

# ESSENTIAL OIL OF CYPERUS ROTUNDUS.

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Although no less than 60 different species of Cyperaceae (Sedges) occur in India<sup>1</sup> none of the oils appears to have been examined. *Cyperus rotundus* Linn. is a common weed found throughout India and Ceylon and according to Watt<sup>2</sup> its occurrence as an enemy of cultivation has been recorded in nearly every tropical country. *Cyperus tuberosus* Rottb. is so closely allied to *C. rotundus* Linn. that it is usually regarded as a variety of the latter. Economically the two plants are identical, and the valuable portion is the tuber or rhizome which is aromatic, and, when mature, quite woody. The dry tubers are a commercial article and can be purchased in the local market at Rs. 2-8-0 per 25 lbs. The vernacular names are:—Motha in Hindustani and Guzerati, Korai in Tamil, Bhadramuste or Tungamuste in Telugu, Barikmotha in Marathi and Mutha in Bengali.<sup>3</sup> They are described as sweet-smelling, round, black and hard like a knot. According to Dymock they have an odour like that of *Acorus*, but the samples of tuber and oil examined in these laboratories have an odour much less pungent than that of *Acorus calamus* Linn. (the sweet flag). Joseph and Whitfield,<sup>4</sup> who examined a sample of oil from Soudan tubers, state that a camphor-odour is noticeable, whereas the Indian oil has no such odour.

Its chief uses are in medicine, in perfumery and for the preparation of fragrant sticks called *oodabatties*. It is not known whether the medicinal properties are due to the oil or to non-volatile constituents. According to Kirtikar and Basu,<sup>5</sup> the tubers are described as a vermifuge and in Indian practice are held in great esteem as a cure for disorders of the stomach and irritation of the bowels; mixed with green ginger and honey they are used in cases of dysentery.

## Steam-distillation.

Table I gives the results of five individual experiments on steam-distilling the tubers. Experiments 1 and 2 were made with the same

<sup>1</sup> Watt, Commercial Products of India, 1908, 464.

<sup>2</sup> *Ibid.*, 465.

<sup>3</sup> Dymock, *Pharm. Indica*, 1893, 2, 552.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1922, 41, 172 T.

<sup>5</sup> Indian Medicinal Plants, 1918, 1356.

sample of material purchased in June, 1923, distillations 3 and 4 were made with a second sample purchased in August, 1923, and distillation 5 with a third sample purchased in February, 1924.

In all cases the tubers were disintegrated using a 0.25-inch screen. The yield of oil per kilo. of steam is comparatively high at the beginning of the distillation, e.g., in distillation No. 5 about 4.4 grams of oil per kilo. of steam during the first two hours, but falls off rapidly and after 20 hours is only 0.7 grams per kilo. of steam.

TABLE I.

*Steam-distillation of disintegrated tubers of Cyperus rotundus.*

Distillation No.	Weight in kilos.	Moisture per cent.	Total steam in kilos.	Total time in hours	Total oil in grams	Ratio oil : steam.	Per cent. yield of oil on dry tubers
1	10.9	8.6	34.5	4.5	53	0.0015	0.53
2	11.6	8.6	32.3	4.0	58	0.0018	0.58
3	52.3	11.0	314	14	362	0.0012	0.78
4	39.3	11.0	229	11	301	0.0013	0.86
5	175.5	9.0	780	36	1116	0.0014	0.71

The yield obtained by Joseph and Whitfield <sup>1</sup> for the Soudan tubers was 0.5 per cent. on the dry tubers.

## ANALYTICAL CONSTANTS OF THE OIL.

Table II gives the analytical data for the five samples of oil obtained from the five distillations given in Table I and in addition the values obtained by Joseph and Whitfield for the Soudanese oil are given.

