ON THE OCCURRENCE OF MANY NEW CONSTITUENTS IN THE UNSAPONIFIABLE MATTER OF SPERM BLUBBER OIL.

By **Sei-ichi UENO** and **Ryosei KOYAMA**.

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The occurrence of some new alcohols (C_8–C_{14}), hydrocarbons and ethers in sperm blubber oil has already been pointed out by the authors(1), and Toyama and co-operators(2) have found $C_{14}\overline{\overline{\ulcorner}}_1$ and $C_{16}\overline{\overline{\ulcorner}}_1$ alcohols in sperm blubber oil.

The present authors have made further investigation on the composition of the new constituents which they found in sperm blubber oil and undertaken the naming of these compounds.

A large amount of the unsaponifiable matters used in this investigation was prepared by the method reported in the preliminary report. The distillates which came out until the temperature of oil bath 200°C. under 70 mm., were further fractionally distilled under 15 mm. For the convenience

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(1) *J. Soc. Chem. Ind., Japan,* **38** (1935), 608B; *J. Chem. Soc. Japan,* **56** (1935), 1145, 1146.

(2) *J. Chem. Soc. Japan,* **56** (1935), 920.

of the experimental course the distillates were divided into two parts. Part 1 distilled out until 160°C. and part 2 at 160–180°C. By the usual method by means of Na-alcoholate, hydrocarbons and alcohols were separated. The percentages of hydrocarbons and alcohols are as follows:

	Alcohols	Hydrocarbons
Part 1	43	57
Part 2	38	62

Separation of Saturated and Unsaturated Alcohols. *Part 1.* The mixed alcohols thus separated from hydrocarbons were subjected to the fractional distillation under 15 mm. and the results of the final distillation and characteristics of each fraction are given in Table 1.

Table 1.

Fraction	Temp. (°C.)	Yield (g.)	Iodine value (Wijs)	d_4^{30}	n_D^{30}
1	85– 90	2.8	50.1	0.8191	1.4329
2	90– 95	3.9	50.8	0.8191	1.4347
3	95–100	5.5	49.1	0.8231	1.4362
4	100–105	12.4	49.2	0.8239	1.4378
5	105–110	6.9	49.2	0.8261	1.4397
6	110–115	6.4	52.6	0.8265	1.4408
7	115–120	3.5	51.9	0.8292	1.4420
8	120–125	4.2	50.6	0.8298	1.4422
9	125–130	2.9	52.6	0.8335	1.4434

From the iodine values of these portions it will be easily seen that each fraction is a mixture of saturated and unsaturated alcohols. For the purpose of separating it into individual alcohols it was acetylated, and then dissolved in ether, and the solution was cooled with ice water and a little excess of bromine was gradually added with constant stirring and care. The ethereal solution was then washed with sodium thiosulphate solution and dehydrated with anhydrous sodium sulphate. The ether was evaporated off on a water bath and the residual liquid was then distilled under 10 mm. The residual bromine was debrominated by usual method and the substance was saponified with alcoholic KOH solution. Free alcohol thus obtained was distilled once more. The results of separation of each fraction are given in Table 2.

Table 2.

	Weight of sample (g.)	Yield (g.)		B. p. (°C.)	d_4^{25}	n_D^{25}	Iodine value (Wijs)
Fraction 3	5.2	sat.	2.1	88–92/14mm.	0.8249	1.4301	17.4
		unsat.	0.7	95–98/15mm.	0.8260	1.4413	111.1
,, 4	3.8	sat.	1.2	104/15mm.	0.8285	1.4330	16.7
		unsat.	0.8	80/15mm.	0.8230	1.4417	67.4
,, 7	5.5	sat.	2.0	111/27mm.	0.8219	1.4346	15.6
		unsat.	1.0	105/15mm.	0.8443	1.4414	80.4

From the results of the above experiment it seemed possible to complete the separation of saturated and unsaturated alcohols, though a remarkable decrease of yield was unavoidable. The samples were so small in quantity that no further separation by the method has been carried out.

