Travancore Essential Oils

Part VI.

From *Cymbopogon Caesius;* Stapf. (*Inchi* Grass).

By

Kishori Lal Moudgill.

This grass grows wild in profusion on the dry hill-slopes of the Western Ghats in South Travancore, and is locally known as 'inchipul'[1] (Ginger grass) because of the aroma given by the leaves and the flowers when they are rubbed. The shoots appear early after the rains in June and the grass flowers between October and January when it attains a height of 6 feet or more. At present it is not put to any use and is invariably destroyed by fire when it dries up.

The botanical identification of the grass presented several difficulties.[2] Ram Rao described the grass as *Andropogon shoenanthus*, Linn., and called it geranium grass (Flowering plants of Travancore) but Professor Rangachari of Coimbatore (*private report*) identified it as *Cymbopogon Caesius*, Stapf. This was subsequently confirmed by the Director of Kew Gardens and is in accord with the results of a detailed chemical examination, for, notwithstanding its aroma, the essential oil obtained from this grass by distillation with steam is quite different in character from the closely allied varieties, *Cymbopogon flexousus*, Stapf. (lemon grass) and *Cymbopogon Martini*,

[1] Lemon grass, *Cymbopogon flexousus*, Stapf is also known as 'inchipul.'

[2] It may be mentioned in this connection that much confusion, which was finally cleared by Stapf, had crept into the nomenclature of the gras es belonging to the family known as *Andropogon*.

Stapf.—formerly known as *Cymbopogon shoenanthus*, Linn., or *Andropogon shoenanthus*, Linn., or the 'motia' and 'sofia' grasses of Western India. Both these oils are well known in commerce, and citral and geraniol, the valuable constituents of the essential oils obtained from the former and the latter grasses respectively, are absent in this oil while borneol, which has not been reported in either of them, appears to be a characteristic constituent of the oil from 'inchi' grass.

A sample of the oil distilled from this grass was analysed at the request of the Department of Industries, Travancore, by Dr. Sudborough of the Indian Institute of Science and the Imperial Institute, London, and the latter reported that the oil might be employed as a substitute for palmarosa oil which it resembles in odour. An account of a preliminary work on this oil was published elsewhere (Moudgill and Krishna Iyer, Perfumery and Essential Oil Record, Vol. xiii, 1922, 292-295) and (Bulletin No. XVII, Department of Industries, Travancore). This paper describes the isolation and the identification of *l*-borneol, *l*-camphene, *l*-limonene and *l*-terpineol as some of the constituents of the oil. In view of the commercial possibilities suggested by the report of the Imperial Institute further work, reported below, was undertaken.

There are two varieties of the grass, one white and the other red. These two grow side by side in the same area and sometimes in the same cluster, and are not distinguishable from one another in odour or in any other respect except the colour of the stem and the base of the spikelets of the flowers, which in the case of the latter variety ranges from discoloured brown to red. The work described below was carried out mostly with the oil obtained from the white variety only, though the essential oils given by both of them as judged by their constants, are identical. (Table I.)

TABLE I.

	Red.	White.
$d\frac{28°}{4°}$ ..	0·9130	0·9110
$n\frac{28°}{D}$	1·4820	1·4815
$\alpha\frac{30°}{D}$ ...	−3·60°	−40·0°
Acid value ...	*Nil.*	*Nil.*
Ester value ...	11·4	9·2
Ester value after acetylation.	121 8	117·4

N. B.—Both the varieties were cut from the same locality and at the same time.

It had been reported (Moudgill and Krishna Iyer, *loc. cit.*), that the difference in ester value caused by slight alterations in the conditions under which the estimation was carried out was due to the presence of terpineol but, in view of the isolation of a sesquiterpene alcohol which can be acetylated with great difficulty, this view has been modified. Consequently, the acetyl value can be used only to characterise the oil and does not afford much help in determining the proportions of alcohols present in the oil.