It is clear that the Indian oils have far higher specific gravities and refractive indices than the Soudanese oil; they also differ in their optical rotation as they are all dextro-rotatory whereas the Soudanese oil rotates to the left: all five Indian samples are insoluble in 80 per cent. (by volume) alcohol.

<sup>1</sup> *loc. cit.*

TABLE II.

*Analytical data for C. rotundus oil.*

$D_{15.5}^{15.5}$	0.9568	0.9907	0.9906	0.9857	0.9880	0.9829
$\alpha_D^{25}$	-19.9	+42.8	+42.8	+33.0	+33.7	+20.1
$n_D^{25}$	1.4967	1.5140	1.5140	1.5156	1.5140	1.5126
Acid value ...	1.0	2.1	2.1	2.1	3.4	2.4
Saponification value.	6.6	11.7	11.7	11.7	12.7	16.1
Acetyl Saponification value.	105	97.0	98.1	66.5	82.5	72.8
Solubility in alcohol.	Insoluble in 70 per cent. Soluble in 4 Parts 80 per cent.	Insoluble in 70 per cent.	Insoluble in 70 per cent.	Insoluble in 80 per cent.	Insoluble in 80 per cent.	Insoluble in 80 per cent.
Source of oil.	Soudan	India 1	India 2	India 3	India 4	India 5

The Indian samples 1-5 gave no absorption with a 30 per cent. solution of sodium hydrogen sulphite nor with a 5 per cent. aqueous solution of potassium hydroxide.

Difficulty was encountered in obtaining a sharp border-line when determining the refractive index with an Abbé refractometer, but sharp readings were obtained with a Pulfrich instrument.

#### DISTILLATION OF THE OIL.

(a) *Distillation under atmospheric pressure (685 mm.).*—The results obtained by distilling 12 grams of the oil under atmospheric pressure from a 30 cc. Claisen flask are given in Table III.

TABLE III.

*Distillation under pressure of 685 mm.*

No. of fraction	Boiling point in degrees cent.	Weight in grams	Per cent. of total oil
1	230-260	2.85	23.7
2	260-280	2.85	23.7
3	280-290	3.60	30.0
Residue.	—	2.00	16.7

There was appreciable fuming and decomposition during the distillation.

(b) *Distillation under reduced pressure (5 mm.).*—The results of four distillations are given in Table IV.

TABLE IV.

*Distillation of Saponified oil under pressure of 5 mm.*

Sample of oil	Fraction No.	Temperature in degrees cent.	Weight in grams	Per cent.	D <sup>15.5</sup> <sub>15.5</sub>	$\alpha$ <sup>25</sup> <sub>D</sub>	$n$ <sup>25</sup> <sub>D</sub>	
(a) No. 4.	1	115-120	1.7	2.6	...	...	1.50835	
	2	120-130	11.2	17.0	0.9520	+24.0	1.50868	
	3	130-140	18.3	27.7	0.9787	+31.3	1.51329	
	4	140-152	15.0	22.7	0.9984	+42.9	1.51932	
	5	152-170	10.7	16.2	1.0130	+46.4	1.52248	
	Residue.	...	9.0	13.8	...	...	...	
(b) No. 1 and 2 mixed.	1	110-120	1.0	1.6	...	...	1.50646	
	2	120-130	7.8	12.8	0.9463	+31.4	1.50812	
	3	130-140	16.6	27.2	0.9811	+35.2	1.51189	
	4	140-152	16.7	27.4	0.9990	+45.8	1.51959	
	5	152-165	11.2	18.4	1.0068	+52.8	1.52239	
	Residue.	...	5.0	8.2	...	...	...	
(c) No. 3	1	110-120	2.3	1.2	...	...	1.50658	
	2	120-130	32.4	16.8	0.9458	+22.7	1.50935	
	3	130-140	33.5	17.4	0.9642	+28.3	1.51199	
	4	140-152	70.0	36.3	0.9925	+38.7	1.51851	
	5	152-178	26.5	13.7	1.0085	...	1.52544	
	Residue.	...	21.0	10.9	...	...	...	
								Saponification value after acetylation.
(d) No. 5.	1	95-125	19.3	19.3	0.9433	...	1.50507	25.4
	2	125-135	18.0	18.0	0.9554	...	1.50885	29.9
	3	135-145	18.3	18.3	0.9802	...	1.51407	69.1
	Residue.	...	44.0	44.4	...	...	...	81.4

