Part IV. The Tar from Cocoanut Shells.

WITH

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During the destructive distillation of cocoanut shells it was observed that the yield of settled tar was high and that it had properties somewhat different from those of the tars from most of the forest woods examined. In thin layers it has a brownish black colour, is relatively mobile and has a specific gravity of about 1·1. When a 600 gram sample was distilled the following fractions were collected : —

TABLE I.

Fraction.	Temperature in degrees centigrade*	Weight in grams.	Per cent.
No. 1.	Below 100	104·4	17·4
No. 2.	100 —150	42·6	7·1
No. 3.	150 —250	267·4	42·9

The first fraction consisted largely of acetic acid solution together with about 2·7 per cent of light oil.

The residue in the flask set, when cold, to an extremely hard, brittle pitch.

As the yield of volatile oils was very high when compared with ordinary wood tars, *viz.*, 5 per cent. of light oils, 10·00 of heavy oils and 64·6 per cent. of pitch (Klar Technologie der Holzverkohlung p. 293), it was decided to make a more complete examination of the tar, more particularly with the view of isolating important phenolic derivatives such as creosote and guaicol.

A large quantity (about 4600 grams) of the tar was distilled under atmospheric pressure (680 mm) and after removal of water and a second distillation the following fractions were collected : —

TABLE II.

Fraction.	1	2	3	4	5	6
Temperature	to 120°	120-160	180-180	180-200	200-220	220-260
Yield in per cent.	8·4	3·5	3·1	11·4	14·2	10·1

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*All the temperatures recorded in this paper, unless otherwise specified, are uncorrected temperatures obtained at the atmospheric pressure of Bangalore, the normal value of which is 685 mm.

These fractions were again distilled and, as the result of a 5th distillation, the following fractions were obtained, after the fractions up to 150° had been treated with 10 per cent. sodium carbonate solution to remove acetic and other acids.

TABLE III.

Temperature in degrees centigrade.			Weight in grams.
180—182	...	...	113·6
182—184	...	...	88·5
184—187	...	...	98·3
187—191	...	...	133·7
191—193	...	...	403
193—195	...	...	55·0
195—197	...	...	198

When the fraction boiling at 180—182° was cooled to 0° an appreciable quantity of colourless crystals melting at 42—43° separated; as the presence of phenol was suspected samples of both this and the next fraction boiling at 182—184°, were treated with excess of bromine water. Both gave solid products which after recrystallisation from alcohol melted respectively at 90° and 92 5—93° whereas *s*-tribromophenol melts at 92·5 to 93°. The melting points of the two compounds when mixed with *s*-tribromophenol were 91·5—93° and 92·5—93°, respectively so that the presence of phenol in the two fractions may be taken as proved.

The higher fractions boiling at 184—187° and 187—191° also reacted with bromine water, but the melting points of the products did not correspond with those of any known derivatives; in all probability they were mixtures. When, however, these fractions were cooled down and seeded with a particle of solid phenol colourless crystals were obtained. From the melting point of the crystals and also from the melting points of the bromo-derivatives obtained from the crystals, it is evident that the crystalline product is phenol although the boiling points of these two fractions are much higher than that of phenol.

Results of distilling tar under reduced pressure.

To ascertain if better yields of volatile oils could be obtained when the tar is distilled under reduced pressure, a quantity of water free tar (the tar being first distilled up to 100° at atmospheric pressure), was distilled under reduced pressure (53 mm). The yield of oil was, if anything, slightly less than that obtained when the distillation was made under atmospheric pressure.

Removal of Neutral substances.

As practically all the fractions contained neutral substances insoluble in sodium hydroxide solution, another quantity of the tar was distilled and the fractions treated with caustic soda solution in order to separate the phenolic constituents from the neutral substances.

Two lots of tar, A, 5148 grams and B, 3819 grams were distilled at atmospheric pressure; four main fractions were collected, viz. (I) below 100° (II) 100—150° (III) 150—200° (IV) 200—260° and a residue.