Part 2. The mixed alcohols freed from hydrocarbons were separated in the same way as in part 1. The experimental results are shown in Table 3 and Table 4.

Table 3. Saturated Alcohols.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}	Iodine value (Wijs)
10	-110	3.3	0.8304	1.4387	28.0
11	110–115	4.1	0.8307	1.4413	23.5
12	115–125	4.5	0.8300	1.4430	27.1
13	125–135	4.7	0.8205	1.4445	22.0
14	135–145	2.4	0.8237	1.4464	24.4
15	145–155	5.6	0.8301	1.4478	22.2
16	155–165	1.9	—	1.4479	13.2
17	165–170	3.0	—	1.4503	14.6
18	170–	0.6	—	—	16.2

Table 4. Unsaturated Alcohols.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}	Iodine value (Wijs)
19	-145	0.4	—	1.4420	115.4
20	145–155	2.5	0.8325	1.4439	107.3
21	155–165	1.4	0.8341	1.4441	91.8
22	165–175	3.2	0.8406	1.4440	68.5
23	175–185	3.2	0.8592	1.4436	58.2
24	-185/8mm.	5.9	0.8583	1.4435	14.6

Detection of Saturated Alcohols in Each Fraction. (1) *Fractions 1 and 2.* It was recognized that these fragrant frations contain a small amount of hydrocarbons. From 5.1 g. of the sample, 1.8 g. of the alcohol were taken. It was difficult to separate the saturated alcohol from the mixed alcohols owing to the small quantity, so that the alcohol was brominated immediately and was distilled with care. As the yield obtained in the distillation was only some drops, the authors could not determine boiling point and characteristics. (Found: C, 72.19; H, 13.92. Calculated for $C_7H_{16}O$: C, 72.33; H, 13.89%.) The results of elementary analysis exactly corresponded to heptanol. Though the reaction product of this alcohol with phenyl isocyanate was a liquid, that with 4-iodo-biphenylyl-4′-isocyanate was crystals melting at 150.5°C. From the experimental results it is assumed that the alcohol corresponds to heptanol-(1), but it can not be confirmed because the oxidation product of this alcohol was not investigated.

(2) *Fraction 3.* The sample (2 g.) was fractionated under 17 mm. as follows: fraction A distilling below 95°; B at 95–97°; and C over 97°. Fraction B was the main distillate, and A and C were very small in quantity. (d_4^{25} 0.8249, n_D^{25} 1.4302. Found: C, 73.53; H, 13.96%; molecular refraction, 40.77. Calculated for $C_8H_{18}O$: C, 73.77; H, 13.94%; molecular refraction, 40.67.) Phenylurethane and α-naphthylurethane of this alcohol melted at 74° and 65° respectively, and no depression was observed in mixed melting points with corresponding urethanes of octanol-(1) (74° and 65°). (Found for phenylurethane: N, 5.32. Calculated for $C_{15}H_{23}NO_2$: N, 5.62%. Found for α-naphthylurethane: N, 4.50. Calculated for $C_{19}H_{25}NO_2$: N, 4.53%.) The acid amide prepared from this alcohol melted at 97°, and it was identified with caprylamide by mixed melting point (97.5°) with an authentic specimen (Found: N, 9.58. Calculated for $C_8H_{17}NO$: N, 9.78%).

(3) *Fraction 4.* After saturated alcohol was separated from this portion, redistillation was carried out under 15 mm. (Table 5).

Table 5.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}
A	–102	0.9	0.8277	1.4322
B	102–105	2.1	0.8285	1.4330
C	105–	0.8	0.8286	1.4330

Fraction B (Found: C, 74.80; H, 14.11. Calculated for $C_9H_{20}O$: C, 74.91; H, 13.98%) was subjected to the oxidation with dil. HCl and chromic acid and the product was transformed into acid amide, m.p. 97°C. (Found: N, 8.77. Calculated for $C_9H_{19}NO$: N, 8.91%). There seemed to exist an alcohol having the molecular formula $C_9H_{20}O$, but the occurrence of C_8- and C_{10}-alcohols has not been determined. A further investigation on this problem will be published in later communication.

