Biochemical Studies on Pityrol, III.
Neutral Constituents of Pityrol

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The tar obtained by the dry distillation of rice bran, which was named "Pityrol" by Professor Matsuura, was a dark-brown viscous liquid of a peculiar unpleasant odour, with some carbon particles.   50 kg. of the tar manufactured in the Shinyaku Kaisha, Kyoto, were kindly presented to us by Mr. Ichinose, Director of the company.   It was subjected to steam distillation to separate into two parts-volatile and non-volatile and each part was subdivided into neutral, acidic and basic fractions by treating with a 7% caustic soda solution and 10% sulphuric acid successively.

Table I

Fraction	Yield	
Volatile part	12. %	10.8 kg.
Non-volatile part	88. „	89.2 „

Fraction	tar	volatile part	non-volatile part
Neutral substance	57 %	89 %	52 %
Acidic „	37 „	6 „	41 „
Basic „	6 „	5 „	7 „

NEUTRAL SUBSTANCES

1.5 kg. of the volatile neutral substances of the dark-brown light oil mentioned above were treated with a 5% solution of sulphuric acid, and then with a dilute caustic soda solution to remove completely the basic and acidic substances from the neutral one, and the light brown residual oil was subjected to fractioned distillation after being dried with anhydrous sodium sulphate.

Table II

	Fraction	Yield		d_4^{25}	n_D^{25}	C	H
1	to 150°	160 gr.	10.3 %	0.8131	1.5578	84.4	11.4
2	150°—180°	369 „	23.8 „	0.8215	1.4547	85.5	11.5
3	180°—210°	524 „	33.8 „	0.8338	1.4615	85.1	11.8
4	210°—240°	359 „	23.1 „	0.8425	1.4683	86.7	12.1
5	240°—270°	140 „	9.0 „	0.8326	1.4620	86.9	13.1

The analytical results of the fractions indicate that the hydrocarbons which composed almost entirely the neutral substance of the pityrol, were of unsaturated nature as indicated in their physical constants.

1. Action of Fuming Sulphuric Acid on Hydrocarbons.

In order to remove the unsaturated hydrocarbons from the fractions

Table III

	Fraction	Yield		d_4^{25}	n_D^{25}
1	to 150°	2.5 c.c.	10 %	0.7115	1.3962
2	150°—180°	3.0 „	12 „	0.7253	1.4020
3	180°—210°	3.3 „	13 „	0.7389	1.4090
4	210°—240°	5.2 „	21 „	0.7557	1.4180
5	240°—270°	7.8 „	31 „	0.7696	1.4250

mentioned above, 25 c.c. of each fraction were treated with 50 c.c. of fuming sulphuric acid with 10% SO_3, under ice-cooled water. The yield of the saturated hydrocarbons which remained unaffected by the acid treatment is shown in Table III with some physical properties.

2. Action of con. Sulphuric Acid on Neutral Substances

25 c.c. of each fraction of the neutral substance were treated with 25 c.c. of con. sulphuric acid (sp. gr. 1.84) under cooling with iced-water. The percentage of the hydrocarbons which remained in each fraction without any reaction from the acid was as follows:

Table   IV

	Fraction	Yield of sat. H. C.		d_4^{25}	n_D^{25}
1	to 150°	5.3 c.c.	21. %	0.7985	1.4455
2	150°—180°	3.5 ,,	14. ,,	0.7671	1.4252
3	180°—210°	3.6 ,,	14 ,,	0.7546	1.4160
4	210°—240°	4.7 ,,	19 ..	0.7822	1.4313
5	240°—270°	7.9 ,,	32 ,,	0.8042	1.4340

The residual hydrocarbons mentioned in the above table were again treated with fuming sulphuric acid (with 10% SO_3) and the residue from the acid treatment was determined as to quantity and also physical constants.