TABLE IV.

Fraction.	B. P.	Per cent. by weight. Expt. A.	Expt. B.
1	Below 100°	14·5	19·1
2	100—150	9·1	10·5
3	150—200	17·6	15·7
4	200—260	28·0	23·9
	Residue	24·4	27·0

In the initial stage of the distillation when fraction (1) was being collected, the operation had to be carefully controlled as the dehydration of the tar is a somewhat difficult operation, the tar tending to froth over. Fraction (1) consisted mostly of dilute acetic acid solution with 2·1 per cent of light oils and these light oils were separated from the acetic acid solution and added to fraction (2).

Estimation of free acids in the fractions:—

Since previous experiments showed that the above fractions, especially No. 2, 100—150°, contained an appreciable amount of acid, it was decided to determine the percentage acidity in each. This was done by taking a weighed quantity of each fraction in a stoppered bottle, shaking well with water and titrating with standard caustic soda (0·5 N) using phenolphthalein as indicator. The values obtained are given in column 4 table V.

TABLE V.

Fraction.	B. P.	Acidity calculated as per cent. of acetic acid. Expt. A	Expt. B.
1	below 100° (aqueous liquid after removal of light oil.)	10·7	10:5.3
2	100—150°	35·3	38·9
3	150—200°	16·9	14·7
4	200—260°	4·5	5·2

As appreciable amounts of phenols were present during these titrations, and as it was possible that these phenolic substances might affect the titration of the acetic acid, a series of experiments was made in which 20 c. c. of a one per cent. solution of acetic acid was well shaken for 5 minutes with varying amounts of pure phenol and then treated with 0·1040 N sodium hydroxide using 1 c. c. of phenolphthalein as indicator. The results are recorded in Table VI.

TABLE VI.

Experiment No.	Acetic acid solution.	Phenol in c. c.	ccs. of 0·1040 N. Sodium hydroxide.
1	20 c. c.	0	33·75
2	„	1	34·85
3	„	2	35·55
4	„	3	36·15
5	„	4	36·60

The acid value for fraction 2 experiment B (see Table V) was checked by treating a weighed quantity of the oil with an excess of standard sodium carbonate solution then heating on a water bath to half the original volume and precipitating the excess of carbonate with barium chloride solution. The precipitate was filtered, treated with standard hydrochloric acid and the excess of acid titrated with standard sodium hydroxide solution. The value obtained was 41·0 per cent. of acid calculated as acetic acid.

Fraction 100—150°.

The fractions No. 2 from experiments A & B (cf. Table IV) were mixed and then divided into two halves and each of these subjected to the following treatment :—

1. Treatment with 20 per cent. sodium carbonate solution in order to remove acidity.

2. Redistillation under atmospheric pressure.

3. Treatment of the fractions with 15 per cent. sodium hydroxide solution in order to separate neutral and phenolic substances and subsequent acidification of the alkaline solution to recover the phenols.

Treated in this manner, 400 grams* of the original fraction gave 113 grams or 28·3 per cent. of oil after removal of acids and water and this oil when distilled gave the following fractions

TABLE VII.

Fraction.	B. P.	Weight in grams
1	75—100°	20·2
2	100—205	76·0
Residue		15·5

The first fraction was largely water and above 205° decomposition took place. Fraction 2 when treated with 15 per cent. sodium hydroxide solution gave 24·5 grams of neutral oil and 42 grams of phenolic compounds. As these latter distilled mainly between 145 and 200° they were added to the main fraction 150—200° before it was distilled,

Fraction 150—300°.

This fraction was treated first with sodium carbonate (20 per cent. solution) and finally with sodium hydroxide (15 per cent. solution).

650 grams of the original fraction after treatment with sodium carbonate gave 483 grams or 87·8 per cent. of oil and this on subsequent treatment with sodium hydroxide gave 27 grams of neutral oil and 431 grams of phenolic compounds. These represent respectively 4·9 and 78·4 per cent. of the original fraction.

