Biochemical Studies on Pityrol, VII Distillation of Oleic Acid

By

Hiroshi Ogata

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The Tsubaki oil (*Thea Japonica Nois*) was regarded by the writer as a good source in Japan for obtaining oleic acid in a pure state, since the oil, according to the investigation by I. Misumi¹, contains 90% or more of oleic acid in its fatty acids.

The oil which was used in this experiment was obtained by the courtesy of Dr. Hiraizumi from seeds grown in Hayaki, Nagasaki ken, and shows the following constants:

 $d_4^{25} = 0.9093$; $n_D^{25} = 1.4626$; acid number 3.9; saponification number 187.7; iodine number 81.5.

A convenient and reliable procedure for the preparation of pure oleic $acid^2$ from Tsubaki oil was proposed after many trials by the writer as follows:

The crude sodium salt of oleic acid prepared from the oil by the usual method was converted into the lead salt which was extracted with ether and then decomposed by means of sulphuric acid into the free oleic acid.

In the purification of the crude oleic acid, it was subjected to distillation under 12-18 mm. pressure after being dried with anhydrous sodium sulphate in its ether solution, and 1.8 kg. of pure oleic acid of the following constants were obtained from 6 kg. of the Tsubaki oil; one operation is enough for obtaining the acid in such a state of purity.

I. J. Chem. Ind., Japan, 9, I (1906).

Refer L. Ubbelohde: Handbuch d. Öle u. Fette I. 55. & F. Ulzer & J. Klimont: Chemie d. Fette. 95 (1906); Monat. f. Chem., 46, 337 (1926).

 $d_4^{25} = 0.8863$; $n_D^{25} = 1.4535$; m.p. = 9.2°;

solid. p.= 4.5° ; b.p.= 235° , 18 mm., light yellow colour. iodine value 90.6.

Sodium oleate was prepared from the interaction of the acid and sodium ethylate, and purified from the alcohol solution¹.

It gave Na = 7.3 on analysis, which agrees quite well with the theoretical value of 7.5 for $C_{13}H_{33}O_2$ Na.

When the salt was heated in Fischer's aluminium retort, gas began to evolve at 390° , tar distils at 440° and the reaction was completed at 550° . The yield of gas, tar and coke was shown in the following table with the results by the distillation of sodium oleate under reduced pressure by Pictet & Potok² and also of the calcium salt under ordinary pressure by Kawai.³

•		Pictet & Potok	Kawai	The writer
	Tar	70%	63%	65%
	Coke	24 ,,	28 "	17 "
	Gas & loss	6 "	9"	18,,

The tar which was obtained by the writer shows the following constants, $d_4^{25}=0.794$; $n_D^{25}=1.445$; iodine number 142., was divided by steam distillation into volatile and non-volatile parts.

	%	В. р.	I. V.	d ₄ ²⁵	n_D^{25}
Volatile part	47	41°—266°	158	0.766	1.427
Non-volatile "	53		105	0.828	1.457

The content of the unsaturated compounds in the fractions was estimated by determination of the volumetric loss to sulphuric acid of 84.5% strength⁴ to be 80%, but the oil which remained unaffected by the sulphuric acid-treatment, still showed the iodine number 87 due to the presence of some unsaturated compounds in it. The liquid sulphur dioxide method proposed by Edeleanu for the determination of unsaturated compounds was tried in the hope that the determination would be an

544

^{1.} L. L. Biscumshaw : J. Chem. Soc., 123, 91 (1923).

^{2.} A. Pictet & G. Potok: Hel. Chim. Acta, 2, 501 (1919).

^{3.} S. Kawai : J. Chem. Soc. Ind. Japan, 28, 52 (1925).

^{4.} E. Leslie: Motor Fuels, 595 (1923).

accurate measure of the unsaturation. The result indicating 92 % of unsaturation is closely in agreement with that of the sulphuric acid method.

VOLATILE PART

This was distilled under ordinary pressure and divided into the following fractions :

	Fraction	Yield	Colour
I	to 90°	8.7%	light yellow
2	90°—150'	41.0%	yellow
3	۲ 50° – 200	32.8%	deep yellow
4	200°-250°	14.8%	greenish yellow
5	250°	2.6%	green

By repeated fractional distillation four times, the volatile part was divided into the following 18 fractions, among which the fractions boiling above 200°, were distilled under 15 mm. pressure. The yield, density, index of refraction and iodine numbers of each fraction were determined and the results are shown in Table I, with the analytical results of carbon and hydrogen.