(4) *Fractions 5 and 6.* The saturated alcohols (6.1 g.) separated from the unsaturated were distilled under 15 mm. (Table 6).

Table 6.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}
A	-100	2.1	0.8277	1.4319
B	100–105	1.3	0.8281	1.4329
C	105–110	0.4	0.8285	1.4331
D	110–	0.7	0.8286	1.4333
Residue		0.9	—	—

M. p. of phenylurethane from fraction A	72°
,, ,, from octanol-(1)	72°
,, ,, from fraction B	60.5°
,, 4-iodo-biphenylylurethane from fraction B	145°
,, phenylurethane from fraction D	71.5°

It was shown fractions B and D were still impure.

(5) *Fraction 7.* Saturated alcohols (4.8 g.) were fractionally distilled under 15 mm. (Table 7).

Table 7.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}
A	-115	0.3	0.8290	1.4339
B	115–120	3.0	0.8292	1.4344
C	120–	0.8	0.8294	1.4346

Further fractional distillation of fraction B was carried out under 15 mm. (Table 8).

Table 8.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}
a	-117	1.4	0.8292	1.4342
b	117-120	1.1	0.8292	1.4345

Fractions a and b were identified with decanol-(1) and the authors propose a name "cachalotyl alcohol" for this alcohol. (Found for fraction b: C, 75.80; H, 14.09%; molecular refraction, 49.84. Calculated for $C_{10}H_{22}O$: C, 75.86; H, 14.02%; molecular refraction, 49.90.) Phenylurethane, m.p. 72.5° (Found: N, 4.88. Calculated for $C_{17}H_{27}NO_2$: N, 5.05%). α-Naphthylurethane, m.p. 66.0° (Found: N, 4.12. Calculated for $C_{21}H_{29}NO_2$: N, 4,15%). Oxidation product of fraction a, m.p. 29°. Acid amide from fraction a, m.p. 106.5° (Found: N, 8.12. Calculated for $C_{10}H_{21}NO$: N, 8.18%).

(6) *Fractions 10, 11, and 12.* Hydrocarbons were completely separated from these fractions in the same way as described above.

(7) *Fraction 13.* After the separation of hydrocarbons the residual alcohol was redistilled under 15 mm.: fraction A (2.0 g.) distilling below 140°, and B (1.4 g.) at 140-150°. Fraction B was combined with next fractions.

(8) *Fractions 14 and 15.* These fractions (7.1 g.) were fractionated under 15 mm.: fraction A (0.4 g.) distilling below 140°, B (6.3 g.) at 140-150°. Fraction B was again distilled under 15 mm. (Table 9).

Table 9.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}
a	140-142	1.9	0.8300	1.4426
b	142-145	2.5	0.8312	1.4440
c	145-150	1.0	0.8322	1.4457

(Found for fraction b: C, 77.36; H, 14.05; molecular refraction, 59.50. Calculated for $C_{12}H_{26}O$: C, 77.33; H, 14.07; molecular refraction, 59.14.) Phenylurethane, m.p. 68° (Found: N, 4.49. Calculated for $C_{19}H_{31}NO_2$: N, 4.59%). α-Naphthylurethane, m.p. 74° (Found: N, 3.69. Calculated for $C_{23}H_{33}NO_2$: N, 3.83%).

The analytical results correspond to $C_{12}H_{26}O$, and the lower melting point of the phenylurethane from b compared with that of lauryl alcohol is due to the presence of two different saturated alcohols. Phenylurethane obtained by the recrystallisation from methyl alcohol showed m.p. 71°C., while that obtained from the mother liquor melted at 69.5°C. (Found for phenylurethane melting at 71°: C, 66.77; H, 10.41. Calculated for $C_{19}H_{31}NO_2$: C, 66.83; H, 10.24%. Found for phenylurethane melting at 69.5°C.: C, 66.71; H, 10.45. Calculated for $C_{19}H_{31}NO_2$: C, 66.83; H, 10.24%). The authors propose to call these alcohols "catadontidaeyl alcohol" and "isocatadontidaeyl alcohol", respectively.