In all cases, with the exception of sample 5, the distillation was conducted in a three-bulb Erlenmeyer flask. The weights of oil taken were  $a=66$  grams,  $b=61$  grams,  $c=191$  grams and  $d=100$  grams. In sample 5 (Table IV*d*) the oil was distilled from an ordinary distillation-flask.

The corresponding fractions obtained by the four distillations given in Table IV were mixed and again carefully fractionated under a pressure of 3.4 mm. from a Claisen flask and the eleven fractions mentioned in Table V collected.

TABLE V.

*Redistillation under pressure of 3-4 mm.*

Fraction No.	Temperature in degrees cent.	Weight in grams	Per cent.	Saponification value after acetylation
1	99-102	6.3	2.0	...
2	102-106	12.8	4.0	...
3	106-110	30.4	9.5	26.4
4	110-116	12.1	3.8	...
5	116-125	6.2	1.9	...
6	125-130	14.5	4.5	...
7	130-135	88.1	27.5	82.0
8	135-137	44.6	13.9	74.8
9	137-139	16.5	5.2	72.2
10	139-150	5.0	1.6	84.8
11	150-156	5.0	1.6	120.6
Residue	...	54.4	17.0	...
Loss	...	24.0	7.5	...

It was hoped that the earlier fractions would be nearly pure sesquiterpene hydrocarbons and the later fractions products rich in alcohols. The results of acetylation and determination of the saponification values of the acetylated products show the presence of appreciable amounts of alcohols in the earlier fractions and the presence of neutral products in the later fractions, as a saponification

value of 85 corresponds with the presence of only 35.7 per cent. of a sesquiterpene alcohol,  $C_{15}H_{24}O$ , in the fraction.

Several attempts were made to isolate the alcohols present in the saponified oil, or in some of the fractions, in the form of their hydrogen phthalates. For this purpose 10 grams of the oil, 10 grams of dry benzene and 10 grams of freshly sublimed and well powdered phthalic anhydride were heated for 6 hours in a reflux apparatus in an oil-bath at temperatures varying between  $90-100^{\circ}$  and  $130-140^{\circ}$ . In one experiment the heating was continued for 20 hours, but in every case, when the product was worked up in the usual manner, the only acid product isolated was a small amount (0-4 per cent.) of phthalic acid, which was identified in each case by melting point and neutralisation value determinations. It is thus clear that the alcohols present cannot be isolated as their hydrogen phthalates, and hence are presumably tertiary. In one case the oil recovered from the phthalic anhydride treatment (6 hours at  $120-125^{\circ}$ ) was acetylated and the saponification value of the acetylated product determined. The value obtained, 50.7, indicates a 20.6 per cent. content of alcohol,  $C_{15}H_{24}O$ , whereas the oil before treatment with phthalic anhydride had a saponification value of 82.5 after acetylation, indicating a content of 34.6 per cent. of alcohols,  $C_{15}H_{24}O$ , and pointing to a loss of alcohols during heating.

A similar loss of alcohols is shown when the fractions given in Table IV*d* are compared with the original oil. The saponification value after acetylation of the latter, 72.8, shows the presence of 30.3 per cent. of alcohols,  $C_{15}H_{24}O$ ; whereas the saponification values after acetylation of the fractions, viz., 25.4, 29.9, 69.1 and 81.4 give a total of 23.6 grams of alcohol in 100 grams of oil. This is equivalent to a loss of 22 per cent. of the total alcohols originally present. A similar result was obtained by taking 40 grams of saponified oil from sample No. 5 distilling at 6 mm. pressure, collecting 12 grams of distillate and 27 grams of residue, and determining the saponification values after acetylation, when a loss of 9 per cent. of the alcohols originally present was found.