The constants of the oil obtained from the plant at different stages of its growth, as well as from different parts of the plant were determined. (Table II.) From these it would appear that the oil from the leaves distilled from the grass cut on different dates does not vary. The flowers yield a different oil and the characters of the oils from the upper third of the grass is to some extent modified after October, when the flowers appear, the alteration being most pronounced in February when the grass begins to dry up. The flowers give a larger yield of oil.

TABLE II.

Dates of distillation.	From the upper third of the plant only.							Leaves.	Flowers.
	5-6-22	10-7-22	13-8-22	12-9-22	12-10-22	13-12-22	6-2-22	6-2-22	6-2-22
Yield (dry) ...	3·75%	...	0·68%	0·78%	...	...	0·85%	0·65%	1·5%
$d\frac{28°}{4°}$ ...	0·9070	0·9040	0·9020	0·9020	0·9030	0·9130	0·9130	0·9056	0·9380
n_D	1·4840	1·4820	1·4826	1·4821	1·4845	1·4885	1·4910	1·4840	1·4925
Rotation ...	−38·0°	−36·8°	−37·5°	−32·8°	−32·0°	−32·5°	−37·5°	−42·5°	−22·9°
Acid value ...	...	1·1	0·9	1·0	0·7	1·6	1·8	1·8	0·4
Ester value ...	14·8	11·1	13·6	13·5	21·6	23·0	7·2	6·8	6·1
Acetyl value ...	93·5	97·0	104·0	117·2	96·0	...	89·0	100·0	78·0
Aldehydes per cent. ...	5·6	...	5·1	6·0	6·2	6·0	4·4	5·4	4·1

In view of the fact that several essential oils change on keeping, the constants of a sample of the oil were determined from time to time after storage for various periods in glass-stoppered bottles and in contact with anhydrous sodium sulphate. They indicate that the oil does not undergo any change, the little variations being well within the range of experimental error. (Table III.)

TABLE III.

	Original oil.	After keeping for			
		3 months.	6 months.	10 months.	20 months.
Solubility in 70 per cent. alcohol.	insol.	insol.	insol.	insol.	insol.
Solubility in 80 per cent. alcohol.	7·0 vols.	7·2 vols.	7·2 vols.	7·0 vols.	7·2 vols.
Solubility in 87 per cent. alcohol.	0·8 vol.	1·0 vol.	0·9 vol.	0·8 vol.	1·0 vol.
$d^{30°}_{4°}$	0·9187	0·9176	0·9180	0·9178	0·9174
Refractive index .	1·484	1·4880	1·4883	1·4885	1·4890
Optical rotation	−38·9°	−37·5°	−38 0°	−34·0°	−34·0°
Acid value .. .	1·7	1·4	2·3	2·4	3·5
Ester value ...	5·6	6·0	6·0	7·1	6·0
Acetyl value .	120·0	118·5	117·0	117·5	111·0

A more detailed examination of the oil has shown that, besides the constituent reported in an earlier paper (Moudgill and Krishna Iyer, *loc. cit.*), it contains a laevo-rotatory terpene alcohol which has not been obtained pure, a sesquiterpene and a liquid sesquiterpene alcohol, an aldehyde ($C_{10}H_{16}O$), and esters of acetic acid, butyric acid and an insoluble acid isomeric with oleic acid.

EXPERIMENTAL.

Fractionation.—An attempt has been made, with considerable success, to separate the oil into several fractions distilling over small ranges of temperature and to locate the major constituents of the oil by a comparative study of the changes in solubility in 80 per cent. and 90 per

cent. alcohols, specific gravity and optical rotation, it being assumed that abrupt changes common to all the three properties would indicate a variation in the composition of the fraction. Fifteen hundred c.c. of the oil were fractionated under reduced pressure, first into three fractions and subsequently into twenty fractions (Table IV), each fraction in the latter case being collected over a range of 5 degrees. It would appear (see diagrams) that the oil consists of four chief fractions, each of which may consist of one or more than one constituent of the same class.

TABLE IV.