Table   V

	Fraction	Yield		d_4^{25}	n_D^{25}
1	to 150°	2. c.c.	8. %	0.7163	1.3965
2	150°—180°	2.4 ,,	9. ,,	0.7354	1.4065
3	180°—210°	3.3 ,,	13 ,,	0.7528	1.4152
4	210°—240°	3.5 ,,	14 ,,	0.7656	1.4220
5	240°—270°	6.1 ,,	24 ,,	0.7730	1.4262

Although the sulphuric acid treatment was not an accurate method for the estimation of the aliphatic, aromatic and other unsaturated hydrocarbons in the mixture, the relative percentage of these hydrocarbons in it would be approximately determined by treating with con. sulphuric acid and fuming sulphuric acid containing 7% SO_3 successively, and the experimental results for the relative amount of these hydrocarbons in the neutral volatile oil of pityrol were as follows:

Table VI

	Fraction	Hydrocarbons.		
		paraffin	aromatic	other unsaturated
1	to 150°	8 (vol. %)	13	79
2	150°—180°	9	5	86
3	180°—210°	13	—	87
4	210°—240°	14	—	86
5	240°—270°	24	—	76

SATURATED HYDROCARBONS

For the study of the chemical nature of the saturated hydrocarbons occurring as a constituent of the neutral substances in pityrol, the isolation of individual compounds in a pure state, was undertaken; 100 — 250 c.c. of each fraction of the crude neutral oil were treated with sulphuric acid of sp. g. 1.84 in a cold state for 30 minutes, and the insoluble oil in the acid, separated from the acid layer, washed with water, dried and distilled, and the saturated hydrocarbons separated from the polymerized and hydrated compounds which were formed from the unsaturated hydrocarbons in the course of the acid treatment, gave the following constants:

Table VII

	Fraction (used)	Yield		d_4^{15}	n_D^{25}
1	to 150°, 145 c.c.	20 c.c.	14 %	0,7888	1.4452
2	150°—180°, 250 „	31 „	12 „	0.7561	1.4235
3	180°—210°, 250 „	40 „	16 „	0.7650	1.4267
4	210°—240°, 250 „	48 „	19 „	0.7782	1.4336
5	240°—270°, 105 „	34 „	32 „	0.7839	1.4370

Each fraction was treated again with fuming sulphuric acid containing 7% SO_3, and then washed with water, dried over calcium chloride and finally distilled on metallic sodium.

For the purification of the saturated hydrocarbons from the hydrocarbons of the polymethylen series which may be present with the former in the fractions, having escaped from the sulphuric acid treatment, each

Table VIII

	Fraction	Yield		d_4^{25}	n_D^{25}
1	to 150°	8.8 c.c.	6.7 %	0.7131	1.3950
2	150°—180°	23.6 „	9.4 „	0.7304	1.4084
3	180°—210°	32.6 „	13.5 „	0.7496	1.4180
4	220°—240°	40.5 „	16.2 „	0.7632	1.4250
5	240°—270°	27.2 „	25.9 „	0.7712	1.4300

fraction was passed, at the rate of 3 grm. an hour, on reduced nickel heated at 300°, under this treatment the polymethylene hydrocarbons should decomposed into unsaturated or aromatic hydrocarbons.

Table IX

	Fraction I	Sample passed	H_2 liberated	Fraction II	Yield	d_4^{25}	n_D^{25}
1	to 150°	4.0 c.c.	60 (c.c.)	(124°—150°)	3.7 c.c.	0.7119	1.3944
2	150°—180°	13.6 „	250 „	(150°—183°)	13.1 „	0.7299	1.4040
3	180°—210°	19.8 „	610 „	(177°—214°)	18.8 „	0.7499	1.4142
4	210°—240°	25.0 „	280 „	(208°—244°)	23.5 „	0.7627	1.4210
5	240°—270°	18.9 „	60 „	(238°—269°)	18.9 „	0.7705	1.4255

The fractions were again distilled after being treated with fuming sulphuric acid containing 10% SO_3, and determined of their physical constants, and the results are shown in Table IX.

