Biochemical Studies on Pityrol, VI : Distillation of Palmitic Acid

AUTHOR(S):

Shoyama, Seiichi

CITATION:

Shoyama, Seiichi. Biochemical Studies on Pityrol, VI : Distillation of Palmitic Acid. Memoirs of the College of Science, Kyoto Imperial University. Series A 1928, 11(6): 533-542

ISSUE DATE:

1928-11-25

URL:

http://hdl.handle.net/2433/256862

Biochemical Studies on Pityrol, VI. Distillation of Palmitic Acid

By

Seiichi Shoyama

(Received September 12, 1928)

I. PREPARATION OF PALMITIC ACID

Palmitic acid, one of the chief constituents of fatty acids occurs in rice oil, which is easily obtained and in a pure state from Haze tallow. According to Dr. Tsujimoto,[1] the fatty acids of Haze tallow are composed of 84 % palmitic acid, 14 % oleic acid and 2 % Japanic acid, and the tallow was regarded by the writer as a good source in Japan, for the preparation in a pure state, of palmitic acid. The raw material which showed the constants, was saponified with a caustic soda solution, and the mixture of sodium salts of the fatty acids separated from the glycerine solution was treated with sulphuric acid. The free fatty acids-mixture was subjected to distillation under 15 mm. pressure after being dehydrated by the melting process, and the fraction B.p. 215°–220° was collected for palmitic acid which shows the following constants:

	Haze tallow	
M. p.	49°–53°	
Saponification number	227 –246	
Acid number	20 –28	
Ester numer	207 –218	
Iodine „	8.5–9	
	Palmitic Acid	
B. p.	(215°–220°)	15 mm.
M. p.	59°	
Iodine number		8.5

The yield was about 60 % of the theory. The purity of the acid was calculated from its iodine number to be about 90 %, assuming the presence of oleic acid to be an impurity.

II. DISTILLATION OF SODIUM PALMITATE

The sodium salt of the acid was prepared by neutralizing the acid with sodium carbonate, and purified by recrystallization from alcohol solution. The sodium content was determined to be Na=9.3% while the theory requires 8.7%.

25 gm. of dry sodium salt were distilled in Fischer's aluminium retort; it appears that gas is evolved up to about 380° and the distillation of tar commenced at 400°, the evolution of tar and gas rapidly increased at about 440° and is finished at about 540°. The yield of tar, coke and gas is 70%, 24% and 6% respectively.

The chemical composition of gas was determined with the following results:

CO	11.8 %
CO_2	12.2 „
C_2H_4	1.7 „
$C_nH_{2n+2}+H$	27.4 „

The coke which shows 27.6% of ignition loss, was assumed to be composed of sodium carbonate, containing Na=44.1, with some organic matter asan impurity.

2 kg. of the salt yielded by the operation 1370 grm. of tar which is a yellowish brown oil of green fluorescence and a burning odour, and was separated first by steam distillation into two fractions-volatile and non-volatile parts:

Volatile part	45 %
Non-valatile „	55 „

A. VOLATILE PART

The volatile part, having as constants, B.p. 80°-270°; d_4^{21}=0.748; iodine-no. 119, was assumed to be a mixture of saturated and unsaturated hydrocarbons of the ratio 60 and 40 by means of conc. sulphuric acid.[1]

1. Z. f. angew. Chem., **33**, 172 (1920).

1. Saturated hydrocarbons

45 grm. of the saturated hydrocarbons which remain without any reaction with conc. sulphuric acid, were fractionated carefuly on metallic sodium six times, and of each distillate the weight, specific gravity, and index of refraction were determined and the results are shown in Table I, II, III. Both the temperature-weight curve and the temperature-mol per cent curve of the fractions shown in Figs. 1 and 2, show the five maxima which indicate the presence of the hydrocarbons of the carbon atom C_8, C_9, C_{10}, C_{11}, C_{12}, and C_{13}. The assumption for the occurrence of the hydrocarbons in the distillates was confirmed by comparison of their physical constants and analytical results with those of the pure substances mentioned in the literature.

2. Unsaturated hydrocarbons

The unsaturated hydrocarbons which occur in the volatile oil were separated from the saturated ones by means of liquid sulphur dioxide according to the method suggested by Edeleanu[1], being divided by fractional

Table I

	Fraction	Yield	Δt^1	$\frac{\Delta W^2}{\Delta t}$
I	−122°	0.2	—	—
II	122°−126°	0.5	4°	0.125
III	126°−148°	3.0	24°	0.125
IV	148°−152°	1.5	4°	0.375
V	152°−171°	2.7	19°	0.142
VI	171°−175°	1.8	4°	0.450
VII	175°−193°	4.9	18°	0.272
VIII	193°−197°	1.7	4°	0.425
IX	197°−212°	3.5	15°	0.233
X	212°−216°	1.7	4°	0.425
XI	216°−232°	3.6	16°	0.225
XII	232°−236°	2.0	4°	0.500
XIII	236°−251°	1.9	15°	0.127
XIV	251°−255°	0.5	4°	0.125
XV	255°−270°	0.3	15°	0.020