Fractions.	B.pt.	Yield%.	Solubility in alcohol.		$d_{4^\circ}^{29^\circ}$	Specific rotation *
			80%	90%		
1	to 55°	7·5	insol.	7·2 vols.	0·8549	.
2	−60°	5·6	,,	4·8 ,,	0·8529	−69·25°
3	−65°	5·9	,,	8·0 ,,	0·8489	−75·78°
4	−70°	3·6	,,	4·8 ,,	0·8498	−70·15°
5	−75°	3·8	,,	3·6 ,,	0·8525	−69·98°
6	−80°	1·7	,,	5·1 ,,	0·8578	−65·30°
7	−85°	2·2	,,	4·2 ,,	0·8682	...
8	−90°	1·4	7 vols.	all	0·9122	−51·46°
9	−95°	1·7	1·2 ,,	,,	0·8932	−40·46°
10	−100°	1·9	0·9 ,,	,,	0·9356	−34·05°
11	−105°	2·8	0·9 ,,	,,	0·9401	−32·73°
12	−110°	8·4	0·9 ,,	,,	0·9423	−31·25°
13	−115°	2·0	0·85 ,,	,,	0·9445	−32·43°
14	−120°	6·3	0·85 ,,	,,	0·9414	−28·24°
15	−125°	2·7	insol.	0·2 vol.	0·9410	−19·95°
16	−130°	2·2	,,	all	0·9450	−15·43°
17	−135°	1·7		..	0·9537	−13·02°
18	−140°	5·6	..	all	0·9683	− 9·99°
19	−150°	6·3	1·2 vols.	,,	0·9828	− 0·55°
20 †	−165°	6·6	0·9 ,,	,,	0·9991	− 0·00°
Solid ...	.	4·2	...	...	..	...
Loss and residue	..	15·0	.	. .	...	...

N.B.—The distillation was carried out under a pressure of 12-14 mm.

* The 19th and the 20th fraction boiled 10° higher than the previous fraction.

† The rotations were determined in 4 decimeter tubes, which alone were available at the time, in alcoholic solution, because, either the rotations of the homogeneous liquid were so high that they did not fall within the range of the polarimeter, or the specimens were so highly coloured that a column 4 decimeters long did not permit light to pass through. Smaller tubes were available in the latter part of the work.

1. *Fractions 1-8.*—Insoluble in 80 per cent. alcohol, soluble with difficulty in 90 per cent. alcohol, specific gravity 0·8500 to 0·8700, optical rotation $-60°$ and above, consisting mainly of terpenes, camphene and limonene.

2. *Fractions 9-13.*—Soluble in equal volume of 80 per cent. alcohol, and in all proportions in 90 per cent. alcohol, specific gravity 0·8900 to 0·9400, optical rotation about $-30°$ consisting mainly of alcohols, borneol, terpineol and another terpene alcohol which has not been isolated so far.

3. *Fractions 14-17.*—Insoluble in 80 per cent. alcohol, easily soluble in 90 per cent. alcohol, specific gravity about 0·9450. The abrupt change in the solubility curve (see diagrams, in 80 per cent. alcohol), indicates the presence of a compound sparingly soluble in alcohol. This was confirmed by the separation described below. The fractions were mixed and saponified with alcoholic caustic potash, the alkaline liquor being reserved for further work. The oil was dried over anhydrous sodium sulphate and distilled when the following fractions were obtained. (Table V.)

TABLE V.

No	B.pt.	$d\frac{30°}{4°}$	$n\frac{30°}{D}$	$\alpha\frac{28°}{D}$	Acetyl value.
1	220°-225°/760 mm.	0 9212	1 4800	..	197 3
2	225-230°/670 mm.	0·9224	1·4840	$-22°$	173·0
3	Up to 112°/16mm	0·9212	1 4928	$-18·5°$	110·0
4	„ 115°/ „	0·9133	1·4930	$-14\ 8°$	42 5
5	„ 123°/ „	0·9308	1 5025	$-12\ 0°$	115·3
6	„ 135°/ „	0·9440	1·5063	$-\ 7\ 5°$	..
7	„ 155°/ „	0 9644	1 5098	..	.