Fig 1



Hiroshi Ogata

Table	I

	Volatile Part							-	
	Fration	Viold	d25	n2ī	I. V.				C II
	Fraction	Tield	4	"D	obs.	calc.	C	п	Cnnm
I	75°-83°	4.4gr.	0.7915	1.4315	83.03		83.82%	10.46%	
п	83°-95°	6.3	0.7810	1.4233	101.60		84.83	10.93	
III	95°–105	1.8	0.7615	1.4124	115.70	259.1	83.78	11.86	C, H14
IV	105°-118°	0.6	0.7561	1.4075	180.27		-	-	
\mathbf{v}	118°-125°	4.I	0.7546	1.4045	137.70	226,8	85.66	13.39	C_8H_{10}
VI	125°-135°	3.5	0.7546	1.4046			84.83	13.42	
VΠ	135°-144°	1.7	0.7547	1.4057	131.50	201.6	84.92	13.51	C_9H_{18}
\mathbf{VIII}	144°158'	7.0	0.7656	1.4104	146 .3 6		83.67	13.43	
\mathbf{IX}	158°-165°	2.6	0.7717	1.4135	147.20	180.15	84.59	13.80	$C_{10}H_{20}$
x	165° 175'	4.8	0.7813	1.4183	126,60	180.15	-	-	$C_{10}H_{20}$
XI	175°-185°	5.6	0.7876	1.4232	160.48		83.36	13.78	
хII	185°-198°	7.9	0.7952	1.4265	155.80	164.93	84.88	13.45	C11H75
$\mathbf{X}\mathbf{III}$	95°–100°	2.7	0.8047	1.4334	138.10	151.19	85.51	13.30	$C_{12}H_{24}$
XIV	100°-110°	2.7	0.8140	1.4392	1 54.88		85.52	14.07	
$\mathbf{x}\mathbf{v}$	110°-120'	3.0	0.8271	1.4437	144.10	139.56	81.81	12.89	$C_{13}H_{26}$
XVI	125°-130°	1,8	0.8377	1.4460	126.01	129.59	83.93	12.78	$C_{14}H_{28}$
$\mathbf{X}\mathbf{V}\mathbf{I}\mathbf{I}$	130°-150°	2.5	0.8389	1.4475	154.00	120.95	_	-	$C_{15}H_{30}$
XVIII	150°-156°	0.7	0.8430	1.4480	-	113.39	85.71	14.29	C16H82

Table II

	Non-volat'le								
	Fraction	Yield	d ²⁵ 4	${}^{n25}_{ m D}$	I. V.				<u>с н</u>
	(15mm.)				obs.	calc.		11	Chille
I	110°-125°	1.0gr.	0,8064	1.4315					
п	125°. 133°	0.9	0.8125	1.4334	118,20	129.59	84.50	13.35	$C_{14}H_{21}$
III	133°-138°	0.2	0.8176	1.4343					
IV	138`-143°	1.9	0.8201	1.4365	131.28	120.95	81.96	11,66	$C_{15}H_{30}$
v	143°-152°	3.8	0.8208	1.4373	127.98				
VI	152`-157°	4.1	0.8225	1.4381	110.80	113 39	85.87	13.92	C_1 H_{a2}
VII	157^-170°	2,2	0.8267	1.4394		106.72			$C_{17}H_{84}$
VIII	170°-178°	4.7	0.8315	1,4425	150.55				
IX	178°–185°	3.1	0.8394	1.4450	126.56	100.79	95.76	13.95	$C_1, H_3;$
x	185°-200°	2,0		1.4492					
XI	200°–210°	0.8	0.8498	1.4519					
хп	210°–220°	1.4	0.8628	1.4585					

NON-VOLATILE PART

The tar separated from the volatile part by steam distillation was of a dark brown colour with a green fluorescence, and shows $d_4^{2i} = 0.828$; $n_D^{25} = 1.457$; iodine value 105.

It contains about 10 % of sodium oleate which was carried out from the retort with the tar during the distillation.

The non-volatile tar separated from sodium oleate, was subjected to fractional distillation under 15 mm. pressure, and after three distillations, it was divided into the following 12 fractions which show the physical constants, iodine value and chemical composition of carbon and hydrogen.

The temperature-mol per cent curves of the results obtained from the volatile and non-volatile parts shown in Fig. 1 indicate the hydrocarbons of the carbon atoms C_8 , C_9 , C_{10} , C_{12} , C_{13} , C_{14} , C_{15} , C_{16} , C_{17} & C_{18} which occur in the tar.

The relative amount of the saturated and unsaturated hydrocarbons of the distillates was estimated by means of their iodine value.

The hydrocarbons of the olefine series of the molecular formulae $C_{3}H_{16}$, $C_{9}H_{13}$, $C_{15}H_{30}$, $C_{16}H_{32}$, $C_{17}H_{31}$ are the main constituents of the tar as the results indicate in the temperature mol per cent ratio curve shown in Fig I.