1. Z. angew. Chem., **25**, 175 (1919).

Table II

Fraction		$d_{4^\circ}^{25^\circ}$ (obs.)	$d_{4^\circ}^{t^\circ}$	$n_D^{25^\circ}$ (obs.)	n_D	C_n
I	-122°	0.6983		1.3890		
II	$122^\circ-126^\circ$	0.7075	$0.7185\left(\frac{0^\circ}{4^\circ}\right)$	1.3924	—	C_8
III	$126^\circ-148^\circ$	0.7150		1.3962		
IV	$148^\circ-152^\circ$	0.7207	$0.733\left(\frac{0^\circ}{4^\circ}\right)$	1.3998	—	C_9
V	$152^\circ-171^\circ$	0.7283		1.4024		
VI	$171^\circ-175^\circ$	0.7333	$0.7303\left(\frac{20^\circ}{4^\circ}\right)$	1.4062	*1.4136	C_{10}
VII	$175^\circ-193^\circ$	0.7398		1.4100		
VIII	$193^\circ-197^\circ$	0.7462	$0.7411\left(\frac{20^\circ}{4^\circ}\right)$	1.4132	1.4158	C_{11}
IX	$197^\circ-212^\circ$	0.7510		1.4152		
X	$212^\circ-216^\circ$	0.7555	$0.7511\left(\frac{20^\circ}{4^\circ}\right)$	1.4181	1.4209	C_{12}
XI	$216^\circ-232^\circ$	0.7589		1.4204		
XII	$232^\circ-236^\circ$	0.7660	$0.7571\left(\frac{20^\circ}{4^\circ}\right)$	1.4227	—	C_{13}
XIII	$236^\circ-251^\circ$	0.7707		1.4251		
XIV	$251^\circ-255^\circ$	0.7817	$0.7645\left(\frac{20^\circ}{4^\circ}\right)$	1.4315	*1.4358	C_{14}
XV	$255^\circ-270^\circ$	0.7965				

Table III

	Found		Calc.		C_n
	C%	H%	C%	H%	
II	84.11	15.91	84.2	15.8	C_8
IV	84.38	15.39	84.4	15.6	C_9
VI	84.42	14.87	84.5	15.5	C_{10}
VIII	84.33	15.21	84.6	15.4	C_{11}
X	84.35	15.28	84.7	15.3	C_{12}
XII	84.44	14.87	84.8	15.2	C_{13}
XIV	84.73	14.43	84.8	15.2	C_{14}

Table IV

	Fraction	Yield	I. V. obs.	I. V. calc.	C_n
I	70°—100°	0.5	—		C_6
II	100°—120°	0.7	166.1	259.2	C_7
III	120°—140°	1.4	167.3	226.8	C_8
IV	140°—160°	1.7	145.6	201.6	C_9
V	160°—180°	2.5	163.1	181.4	C_{10}
VI	180°—200°	2.4	131.6	164.9	C_{11}
VII	200°—220°	2.1	126.1	151.2	C_{12}
VIII	220°—240°	2.0	109.9	139.6	C_{13}

Table V

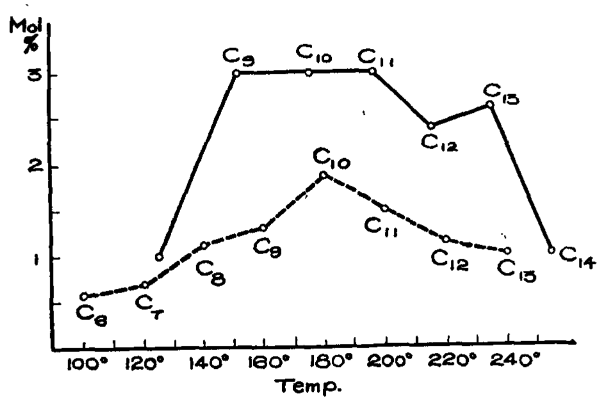
	Fraction	$d^{25°}_{4°}$ (obs.)	$d^{t°}_{4°}$(Beilstein)	$n^{25°}_D$	$n^{t°}_D$	C_n
I	70°—100°	—	$0.683\left(\frac{20°}{4°}\right)$	1.4022	—	C_6
II	100°—120°	0.736	$0.699\left(\frac{15°}{4°}\right)$	1.3958	—	C_7
III	120°—140°	0.737	$0.723\left(\frac{0°}{4°}\right)$	1.3966	—	C_8
IV	140°—160°	0.751	$0.743\left(\frac{20°}{4°}\right)$	1.4023	* 1.4286	C_9
V	160°—180°	0.762	$0.763\left(\frac{0°}{4°}\right)$	1.4090	* 1.4301	C_{10}
VI	180°—200°	0.773	$0.773\left(\frac{15°}{15°}\right)$	1.4147	*{1.4219 1.4376	C_{11}
VII	200°—220°	0.779	$0.773\left(\frac{0°}{4°}\right)$	1.4193	*{1.4212 1.4231	C_{12}
VIII	220°—240°	0.785	$0.844\left(\frac{0°}{4°}\right)$	1.4215	* 1.4488	C_{13}

