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

By P. Parameswaran Pillay, B. Sanjiva Rao, and John Lionel Simonsen.

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 considefed 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 Tinnevelly 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°, $[\alpha]_D^{30} - 82{\cdot}3°$ (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.

* Reprinted from the *Journal of the Society of Chemical Industry*, 1928, **47**, 52T.

TABLE I.

——	*C. coloratus*	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	...	...
$[\alpha]_D^{30}$	−20·7°	−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°	19·5
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°	0·9383	1·4928	+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	1·4669	−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-iso*borneol, 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 camphene-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./100 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; $C_{18}H_{22}O_4$ 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 $C_{15}H_{24}O$, 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°, 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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THE CONSTITUENTS OF SOME INDIAN ESSENTIAL OILS. PART XXIII. THE ESSENTIAL OIL FROM THE FRUITS OF 'PIPER CUBEBA,' LINN.*

By B. Sanjiva Rao, Vishnu Purushottam Shintre and John Lionel Simonsen.

Oil of cubeb is obtained from the dried, full-grown but unripe fruits of *Piper cubeba*, Linn. Although *P. cubeba* is not indigenous to India, and is not widely cultivated, the fruits are imported in considerable quantity. It appeared to us desirable, therefore, to examine carefully the oil obtained from fruits grown in Mysore. A quantity of oil from this source was prepared in 1923, but it was not studied in detail at the time (*J. Ind. Inst. Sci.*, 1925, 8A, 159).

Although oil of cubeb is official in the British Pharmacopœia, and has been repeatedly examined (cf. Finnemore, 'The Essential Oils,' 192 *seq.*), there would appear to be considerable doubt as to its main constituents, only the presence of *l*-cadinene having been established with certainty.

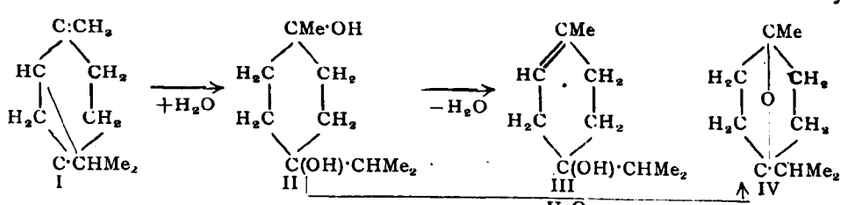
The fruits used in this investigation, which were of undoubted authenticity, gave on distillation in steam 7·5 per cent. of an oil as compared with a yield of 11·9 per cent. obtained in 1923 from fruits from the same source. It is possible that the fruits were slightly immature.

The terpene fraction of the oil (about 35 per cent.) consisted essentially of *d*-sabinene, which was identified by conversion into terpinene dihydrochloride, and by oxidation with potassium permanganate to *d*-sabinenic acid. From amongst the oxidation products a small quantity of *cis*-caronic acid was isolated indicating the presence of either Δ^3-carene or Δ^4-carene. By the oxidation of the appropriate fraction with potassium permanganate in acetone solution a small amount of a keto-acid was obtained, and this was identified as *d*-1:1-dimethyl-2-γ-ketobutyl*cyclo*propane-3-carboxylic acid by the preparation of the semicarbazone, m.p. 178–180°, thus confirming the presence of *d*-Δ^4-carene. No evidence was obtained of the presence of any other terpenes, although pinene, camphene, and dipentene were specially tested for.

The terpene fraction (b.p. 105–110°/100 mm.) had a camphoraceous odour resembling that of cineole and analysis indicated the

* Reprinted from the *Journal of the Society of Chemical Industry*, 1928, **47**, 92T.

presence of an oxygenated compound. No derivatives of 1 : 8-cineole could be obtained, but on saturating a glacial acetic acid solution of this fraction of the oil with hydrogen chloride, an excellent yield of terpinene dihydrochloride separated, although the parent hydrocarbon itself was absent. The formation of this hydrochloride appeared to point to the presence of 1 : 4-cineole. This oxide has so far not been found to occur in nature, and was prepared synthetically by Wallach (*Annalen*, 1912, **392**, 62) by the dehydration of 1 : 4-terpin. Unfortunately, it is somewhat difficult to identify, since its only recorded properties are its conversion into terpinene dihydrochloride on treatment with hydrogen chloride, and its oxidation by potassium permanganate to an unidentified acid, m.p. 157°, which is sparingly soluble in water. Our specimen, which was contaminated with *d*-Δ^4-carene, yielded on oxidation under the conditions used by