The phenolic substances were mixed with the phenols obtained from the earlier fraction 100—150°. (cf. above) and the whole subjected to fractional distillation under atmospheric pressure (683 mm).

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* The 400 grams was treated in two lots of 200 grams each and fairly concordant results were obtained.

		Expt. A.	Expt. B.
Weight of oil taken		200 gtama	200 grama.
Weight of oil obtained after treatment with 20 per cent. sodium carbonate solution.		57	56
Fractions obtained on distilllation	a to 100°	11·0	9·2
	b 100—205°	38·0	38·0
	c Residue	8·0	7·5
Treatment of fraction 100—205° with caustic soda and liberation of phenols		21·	20·5

The following fractions were obtained:—

TABLE VIII.

Fraction.	B. P.	Weight in grams.
1	Below 100°	65·0
2	100—170	17·0
3	170—177	11·0
4	177—180	21·5
5	180—185	132·0
6	185—190	87·0
7	190—196·5	25·5
8	196·5—220	61·0
Residue	„	45·0

Fraction 1 consisted of water and contained no oily drops. Distillation could not be continued beyond 220° as decomposition set in at this temperature and dense white fumes were given off.

Fraction 200—260°

800 grams of this fraction were distilled under a pressure of 684 mm. and the fractions mentioned in Table IX collected. The whole fraction was not treated with sodium hydroxide solution before redistillation as the caustic soda solution (15 per cent) gave a solid sodium derivative which rendered the separation of the neutral oil difficult.

TABLE IX.

Fraction.	B. P.	Weight in grams.
1	Below 100°	56
2	100—200	94
3	200—230	346
4	230—268	225
Residue		76

The first fraction was mainly water with only a few drops of oil floating in it. Fraction 4 gave a solid sodium derivative on treatment with caustic soda solution.

Fractions 2 and 3 were separately treated with sodium hydroxide solution to remove neutral oils and the recovered phenolic compounds fractionated.

Fraction IX. 2., when treated with 15 per cent. sodium hydroxide solution, gave 20 grams of neutral oil equivalent to

2·5 per cent of the original fraction 200—260 and 69 grams of phenolic substances equivalent to 7·4 per cent of the original fraction. When distilled these phenols gave the following fractions :—

TABLE X.

Fraction	B. P.	Weight in grams.
1	Below 100°	8·0
2	100 - -185	14·0
3	185 - -190	12·4
4	190 - -196·5	6·4
5	196·5- -221	13·0
Residue.		5·0

Fraction IX. 3. treated in the same manner gave 26·5 grams of neutral oil equivalent to 3·3 per cent of the original 200—260° fraction, and 288 grams of phenolic compounds equivalent to 36 per cent. of the original fraction.

When distilled under a pressure of 683 mm, the following fractions were obtained :—

TABLE XI.

Fraction.		B. P.		Weight in grams.
1	...	Below 100°	...	13·5
3	...	100—190	...	9
8	...	190 —196·5	...	64
4	...	196·5—216·5	...	110
5	..,	216·5—226·5	...	26
6	...	226·5—237	...	27
Residue		...	...	47

Fraction XI. 1 contained 1·5 grams of oil which was separated from the water and added to XI. 2.

Isolation of Phenol and Creosote Oil.

As the preliminary examination (cf. p 294) had proved the presence of appreciable amounts of phenol, $C_6H_5.OH$, in the fractions the next stage was the isolation of phenol crystals from the suitable fractions mentioned in Tables VIII, X and XI.

For this purpose the corresponding fractions of X and XI were mixed and the whole redistilled and the fractions obtained mixed with the corresponding fractions of VIII and again fractionated.

In this way the following series of fractions (a) was obtained:—

TABLE XII.

