KACHI-GRASS OIL.

By Bijoor Sanjiva Rao and J. J. Sudborough.

The Andropogon grasses (natural order Gramineae) are characterised by the essential oils contained in their leaves, efflorescence or roots, and several of these oils are products of commercial importance.

In 1906 Stapf[1] reorganised the classification of these grasses and introduced the three genera :—

Cymbopogon with ten species,
Andropogon with one species,
Vetiveria with one species.

Since this date, new species of Cymbopogon have been introduced and in some cases their oils have been examined. The following list comprises sixteen fairly well-defined species of Cymbopogon grasses, including the ten recognised by Stapf which are denoted by an asterisk.

CYMBOPOGON GRASSES.

* 1. *C. caesius* Stapf. This is allied to the well-known species *Martini* and is quite common in the Carnatic. The oil is dealt with in this paper.

* 2. *C. citratus* Stapf. This is not known wild, but is cultivated especially in Ceylon, the Straits Settlements and Malay. It yields the Ceylon lemon-grass oil, which resembles the oil from *flexuosus* but contains less citral and is less soluble in alcohol.[2]

* 3. *C. coloratus* Stapf. This is a lemon-grass oil occuring in South India but is smaller than *flexuosus*. It contains about 42 per cent. of citral, 33 per cent. of geraniol and geranyl acetate and 7 per cent. of terpenes.[3]

* 4. *C. confertiflorus* Stapf. This grass occurs in South India between the Nilgiris and Ceylon, and is thought by some to be the mother plant of the Citronella grasses. The yield of oil is very low.

* 5. *C. flexuosus* Stapf. This is the lemon-grass of Malabar, Tinnevelli and Tuticorin and is often planted. The important constituent of the oil is citral (70–85 per cent.), and other compounds present are geraniol and its esters and methylheptenone.

[1] *Kew Bull.*, 1906, 297.
[2] Schimmel's Report, 1908, October, 81.
[3] Schimmel's Report, 1910, April, 85 ; *Bull. Imp. Inst.*, 1912, **10**, 27 ; *Proc. Chem. Soc.*, 1914, **30**, 10.

*6. *C. Iwarancusa* Schult, known also as fever-healing grass. It occurs on the Bombay plains and upwards to the Himalayas. It yields 1 per cent. of an oil with an odour of peppermint and contains Δ^4-carene 20, and *d*-piperitone 77 per cent.[1] A sample from Sind gave 44 per cent. of piperitone, 24 per cent. of terpenes and 28 per cent. of sesquiterpene alcohols and closely resembles the oil from *C. sennaarensis*.[2]

7. *C. javanensis* Hofman[3] yields an oil resembling palmarosa and contains geraniol, methylisoeugenol, citral and methylvanillin.

*8. *C. Martini* Stapf occurs in two varieties known as *motia* and *sofia*. The former yields the well-known palmarosa oil, the chief constituents of which are geraniol (75–95 per cent.) and farnesol;[4] the latter yields the less valuable ginger-grass oil containing terpenes, geraniol and perillic alcohol. Both grasses grow largely in the North of the Bombay Presidency and in the Central Provinces.[5]

*9. *C. Nardus* Rendle is the true Citronella-grass. It is found wild in Ceylon, but is cultivated in Ceylon, Java, and the Malacca Peninsula. Stapf recognises two varieties: old Citronella-grass, Winter's grass or *Maha pengiri*, and new Citronella-grass or *Lenabatu*. The constituents of the oil are geraniol, nerol, citronellol, citronellol together with methyleugenol, terpenes and sesquiterpenes. The new grass is largely grown in Ceylon, the oil is less valuable than that from the old grass and is less soluble in alcohol. It possesses the advantage of not being so readily exhausted as the old grass, which usually does not last more than 10–15 years.

10. *C. nervatus* Chiov, is the Naal-grass of the Soudan. The yield of oil from the inflorescence is 0·8–1·5 per cent. The odour resembles that of Ginger-grass oil and it contains *l*-limonene and perillic alcohol (60–64 per cent.)[6]

11. *C. odoratus* Lisb is used as a domestic remedy on the West Coast of India and yields as much oil as Rosha-grass.[7]

12. *C. pendulus* Stapf occurs in North Bengal and yields an oil containing 83–90 per cent. of aldehydes.[8]

[1] *Simonsen, J. Chem. Soc.*, 1921, **119**, 1644.
[2] *Indian Forest Records*, 1922, **9**, 128.
[3] *Pharm. Weekblad*, 1919, **56**, 1279; Schimmel's Report, 1919, 20. It is doubtful if this is a definite new species.
[4] *Chem. Zeit.*, 1910, **34**, 857.
[5] Pearson, *Indian Forest Records*, 1916, **5**, 191. Walbaum And Huthig, *J. Pr. Chem.*, 1905, **71**, 459.
[6] Joseph and Whitefield, *J. Soc. Chem. Ind.*, 1922, **41**, 144 T. Also Schimmel's Report, 1911, April, 19.
[7] *Pharm. Ind.*, edition 1893, vol. iii, p. 569; Schimmel's Report, 1892, April, 44.
[8] Schimmel's Report, 1911, October, 59.