In order to isolate the pure hydrocarbons from the fractions, the fractional distillation was repeated 13 times for each fraction the following 15 portions resulted from the physical constants and analytical results of carbon and hydrogen.

Octane (B. p· 135.8°); nonane (B. p. 149.5°); decane (B. p. 172°); undecane (B. p. 194.5°), dodecane (B. p. 95°. 15 mm.), tridecane (B. p. 114°. 15 mm.), tetradecane (B.p. 129°. 15 mm.), and pentadecane (B. p. 144°. 18 mm.), were found to be isolated in a fairly pure state from their physical constants and analytical results, from the neutral oil of pityrol among which decane $C_{10}H_{22}$, undecane $C_{11}H_{24}$, dodecane $C_{12}H_{26}$ and tridecane $C_{13}H_{28}$ occupy the principal parts of the oil.

Table X

	Fraction	Yield	n_D^{25}	d_4^{25}	Mean	
					C	H
1	to 120° ord. press.	0.5 grm.	1.3870	0.6962	84.0	15.9
2	120°—130°	1.0	1.3908	0.7047	84.0	15.7
3	130°—140°	1.1	1.3942	0.7115	84.0	15.8
4	140°—150°	3.4	1.3982	0.7205	84.1	15.7
5	150°—160°	2.2	1.4015	0.7256	84.2	15.6
6	160°—170°	3.3	1.4050	0.7327	84.3	15.5
7	170°—180°	4.0	1.4073	0.7372	84.5	15.5
8	180°—190°	3.0	1.4113	0.7447	84.4	15.3
9	190°—200°	7.4	1.4138	0.7495	84.6	15.3
10	— 95°	2.5	1.4180	0.7585	85.0	15.2
11	95°—105°	6.0	1.4185	0.7588	84.8	15.2
12	105°—115°	7.7	1.4208	0.7625	84.8	15.2
13	115°—125° 12 mm.	3.0	1.4228	0.7663	85.0	15.1
14	125°—135° „	5.7	1.4248	0.7698	84.0	15.0
15	Above 135° „	2.8	1.4260	0.7712	85.0	15.0

UNSATURATED HYDROCARBONS

The volatile neutral part of pityrol, which, being assumed to be a mixture of saturated and unsaturated hydrocarbons, was treated with con. sulphuric acid to remove the unsaturated compounds. The results of the treatment with conc. sulphuric acid would involve some chemical changes in the unsaturated compounds of polymerisation, the formation of sulphuric acid esters, and hydration to alcohols.

The researches into the polymers and alcohols which were formed by the treatment are therefore of considerable interest in connection with the identification of the unsaturated hydrocarbons which occurred with the saturated compounds in the volatile neutral oil.

Five fractions mentioned in the foregoing paragraph, had contained the saturated & unsaturated hydrocarbons, and the latter were supposed to yield by the action of the acid polymers which were separated by fractional distillation and their physical constants determined.

Table XI

	Original sample		B.p. polymer.	Yield of	
	B. p.	c.c.	(10—11 mm.)	Polymer.	High boiling fraction
1	to 150°	145	60°—195°	25 grm.	3 grm.
2	150°—180°	250	90°—210°	50 „	19 „
3	180°—210°	250	120°—225°	33 „	30 „
4	210°—240°	250	150°—250°	42 „	17 „
5	240°—270°	105	180°—275°	10 „	10 „

Table XII

	Fraction (10—11 mm.)	d_4^{25}	n_D^{25}
1	60°—195°	0.8672	1.4840
2	90°—210°	0.6895	1.4856
3	120°—225°	0.8733	1.4880
4	150°—260°	0.8832	1.4950
5	180°—275°	0.8857	1.4954

Each fraction was again distilled 4 times under 12 mm. to isolate, if possible, definite polymers, and divided into three parts which show physical constants, analytical results and molecular weight.