As the alcohols present in the oil appear to be tertiary since they do not react with phthalic anhydride, and as when heated they appear to undergo decomposition probably into water and hydrocarbons, it was thought possible that similar decomposition may occur during acetylation. Comparative experiments were conducted in order to ascertain the alcohol-content by (a) acetylation, (b) formylation and (c) estimation of hydroxyl by Hibbert and Sudborough's method using magnesium methyl iodide in phenetole solution. The values obtained for the oil from distillation No. 5 are given in Table VI.

TABLE VI.

*Percentage of alcohols in oil No. 5.*

—	Method employed	Per cent. of alcohols Calculated as $C_{15}H_{24}O$
1	Ordinary acetylation process ... ..	30.3
2	Boulez method of acetylation <sup>1</sup> ... ..	37.5
3	Formylation by Glichitch's method <sup>2</sup> ... ..	29.3
4	Hydroxyl estimation by Grignard's reagent. <sup>3</sup>	31.7 <sup>4</sup>

The results prove that little or no decomposition occurs during acetylation or formylation.

*Sesquiterpenes*,  $C_{15}H_{24}$ .—As the low-boiling fractions are poor in alcohols, attempts were made to isolate sesquiterpenes from them.

The alcohols were removed as far as possible as benzoyl derivatives by Walbaum and Huthig's <sup>5</sup> or by Erdmann's method. <sup>6</sup> The oil used was sample No. 5, which was distilled under a pressure of 10 mm., when 50 per cent. of the oil collected boiled between 100° and 150°. This fraction had a sp. gr. 0.9576 at 15.5°, a refractive index 1.5094 at 25° and a rotation of +13.0° at 25°. The saponification value after acetylation was 35.7, indicating the presence of 14.3 per cent. of alcohols calculated as  $C_{15}H_{24}O$ . After one benzoylation with twice the theoretical amount of benzoyl chloride and subsequent distillation, the alcohol content was reduced to 10 per cent. and after a second treatment by Erdmann's method was further reduced to 4.3 per cent. The recovered oil was repeatedly distilled over sodium to remove the alcohols still present and was then carefully fractionated under a pressure of 4.5 mm., when the two fractions given in Table VII were collected.

<sup>1</sup> In this method a diluent, e.g., xylene is used (*Bull. Soc. Chim.*, 1907, [IV], 1, 117) and experiments made with pure geraniol and santalol indicate that high results are obtained.

<sup>2</sup> *Bull. Soc. Chim.*, 1923, [IV], 33, 1284.

<sup>3</sup> *J. Chem. Soc.*, 1904, 85, 933.

<sup>4</sup> As the first three methods give total alcohols, i.e., free and combined as esters, in this estimation the alcohol present as esters, viz., 6.4, was added to the free alcohol found (25.3), making a total of 31.7 per cent.

<sup>5</sup> *J. pr. Chem.*, 1905, [II], 71, 465.

<sup>6</sup> *Ibid.*, 1897, [II], 56, 14.

TABLE VII.

*Hydrocarbon fractions from the oil.*

Fraction No.	Temperature	$D_{15.5}^{15.5}$	$n_D^{25}$	$\alpha_D^{25}$	Mol. Ref.
1	100-103°	0.92967	1.50196	- 2.3	65.4
2	106-109	0.92987	1.50483	+ 12.3	65.7

*Analyses :*

Fraction 1. 0.1797 gave 0.1934 of water and 0.5798 of carbon dioxide.

Fraction 2. 0.1601 gave 0.1722 of water and 0.5170 of carbon dioxide.

