

NOTES ON SOME LESS KNOWN AQUATIC ANIMAL OILS

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This paper records the results of our study on oils obtained from several kinds of aquatic animals caught in the Japanese waters. These oils have been little or not studied. Only some data on the properties of a few specimens of some of these oils have been recorded in previous literatures.

1. Grampus oil

A specimen of oil produced from a grampus, *Grampus orca* (Linné), caught in Sea of Japan, was submitted to us for examination from the former Teikoku Yuryo Tosei Co. (a control concern for fats and oils; now dissolved). Bull and Sörvig¹⁾ reported that grampus oil has high saponification and Reichert-Meissl values; oil from upper jaw having S.V. 257.8 and R.M.V. 43.7 resembles dolphin jaw and head oils. Although saponification value of the oil examined by us was not high, the results of our experiments described below on volatile fatty acid components and unsaponifiable matter indicated that this oil, like dolphin oil, contains isovaleric acid and cetyl and oleyl alcohols.

Three hundred g of oil was saponified with potassium hydroxide in ethanol. After completion of the saponification, ethanol was distilled off, and dilute sulfuric acid was added to the residue. The mixture was then subjected to steam distillation, and the distillate was neutralized with sodium hydroxide and evaporated to dryness. The residue was acidified with sulfuric acid, and then extracted with large amounts of ether. The ether solution obtained was washed with a saturated solution of sodium chloride. On distilling off ether from the ether solution, there was obtained 3 g of liquid having an odor suggestive of isovaleric acid. This was converted into methyl ester from which a fraction of B.P. 115°-116° C was separated as methyl isovalerate; d_4^{20} 0.8785 and n_D^{20} 1.3918.

The unsaponifiable matter separated from the oil was dissolved in three times its weight of acetone, the solution was cooled to -10° C, and a solid material was separated. The liquid material obtained from the filtrate gave on acetylation a product which had S.V. 179.2 and I.V. 87.4 and was considered to consist mainly of oleyl acetate (calculated, S.V. 180.7 and I.V. 81.7). The solid material had M.P. 49.5°-50° C. Fractional crystallization of the solid material from acetone gave the crops of M.P. 49.5°-51° C, M.P. 51°-51.5° C and M.P. 50°-50.5° C, all of which were considered to consist chiefly of cetyl alcohol.

2. Right whale oil

This oil was prepared by rendering a small lot of blubber which was received

by the courtesy of the former Ogasawara Whaling Base of the Nihon Suisan Co. The blubber had been obtained from a male right whale, *Balaena glacialis sieboldii* Gray, of 12 m in length.

3. Mullet oil

Tsuchiya and coworkers²⁾ have recently reported some properties of an ether extracted mullet viscera oil. The mullets, *Mugil cephalus* L., used in the present study were mature ones, "Bora" in Japanese, of an average weight of 708 g caught in the Kishu waters and young mullets, "Ina" in Japanese, of an average weight of 218 g caught in the coast waters of Chita, Aichi Prefecture, both having been procured in the autumn, 1952. Fish bodies excepting viscera, which were previously separated, were boiled with water, and the creamy layer formed on the upper part was separated, washed several times with hot water and then taken up with ether. The ether solution was dehydrated, and the ether was distilled off. The viscera were heated at 60°-80° C for a short time, and then extracted with ether. The ether extract (lipid) was treated with acetone for the removal of insoluble phosphatide, and an acetone soluble oil was obtained. The yields of oil were low; 1.2% for body oil of mature mullet; 2.7% for body oil of young mullet and 3.3% for viscera oil of young mullet.

4. Oil from *Trachurus japonicus* (Temminck and Schlegel)

Some properties of a specimen of viscera oil from this fish have recently been reported by Tsuchiya and coworkers.²⁾ The fish caught in the autumn, 1952, in the coast waters of Aichi Prefecture were divided according to their size into two groups; the one having an average weight of 34 g and the other having an average weight of 222 g. Each one excepting viscera, which were previously separated, was boiled with water, and the fluid was separated from the residue by using a hand press. The creamy layer formed on the upper part of the fluid was separated and treated in the same way as described in the case of mullet body oil. The yields of oil were below 1% both for small and large fish. The viscera were treated in the same way as described in the case of mullet viscera oil, yielding 8.2% of oil from the viscera of small fish and 13.3% of oil from the viscera of large fish.

5. Oil from *Hexagrammos otakii* Jordan and Starks

The mature fish of this kind is called "Ainame" in Japanese, while the young fish is locally called "Kujime". The fish used in the present experiments were young fish caught in the coast waters of Chita in the autumn, 1952. Oil was prepared from the body excepting viscera in the same way as described for mullet. The yield of oil was below 1%.

6. Oil from "Raigyo", *Ophiocephalus tadianus* Jordan and Everman

The fish used in the present experiments were caught in a river in Aichi Prefecture in the autumn, 1952. Since the body excepting viscera did not yield oil by rendering, it was extracted with ether and the ether-extract was treated with acetone. The viscera were similarly treated.