The middle part (b) of each fraction was assumed to be composed mostly of a definite compound from its physical constants, analytical results and also molecular weight measured by the cryoscopic method of the benzene solution; the hydrocarbons of the molecular formulae $C_{16}H_{26}$, $C_{18}H_{30}$, $C_{20}H_{34}$, $C_{24}H_{38}$ & $C_{28}H_{46}$ were found actually to occur in the main part of each fraction shown in Table XII.

The occurrence of these compounds in the polymers can be explained by assuming the polymerisation of the unsaturated hydrocarbons C_8H_{13}, C_9H_{15}, $C_{10}H_{17}$, $C_{12}H_{19}$ & $C_{14}H_{23}$, which takes place during the acid-treatment. It seems, however, very reasonable to assume that the mother substances which occur in the original tar and yield polymers by the acid treatment should be hydrocarbons of the C_nH_{2n} or C_nH_{2n-2} series, namely the unsaturated hydrocarbons of C_9H_{16}, $C_{10}H_{18}$, $C_{12}H_{20}$ and $C_{14}H_{24}$ are the main constituents of the volatile neutral part of pityrol.

Table XIII

		Fraction	Yield	d_4^{25}	n_D^{25}	C	H	M. W.
	(a)	45°—135°	5.7 grm.	0.8287	1.4620	87.3	12.7	—
1	(b)	135°—150°	10.4	0.8722	1.4878	88.2	11.9	218
	(c)	150°—190°	4.3	0.8915	1.4968	88.2	11.6	—
	(a)	90°—155°	6.4	0.8153	1.4530	86.6	13.3	—
2	(b)	155°—175°	30.2	0.8741	1.4882	87.9	12.2	216
	(c)	175°—210°	9.7	0.8888	1.4952	87.6	11.9	—
	(a)	105°—185°	4.1	0.8280	1.4594	86.6	13.3	—
3	(b)	185°—195°	17.4	0.8748	1.4890	87.1	12.2	287
	(c)	195°—220°	7.9	0.8870	1.4958	87.2	12.0	—
	(a)	125°—215°	4.5	0.8161	1.4516	85.5	13.8	—
4	(b)	215°—230°	19.8	0.8891	1.4982	87.1	12.0	362
	(c)	230°—260°	8.9	0.9003	1.5050	87.2	11.9	—
	(a)	150°—240°	3.0	0.8717	1.4851	86.4	12.5	—
5	(b)	240°—255°	4.3	0.8932	1.4998	87.5	12.1	383
	(c)	255°—270°	0.9	0.8988	1.5028	87.3	12.1	—

In order to isolate alcohol formed from alkyl sulphuric acid esters, as an intermediate reaction substance from the unsaturated hydrocarbon of the olefine series and sulphuric acid, by hydrolysis, the aqueous acidic solution in each fraction, which is separated from the oily layer of

Table XIV

	Fraction	Yield	d_4^{25}	n_D^{25}
1		0.9 grm.	0.8602	1.4329
2		5.0 „	0.8322	1.4257
3		6.7 „	0.8382	1.4364
4		4.7 „	0.8368	1.4435
5		1.4 „	0.8433	1.4469

hydrocarbons, was diluted with water at 0°, and the alcohols which resulted from the hydrolysis of the sulphuric acid esters were extracted by means of ether.

Distilling off the solvent, there remained an oily residue which was

composed mostly of alcohols, this was subjected to steam distillation, the oily distillate separated from water, dried and then distilled.

Each fraction was distilled again under 18 mm. 4 times and was divided into the following parts, and the physical constants and the contents of carbon & of hydrogen in the molecule determined.

