

I.—THE CONSTITUENTS OF SOME INDIAN ESSENTIAL OILS. PART XXII. THE ESSENTIAL OIL FROM THE FLOWER HEADS OF 'CYMBOPOGON COLORATUS, STAPF.'*

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Cymbopogon coloratus, Stapf (synonyms: *Andropogon nardus*, var. *coloratus*, Hook.; *A. coloratus*, Nees.), one of the lemon grasses of the Malabar District, was first recognised as a definite species by Stapf (*Kew Bull.*, 1906, 8, 321), having been considered by Hooker (*Fl. Brit. Ind.*, 1897, 7, 206) to be a variety of *C. nardus*. It occurs throughout the Carnatic from the extreme south as far as the Cuddapah District and from the Tinnevely Hills to the Annamalais. Seeds of this grass were planted in Fiji in 1907, and oils obtained from Fiji have been examined at the Imperial Institute (*Bull. Imp. Inst.*, 1912, 10, 670; *Proc. Chem. Soc.*, 1914, 30, 10). The yield of oil was stated to be 0.36 per cent. the principal constituents being *l*-limonene and other terpenes (7 per cent.), aldehydes mainly citral (40 per cent.), and geraniol (23 per cent.). As will be seen from the sequel, the Indian oil examined by us had a completely different composition.

The oil used in this investigation was obtained from the flower heads of a grass grown in the North Arcot District. The grass, which is known locally as 'Botha' grass, was identified as *C. coloratus*, Stapf, by Mr. R. N. Parker, Forest Botanist, Forest Research Institute, Dehra Dun, and the oil was distilled at the Kangundi Industrial Works, Kuppam. A detailed examination of the oil, the constants of which are given in Table II, has shown it to have the following composition: *l*-camphene (15 per cent.), *l*-limonene (7 per cent.), camphor? (trace), *l*-borneol (8 per cent.), geraniol (10 per cent.), sesquiterpenes (35 per cent.), sesquiterpene alcohols (8 per cent.), sesquiterpene oxide? (2-3 per cent.), unidentified (14 per cent.).

The major portion of the *l*-camphene crystallised on cooling the terpene fraction of the oil and after recrystallisation from alcohol had m.p. 51°, $[\alpha]_D^{20} - 82.3^\circ$ (in chloroform solution). Although camphene has been found in a large number of essential oils, it has apparently only been obtained crystalline on two previous occasions, namely, from citronella oil (*Schimmel's Rep.*, April, 1912, 44) and from Siberian pine needle oil (Golubeff, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 1004). The constants of these three crystalline camphenes are given in Table I.

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TABLE I.

---	<i>C. coloratus</i>	Citronella oil	Siberian pine needle oil
M.p. ...	50-51°	49-50°	50°
B.p. ...	153-154°/686 mm.	...	159-160°
d_{30}^{30} ...	0.8616
n_D^{30} ...	1.4644
$[\alpha]_D^{30}$...	- 82.3° (in CHCl ₃)	- 173.3° (in CHCl ₃)	- 92.37°

After the removal of the alcohols referred to above, which were identified as described in the experimental portion of the paper, a small quantity of an oxygenated compound, which distilled unchanged over sodium, was separated. This substance, which analysis showed to have the composition $C_{15}H_{24}O$, had a pleasant musk-like odour; it did not contain a methoxyl group nor did it react with the ordinary ketonic reagents. It is possible that it was a sesquiterpene oxide, but the quantity available was insufficient for a detailed examination. The sesquiterpene fraction gave a nitrosochloride, nitrosate and benzylamine derivative with melting points agreeing fairly closely with the corresponding derivatives prepared from α -caryophyllene. Attempts to confirm the identity of this hydrocarbon by the preparation of caryophyllene alcohol and caryophyllene dihydrochloride were unsuccessful, and the nature of the sesquiterpene must therefore remain somewhat doubtful.

It is interesting to note that the oil showed no absorption when treated with sodium bisulphite solution, and careful examination failed to reveal any trace of either citral or citronellal, the characteristic constituents of lemon grass oil. In spite, therefore, of the close botanical relationship of these two grasses, they show a marked difference in their chemical constituents.