* 13. *C. polyneuros* Stapf occurs in south-west India especially in the Nilgiris. It has an odour of anise or fennel, but yields only 0·25 per cent. of oil containing 39–52 per cent. of alcohols.[1]

* 14. *C. Schoenanthus* Spreng or Camel-grass is common in North Africa, Arabia, Afghanistan, Beluchistan, and the Punjab, and contains phellandrene.[2]

15. *C. sennaarensis* Chiov, grows in British Sudan and yields 1·0 to 1·2 per cent. of oil resembling pennyroyal, but is more fragrant and contains 45 per cent. of *d*-piperitone (Δ^1-menthen-3-one), 13 of terpenes and 25 of sesquiterpene alcohols.[3]

16. *C. Winterianus* Jowett. This is the Java variety of *C. Nardus*, viz., old Citronella-grass or *Maha pengiri* which has been raised to a distinct species by Jowett.[4]

A grass which is quite common around Bangalore and generally on the Mysore Plateau is Kachi-grass, which has a pronounced aromatic odour. Specimens of this grass sent to the Agricultural College, Coimbatore, and to the Royal Botanic Gardens, Kew, were identified as *Cymbopogon caesius* Stapf. According to Rao Bahadur K. Rangachariar of Coimbatore, the difference between *C. Martini* and *C. caesius* is to be found in the general habit of the plants and the size of the leaves; he states that it is difficult to distinguish the narrow-leaved forms of *Martini* from the closely allied *caesius*. The following are the descriptions of the two species given by Stapf:

C. Martini. Culms in loose, rather scanty fascicles, erect and simple or nearly so, usually tall and robust, basal sheaths soon withering, blades 10-30 mm. wide (rarely under 10), somewhat fat, rich green at least above, panicles 10-30 mm. long, rather loose, turning reddish (often very bright) when mature.

C. caesius. Culms in somewhat loose, often in copious fascicles, erect or geniculately ascending, very slender, frequently branched, the branches often in fascicles from the culms, sheaths soon withering, blades 2-6 mm. wide, thin glaucous, panicles usually loose, 10-20 mm. long, glaucous or straw-coloured when mature.[5]

Rangachariar[6] gives the following description of Kachi-grass. 'This is a perennial grass with stout or slender erect stems rising

[1] *Bull. Imp. Inst.*, 1912, 10, 27.
[2] Schimmel's Report, 1892, April, 44.
[3] Roberts, *J. Chem. Soc.*, 1915, 107, 1465.
[4] *Annals Royal Botanic Gardens*, Peradeniya, 1908, IV, 4, 185.
[5] *Bull. Misc. Information, Royal Bot. Gardens, Kew*, 1906, 351.
[6] *Hand-book of Some South Indian Grasses*, 1921, pp. 209–210.

from a woody base, leaf upward, simple or branched. The grass grows all over the Madras Presidency in open dry situations, and is very widely distributed throughout India to tropical Africa.'

Cameron in 1894 termed Kachi-grass *C. pachnodes*.[1]

According to Messrs. Volkart Brothers, there is a large area near Madras in which a grass yielding an oil somewhat similar to *C. Martini sofia* is available and this finds its way to Bombay *via* Vaniambady Station.[2] It is probable, though not certain, that this grass is *C. caesius*.

Although small quantities of Kachi-grass are distilled locally, there appears to have been no attempt made to cultivate an industry comparable with that of the *Motia* and *Sofia* industry of N. India.

As no description of the oil could be found in the literature, we distilled some of the grass growing on the Institute site and a determination of its analytical data at once showed that these fall within the limits usually given for Ginger-grass oil, i.e., the oil from *C. Martini sofia*. A more detailed examination showed that the main constituents of Ginger-grass oil, viz., limonene, dipentene, geraniol and perillic alcohol are also present in the oil from Kachi-grass.

It is thus clear that the oils from *C. Martini sofia* and *C. caesius* contain practically the same constituents, and this affords another example of two distinct species yielding much the same oil. Other examples among the Cymbopogon genus are *Iwarancusa* from Sind and *sennaarensis* from Soudan, also *citratus* of Ceylon and *flexuosus* of Malabar.

Recently the oil from Inchi-grass of Travancore has been examined by Moudgill and K. R. Krishna Iyer[3] and has been found to be different from the other oils derived from Cymbopogon species. The constituents of the oil from the white variety are *l*-borneol, *l*-terpineol, *l*-camphene, *l*-limonene and sesquiterpenes. The identity of this grass cannot be regarded as settled. According to Rao Bahadur K. Rangachariar of Coimbatore the white Inchi-grass is *C. cæsius* Stapf and the red variety is *C. flexuosus* Stapf, whereas according to the Kew authorities both varieties are the same species, viz., *C. flexuosus* Stapf forma *albescens*. If the former classification is correct, then the same species can give rise to quite different oils in different localities.

The experimental work described in this paper falls under the following headings :—

[1] *The Forest Trees of Mysore and Coorg*, 3rd edition, appendix, p. 29.
[2] Pearson, *Indian Forest Records*, 1916, 5, part 7, p. 5.
[3] *Perf. Essent. Oil Rec*, 1922, 13, 293.