Fraction.	Boiling point.	Weight in grams.		
		(a)		(b)
1	Below 100°	8·5	—	1·8
2	100—170	6·5	—	2·0
3	170—177	10·3	—	15·0
4	177—180	94·0	—	149·0
5	180—185	147·0	—	109·0
6	185—190	76·0	—	57·0
7	190—196·5	57·0	—	38·5
8	196·5—226·5	182·9	—	196·0
9	226·5—236·5	19·3	—	21·6
10	236·5—250	12·3	—	9·2
Residue	...	9·0	—	3·0

On further fractionation after removing the water from fractions 1 and 2 the weights given in column 4 Table XII were obtained.

These fractions were derived from 400 grams of the original fraction 2, 660 grams of original fraction 3, and 800 grams of original fraction 4, Table IV which in their turn were obtained from 3450 grams of original tar.

Fraction XII. 4 b when seeded with a crystal of pure phenol readily solidified and fraction XTI. 5 b also gave crystals when cooled in ice and seeded with a little pure phenol. Fractions XII. 3 b and XII. 6 b treated in the same manner gave no crystals.

By draining the crystals from the fraction XII. 4 b at the ordinary temperature (22°) 140·2 grams of crystals were obtained and by cooling fraction XII. 6 b and removing the crystals at 0° and repeating the process with the liquid portion 74 grams of crystals were obtained making a total of 214·2 grams or a 6·2 per cent. yield on the weight of the original tar.

Properties of the Crystals.

The fractions from which the crystals were obtained, although quite colourless when freshly distilled, turned a yellowish brown when kept for some time in contact with the air. The crystals were quite colourless needles, they turned yellowish in colour on exposure to the air and melted between 37·5 and 38·5°.

A portion of the crystallised phenol was transformed into its bromo-derivative by treatment with excess of bromine water. A 93·2 per cent yield of crude tribromo-derivative melting at 80·5—81·5° was obtained and this after recrystallisation from light petroleum (b. p. 65 to 70°) melted at 90·5 to 91·5° whereas pure tribromophenol melts at 92·5 to 93°.

Cresote.

As wood cresote is a substance of considerable value several attempts were made in order to obtain from the higher boiling fractions a product which would fulfil the requirements of the United States Pharmacopoeia.

These requirements are (cP. U. S. P. Edition 1916. pp. 125—126):—

1. " Cresote is an almost colourless or yellowish, highly refractive oily liquid, having a penetrating smoky odour, and a burning, caustic taste; it does not readily become brown on exposure to light.

2. Cresote is slightly soluble in water; it is mixable with alcohol, ether, or fixed or volatile oils. It is neutral or faintly acid to litmus. Specific gravity not below 1·073 at 25°C.

3. It begins to distil between 195 and 200°C and not less than 80 per cent by volume distils between 200 and 220°C.

4. Add one drop of $FeCl_3$ (T. S.) to 10 units of a saturated aqueous solution of cresote ; the liquid develops a violet blue colour which is very transient; it then clouds almost instantly, the colour passing from a greyish-green to a muddy brown, with finally the formation of a brown precipitate.

5 Mix equal volumes of creosote and collodion in a dry test tube; no permanent coagulum is produced (phenol and so-called " coal-tar creosote ").

6. Mix 4 mils. of creosote with 4 mils. of glycerine, a clear mixture results, from which a creosotic layer equal to or greater in volume than the creosote taken separates on the addition of 1 mil. of water (" coal-tar creosote ").

7. Two mils. of creosote require not less than 10 mils. nor more than 18 mils. of normal sodium hydroxide (V. S.) to produce

a clear liquid. This liquid remains unclouded on diluting with 50 mils. of distilled water (hydrocarbons and bases).