The acetyl values of the different fractions indicate that No. 4 (b.pt. 112-115/16 mm.) consists probably of a hydrocarbon. It was distilled repeatedly over sodium

and finally a nearly homogeneous colourless sesquiterpene ($C_{15}H_{24}$), which did not alter on repeated fractionation, was obtained $d^{30°}_{4°}$ 0·9064, $n^{30°}_{D}$ 1·5005, $\alpha^{30°}_{D}$ 12°

Found: C = 87·7; H = 11·2 per cent.

$C_{15}H_{24}$ requires C = 88·2; H = 11·8 per cent.

Unfortunately, only a small quantity of the oil was available for characterisation, and no solid derivative could be obtained. From a study of the molecular refraction and analysis of the liquid hydrobromide and dibromide (both unpurified), it appears that the hydrocarbon is a bicyclic sesquiterpene containing one double bond which is easily saturated. On treating it in glacial acetic acid solution in an ice-bath, with a cooled solution of bromine in the same solvent, nearly 1·1 molecules of bromine were absorbed for each molecule of the hydrocarbon. The *dibromide* was obtained as a liquid by pouring the above reaction mixture on ice and removing the oil by extraction with ether. The ethereal solution was dried over anhydrous sodium sulphate, the ether recovered and the oil kept in a vacuum desiccator for six weeks.

Found: Br = 41·37.

$C_{15}H_{24}Br_2$ requires Br = 43·05 per cent.

A liquid *monohydrobromide* was obtained in the usual way.

Found: Br = 30·58 per cent.

$C_{15}H_{25}Br$ requires Br = 28·07 per cent.

When the hydrocarbon was dissolved in acetone or acetic anhydride and the solution was treated with a trace of concentrated sulphuric acid, a green colouration was produced which turned blue on keeping. Solutions of the hydrocarbon in chloroform or glacial acetic acid, treated similarly, gave varying shades of purple.

Fraction 1-3 (Table V) were evidently mixtures of alcohols with the hydrocarbon. All attempts to obtain geraniol from these by treating with powdered calcium chloride in the cold and subsequent regeneration of the alcohol were unsuccessful. As they could not be purified further, their identity could not be established. Fractions 6 and 7 consist partly of a sesquiterpene alcohol and were added to the corresponding fractions below.

4. *Fractions 18 to 20.*—These were mixed and saponified with excess of alcoholic caustic potash, the alkaline extracts being reserved. Fractions 6 and 7 above (Table V) were mixed with the oil which was distilled and the following fractions obtained.

TABLE VI.

No.	B pt /16mm pressure	$d\frac{30°}{D}$	$n\frac{30°}{D}$	Rotation.
1	135°-140°	0 9543	1 5040	−9·0°
2	140°-145°	0 9700	1 5090	−1 25°
3	145°-150°	0 9863	1 5108	±0°
4	150°-160°	0 9776	1·5092	±0°
5	Above 160°	0·9640	1 5090	±0°

The major portion of the oil distilled at 147°-149°/16 mm. and consisted of an optically inactive sesquiterpene alcohol ($C_{15}H_{26}O$). It would appear from the constants of fractions 4 and 5 that the alcohol undergoes decomposition on prolonged heating probably getting dehydrated and giving a lighter hydrocarbon. The alcohol cannot be acetylated easily. Under the normal conditions of acetylation, the acetyl value was 32, which corresponds to acetylation to the extent of only 13 per cent. In such cases, Boulez has recommended that a diluent with a low acetyl value should be employed and, if necessary, correction made to allow for the acetyl value of the diluent.

When acetylation was carried out in camphene solution and the period of heating with acetic anhydride prolonged, better results were obtained. Table VII gives the extent of acetylation under varying conditions of experiments. It appears that the alcohol is tertiary because the difficulties of acetylation met with in the case of this body are commonly experienced with tertiary alcohols.

TABLE VII.

Alcohol (4·6 parts) : *camphene* (25·6 parts).
Acetyl value of camphene=6·0.