1. Distillation of different samples of grass and the analytical data for the oils obtained.

2. Isolation of the more important constituents.

3. Conversion of insoluble into soluble oils.

4. Changes in the oil on storage.

EXPERIMENTAL.

1. Distillation of Different Samples of Kachi-grass and the Analytical Data for the Corresponding Oils

In Table I are given the relative proportions of flower-heads and stems for the species *caesius*, *Martini motia*, *Martini sofia*.

TABLE I.

—	Caesius	Martini	
		Motia	Sofia
Flower-heads	42	40[2]	60[2]
Stalks	58[1]	60	40

In Table II are given the results of a number of distillations of the grass carried out between 1917 and 1923. The results show that the stalks (with leaves) contain very little oil compared with flower-heads.

The percentages of oil are all calculated to dry grass. A number of determinations of moisture were made in different samples and they varied according to the number of days the grass had been kept.

In experiments 20 to 25, note was made of the condition of the grass and of the time elapsing between picking and distillation. The yield from immature flower-heads (Nos. 20 and 24) is much the same as from mature (Nos. 22 and 25). It is rather lower if the flower-heads are dead (No. 23) or if they are kept some days before distillation (No. 21).

The values are interesting when compared with those given by Pearson[3] for *Martini motia* and *sofia*. (See Table III.)

[1] Including leaves.
[2] Including leaves, cf. Pearson, *loc. cit.*, pp. 11, 12.
[3] *loc. cit.*, pp. 14, 15, 17.

TABLE II.

Steam-distillation of Kachi-grass—whole grass, stalks and leaves, and flower-heads.

No.	Date of distillation	Description of materials	Weight of raw material in kilos.	Moisture per cent.	Grams of oil obtained	Percentage yield on weight of raw material	Percentage yield on weight of dry material
1	Dec. '20 ...	Whole grass ...	52·3	...	155	0·30	0·42
2	Do. ...	Do. ...	53·6	...	186	0·37	0·53
3	Do. ...	Do. ...	50·5	...	165	0·33	0·47
4	Do. ...	Do. ...	53·2	...	170	0·32	0·46
5	Do. ...	Do. ...	50·0	...	162	0·33	0·46
6	Do. ...	Do. ...	53·0	...	100	0·20	0·30
7	Do. ...	Do. ...	39·3	...	57	0·14	0·22
8	Do. ...	Stalks and leaves.	33·4	...	45	0·14	0·20
9	Do. ...	Do. ...	56·8	...	74	0·13	0·16
10	Jan. 31, '22 ...	Do. ...	52·3	30·2	64	0·11	0·18
11	Nov. 10, '17 ...	Flower-heads ...	33·6	*...	300	0·90	1·25
12	Nov. 17, '17 ...	Do. ...	27·0	...	314	1·16	1·61
13	Dec. 31, '17 ...	Do. ...	63·0	...	655	1·33	1·45
14	Jan. 28, '18 ...	Do. ...	28·2	...	276	0·98	1·36
15	.....	.....	...	...	...	...	...
16	Dec., '20 ...	Flower-heads ...	32·7	...	301	0·92	1·20
17	Do. ...	Do. ...	23·6	...	188	0·80	1·10
18	Do. ...	Do. ...	23·9	...	235	0·99	1·36
19	Do. ...	Do. ...	14·5	...	127	0·88	1·12
20	Dec. 15, '21 ...	Do. ...	43·6	28·0	410	0·94	1·28
21	Jan. 26, '22 ...	Do. ...	33·2	24·0	282	0·85	1·13
22	Jan. 31, '22 ...	Do. ...	53·2	36·3	550	1·03	1·61
23	Feb. 7, '22 ...	Do. ...	54·6	19·2	502	0·92	1·13
24	Nov. 20, '23 ...	Do. ...	38·6	27·2	389	1·00	1·40
25	Dec. 13, '23 ...	Do. ...	55·0	26·0	619	1·11	1·52

* Moisture not estimated but taken as 28 per cent. for Nos. 11–19.

TABLE III.

——	Motia	Sofia
Fresh green (reduced to Sun-dried)...	1·90	1·42 per cent.
Sun-dried	1·26	...
Stalks	0·67	...
Total grass (Sun-dried)	...	0·4-0·6 per cent.

All the distillations were carried out in a small copper still of the tilting type capable of taking about 60 kilos of grass or flower-heads at a charge. The still was lagged and the steam entered below the false bottom; steam and oil were cooled in a copper tube-condenser well tinned. The rate of steam was 20 kilos per hour and the average duration of a distillation 2·5 hours. Three florentine flasks were used for separating oil and water, and the aqueous liquid on further standing for 24 hours gave no appreciable quantity of oil.

In Table IV are given the results of the analyses of most of the samples of oil prepared. These results show that:—

1. The yield of oil from mature and immature flower-heads is much the same. The low yield in distillation No. 21 is probably due to the fact that most of the grass had been kept for several days in the shade before distillation, losing moisture and oil.

