

## II.—ESSENTIAL OIL FROM FLOWER-HEADS AND STALKS OF *ANDROPOGON KUNTZEANUS*, HACK, VAR. *FOVEOLATA*, HACK.

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For the purpose of examining the oil from *Andropogon odoratus*, Dna, Lisboa, a quantity of grass, believed to be of this species was collected at Lonawala near Poona. A specimen was, however, identified by R. N. Parker, the Forest Botanist at Dehra Dun as *Andropogon Kuntzeanus*, Hack, var. *foveolata* Hack, an opinion confirmed by the botanist at Coimbatore who stated that *Andropogon odoratus*, Dna, closely resembles this species, but is aromatic. Hooker (*Flora of British India*, 1897, 7, 177) dealing with *A. odoratus*, Dna, says 'The compressed sheaths, paniced spikes, villous gl. 1 of the sessile spikelets, and aroma, seem to distinguish this from *A. Kuntzeanus*, which it strongly resembles in a dry state.' Thus, although the two grasses are similar, the differences are sufficient to admit of definite discrimination and the identity of the specimen collected in the present case may be regarded as established. The lack of aroma indicated the absence of an admixture of *A. odoratus*. On steam distillation the grass yielded 0.27 per cent. of oil, a quantity greater than was expected. About 40 per cent. of this oil consisted of bicyclic tertiary sesquiterpene alcohols, belonging to the cadalin group. About 10 per cent. of solid *l*-camphene was isolated with an equal amount of material giving a good yield of the chief derivatives of *l*-camphene, but this could not be solidified. Probably there is present an isomeric form of camphene similar to that found in citronella oil (Gildemeister and Hoffmann, *The Volatile Oils*, 1916, 2, 225). Tricyclene could not be detected, but  $\alpha$ -pinene and borneol were present in small quantities.

### *Experimental.*

The grass was cut 2-3 inches above ground and included inflorescence and stalk (moisture 33.3 per cent.); 252 lbs. yielded 203 g. of oil, or 0.27 per cent. calculated on the dry grass, on distillation in steam. This oil was deep brown and had a characteristic sesquiterpenic odour. The more important constants were:— $d_{30}^{30}$  0.9208;  $n_D^{30}$  1.4813;  $[\alpha]_D^{30}$  —36.5°: acid value 1.7; ester value 0.3; ester value after acetylation 80.8. There was no appreciable absorption either with sodium sulphite or potassium hydroxide. Gildemeister and Hoffmann (*loc. cit.*, 247) give for *A. odoratus*  $d_{31}^{31}$  0.931;  $[\alpha]_D$  —22.75°.

The oil (165 g.) was saponified with alcoholic potash, washed free of alkali and dried over anhydrous magnesium sulphate. The saponified oil (150 g.) distilled under diminished pressure (100 mm.) using a Young's column yielded the following fractions:—

TABLE I.

Fraction	B.P.	$d_{30}^{30}$	$n_D^{30}$	$[\alpha]_D^{30}$	Weight in grams	Yield per cent. on saponified oil
1	90—95°	0.8626	1.4653	—77.2°	22.9	15.3
2	95—105	0.8636	1.4663	—77.8	18.0	12.0
3	105—110	0.8670	1.4676	—74.3	9.0	6.0
4	110—115	..	1.4685	..	3.2	2.1
5	120—140	..	1.4708	—56.6	5.8	3.9
6	140—150	0.9073	1.4800	—28.2	18.0	12.0
7	175—200	0.9378	1.4887	—3.8	27.0	18.0
8	200—215	0.9670	1.4995	—4.6	37.0	24.7
Residue and loss					9.1	6.0

The first three fractions contained the greater part of the terpenes and were redistilled repeatedly under 100 mm. pressure, the following fractions being obtained:—

TABLE II.

Fraction	B.P.	$d_{30}^{30}$	$n_D^{30}$	$[\alpha]_D^{30}$	Weight in grams	Yield per cent. on saponified oil
a	90—91°	0.862	1.4643	—73.3°	3.0	2.0
b	91—93	0.861	1.4654	—79.3	19.8	13.2
c	93—94	0.861	1.4658	—77.1	5.8	3.9
d	94—96	0.862	1.4663	—76.4	5.2	3.5
e	96—100	0.861	1.4668	—74.3	3.6	2.4
f	100—110	..	1.4678	..	1.5	1.0
g	110—118	..	1.4693	—56.2	1.5	1.0

*Fraction a.*—On treating this fraction (1 g.) with amyl nitrite and hydrochloric acid a small quantity of solid nitrosochloride was obtained, but the amount was insufficient for satisfactory purification. It is probable that a small proportion of  $\alpha$ -pinene, which boils at this temperature and gives a nitrosochloride, is present.