Duration of heating.	* 2 hrs.	4 hrs.	* 6 hrs.	8 hrs.	9 hrs.	11 hrs.
Ester value (found) ..	26 12	31·99	36·91	37·08	37·65	43·8
Corrected ..	20·12	25 99	30·91	31 08	31·65	37 8
% Acetylation in mixture ..	8·0	10·42	12·43	12 5	13·10	15 29
Acetylation for homogeneous liquid (calculated).	47 89	68.13	74·35	81·72	80·74	99·95

An attempt to prepare the benzoyl derivative by the Schotten-Baumann method proved equally unsuccessful, the resulting oil, changed in so far that it had a sweeter smell and different constants, gave an ester value of 63·2 which corresponds to benzoylation to the extent of 28 per cent. only. The alcohol is still under examination.

Treatment of the oil for isolating the aldehyde.—The oil is found to contain a small percentage of aldehyde (or ketone) at all stages of its growth. One litre of the oil was shaken repeatedly with a concentrated solution of sodium bisulphite, 100 cc. at a time. The extracts were mixed together, washed with ether ten times to remove traces of the adhering oil and warmed with excess of a solution of sodium carbonate when an oily layer separated. This was extracted with ether, the ethereal solution dried over anhydrous sodium sulphate and the

* The dilution in these two determinations was 4·7545 parts alcohol, 23·71 parts camphene

ether removed. It was noticed that a portion of the oily layer did not dissolve in ether. On addition of some sodium chloride to the aqueous layer further quantities of this oil separated. It was removed with benzene, the benzene solution dried and the benzene recovered.

The sweet smelling oil recovered from the dry ethereal solution possessed the following constants. B.pt. 92°-94°/4-5 mm. $\alpha \frac{30°}{D}$ —6·5°, $d \frac{30°}{4°}$ 0·9694, $n \frac{30°}{D}$ 1·4980.

Found: C = 79·6; H = 9·7.

$C_{10}H_{14}O$ requires C = 80; H = 9·3 per cent.

$C_{10}H_{16}O$ requires C = 79·0; H = 10·5 per cent.

Preparation of the Semicarbazone.—A mixture of alcoholic solution of sodium acetate (1·3 grams) and semicarbazide hydrochloride (1·9 grams) was added to an alcoholic solution of the aldehyde (2·1 grams) and heated on a boiling water-bath during 30 minutes. It was allowed to stand for 24 hours and then poured into excess of water, when, on keeping for some hours, a semi-solid separated which was collected and drained on a porous plate. The solid thus obtained was crystallized from methyl alcohol, m.p. 170°-175°. The crystals were washed several times with anhydrous ether and the washings when evaporated deposited crystals, m.p. 164°. The residue was recrystallised from ethyl acetate, m.p. 181°. It would appear that the aldehyde extract obtained above contains two aldehydes, or, alternatively, the aldehyde in the mixture gives two semicarbazones, but owing to the scarcity of available material it was not possible to study this point further.

Attempts to prepare a solid oxime or a phenyl hydrazone were unsuccessful.

The benzene extract was found to solidify on keeping in a desiccator for a week. It is very hygroscopic and dissolves in water giving a colloidal solution from which it can be precipitated by adding concentrated aqueous solution of sodium chloride or any other inorganic salt. Attempts to crystallise it from organic solvents were unsuccessful. Qualitative analysis showed that the compound contained sodium and sulphur, and this and other characters of the solid suggested that a molecular compound of the aldehyde with sodium bisulphite had been obtained. This has been observed with several unsaturated aldehydes, most notably acraldehyde. The solid was purified as far as possible by dissolving it in water, precipitating with sodium chloride and extracting with benzene. Unfortunately, sufficient quantities for a complete analysis could not be obtained.

Found : Na = 5·4, 5·6 ; S = 8·78.

$(C_{10}H_{16}O)_2NaHSO_3$ requires Na = 5·63; S = 7·85 per cent.

The formula $(C_{10}H_{16}O)_2NaHSO_3$ has been deduced from the above results of analysis. In view of the discordant figure obtained for sulphur and the fact that the purity of the compound under analysis may be questioned, it is put forward tentatively and must be accepted with reserve.