2. The oil becomes richer in oxygenated compounds as the flowers ripen.[1] There is thus a gradual increase in the total alcohols and esters present. As the result of this the oil becomes more soluble in 70 per cent. (by volume) alcohol. Puran Singh [2] in the case of Rosha-grass, and Moudgill and Krishna Iyer [3] in the case of Inchi-grass state that the oils from over-ripe grass contain less alcohols. The specific gravity and the refractive index also tend to rise as the grass matures.

3. The properties of the oils from the stalk and flower-heads do not vary much.

4. An interesting point is the relatively high optical rotation of samples of oil from green flowers.[4] The rotation may be either positive or negative, and appears to be due to the presence of *d*-or *l*-limonene, as the high rotation is due to the lower terpene fraction and not to the higher alcohol fractions, cf. Table X.

[1] The flowers ripen about the end of January, if the rainfall is good or in December itself, if the rainfall is small.

[2] *Indian Forest Records*, 1916, **5**, 240

[3] *Perf. Essent. Oil Rec.*, 1922, **13**, 292.

[4] Samples 20 and 24 in Table IV.

TABLE IV.

No.	Specific gravity at $\frac{15{\cdot}5°}{15{\cdot}5}$	Refractive Index at 25°	Optical rotation at 25°	Acid value	Saponification value	Saponification value after acetylation	Percentage of total alcohols as $C_{10}H_{18}O$	Solubility in volumes of 70 per cent. (vol.) alcohol	Source of the oil
1	0·9274	1·4847	— 43·1	0·9	15·9	150·6	46·7	Insoluble.[1]	Whole grass.
2	0·9332	1·4857	— 18·3	0·9	18·4	150·4	46·6	do.	
3	0·9319	1·4855	— 43·8	0·9	16·3	151·5	47·0	do.	
4	0·9288	1·4848	— 45·6	1·0	17·6	153·1	47·8	do.	
5	0·9372	1·4867	— 41·3	0·6	13·2	155·8	48·5	do.	
6	0·9267	1·4846	— 37·5	1·7	31·2	164·0	51·4	do.	
7	0·9339	1·4856	— 34·4	2·5	24·0	155·6	48·4	do.	
8	0·9497	1·4855	— 38·9	4·9	21·1	149·5	46·3	do.	Stalks and leaves.
9	0·9564	1·4907	— 38·8	4·1	24·8	164·0	51·4	do.	
10	0·9356	1·4875	— 31·6	3·4	22·3	145·8	45·0	do.	
11	0·9281	1·4857	— 23·7	5·9	12·0	123·5	37·4	do.	Flower-heads.
12	0·9345	1·4857	+ 2·7	9·2	19·0	131·7	39·2	do.	
13	0·9311	1·4889	+ 4·2	8·3	19·3	124·7	37·8	do.	
14	0·9328	1·4851	— 20·1	7·8	21·2	133·6	40·8	do.	
15	0·9181	1·4838	— 62·5	1·7	12·6	114·6	34·5	do.	
16	0·9399	1·4867	— 32·0	4·3	32·1	149·2	46·2	do.	
17	0·9350	1·4863	— 58·5	2·7	19·9	146·5	45·3	do.	
18	0·9367	1·4875	— 30·3	0·5	16·8	146·2	45·2	do.	
19	0·9306	1·4860	— 39·1	0·5	15·6	149·3	46·2	do.	
20	0·9291	1·4857	— 62·1	4·2	18·8	138·9	42·6	do.	
21	0·9387	1·4867	+ 9·9	3·4	24·9	147·9	45·8	4 at 14° ; 5 at 25°.	
22	0·9409	1 4871	— 32·6	3·4	27·2	158·7	49·5	3 at 10° ; 5 at 25°.	
23	0·9789	1·4887	— 25·1	...	32·4	172·3	54·4	2 at 10° ; 6 at 25°.	
24	0·9381	1·4867	— 61·5	2·6	22·4	139·8	43·0	Insoluble.	
25	0·9777	1·4873	— 40·0	3·1	26·9	171·0	53·9	3 at 10° ; 5 at 25°.	

[1] This means that the oil is insoluble even in 10 volumes at 25°.
[2] The oil becomes turbid on addition of more alcohol.

5. The four samples, Nos. 20, 21, 22 and 23, showed an absorption of 12–14 per cent. when treated in the usual manner with concentrated sodium bisulphite solution. A sample of Ginger-grass oil from Baroda gave an absorption of 12 per cent., and a genuine sample of Ginger-grass oil examined at the Imperial Institute gave an absorption of 10 per cent.[1] A more detailed study of this reaction renders it extremely doubtful if this absorption is due to the presence of aldehydes or ketones.

2. Isolation of the More Important Constituents of the Oil.

Geraniol.—Geraniol is a common alcoholic constituent of many Cymbopogon oils and attempts were made to isolate this alcohol from Kachi-grass by (*a*) the calcium chloride method recommended by Jacobson [2] and (*b*) the conversion into its hydrogen phthalate.