fractions 5 times into 8 parts. The occurrence of the hydrocarbons of the carbon atoms C_7, C_8, C_9, C_{10}, O_{11}, C_{12}, C_{13}, was indicated from the analytical results and the determination of physical constants of the fractions as will be seen in Table IV, V, VI. and figure. I. (dotted line)

Table VI

	Fraction	Found		Calc.		C_n
		C%	H%	C%	H%	
I	70°–100°	—	—	85.7	14.3	C_6
II	100°–120°	85.41	13.97	85.7	14.3	C_7
III	120°–140°	85.22	13.91	85.7	14.3	C_8
IV	140°–160°	85.76	13.92	85.7	14.3	C_9
V	160°–180°	84.87	13.86	85.7	14.3	C_{10}
VI	180°–200°	85.12	13.88	85.7	14.3	C_{11}
VII	200°–220°	84.42	13.71	85.7	14.3	C_{12}
VIII	220°–240°	84.61	13.99	85.7	14.3	C_{13}

Fig. 1



B. NON-VOLATILE PART

1. Palmitone, $(C_{15}H_{31})_2CO$

The occurrence of this ketone in the non-volatile part of the tar was previously assumed from the experiment which was carried out by Kraft,[1] and 20 grm. of the ketone were actually isolated from 270 grm. of the tar by treating with ether, and the ketone was confirmed by converting it into its oxime of m.p. 58°.[2]

1. Ber. D. Chem. Ges., **15**, 1711 (1882).
2. Kipping: J. Chem. Soc., **57**, 985 (1890).

2. Hydrocarbons

The oily part separated from the ketone, which showed by its iodine number 69 about 85% of unsaturated hydrocarbons, was fractionated under 10–12 mm. pressure.

150 grm. of the non-volatile oil free from the ketone, were divided into 18 fractions by repeating fractional distillation fives times which were confirmed as composed of hydrocarbons by determining the physical constants and chemical properties and also by analysis of the fractions. (Table VII, VIII, IX.) The proportion of saturated and unsaturated hydrocarbons in the non-volatile oil was estimated by means of iodine number of the oil, and the results are shown in Table X. Among these hydrocarbons, unsaturated compouds of the carbon atom C_{15}, C_{19}, C_{20} and C_{30} as will be seen in Table X, composed the main part of the oil and the chief saturated hydrocarbons are $C_{14}H_{30}$, $C_{18}H_{38}$ and $C_{20}H_{42}$.

Table VII

	Fraction (10–12mm.)	Yield	I. V. (obs.)	I. V. (calc.)	C_n
I	–120°	12.6	94.4	139.6	C_{13}
II	120°–130°	11.5	87.4	129.6	C_{14}
III	130°–140°	27.1	114.8	121.0	C_{15}
IV	140°–150°	7.9	111.0	113.4	C_{16}
V	150°–160°	5.5	150.8	106.7	C_{17}
VI	160°–170°	5.1	18.8	100.9	C_{18}
VII	170°–180°	6.7	59.0	96.2	C_{19}
VIII	180°–190°	10.8	42.8	90.7	C_{20}
IX	190°–200°	5.2	46.6	85.8	C_{21}
X	200°–210°	4.0	61.4	82.4	C_{22}
XI	210°–220°	4.5	58.2	78.8	C_{23}
XII	220°–230°	3.7	59.0	75.6	C_{24}
XIII	230°–240°	3.8	62.0	72.6	C_{25}
XIV	240°–250°	2.9	71.0	69.8	C_{26}
XV	250°–260°	2.9	69.2	67.2	C_{27}
XVI	260°–270°	1.2	57.5	64.8	C_{28}
XVII	270°–280°	0.7	59.0	62.6	C_{29}
XVIII	280°–290°	2.0	61.4	60.5	C_{30}
XIX	290°–300°	3.2	53.4	58.5	C_{31}