*Fractions b, c, d and e.*—Each of these fractions on keeping in the ice-chest partly solidified. The solid was separated and the combined liquid portions were distilled from sodium and then fractionated under 14 mm. pressure with the following results:—

B.P.	$d_{30}^{30}$	$n_D^{30}$	$[\alpha]_D^{30}$	Yield per cent. on saponified oil	Found	Calc. for camphene
55°	0.8592	1.4657	—70.4°	14.0	43.80	43.91
• 55	0.8602	1.4661	—70.5	4.0	43.82	..
55—57	0.8591	1.4661	—74.2	3.0	..	..

A further quantity of solid camphene was obtained by freezing these distillates. The process of distillation and freezing was repeated several times until the final fraction (12 g.) remained liquid. The *l*-camphene (14 g.; 9.3 per cent. on the whole oil) was isolated, had m.p. 45° and  $[\alpha]_D^{30}$  —83.2° in absolute alcohol ( $C = 8.180$ ); it was converted into *isoborneol*, m.p. 212°.

The liquid (12 g.) was distilled from sodium and had then the following constants:— B.p., 55—56°/14 mm;  $d_{30}^{30}$  0.8574;  $n_D^{30}$  1.4660;  $[\alpha]_D^{30}$  —71.9°. It was thought that this might be a mixture of camphene and tricyclene but the following experiments indicated that it was mainly camphene. Neither a nitrosochloride nor a bromide could be obtained; 4 c.c. in anhydrous ether (20 c.c.) when saturated with dry hydrogen chloride yielded camphene hydrochloride (3.9 g.; calculated, 4.3 g.) m.p. 145°. Oxidation with alkaline permanganate gave camphene-camphoric acid, m.p. 142°, while the portion unoxidised, when distilled over sodium and treated with hydrogen chloride, again gave camphene hydrochloride. It is thus probable that the liquid was an isomeric form of camphene which has been found in citronella oil (Gildemeister and Hoffmann, *loc. cit.*).

Alcohol fractions 4, 5, 6, 7 and 8 (Table I) were systematically refracted under 12 mm. pressure as follows:—

TABLE III.

Fraction	B.P.	$d_{30}^{30}$	$n_D^{30}$	$[\alpha]_D^{30}$	$[R_L]_D$	Weight in grams	Yield per cent. on saponified oil
A	100—110°	..	1.4759	—30.0°	..	2.3	1.5
B	110—120	..	1.4789	—27.5	..	1.5	1.0
C	120—140	..	1.4819	—11.8	..	2.2	1.5
D	142—143	0.9128	1.4809	— 2.4	..	8.1	5.4
E	145—155	0.9448	1.4889	— 5.4	..	7.5	5.0
F	158—160	0.9601	1.4945	— 7.4	66.86	7.5	5.0
G	165	0.9674	1.4987	— 8.8	66.80	16.5	11.0
H	165—168	0.9690	1.4995	— 9.2	66.71	25.0	16.7
Residue						15.0	10.0

*Fractions A, B and C.*—On cooling these fractions 0.3 g. of borneol was obtained melting at 202—204°. Tests for geraniol were negative.

*Fraction D* on treatment with sodium was almost completely decomposed and no distillate could be obtained. Sesquiterpenes are therefore not present, excepting possibly in very small quantity.

*Fractions F, G and H.*—The boiling points of these fractions indicate that they consist mainly of sesquiterpene alcohols, which thus comprise nearly 50 per cent. of the oil, and as they did not react with phthalic anhydride at 130-140° belong to the tertiary group. Attempts to prepare a hydrochloride or nitrosate were unsuccessful. Fraction H on being heated with selenium at 260° gave a hydrocarbon, b.p. 140—165°/12 mm. yielding cadalin picrate, m.p. 114-115° (mixed m.p. 114-115°), showing that the alcohols belong to the cadalin group of bicyclic sesquiterpene alcohols.