(i) *Calcium chloride method.*—100 grams of oil with an acetyl value of 124·7 was saponified with alcoholic potash and the product mixed with 100 grams of finely powdered anhydrous calcium chloride and kept overnight in a closed vessel immersed in freezing mixture contained in a vacuum flask. The product was well washed with light petroleum (b. p. 40–60°) to remove all terpenes and uncombined alcohols and the residual solid decomposed by means of ice.[3] The oil which had not reacted with calcium chloride was treated again and finally 30 grams of an oil derived from the calcium chloride additive compound was collected. This oil had the following constants: $n_D^{25} = 1{\cdot}4870$, $[\alpha]_D^{25} = +0{\cdot}7^0$ and saponification value of 172·4, as compared with the values 1·4760, nil and 286 required by pure geraniol. The method appears therefore to be useless for separating geraniol in a pure state from Kachi-grass oil. When 20 grams of pure geraniol were mixed with 80 grams of the terpene fraction derived from the original Kachi-grass oil by distillation and the mixture treated with calcium chloride as described above, 25 per cent. of the pure alcohol was recoverd from the additive compound. In another experiment using the same proportions, but only one-fourth the amounts, 30 per cent. of the geraniol was found to have combined with the calcium chloride.

These results show that it is not possible to separate all the geraniol from an oil by means of calcium chloride,[4] but that geraniol free from hydrocarbons can be isolated, indicating that in the treatment

[1] *Bull. Imp. Inst.*, 1920, **18**, 345.
[2] *Annalen*, 1871, **157**, 234.
[3] Decomposition with water engendered much heat and the product was resinous.
[4] Cf. Brooks, *The Non-benzenoid Hydrocarbons*, 1922, p. 193.

of the original oil with calcium chloride, in addition to geraniol calcium chloride a product was formed which, on treatment with water, gave rise to hydrocarbons or non-acetylisable alcohols.

(ii) *Geranyl hydrogen phthalate method.*—A given weight of oil, freed from terpenes and hydrolysed, was heated with its own weight of phthalic anhydride and half its weight of benzene for 10 hours in an oil bath at 110–120°. The neutral oil was removed and again treated with phthalic anhydride in the same manner. The first operation gave 18 and the second 4 grams of hydrogen phthalate or a total of 22 grams corresponding with 11 grams of an alcohol, $C_{10}H_{17}\cdot OH$, or 24 per cent. of the total alcohols present in the oil.

Another sample of oil freed from terpenes and hydrolysed, and with an acetyl value 226 corresponding with 74·8 per cent. of alcohols $C_{10}H_{17}\cdot OH$, gave hydrogen phthalate corresponding with 20 per cent. of the total alcohols present.

The geraniol isolated from the hydrogen phthalate had the following properties: b.p. 105–109°/8 mm., $[\alpha]_D^{25} = -0{\cdot}2$ and $n_D^{25} = 1{\cdot}4800$, as compared with the values usually given, viz., b.p. 110–111°/10 mm., $[\alpha]_D^{25} = 0$ and $n_D^{25} = 1{\cdot}4766$–$1{\cdot}4786$; it was characterised as geraniol by

(*a*) its oxidation to citral with dichromate and sulphuric acid and the isolation of citral-semicarbazone melting at 132–133° [1] and with nitrogen content 20·05 as compared with the theoretical value 20·1 per cent.

(*b*) its oxidation to citral and the condensation of this with pyruvic acid and β-naphthylamine to α-citryl-β-naphthylcinchoninic acid melting at 199° after crystallisation from alcohol.[2]

(*c*) the formation of silver geranyl phthalate melting at 132–133° [3].

Perillic alcohol [4].—The method of isolation was the same as that adopted by Walbaum and Huthig, viz., conversion of alcohols into benzoyl derivatives by the pyridine method and removal of non-benzoylated compounds by steam distillation; hydrolysis of the benzoates to the alcohols by alcoholic potash and removal of the geraniol from the mixed alcohols by treatment first with calcium

[1] Tiemann, *Ber.*, 1898, 31, 3330.
[2] *Ibid.*, 3327.
[3] H. and E. Erdmann, *J. Pr. Chem.*, 1897, [ii.], 56, 19.
[4] This alcohol was first isolated by Walbaum and Huthig (*J. Pr. Chem.*, 1905, [ii.], 71, 459) from Ginger-grass oil and termed dihydrocuminic alcohol, but was afterwards shown by Semmler and Zaar (*Ber.*, 1911, 44, 466) to be identical with perillic alcohol obtained by reducing perillic aldehyde from *Perilla arguta* Benth (*ibid.*, p. 54).

chloride, then with phthalic anhydride and finally with anhydrous formic acid to destroy the last traces of geraniol. In carrying out these operations it was found that considerable resinification occurred during benzoylation and hydrolysis. From 237 grams of oil with an acetyl value of 213, only 45 grams of mixed alcohols were obtained after twice benzoylating and hydrolysing. The values for this oil were :—

Acetyl value 282·4 corresponding with 98·5 per cent. of alcohols as $C_{10}H_{17}\cdot OH$; $[\alpha]_D^{25} = -7\cdot5^\circ$ and $n_D^{25} = 1\cdot4989$.

