professor of Kyoto University, classified the fish. Dr. Toyama, professor of Nagoya University, gave us advice. The authors wish to express their sincere thanks to these individuals.

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[Received March 7, 1955]

Studies on the Oxygen Uptake of Fat Emulsions Used in Intravenous Alimentation[1]

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THE PARTICLES of fat in an emulsion which is suitable for intravenous nutritional purposes (1, 2, 3, 4) must be extremely small to avoid undesirable physiological reactions and to insure maximum stability. In such emulsions most of the particles of fat are well below 1 micron in diameter, resulting in an enormous surface area of lipids which might favor hydrolytic and oxidative reactions. Preliminary experiments, however, in which a coconut oil emulsion (1) was used, disclosed almost complete stability to both types of degradation reactions under normal conditions of storage.[2] To gain a better understanding of the factors involved in the oxidation of the highly dispersed lipid in such emulsions, a number of experiments were subsequently done in which the uptake of molecular oxygen by various emulsions and their individual components was studied manometrically. As pointed out by Holman (5), relatively little work has been done on the oxidation of emulsions of fat.

The problems investigated were a) the relative rates of oxidation of a typical emulsion and its components, b) the influence of the type of oil on the uptake of oxygen by emulsions, c) the influence of the type and concentration of stabilizer on the uptake of oxygen by both emulsions and the stabilizers themselves, d) the influence of particle size of the oil droplets on the oxygen uptake of emulsions, and e) the influence of temperature on the oxidation rate of emulsions and stabilizers. Although the conditions used for these measurements were not those dealt with in the actual use of the emulsions, they allowed comparisons to be made between various preparations in a relatively short period of time. Furthermore data so obtained should prove useful as a complement to results found when the more usual but more time-consuming procedures are used. The usefulness of the Warburg manometric method in studies on the oxygen uptake of oils has been shown (6, 7, 8).

Experimental

Preparation of Emulsions. The preparations used in the present studies were made by means of high pressure homogenization. The homogenizer was preheated to approximately 65°C. by means of hot water, rinsed with distilled water, and then flushed with nitrogen. The emulsion ingredients were added to the required amount of warm 5% dextrose solution, and the entire mixture was premixed in a blender for 5 min. The blender jar was provided with a thermometer and an inlet tube for nitrogen. The preparation was then transferred to the homogenizer[3] and emulsified at 3,000 lbs. p.s.i. until the diameter of the particles was well below 1 micron as determined by visual phase microscopy. Samples removed before the particles were this small are so designated under the proper experiment. In all cases the temperature was kept below 85°C., and a nitrogen atmosphere was maintained over the liquid in the reservoir. The finished emulsions were sealed in glass containers after flooding with nitrogen and autoclaved for 15 min. at 15 lbs. p.s.i. The sterile preparations were stored in the dark at room temperature and were used within two days from the time of preparation.

Method of Studying the Oxygen Uptake. The oxygen uptake was measured by conventional technique (9), using a Precision circular, twenty-place Warburg apparatus at 38°C. The shaking speed was 90 strokes per minute with an amplitude of 3 cm. Flasks with a capacity of 15 ml. were used, and the total liquid volume in the flask was 3 ml. Gassing was done with 100% oxygen for 10 min. and was followed by a 5-min. equilibration period. Resetting of the manometers was accomplished when necessary by opening the stopcock to air.

Oxygen Uptake Experiments. A large number of

[1] Supported in part by grants-in-aid from the Research and Development Division, Office of Surgeon General, Department of the Army (DA-49-0070MD-49); The Upjohn Company, Kalamazoo, Mich.; Atlas Powder Company, Wilmington, Del.; and Armour and Company, Chicago, Ill.

[2] Unpublished data obtained in this laboratory.

[3] Model 124 E, Manton Gaulin Manufacturing Company Inc., Everett, Mass.