Table XV

II.	Fraction	Yield	d_4^{25}	n_D^{25}	C	H	O
1	40°—50°	0.2 grm.	—	1.4115	—	—	
2	50°—60°	0.7	0.8143	1.4162	76.3	12.7	11.0
3	60°—70°	0.9	0.8257	1.4218	76.6	12.4	11.0
4	70°—80°	1.0	0.8388	1.4281	75.6	12.0	11.4
5	80°—105°	0.8	0.8702	1.4449	74.4	11.2	13.4
III.							
1	60°—70°	0.6	0.8041	1.4213	78.7	13.1	8.3
2	70°—80°	1.6	0.8176	1.4277	78.5	12.7	8.8
3	80°—90°	1.7	0.8381	1.4366	78.5	12.2	9.3
4	90°—100°	1.0	0.8571	1.4442	77.9	11.7	10.3
5	100°—117°	0.5	0.8781	1.4534	76.9	11.4	11.6
IV.							
1	80°—90°	0.6	0.8171	1.4330	80.6	12.9	6.4
2	90°—100°	1.1	0.8261	1.4388	80.4	12.9	6.7
3	100°—110°	1.0	0.8364	1.4429	79.8	12.6	7.5
4	110°—120°	0.9	0.8486	1.4489	79.2	12.3	8.4
5	120°—	0.3	—	1.4642	—	—	—

The experimental results shown in the table above, indicate alcohols of the molecular formulae from $C_8H_{18}O$ to $C_{14}H_{30}O$ occurring in the distillates, which were evidently derived from the hydrocarbons of the olefine series C_8H_{16} $C_{14}H_{28}$ by hydration in presence of con. sulphuric acid.

NEUTRAL SUBSTANCE IN THE NON-VOLATILE OIL

The non-volatile oil of pityrol was treated with a 5% sulphuric acid & a 3% caustic soda solution successively to separate neutral substance, and

1700 grm. of the remaining oil after being washed with water and dried were subjected to fractional distillation 3 times under 20 mm. and the results were :

| | Fraction | Yield | | d_4^{25} | n_D^{25} |
		wt.	%		
1	90°—150°	167 gr.	9.8	0.8693	1.484
2	150°—200°	356	20.9	0.8564	1.477
3	200°—250°	357	21.0	0.8996	1.491
4	250°—280°	64	3.8	0.9526	1.529
	Residue	530	31.2		

These fractions were again distilled 5 times under 10 mm.

| | Fraction | Yield | | d_4^{25} | n_D^{25} |
		wt.	%		
1	to 130°	151 gr.	10.1	0.8804	1.4837
2	130°—180	347	23.1	0.8616	1.4750
3	180°—230°	353	23.5	0.8999	1.4870
4	230°—300°	189	12.6	0.9445	1.5270

Fig. 2
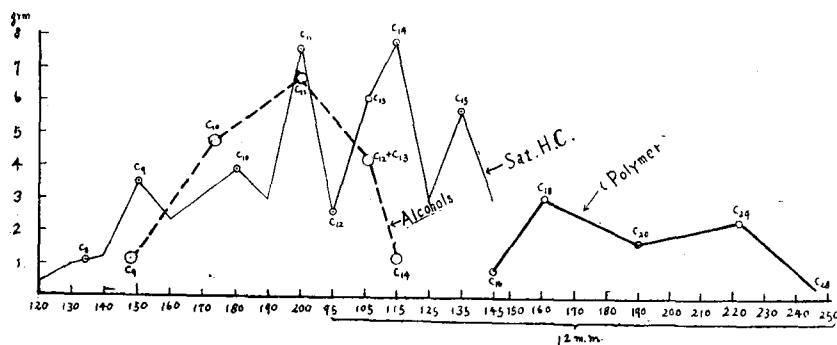
From these experimental results, the neutral non-volatile part of pityrol was assumed to be composed mostly of the hydrocarbons of the polymethylene series, which are similar in properties with those that occur

C	H	N	S
85.6	11.5	1.5	0.2
85.6	12.4	1.9 ·	0.2
82.3	12.0	2.5	0.1
84.3	11.4	4.2	0.1

in Russian or some Japanese Petroleums and in low temperature coal tars.

The neutral constituents of pityrol, as will be indicated in the Fig 2, consist mostly of the hydrocarbons of the carbon atoms C_{10}, C_{11}, C_{14} & C_{15}.