After removal of geraniol an oil was obtained boiling at 90–95° under a pressure of 4 mm. and with the constants given in Table V.

TABLE V.

Constants for Perillic alcohol.

—	From Perillic aldehyde[1]	From Kachi-grass	From Ginger-grass[2]	From Ginger-grass[3]
Boiling point	119–121°/11 mm.	90–95°/4 mm.	92·0–93·5°/5 mm.	107–110°/12·5 mm.
d_{15}^{15}	0·964	0·9630	0·9510	d_{20}^{20} 0·946
$[\alpha]_D^{25}$	− 68·5°	− 12·9°	− 13·3°	− 7·0
n_D^{25}	1·4996	1·4996	...	1·4968

The perillic alcohol was characterised by conversion into (*a*) its aldehyde semicarbazone melting at 200°. (*b*) Perillic chloride b.p. 97–105°/5 mm. and $[\alpha]_D^{25} = -28\cdot0^\circ$ and $d_{15}^{15} = 0\cdot9879$. (*c*) Reduction of the chloride to dipentene and the formation of the tetrabromide melting at 123–124°. All these operations were carried out according to the methods given by Semmler and Zaar.

Terpenes.—The low boiling fractions from a number of preparations were mixed, carefully fractionated, the fractions distilled over sodium and again fractionated. By this process two main fractions were obtained with the properties given in Table VI.

[1] Semmler and Zaar, *Ber.*, 1911, 44, 54.
[2] Walbaum and Huthig, *J. Pr. Chem.*, 1905, [ii.], 71, 466.
[3] Semmler and Zaar, *Ber.*, 1911, 44, 460.

TABLE VI.

Terpenes.

Fraction	B. P. under 6 mm. pressure	Weight in grams	$d_{15\cdot5}^{15\cdot5}$	n_D^{25}	$[\alpha]_D^{25}$
1	49–53°	65	0·8539	1·4728	— 17·2
2	53–58°	24	0·8517	1·4728	— 18·2

Fractions 1 and 2 when brominated in glacial acetic acid solution gave respectively 28 and 23 per cent. of solid tetrabromides melting at 119–121° and at 123–124° after crystallisation from ethyl acetate. By using Godlewsky's method of bromination in amyl alcohol and ether[1] the yield of tetrabromide from fraction 1 was raised to 79 per cent. of the theoretical. The properties and analysis proved the compound to be the tetrabromide of dipentene. By the addition of hydrogen chloride in glacial acetic acid a dihydrochloride melting at 49–50° was obtained. The formation of these compounds points to the presence of dipentene. The presence of *l*-limonene in a similar fraction having a strong lævo-rotation was proved by the isolation of a tetrabromide melting at 104° after crystallisation from ethyl acetate.

Phellandrene and terpinene could not be isolated as nitrite or nitrosite and no trace of *iso*borneol could be detected by heating the terpene fractions with a mixture of acetic and sulphuric acids, thus pointing to the absence of camphene.

3. Conversion of Insoluble into Soluble Oils.

From the early part of the paper it is clear that there is a close similarity between Ginger-grass and Kachi-grass oils. The former is met with in what are termed the soluble and insoluble[2] varieties and purchasers always buy on sample and give higher prices for the soluble oil. Similarly Kachi-grass oil is found in soluble and insoluble forms and it has already been shown that, as a rule, the oil from mature flower-heads is more soluble than that from the immature flowers, as it contains less of terpenes and therefore a higher percentage of alcohols. It is thus clear that to render an insoluble oil soluble it is only necessary to remove a certain portion of the terpenes present and thus bring

[1] *Chem. Zeit.*, 1898, 23, 827.

[2] This refers to the solubility or insolubility of the oil in three volumes or less of 70 per cent. (by volume) alcohol.

up the percentage of alcohols. To ascertain the percentages of terpenes, a number of different samples of oil were subjected to fractional distillation under a pressure of 6–7 mm., and the fractions passing over below 70° regarded as terpenes. The value of n_D^{25} for such fractions is always below 1·480 and the saponification value of the acetylated oil is always low, e.g., 7, indicating the presence of only 2·5 per cent. of alcohols $C_{10}H_{17}\cdot OH$.

The results of distilling six different samples of oil are given in Tables VII to XII. In Table XI the results of a complete distillation are given and the rotation, refractive index and solubility of each fraction indicated: in Table XII are given the results of fractional distillation of a sample of Kachi-grass oil having a relatively high positive rotation and in Table XIII of a sample of Ginger-grass oil from Baroda.

TABLE VII.

Distillation of 50 grams of Dist. No. 11 under a pressure of 6–7 mm.

No. of fraction.	Temperature in degrees centigrade	Weight of fraction in grams	Refractive Index at 25°
1	44–64	17·5	1·4716
2	64–70	2·5	1·4761
3	70–80	1·5	1·4810
4	80–82	1·5	1.4846
5	82–85	2·5	1·4874
6	85–95	23·0	1·4901
	Residue	1·0	

TABLE VIII.

. Distillation of 50 grams of Dist. No. 14 under a pressure of 6–7 mm.