Combined acids.—The alkaline extracts obtained after the saponification of the various fractions were mixed together, washed several times with ether to remove adherent oil and acidified with dilute sulphuric acid. An oil, smelling strongly of rancid butter, separated and was removed. The aqueous layer was neutralized with sodium hydroxide, reduced in bulk to about 200 cc., extracted again with ether, acidified with dilute sulphuric acid and distilled with steam. The volatile acids were collected in three fractions, converted into their silver salts and analysed.

Fraction 1. Found: Ag=65·62. $C_2H_3O_2Ag$ requires Ag=64·7 per cent.

Fraction 2. Found: Ag=60·1 per cent.

Fraction 3. Found: Ag=56·4. $C_4H_7O_2Ag$ requires Ag=55·4 per cent.

Fractions 1 and 3 consist of acetic acid and butyric acid respectively. Even though the results of the silver salt obtained from fraction 2 would indicate the presence of propionic acid, it was neutralized, reduced in bulk, acidified and distilled with steam again. Three fractions were obtained and as the silver salts obtained from these did not give a figure for silver to correspond to silver propionate, fraction 2 was taken to have been a mixture of acetic acid and butyric acid.

The oily portion which had been removed with ether was repeatedly distilled with steam and finally obtained as a yellow oil smelling strongly of rancid fats. $d\ \frac{30°}{4°}$ 0·8732, $n\ \frac{30°}{D}$ 1·4583. It was optically inactive, insoluble in water hot and cold, but readily soluble in all the common organic solvents. A suspension in water rapidly cleared when a dilute aqueous solution of caustic soda was added but after a moment the solution became turbid and gave a lather, characteristic of soaps. The silver salt prepared from an alcoholic solution of the oil was a white solid insoluble in water and very sparingly soluble in alcohol.

Found: Ag=30·18, 29·40.

$C_{16}H_{31}O_2Ag$ requires Ag=29·75 per cent.

$C_{16}H_{32}O_2Ag$ „ Ag=29·87 „

A solution of the acid in alcohol readily absorbs bromide. This fact and the high specific gravity and refractive index of the compound would point to its being

an unsaturated compound, because the values for the latter two increase, in the case of the acids containing the same number of carbon atoms, with the increase in the degree of unsaturation. The acid is probably an isomer of oleic acid with the formula $C_{16}H_{30}O_2$.

Conclusions.

1. *Cymbopogon Caesius*, Stapf. gives a sweet-smelling essential oil which is quite different in character from the oils obtained from similar grasses but resembles palmarosa oil in odour.

2. The oil occurs in the flowers and the leaves. The former yields more oil than the latter.

3. The oil does not undergo any change on storage.

4. The oil obtained from the leaves is fairly uniform during the different stages of the growth of the plant. The oil from the flower is richer in sesquiterpene constituents and has a much lower acetyl value than the oil from the leaves.

5. The constituents of the oil are:—*l*-limonene, *l*-camphene, *l*-borneol, *l*-terpeneol, a bicyclic sesquiterpene $d\ \frac{30°}{4°}\ 0{\cdot}9064, n\ \frac{30°}{4°}\ 1{\cdot}5005$, specific rotation at $\frac{30°}{D}$ —12°, a tertiary sesquiterpene alcohol ($C_{15}H_{26}O$) and a terpene alcohol which could not be obtained in a pure state for characterisation. Besides these, the oil contains an aldehyde which gives a sodium salt of a sulphonic acid on treatment with sodium bisulphite, and esters of acetic acid, butyric acid, and an unsaturated acid $C_{16}H_{30}O_2$.