EXPERIMENTAL.

The oil, which was pale yellow in colour had, after drying over magnesium sulphate, the constants given in Table II (a); for comparison the constants of the oils obtained from Fiji are given in adjoining columns.

TABLE II.

	a	b	c
d_{30}^{30}	0.9183	0.9111-0.920	d_{15}^{15} 0.912
n_D^{30}	1.4819
$[\alpha]_D^{30}$	-26.7°	-7.7-10.7°	$[\alpha]_D^{24}$ -10.3°
Acid value	2.3
Saponif. value	39.8
Do. after acetylation	111.2
Aldehydes by NaHSO_3	Nil	37.5-43%	34%

(b) *Bull. Imp. Inst.*, loc. cit.(c) *Proc. Chem. Soc.*, loc. cit.

The oil, which was free from phenols, was digested with an alcoholic solution of potassium hydroxide to hydrolyse any esters present and fractionated at 100 mm. using a Young still head, when the following fractions were obtained:—

TABLE III.

No	B.p./100 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent.*
1	90-92°	0.8668	1.4651	-71.0°	13.5
2	92-95°	0.8728	1.4679	-70.8°	3.5
3	105-115°	0.8865	1.4697	-67.5°	4.5
4	115-135°	0.9126	1.4731	-50.0°	3.8
5	135-150°	0.9315	1.4785	-23.2°	11.2
6	150-170°	0.9303	1.4838	-11.3°	10.2
7	170-200°	0.9385	1.4926	+4.4°	42.5
Residue and loss	10.8

The first three fractions, which contained the greater part of the terpenes present in the oil, were redistilled at the ordinary pressure with a column and finally over sodium.

* The percentage weight is in all cases calculated on the original weight of the oil used.

TABLE IV.

No.	B.p./686 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent.
I	153-154°	0.8616	1.4644	-70.3°	4.5
II	154-157°	0.8602	1.4651	-77.0°	3.5
III	157-160°	0.8565	1.4662	-84.5°	2.7
IV	160-163°	0.8545	1.4659	-89.9°	1.6
V	163-167°	0.8523	1.4679	-94.7°	1.3
VI	167-171°	0.8521	1.4693	-96.3°	1.5

Fractions I, II and III on keeping in a freezing mixture crystallised almost completely, and after repeated crystallisation from alcohol pure *L*-camphene was obtained, m.p. 50-51°, $[\alpha]_D^{30}$ -82.3° in chloroform solution ($c = 5.937$). The identification of this substance with *L*-camphene was confirmed by its conversion into *L*-isoborneol, m.p. 212° (mixed m.p. 212°), the phenylurethane of which had m.p. 138°. Fractions I to IV consisted essentially of *L*-camphene; β -pinene was not found to be present in Fraction IV, which on oxidation with alkaline potassium permanganate gave an excellent yield of camphenic camphoric acid, m.p. 142°.

Fractions V and VI were found to consist of *L*-limonene. When Fraction V was treated with hydrogen chloride in acetic acid solution it gave an excellent yield of dipentene dihydrochloride, m.p. 50°, which was not depressed on admixture with an authentic specimen, whilst from Fraction VI *L*-limonene tetrabromide, m.p. 104°, was prepared. This had $[\alpha]_D^{30}$ -73.4° in chloroform solution, which is in excellent accord with the value observed by Wallach and Conrady (*Annalen*, 1889, 252, 145). Found: Br. 70.0; calc. 70.2 per cent.

Fractions 4, 5 and 6 (Table III) were systematically refractionated at 100 mm. and the following fractions obtained:—

TABLE V.