1	45–60	15·0	1·4710
2	60–70	3·5	1·4768
3	70–82	2·5	1·4830
4	82–85	1·0	1·4865
5	85–95	20·0	1·4898
	Stopped		

TABLE IX.

Distillation of 50 grams of Dist. No. 15 under a pressure of 6–7 mm.

No. of fraction	Temperature in degrees centigrade	Weight of fraction in grams	Refractive Index at 25°
1	44–64	12·0	1·4720
2	64–70	5·5	1·4769
3	70–82	1·5	1·4860
4	82–85	4·5	1·4880
	Stopped		

TABLE X.

Distillation of 50 grams of sample No. 20 under a pressure of 6–7 mm.

No. of fraction	Temperature in degrees centigrade	Weight in grams	Refractive Index at 25°	Optical rotation at 25°	Solubility in volumes of 70 per cent. (vol.) alcohol
1	45–60	3·5	1·4714	— 89·8	...
2	60–62	6·0	1·4714	— 91·6	...
3	62–66	5·5	1·4728	— 88·8	...
4	66–70	6·0	1·4744	— 83·8	...
5	70–76	2·0	1·4754	...	...
6	76–80	1·5	1·4794	...	...
7	80–85	1·5	1·4844	...	...
8	85–90	2·5	1·4870	— 60·0	...
9	90–92	3·5	1·4884	— 58·0	...
10	92–94	4·5	1·4892	— 55·0	...
11	94	5·0	1·4904	— 47·6	...
12	94	1·5	1·4914	...	...
13	94–110	5·5	1·4923	— 21·8	...
...	Residue	1·0	...	...	...

TABLE XI.

Distillation of 50 grams of sample No. 22 under a pressure of 6–7 mm.

1	45–60	3·5	1·4746	— 46·5	Insoluble.
2	60–65	5·3	1·4731	— 48·0	Do.
3	65–66	2·8	1·4738	— 46·5	Do.
4	67–69	1·0	1·4752	— 45·0	Do.
5	69–70	1·5	1·4753	— 38·6	Do.
6	75–80	2·5	1·4845	— 35·0	2 at 22°
7	80–84	2·0	1·4878	— 34·4	2 at 2°
8	84–85	3·5	1·4886	— 34·4	2 at 0°
9	85–91	4·5	1·4900	— 33·4	2 below—6°
10	91–92	3·5	1·4910	— 31·0	2 at—5°
11	92–95	6·5	1·4919	— 26·4	Do.
12	95–96	4·0	1·4926	— 20·5	2 at − 3°
13	96–98	2·5	1·4925	— 14·0	2 at + 6°
14	98–110	2·0	1·4928	— 9·0	2 at − 3°
...	Residue	3·0	...	...	...

TABLE XII.

Distillation of 50 grams of sample No. 21, Table IV.

No. of fraction	Pressure in mm. of mercury	Temperature in degrees centigrade	Weight in grams	Refractive index at 25°	Optical rotation at 25°
1	5–6	44–60	3·4	1·4731	+ 11·8
2	,,	60–63	5·0	1·4726	+ 16·0
3	,,	63–66	5·0	1·4734	+ 15·9
4	,,	66–70	4·0	1·4756	+ 14·8
5	,,	70–76	3·0	1·4796	+ 12·0
6	,,	76–80	2·5	1·4851	+ 10·2
7	,,	80–85	2·5	1·4866	+ 10·0
8	,,	85–88	3·5	1·4876	+ 9·3
9	,,	88–90	4·0	1·4886	+ 8·8
10	,,	90	5·0	1·4898	+ 7·8
11	,,	90	3·0	1·4906	+ 6·3
12	,,	90–92	3·0	1·4924	+ 5·1
13	,,	92–94	2·5	1·4926	+ 2·8
14	,,	94–100	1·0	1·4926	+ 1·0

TABLE XIII.

Distillation of 50 grams of Ginger-grass oil from Baroda.

1	10	65–67	3·0	1·4729	+ 53·3
2	8	,,	3·5	1·4738	+ 58·4
3	7	67–69	3·0	1·4746	+ 54·0
4	,,	69–71	4·0	1·4755	+ 48·0
5	,,	71–78	4·5	1·4788	+ 41·4
6	,,	78–84	4·2	1·4865	+ 39·9
7	,,	84–94	4·3	1·4889	+ 35·9
8	,,	94–98	4·3	1·4900	+ 29·2
9	,,	98	3·3	1·4910	+ 24·0
10	,,	98–104	5·5	1·4910	+ 16·0
11	,,	104–110	4·6	1·4935	+ 14·8

Table XIV gives the analytical data for two samples of oil the terpene contents of which have been reduced to just below 30 per cent. by removal of a portion of the more volatile constituents.

TABLE XIV.

Analytical constants for two Soluble oils.

Date of distillation	Dec. 1921 Sample No. 20	Dec. 1917 Sample No. 13
$d_{15\cdot5}^{15\cdot5}$	0·9538	0·9439
n_D^{25}	1·4873	1·4874
$[\alpha]_D^{25}$	−28·3	+3·6
Saponification value after acetylation	163·8	159·8
Per cent. of alcohols $C_{10}H_{17}\cdot OH$	73·7	71·4
Solubility in 70 per cent. alcohol	Soluble in 3 vols. at 18°	Soluble in 2·5 vols. at 15°.