8. Shake gently 1 mil. of creosote with 2 mils. of petroleum benzin and 2 mils. of freshly prepared barium hydroxide (T. S.) until a uniform mixture is produced. Upon complete separation three distinct layers are visible, a middle layer containing the creosote, a benzin layer which is neither blue nor muddy, and an aqueous layer which does not acquire a red tint (coerulignol and some other high-boiling constituents of wood tar.) ”

The fraction XII. 8b was examined to see if it fulfilled these requirements (for results see Table XIII). As the sp. gr. of this fraction was below the standard and too small a portion of it passed over at 196·5 to 216·5° the fraction was redistilled and the fraction 195—214° (683 mm) which constituted 80 per cent. of the original fraction XII. 8b was examined.

A further portion of the fraction XII. 8b was distilled and the portion boiling at 196·5—220° separately collected and examined, it was thought possible that such a fraction might not contain the substance which gave the reaction with barium hydroxide.

The results obtained for the three samples examined are given in Table XIII.

These show that no one of the three samples examined satisfies the U, S. P. tests. In all cases the sp. gr. is low, in the case of samples 2 and 3 the amount of sodium hydroxide required is too large and a blue colour is obtained by shaking with light petroleum and barium hydroxide solution.

British Pharmacopœia Creosote.

As the different fractions did not fulfil the requirements of the U. S. Phaomacopoeia they were examined in order to see if they came up to the B. P. Standard.

The requirements of the British Pharmacopoeia (1914) P. 106 are :—

A colourless or pale yellow highly refractive liquid, neutral or faintly acid to litmus. Freely soluble in alcohol (90 per cent), in ether, chloroform and in glacial acetic acid. Sp. gr. not below 1·080. Commences to boil below 200°. Not less than 75 per cent distils between 200 and 220°.

A solution (1 in 100) in alcohol (90 per cent.) produces with a drop of test solution of ferric chloride a green coloration rapidly changing to reddish-brown.

TABLE XIII.

	Fraction tested.	$D_{25°}^{25°}$	Per cent. by volume distilling between 196·5—216·5°.†	Reaction with $FeCl_3$.	Reaction with collodion.	Reaction with glycerine.	Reaction with normal sodium hydroxide.	Reaction with barium hydroxide.	Other tests.
1	196·5—226·5° cf. Table rii fraction 8.	1·070	84	A very transient violet colour was seen with the formation of a small brown precipitate at the end.	The coagulum which was produced on mixing 0·5 c.c. of the fraction with 0·5 c.c. of collodion equal volumes) soon disappeared	No clear mixture resulted on adding 1 c.c. of glycerine to 1 c.c. of the fraction, even on warning.	1 c.c. required 19 c.c. of sod. hydroxide to give a clear solution. Became slightly turbid on adding 25 c.c. of water.	1 c.c. shaken gently with 2 c.c. of petrol (60°— 75°) and 2 c.c. of baryta soln. Three layers were visible: a benzin layer which gradually became dark blue, a yellowish middle layer and an aqueous layer. No red tint.	Refractive index 1·4894 at 25°C. 1 part of oil soluble in 120 c.c. of water. Miscible with alcohol, ether, sesame oil, lemon grass oil. It is faintly acid to litmus. It is inflammable burning with a luminous, smoky flame
2	195—214° obtained by redistilling No. 1.	1·070	72	Same as above. The colour changed to a grey and then muddy brown.	,,	1·2 c.c. of the fraction mixed with 1·2 c.c. of glycerine mixture became clear on slight warning and remained so on cooling. 1·2 c.c. of creosote separated on adding 0·3 c.c. of water.	1 c.c. of the fraction required S c.c. of sodium hydroxide to give a solution, which became slightly clouded on adding 25 cc. of water.	Only two layers were seen, the top layer slightly reddish and the bottom layer yellowish.	Refractive index 1·5294 at 25°C. 1 part of oil soluble in 110 c.c. of water. Other tests as above.
3	196·5—220° obtained by redistilling No. 1.	1·070	84·4	Same as above	,,	The two liquids mixed on slight warming but separated again on cooling.	1 c.c. required 18 c.c. of sod. hydroxide to produce a solution and on diluting with 25 c.c. of water suspended particles were seen.	A blue colour was formed but soon disappeared. On separation, only two layers were seen the top one yellowish.	Refractive index 1·5308 at 26·2°C. Other tests same as above

†Corresponding with 200—220° at 760 mm.