No.	B.p./160 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent.
a	140°	—	—	—	0.1
b	140-145°	0.9357	1.4750	-23.7°	1.2
c	145-150°	0.9327	1.4759	-21.0°	1.8
d	150-155°	0.9209	1.4766	-18.3°	3.0
e	155-156°	0.9133	1.4769	-12.6°	1.7
f	156-160°	0.9104	1.4779	-10.2°	1.0
g	160-165°	0.8986	1.4801	-8.1°	0.7

Fraction *a* on treatment with semicarbazide acetate gave a small quantity of a crystalline semicarbazone, m.p. 234–236°. This appeared to be camphorsemicarbazone, but owing to the small quantity of material available it was not possible to confirm this. On keeping, fractions *b*, *c* and *d* deposited a considerable quantity of a crystalline solid. This was collected, and after draining on porous porcelain was recrystallised from light petroleum, when it was found to melt at 204° and to yield a phenylurethane m.p. 138°. Its identity with *l*-borneol was confirmed by the method of mixed melting point. The filtrate from which the borneol had been separated was treated with phthalic anhydride at 130°. From the reaction product only bornyl hydrogen phthalate, m.p. 104–105°, could be isolated (Found: C, 71.5; H, 7.6; C₁₈H₂₂O₄ requires C, 71.5; H, 7.3 per cent.).

Fraction *e* probably consisted of a mixture of *l*-borneol and geraniol; no terpineol could be detected. Fractions *f* and *g* were shown to contain geraniol by the preparation of geranyldiphenylurethane, m.p. 81.5–82° (Found: N, 4.4; calc., 4.0 per cent.). No traces of citral, nerol, or citronellol were found in these fractions of the oil.

The fractions boiling above 165°/100 mm. (Tables IV and V) were combined and repeatedly distilled at 6 mm., using a four-pear Young still-head, when the following fractions were ultimately obtained:—

TABLE VI.

No.	B.p./6 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent.
A	110–118°	0.9171	1.4992	5.3°	1.9
B	120–130°	0.9238	1.4990	7.1°	1.8
C	135–140°	0.9348	1.4953	8.3°	20.3
D	140–145°	0.9542	1.4983	...	1.3
E	145–160°	0.9738	1.5032	...	5.8

Fractions A and B, after distillation over sodium until this was no longer acted upon, still contained oxygen as is shown by the following analyses: (A) Found: C, 82.1; H, 11.4; (B) C, 83.1, H, 11.4 per cent. These figures point to the presence in these fractions of an oxygenated compound of the formula C₁₅H₂₄O, which requires C, 81.8; H, 10.9 per cent. These oils, which had a characteristic pleasant odour differing from that of the sesquiterpene fraction C, did not contain a methoxyl group, nor did they react with the usual ketonic reagents. On treatment with potassium nitrite and acetic acid at a low temperature a crystalline nitrosite was formed which melted below 0°

and could not be isolated. It is not improbable that these fractions contained a sesquiterpene oxide, but unfortunately no crystalline derivatives could be prepared. From Fraction C a crystalline nitrosochloride, m.p. 171° (Found: N, 5.5; $C_{15}H_{24}ONCl$ requires N, 5.2 per cent.), and a crystalline nitrosate, m.p. 154° (Found: N, 9.6; $C_{15}H_{24}O_4N_2$ requires N, 9.4 per cent.), were prepared. Both these substances yielded, when treated with benzylamine, a derivative of m.p. $126-128^{\circ}$, which pointed to the presence of *d*- α -caryophyllene, the corresponding derivatives of which melt at 177° , 158° and 128° . Attempts to confirm the presence of this hydrocarbon by the preparation of α -caryophyllene alcohol and α -caryophyllene dihydrochloride were not successful; we consider, however, that the principal sesquiterpene present is α -caryophyllene.

Fractions D and E consisted of sesquiterpene alcohols, but since they did not yield crystalline derivatives they were not further examined.

FREE AND COMBINED ACIDS.

The alkaline solution separated from the treatment of the original oil with alcoholic potassium hydroxide solution was after the removal of the alcohol acidified with sulphuric acid and distilled in steam, three fractions being collected. The silver salts of the volatile acid were analysed: (1) Ag, 59.5; (2) Ag, 38.1; (3) Ag, 36.1 per cent. These figures indicate the presence of propionic acid in the first fraction (Ag, 59.6 per cent.), and of a mixture of capric and lauric acids in the less volatile fractions (Ag, 38.6 and 35.0 per cent.).

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