An insoluble oil is also readily rendered soluble by removing a portion of the terpenes by steam distillation.

Several samples of oil were steam distilled and the residual oil examined after each successive removal of 2 to 3 per cent. of terpenes. The quantity of terpene that has to be removed in each case in order to render the oil soluble is shown in Table XV.

TABLE XV.

Date of distillation of original oil	Per cent. of terpenes removed to render oil soluble given as per cent. of total oil	Percentage of terpenes in soluble oil
Nov. 1917, Sample No. 11 ...	13·8	26·2
Jan. 1918 do. 14 ...	11·9	25·1
Dec. 1918 do. 15 ...	4·0	31·0
Dec. 1921 do. 20 ...	12·0	30·0

From these results it is clear that an insoluble sample of Kachi-grass oil may be rendered soluble by reducing the terpene-content to 30 per cent., either by removal under reduced pressure or by steam.

The results recorded in Table XVI show that the higher boiling fractions are also insoluble in alcohol and it has been shown that freshly distilled oils, if insoluble, can often be rendered soluble by rejecting a portion of the higher boiling fractions, usually the last 12 per cent. Samples of oil which have been kept for some time do not give soluble products under such treatment.

TABLE XVI.

Solubility of fractions from distillation No. 23.

Percentage of total distillate	Solubility in volumes of 70 per cent. (by volume) alcohol
First 63·0	2 at 12°
Next 12·2	2 at 13°
,, 12·6	2 at 15°
,, 8·0	2 at 16·5°
,, 4·2	Insoluble

4. CHANGES IN KACHI-GRASS OIL ON STORAGE.

It has been observed that, although a sample of oil may have a pale yellow colour when freshly distilled, it turns a deep reddish brown when kept for some time. Samples from different distillations and also from different fractions of the same distillation have been examined. The result has been to show that the refractive index shows an increase on storage and that the solubility tends to improve. At the same time there is a slight diminution in optical activity. The change is most marked in the higher fractions containing the oxygenated compounds.

The results of the experiments are recorded in Table XVII.

A determination of the total alcohols by the acetylation process in different samples after several years' storage shows that there is no diminution in alcohol-content.

TABLE XVII.

Change in physical properties of the oil on storage.

Sample No.	Date of examination	Refractive Index at 25°	Optical rotation at 25°	Solubility in parts of 70 per cent. (vol.) alcohol
	January 4, 1922 ...	1·4857	−62·1°	Insoluble
20	September 26, 1922 ...	1·4860	−60·0°	,,
	September 30, 1923 ...	1·4864	−60·0°	,,
	January 28, 1922 ...	1·4867	+9·9°	4 at 14°
21	September 26, 1922 ...	1·4872	+9·3°	...
	September 30, 1923 ...	1·4878	+8·4°	3 at 18°
	February 4, 1922 ...	1·4871	−32·6°	3 at 10°
22	September 26, 1922 ...	...	−25·6°	...
	September 30, 1923 ...	1·4951	−22·5°	2 at 0°
23	February 8, 1922 ...	1·4853	−29·3°	2·5 at 16°
First 38	September 23, 1922 ...	1·4877	−26·8°	,,
percent.	September 30, 1923 ...	1·4884	−26·2°	2·5 at 17°
23	February 8, 1922 ...	1·4878	−28·5°	2 at 13°
Next 26	September 23, 1922 ...	1·4892	−26·8°	2 at 10°
percent.	September 30, 1923 ...	1·4896	−26·8°	2 at 8°
23	February 8, 1922 ...	1·4878	−25·9°	2 at 17°
Next 12·7	September 23, 1922 ...	1·4930	−20·6°	2 at −2°
percent.	September 30, 1923 ...	1·4996	−18·0°	2 at −5°
23	February 8, 1922 ...	1·4868	−21·6°	2 at 17°
Next 13	September 23, 1922 ...	1·4914	−17·2°	2 at 12°
percent.	September 30, 1923 ...	1·4976	−14·0°	2 at −8°

SUMMARY.

1. Kachi-grass oil, the oil from *C. caesius* Stapf, closely resembles Ginger-grass oil from *C. Martini sofia* Stapf. The analytical values for the former oil fall within the limits accepted for Ginger-grass oils. The similarity extends to the presence of the following constituents in the two oils:—Dipentene, limonene, geraniol and perillic alcohol.

2. Kachi-grass oil when freshly obtained can be either soluble or insoluble in alcohol. The oils from more mature flower-heads, as a rule, are richer in oxygenated compounds and more soluble in 70 per cent. alcohol.

3. An insoluble sample of oil can usually be rendered soluble by reducing the percentage of terpenes to 30, either by distillation under reduced pressure or by steam distillation.

4. The physical properties of the oil alter on storage. The refractive index rises and the rotation falls. The change is more marked in the fractions containing alcohols than in those containing terpenes, but the total percentage of alcohols, as determined by acetylation, does not change appreciably.

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