Dropped on white filter paper and exposed to a temperature of 100° it leaves no translucent stain. (absence of less volatile oils).

The results of the tests are given in Table XIV, and from these results it is clear that the fraction 196·5—226·5° and the fraction 196·5—220° fulfil the requirements with the exception of specific gravity which is too low.

Attempts were made to increase the density and the proportion of oil distilling between 196·5 and 216·5° by repeated fractionation both at atmospheric and at reduced pressure, but these were not successful owing to the decomposition of the oil during distillation.

Estimation of Guaiacol in the fraction boiling at 197—217°.

The method adopted was that due to Kebler (Amer. J. Pharm. 1899, 409). cf. Allen's Commercial Organic Analysis Vol. III, 356.

The method was first tested by using a synthetic mixture containing guaiacol and *m*-cresol. The yield of potassium derivative corresponded with 98·2 per cent. of the guaiacol actually taken and the free guaiacol recovered corresponded with 92·3 per cent.

The fraction 197—217° was redistilled and the fractions 197—205° and 205—217° collected and analysed for guaiacol and creosole.

TABLE XV.

	Fraction 197—205°		Fraction 205—217°.	
	a,	b.	a.	b.
Weight taken ...	20·23	9·37	13·62	9·08
Weight of potasium compound of guaiacol and creosole.	2·07	1·01	4·50	2·99
Weight of free guaiacol ...	1·00	0·485	2·42	1/65
Percentage of Guaiacol and Creosol	8·10	816	26·16	26·02
Percentage of Guaiacol ...	4·95	4·91	18·20	17·77

The total guaiacol works out at about 0·43 per cent. on the original tar and at about 6·2 per cent on the fraction 197-217°.

The purity of the recovered guaiacol was tested by conversion into tetrabromoguaiacol melting at 162° (cf. Jackson and Torrey, Am. Chem. J., 1898, £0 424). The fractions boiling above

TABLE XIV.

	Fraction tested	Reaction with Solvents	$D_{15·5}^{15·5}$	Per cent. by volume distilling between 196·5—216·5°	Reaction with FeCl$_3$		Reaction with litmus
1	196·5 -226·5° Table XII fraction 8	Freely soluble in alcohol (90 % by vol). in ether, chloroform and glacial acetic acid	1·076	84	0·1 cc dissolved in 9·9cc of 90 per cent alcohol produced with a drop of FeCl$_3$, a light green colouration which became dark green and then turned brown	No translucent stain was left when a few drops were thrown on a white filter paper and exposed to a temp of 100°	It is faintly acid to litmus
2	195 -214° obtained by distilling No. 1	,,	1·076	72	,,	,,	,,
3	196·5-220° obtaining by distilling No. 1.	,,	1·076	84·4	,,	,,	,,

217° also gave potassum derivatives by Kebler's method, but the recovered phenol did not give the characteristic tetrabromoguaiacol.

SUMMARY.

1. A sample of the settled tar from cocoanut shells has been examined and found to give a very high yield of volatile constituents when compared with ordinary hardwood tar, 69 per cent. of the original tar being volatile below 260°C at 685 mm. pressure.

2. The tar on distillation yielded about 2-1 per cent. of aqueous distillate with 8 per cent. of acetic acid and 44 per cent. of oils volatile below 260° which gave 30 per cent. of phenolic bodies soluble in caustic soda solution. The latter on fractionation gave 6·2 per cent. of phenol and 5·86 per cent. of creosote boiling between 200 and 230° at normal pressure, while this last contained 0·43 per cent. of guaiacol, all these percentages being calculated on the original tar.

3. The creosote obtained did not satisfied the requirements of either the British or United States Pharmacopoeia mainly owing to its low density.

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