6. There are two varieties of the grass, one white and the other red, but they both give the same oil.

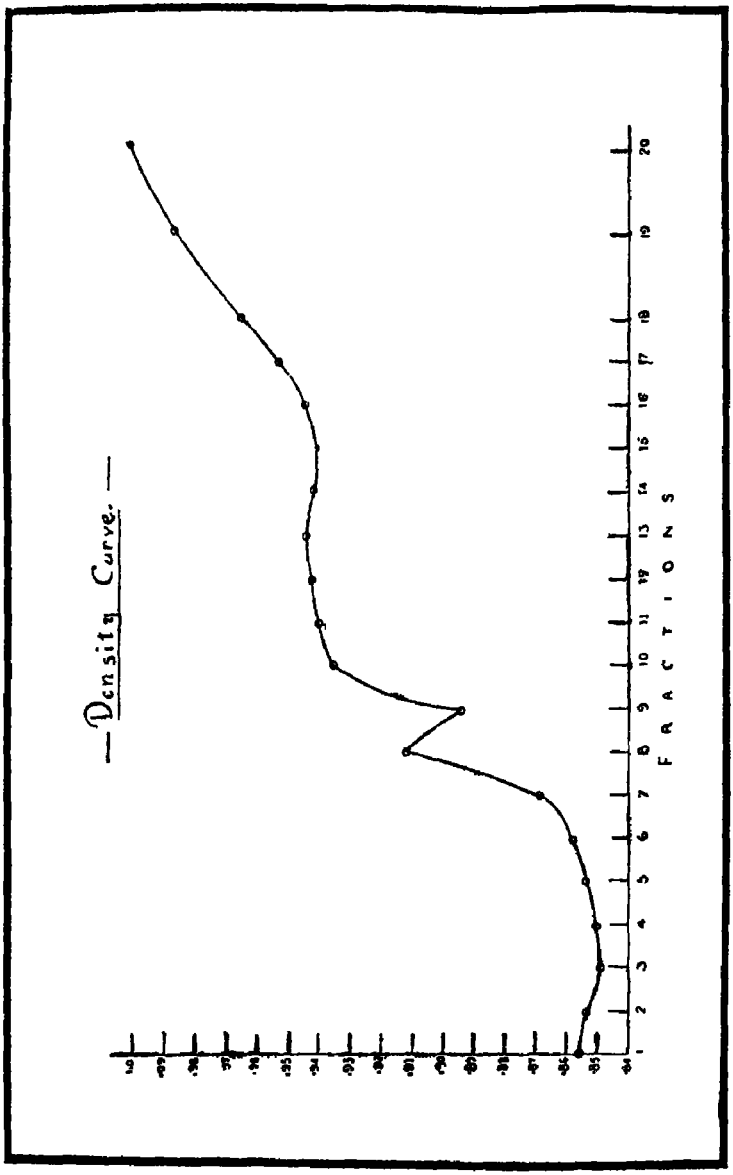
The work described in this paper was carried out mostly with the oil from the white variety.

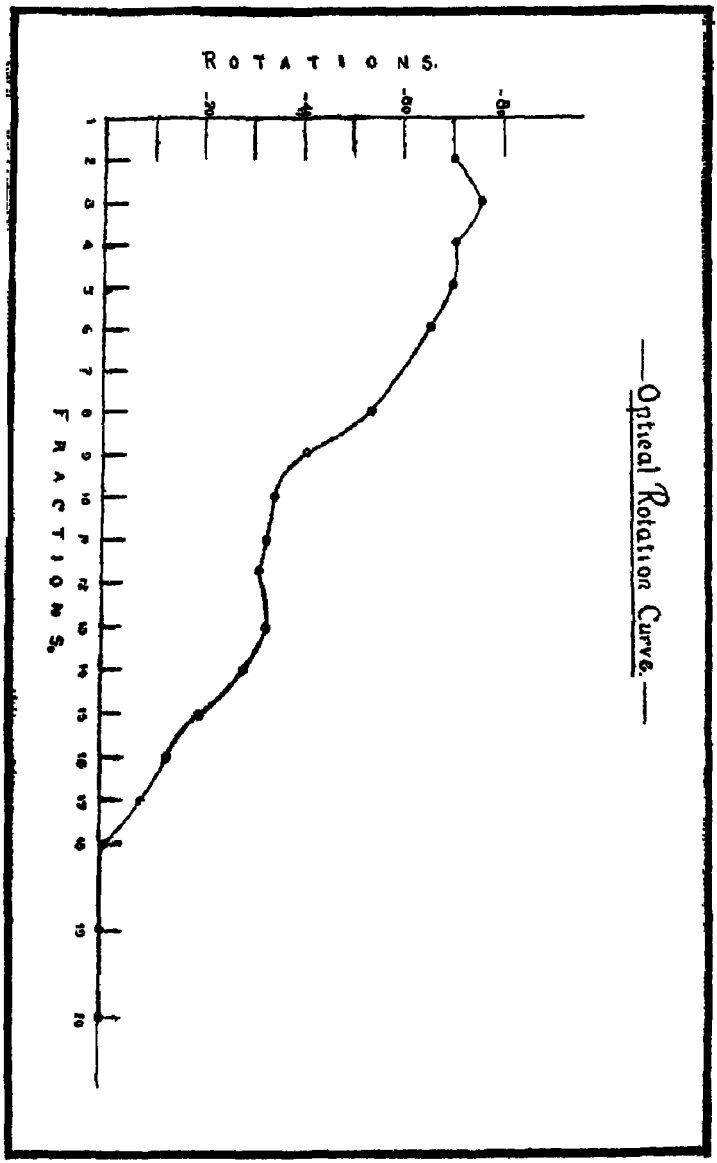
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CHEMICAL LABORATORY