(9) *Fraction 16*. This fraction is under experiment.

(10) *Water-soluble material*. The sample used in this investigation was collected in the case of distillation of the unsaponifiable matter. The alcohol in this sample was extracted with ether, and transformed into phenylurethane melting at 70°C. The experiments with the acid amide melting at 95–96°C. also showed that this water-soluble material mainly contains octanol-(1).

Detection of Unsaturated Alcohols. The authors could not determine the constituents because of minute amounts of the samples compared with saturated alcohols. The results of analyses are given below.

(1) *Fraction 3*. The characteristics and the results of analysis are as follows: B.p. 94–95°C./15 mm., d^{25}_{4} 0.8261, n^{25}_{D} 1.4414. (Found: C, 75.07; H, 12.77%; molecular refraction, 40.99. Calculated for $C_8H_{16}O$: C, 74.92; H, 12.59%; molecular refraction, 40.20.) The authors propose for this alcohol a name "agorophyl alcohol".

(2) *Fraction 4*. Characteristics: B.p. 100–102°C./15 mm., d^{25}_{4} 0.8340, n^{25}_{D} 1.4417. (Found: C, 76.71; H, 13.09. Calculated for $C_{10}H_{20}O$: C, 76.84; H, 12.91%.) For the alcohol the authors propose a name "macrocephalyl alcohol".

(3) *Fraction 20*. Characteristics: B.p. 140–141°C./17 mm., d^{25}_{4} 0.8361, n^{25}_{D} 1.4433. (Found: C, 77.74; H, 13.27%; molecular refraction, 53.99. Calculated for $C_{11}H_{22}O$: C, 77.75; H, 13.03%; molecular refraction, 53.06.)

By the oxidation with 5% ozone in chloroform solution, a pale yellow ozonide was obtained. The ozonide was decomposed with chromic acid in dilute acid solution and an acidic substance was obtained. It was extracted with ether, and on distilling off the ether an oily substance remained, which was separated into hardly soluble and soluble parts by shaking with water. The melting point of the acid amide obtained from the hardly soluble part through acid chloride, corresponds to peralgonic acid amide. From the soluble part the formation of oxalic acid was recognised. Though the authors could not identify it with certainty owing to the small quantity of the sample the constitution may be assumed to be as follows: $CH_3\cdot(CH_2)_7\cdot CH{=}CH{-}CH_2OH$.

(4) *Fraction 2.* Characteristics: B.p. 156–158°C./17 mm., d_4^{25} 0.8405, n_D^{25} 1.4440. (Found: C, 78.25; H, 13.37%; molecular refraction, 58.21. Calculated for $C_{12}H_{24}O$: C, 78.18; H, 13.13%; molecular refraction, 58.67.) The name "odontocetyl alcohol" is proposed.

Hydrocarbons and Ethers. The mixtures of hydrocarbons and ethers obtained by separating alcohols from part 1 and part 2 were fractionally distilled under 70 mm. (Tables 10 and 11).

Table 10. Part 1.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}	Iodine value (Wijs)
1	100–105	3.5	0.8193	1.4390	90.5
2	105–112	2.6	0.8195	1.4410	97.7
3	112–114	3.5	0.8237	1.4452	95.9
4	114–118	2.9	0.8245	1.4470	96.4
5	118–120	8.0	0.8242	1.4523	98.3
6	120–130	4.6	0.8155	1.4550	105.0
7	130–135	3.4	0.8149	1.4542	105.8
8	135–145	2.7	0.8053	1.4520	
Residue and loss		3.7			