Table VIII

	Fraction (10—12mm.)	$d^{25°}_{4°}$ (obs.)	$d^{t°}_{4°}$ (Beilstein)	$n^{25°}_{D}$	C_n
I	−120°	0.7837	{0.7977(20°) {0.8445(0°)	1.4203	C_{13}
II	120°−130°	0.7825	0.7638(30°)	1.4210	C_{14}
III	130°−140°	0.7853	—	1.4226	C_{15}
IV	140°−150°	0.7974	0.7842(0°)	1.4288	C_{16}
V	150°−160°	0.8118	0.7977(10°)	1.4345	C_{17}
VI	160°−170°	0.8033	0.7881(22°)	—	C_{18}
VII	170°−180°	0.8110	—	—	C_{19}
VIII	180°−190°	0.8166	0.7810(0°)	—	C_{20}
IX	190°−200°	0.8224	—	—	C_{21}
X	200°−210°	0.8307	—	—	C_{22}
XI	210°−220°	0.8347	—	—	C_{23}
XII	220°−230°	0.8372	—	—	C_{24}
XIII	230°−240°	0.8412	—	—	C_{25}
XIV	240°−250°	0.8433	—	—	C_{26}
XV	250°−260°	0.8458	—	—	C_{27}
XVI	260°−270°	0.8479	—	—	C_{28}
XVII	270°−280°	0.8490	—	—	C_{29}
XVIII	280°−290°	0.8500	—	—	C_{30}
XIX	290°−300°	0.8545	—	—	C_{31}

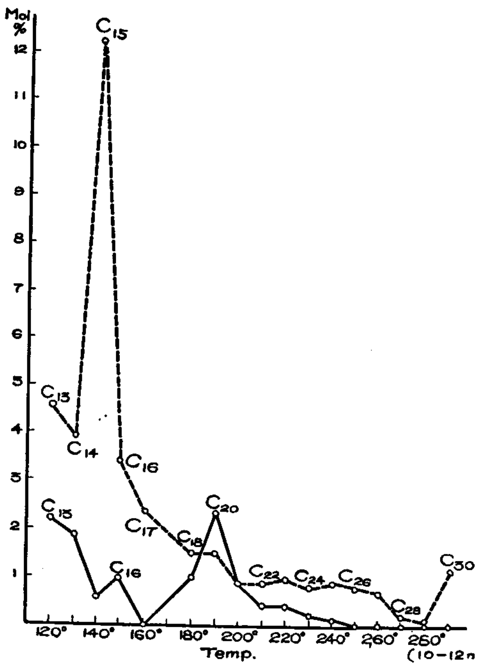
Table IX

	C%	H%	O% (by diff)
I	83.85	13.88	2.27
II	84.30	13.97	1.73
III	84.66	13.99	1.35
IV	83.20	13.33	3.47
V	82.68	13.53	3.79
VI	81.17	13.33	3.50
VII	79.09	12.80	8.11
VIII	81.89	13.54	4.57
IX	81.64	12.55	5.81
X	82.57	13.32	4.11
XI	82.52	13.22	4.26
XII	82.50	12.95	4.55
XIII	80.69	12.73	6.58
XIV	82.77	13.00	4.23
XV	83.22	13.25	3.53
XVI	83.82	12.83	3.35
XVII	82.88	12.91	4.21
XVIII	81.43	12.98	5.59
XIX	82.51	12.63	4.86

Table X

	Olefine			Paraffine	
		Yield		Yield	
	C_n	(gr.)	Mol%	(gr.)	Mol%
I	C_{13}	8.5	4.6	4.1	2.2
II	C_{14}	7.7	3.9	3.8	1.9
III	C_{15}	25.7	12.2	1.4	0.6
IV	C_{16}	7.6	3.4	0.3	0.1
V	C_{17}	5.5	2.3	0.0	0.0
VI	C_{18}	0.9	0.4	4.2	1.6
VII	C_{19}	4.0	1.5	2.7	1.0
VIII	C_{20}	4.4	1.5	6.4	2.3
IX	C_{21}	2.8	0.9	2.4	0.9
X	C_{22}	2.8	0.9	1.2	0.4
XI	C_{23}	3.2	1.0	1.3	0.4
XII	C_{24}	2.9	0.8	0.8	0.2
XIII	C_{25}	3.2	0.9	0.6	0.1
XIV	C_{26}	2.9	0.8	0.0	0.0
XV	C_{27}	2.9	0.7	0.0	0.0
XVI	C_{28}	1.0	0.2	0.2	0.0
XVII	C_{29}	0.6	0.1	0.1	0.0
XVIII	C_{30}	5.2	1.2	0.0	0.0

Fig 2



In conclusion, sodium palmitate, when distilled in Fischer's aluminum retort produces 70% of a theory-yield of tar which is composed of the following constituents.

Volatile oil	acidic oil	trace
	saturated hydrocarbons	25%
	unsaturated ,,	23%
Non-volatile oil	palmitone	3%
	saturated hydrocarbons	8 ,,
	unsaturated ,,	47 ,,