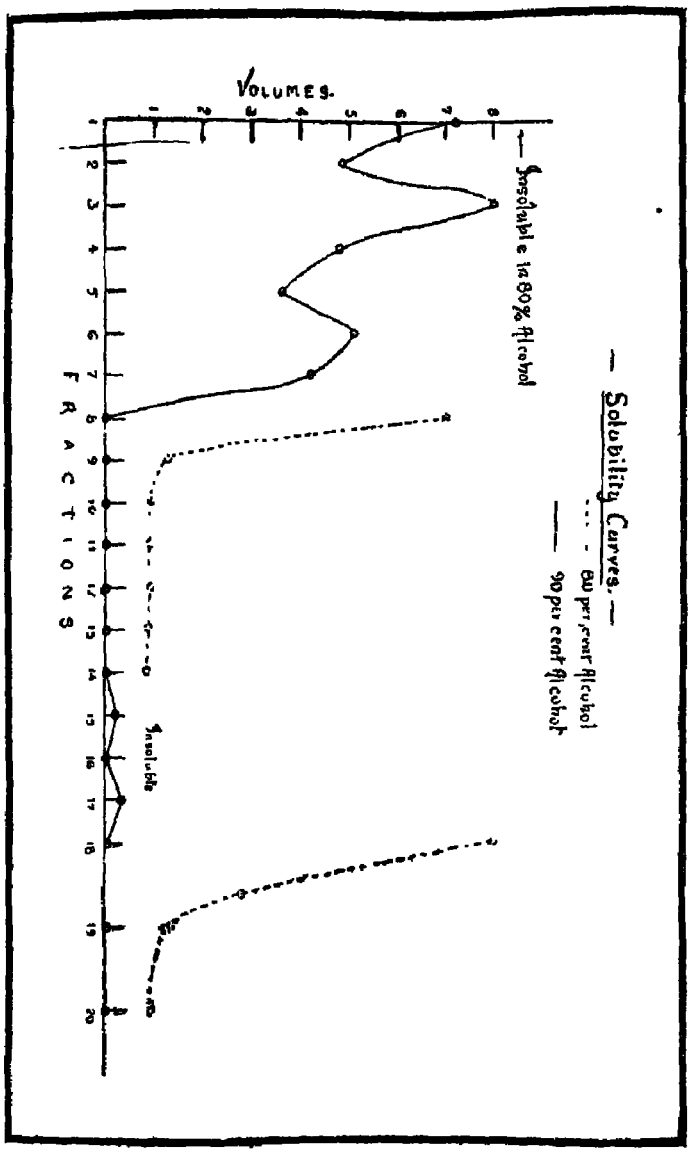
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— Density Curve. —
FRACTIONS



—Optical Rotation Curve.—


VOLUMES.
1
2
3
4
5
6
7
8
FRACTIONS
Insoluble in 80% Alcohol
Solubility Curves.
60 per cent Alcohol
90 per cent Alcohol
Insoluble