	Found		Calculated for
	(i)	(ii)	$C_5H_8$
C	88.03	88.04	88.22 per cent.
H	11.98	11.99	11.78     ,,

The molecular refraction for fraction 1, calculated from the data  $d_4^{15} = 0.92644$  and  $n_D^{15} = 1.50596$ , is 65.4, and for fraction 2, calculated from the data  $d_4^{15} = 0.92724$  and  $n_D^{15} = 1.50883$ , is 65.7. The usual value for monocyclic sesquiterpenes is 67.76, for bicyclic 66.15 and for tricyclic 64.45.

The two fractions isolated appear to consist of sesquiterpenes and probably a mixture of bi- and tricyclic.

*Alcohols from the benzoyl derivatives.*—The benzoyl derivatives obtained in isolating the sesquiterpenes were non-volatile with steam, were saponified with alcoholic potash and the resulting alcohols isolated; but it was not found possible to isolate any definite compound. After several distillations a fraction consisting of 81 per cent. of the total product and weighing 11 grams was obtained. It boiled at 130–175° under 4 mm. pressure, had a rotation +22.8°, a refractive index 1.51756 at 25° and was obviously a mixture. The result of the determination of OH by Hibbert and Sudborough's method gave 94 per cent. of alcohols  $C_{15}H_{24}O$ . The molecular refraction was 67.0.

An attempt was made to examine the higher boiling fraction. For this purpose a sample of the oil from distillation No. 5 was distilled under a pressure of 10 mm. and two fractions boiling at 100–150° and 150–170° separately collected. The yields were 50.0 and 48.7 per cent. respectively calculated on the weight of the original



oil, and the respective specific gravities at  $15.5^{\circ}$  were 0.95757 and 1.01328. The second fraction was redistilled and 30 grams of distillate with  $n_D^{25} = 1.5186$ ,  $a_D^{25} = +32.0$  and saponification value after acetylation = 81 were collected. After two distillations over sodium 7.5 grams of an oil were obtained boiling at  $126-131^{\circ}$  under a pressure of 3-4 mm. and with a specific gravity 0.983 at  $15.5^{\circ}$ . The yield of this fraction corresponds with 12.1 per cent. of the original oil and the following results were obtained on combustion:—

*Analyses:*

	(i)	0.2205	gave	0.6678	of carbon dioxide	and	0.2037	of water.
	(ii)	0.1506	„	0.4576	„	„	0.1374	„
			Found.			Calculated for		
		(i)		(ii)		$C_{15}H_{24}$	$C_{15}H_{24}O$	
C		82.59		82.87		88.23	81.82	per cent.
H		10.26		10.14		11.76	10.91	„

Another sample was prepared in a similar manner and a product boiling at  $133-137^{\circ}$  under a pressure of 6 mm. was obtained. This had  $d_{15.5}^{15.5} = 0.9836$ ,  $n_D^{25} = 1.5087$  and  $a_D^{25} = +23.7$ . It contained 83.1 per cent. of carbon and 11.0 per cent. hydrogen and when acetylated and saponified gave a saponification value of 61.3 corresponding with 25.2 per cent. of an alcohol  $C_{15}H_{24}O$ .

It is therefore clear that the treatment with sodium had not removed all the oxygen and that the product is a mixture of hydrocarbon, alcohol and perhaps an ether.

### SUMMARY.

1. The oils obtained from the tubers of Indian *Cyperus rotundus* differ appreciably from Soudanese oil especially as regards specific gravity, refractive index and optical rotation.

2. The lower fractions contain at least two sesquiterpenes with molecular refraction 65.5.

3. Two or more alcohols are also present. The percentage of total alcohol calculated as  $C_{15}H_{24}O$  is about 30. The alcohols do not react with phthalic anhydride and hence are presumably tertiary.

4. In addition to alcohols large quantities of neutral substances, probably hydrocarbons, are present in the higher fractions.

5. So far it has not been found possible to isolate pure substances from the oil.

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