TABLE 1

Oil	Appearance ^{a)}	d_4^{20}	n_D^{20}	A.V.	S.V.	I.V.	Unsap. M. (%)	Fatty acid			Poly-bromide ^{e)} (%)	Remarks
								N.V.	I.V.	Solid F.A. (%) ^{b)}		
<i>Grampus orca</i>	Orange yellow	0.9135	1.4701	1.04	186.5	112.3	7.54	—	—	—	21.77	R.M.V. 6.72
<i>Balaena glacialis sebolitii</i>	Light yellow	0.9196	1.4760	2.64	186.6	132.2	0.46	—	—	—	30.00	Br in Poly-bromide 70.02%; I.V. of solid F.A. 3.1
<i>Mugil cephalus</i> ; mature; body	Orange yellow; with solid	0.9306	1.4803	1.50	197.8	159.0	0.72	—	—	18.30	—	I.V. of solid F.A. 3.1
<i>Mugil cephalus</i> ; young; body	Orange yellow; with solid	0.9298	1.4787	1.44	200.2	163.1	0.65	—	—	20.36	—	I.V. of solid F.A. 3.4
<i>Mugil cephalus</i> ; young; viscera	Dark reddish orange; with much solid	0.9361	1.4817	28.4	195.6	151.7	4.43	212.3	155.3	—	—	—
<i>Trachurus japonicus</i> ; small size; body	Orange yellow; with solid	0.9248*	1.4818	10.6	193.6	150.4	1.48	199.2	156.3	—	58.76	—
<i>Trachurus japonicus</i> ; small size; viscera	Dark reddish orange; with much solid	0.9327*	1.4827	14.9	188.2	155.2	2.58	—	—	—	56.74	—
<i>Trachurus japonicus</i> ; large size; body	Orange yellow; with a little solid	0.9165*	1.4767	3.26	192.4	136.7	1.56	198.6	141.9	20.57	47.45	I.V. of solid F.A. 8.7
<i>Trachurus japonicus</i> ; large size; viscera	Dark reddish orange; with much solid	0.9223*	1.4778	12.3	188.5	135.8	2.47	197.7	139.9	24.81	48.01	I.V. of solid F.A. 7.0
<i>Hexagrammos otakii</i> ; male; body	Orange yellow	—	1.4801	55.0	184.7	153.9	2.19	190.0	159.8	12.81	35.70	I.V. of solid F.A. 8.9
<i>Hexagrammos otakii</i> ; female; body	Orange yellow	—	1.4807	22.5	185.2	157.1	1.02	192.1	164.4	13.59	32.83	I.V. of solid F.A. 8.9
<i>Ophiocephalus tadius</i> ; body	Dark reddish orange; with solid	0.9344	1.4776	19.5	173.3	116.7	9.95	201.5	119.2	23.80	24.49	I.V. of solid F.A. 9.7
<i>Ophiocephalus tadius</i> ; viscera	Dark reddish orange; with solid	0.9239	1.4747	2.01	189.1	124.2	4.01	—	—	21.40	27.19	I.V. of solid F.A. 3.7
<i>Katsuonus vagans</i> ; liver; sample A	Dark reddish orange; with much solid	0.9590	1.4954	75.8	166.0	219.3	13.76	186.8	237.8	—	82.73	E=35.3 ^{c)} ; sterol 26.87% ^{e)}
<i>Katsuonus vagans</i> ; liver; sample B	Dark reddish orange; with much solid	0.9617	1.4968	82.3	161.7	223.7	16.11	187.1	244.2	—	91.56	E=38.5; sterol 30.28%
<i>Katsuonus vagans</i> ; liver; sample C	Orange yellow	0.9200	1.5035	2.14	132.6	239.4	28.64	188.0	241.0	—	87.25	E=84.7
<i>Spheroides pardalis</i> ; liver	Light yellow; with solid	0.9243	1.4786	6.00	182.4	157.2	2.37	—	—	—	49.70	E=0.202
<i>Spheroides pardalis</i> ; liver	Light yellow; with solid	0.9259	1.4796	2.94	180.3	171.9	2.48	—	—	—	56.92	E=0.219; Br in polybromide 70.47%; sterol 28.66%

Notes. ^{a)}: Appearance at ordinary temperature; ^{b)}: By lead salt ethanol method; ^{c)}: Ether-insoluble bromide from the mixed fatty acids; ^{d)}: E denotes $E_{1\text{cm}}^{1\%}$ at 328 m μ ; ^{e)}: Sterol content of unsaponifiable matter; *: d_4^{25} .

7. Bonito liver oil

Frozen bonito livers prepared from bonito, *Katsuwonus vagans* (Lesson), caught off the coast of Kanagawa Prefecture were used in the present experiments.

For preparation of liver oils, a portion of livers was heated for a short time and then extracted with ether, giving the sample oils *A* and *B*. These sample oils were not treated with acetone. Accordingly they are afraid of being contaminated with phosphatides to a large proportion. Another portion of livers was digested with a solution of caustic soda, and the mixture was allowed to stand over a night. The oily layer formed on the upper part was separated, washed with water, and then taken up with ether. Dehydration of the ether solution followed by distillation of ether gave the sample oil *C*. The yields were 7.4%, 8.6% and 2.6% for the sample oils *A*, *B* and *C*, respectively. According to a recent study of Tsuchiya and coworkers,²⁾ bonito liver oils have iodine values of 222.9-224.0, while the iodine values of bonito liver oils produced in Formosa were reported by Kafuku and coworkers³⁾ to be 114.09-132.56. The bonito liver oils examined by us, like liver oils reported by Tsuchiya and coworkers, had very high iodine values in contrast to lower iodine values reported for the Formosan oils.

8. Swellfish liver oil

Oil samples examined by us were prepared by the melting out process from livers of swellfish, *Spheroides pardalis* (Temminck and Schlegel) caught in the coast waters of Shimonoseki.

The properties of the oils examined by us are given in Table 1.

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References

- 1) Halden-Grün: "*Analyse der Fette und Wachse*," II, 431.
- 2) T. Tsuchiya, R. Kaneko and T. Endo: *J. Chem. Soc. Japan, Ind. Chem. Sect.* **56**, 350 (1953).
- 3) K. Kafuku, T. Ikeda and R. Kato: *J. Chem. Soc. Japan* **54**, 325 (1933).