Table 11. Part 2.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{25}	n_D^{25}	Iodine value (Wijs)
9	112–115	1.0	0.8651	1.4762	100.3
10	115–120	2.4	0.8651	1.4741	91.3
11	120–125	2.2	0.8592	1.4708	85.4
12	125–130	3.0	0.8584	1.4680	75.2
13	130–135	2.2	0.8450	1.4657	75.5
14	135–140	4.0	0.8348	1.4600	75.4
15	140–145	2.9	0.8318	1.4600	79.1
16	145–150	8.6	0.8285	1.4600	85.9
17	150–155	5.0	0.8248	1.4593	85.7
18	155–160	9.5	0.8220	1.4581	82.1
19	160–165	5.8	0.8189	1.4568	86.8
20	165–170	7.3	0.8132	1.4552	93.5
21	–140/4mm.	5.3	0.8266	1.4532	83.9

The lower fractions have very sweet odour. With the lapse of time they gradually changed from orange to brown in colour. When these fractions were distilled under atmospheric pressure polymeric substances having high melting points were produced.

Colour Reactions of the Fractions Distilling below 120°/70 mm. The fractions distilling below 120°/70 mm. gave the following colour reactions: (1) On the addition of bromine the colour changed from pink to dark purple through purple. (2) On dropping conc. HCl-alcoholic solution and conc. potassium nitrite solution in the sample and cooling with ice, it gets green colour and the solution showed orange colour on adding to ether. (3) In Denigé's reaction light yellow precipitate was obtained.

The Results of Analyses of the Above-mentioned Fractions (Table 12).

Table 12.

Fraction	Found		Fraction	Found	
	C	H		C	H
3 b.p. 112-114°/70mm. d_4^{29} 0.8200 n_D^{29} 1.4511 iodine value (Wijs) 40.8	81.15	12.64	18	85.40	13.39
	81.43	12.51		85.79	13.00
16	83.39	15.20	20	90.19	9.39
	83.40	15.09		88.89	9.30

Examination of the Fractions below 120°/70 mm.; Detection of a Tertiary Alcohol. The existence of a tertiary alcohol in this fraction was recognised by Denigé's reaction, but separation of it from unsaturated hydrocarbon was very difficult. A further investigation of this problem will be continued.

Ethers. A substance which seemed to be ethers was obtained from the fraction distilling below 120°C./70 mm. by separating alcohols, (Found: C, 81.36, 81.21; H, 12.70, 12.91. Calculated for $C_{18}H_{34}O$: C, 81.12; H, 12.87%). The absence of tertiary alcohols in this fraction was shown by the negative result of Denigé's reaction. Also the existence of OH-group was not recognised by Tschugajeff-Zerewitinoff's reaction. Accordingly the authors assumed that the oxygen detected by analysis was ethereal oxygen, and gave a general name "sperm oil ethers" and the naming of the individuals is preserved for next report.

The tetrahydro-compound obtained by hydrogenation in the presence of Adams Pt-black catalyst under high pressure (100 atm.) was distilled. The distillate gave the following characteristics: b.p. 223–224°C./75 mm., d_4^{30} 0.8191, n_D^{30} 1.4463 (Found: C, 79.88; H, 14.33%; molecular refraction, 86.64. Calculated for $C_{18}H_{38}O$: C, 79.92; H, 14.16; molecular refraction, 86.03).

The reaction product obtained by heating the tetrahydro-compound (4.2 g.) with HI (sp. gr. 1.7, 10 g.) in a sealed tube 6 hrs, 160°C.), was extracted with ether, washed with water, and fractionally distilled under 15 mm.: A –100°C., 0.2 g.; B 100°C.–, 0.3 g.; C residue, 2.2 g. Crystals obtained from fraction B and 4-iodo-biphenylyl-4′-isocyanate melted at 145°C. corresponding to decanol-(1). From fraction A crystals could not be expected. Though the authors could not give a determinate constitution for this hydrogenated ether, they assumed the following: $C_{10}H_{21}–O–C_8H_{17}$.

In the same way as mentioned above ethers were separated from fraction 6, yield 0.2 g., b.p. 126°C./70 mm. (Found: C, 81.82; H, 13.40. Calculated for $C_{20}H_{38}O$: C, 81.55; H, 13.02%).

Department of Chemical Technology,
Faculty of Engineering,
Imperial University of Osaka.