Wallach a sparingly soluble acid, m.p. 157°, which is at present under investigation, and there can therefore be little doubt that 1 : 4-cineole was present in the oil. In veiw of the probable occurrence of this oxide in other essential oils one of us (J.L.S.) proposes to make a further study of its properties.

The alcohols, which formed about 11 per cent. of the oil, were mainly tertiary. On hydration with dilute sulphuric acid *trans*-terpinene-terpin was formed together with what appeared to be *cis*-terpin. The latter was not obtained in sufficient quantity for complete characterisation, and it was not possible to confirm the presence of terpineol by other means. The *trans*-terpinene-terpin resulted from the hydration of *d*-1-methyl-4-*iso*propyl-Δ^1-*cyclo*hexen-4-ol (*d*-Δ^1-terpinen-4-ol), the presence of which was confirmed by oxidation to the glycerol, 1-methyl-4-*iso*propyl-1 : 2 : 4-trihydroxy*cyclo*hexane, m.p. 116–117° and m.p. anhyd. 128–129° (cf. Wallach, *Annalen*, 1906, **350**, 169).

The co-existence of *d*-sabinene (I), *d*-1-methyl-4-*iso*propyl-Δ^1-*cyclo*-hexen-4-ol (III), and 1 : 4-cineole (IV) in the same oil is of considerable interest, since, as will be seen from a study of their formulæ, these substances are extremely closely related, their interconversion merely involving the addition or loss of water with the intermediate formation of 1 : 4-terpin (II).

In the sesquiterpene fraction *l*-cadinene was readily identified by the preparation of the dihydrochloride, but the low rotation pointed to the presence of a second hydrocarbon, the nature of which could not be determined.

In view of the marked difference in the rotation of the oil distilled in 1923 (Table I, sample B), it appeared desirable to determine if possible the cause of this, and the small remaining quantity of this oil was fractionated. The terpene fraction was found to be almost inactive and consisted of *dl*-sabinene, a hydrocarbon which has only once previously been described (Penfold and Simonsen, *J. Proc. Roy. Soc. N. S. W.*, 1925, **59**, 147). It was characterised by the preparation of *dl*-sabinenic acid, which was compared with the specimen obtained by the above-mentioned authors. The *l*-cadinene isolated from the sesquiterpene fraction had a much higher rotatory power than that which was obtained from sample A, and these two factors account for the marked difference in the rotatory powers of the two oils.

The composition of Mysore oil of cubeb is approximately the following:—*d*-sabinene (33 per cent.), *d*-Δ^4-carene and 1 : 4-cineole (12 per cent.), *d*-Δ^1-terpinene-4-ol and other alcohols (11 per cent.), sesquiterpenes mainly *l*-cadinene (14 per cent.), sesquiterpene alcohols (17 per cent.), unidentified (13 per cent.).

EXPERIMENTAL.

The crushed fruits (21·8 kg.) were distilled in steam, yielding a light green oil (1·63 kg.). After drying over magnesium sulphate the oil had the constants given in Table I, column A, the constants for the sample of oil obtained in 1923 being given in column B.

TABLE I.

	A	B
d_{30}^{30}	0·8937	0·9167
n_D^{30}	1·4811	1·4894
$[\alpha]_D^{30}$	+25·6°	−29·9°
Acid value	0·78	Nil
Sap. value	5·2	0·5
Do. after acetylation	54·6	24·1
Colour	Light green	Pale green, yellow on long keeping.

A quantity of the oil (A) was treated with an alcoholic solution of potassium hydroxide to hydrolyse the esters present, dried over magnesium sulphate, and distilled under diminished pressure, yielding the fractions given in Table II.

TABLE II.

No.	B.p./100 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent.
1	1–100°	...	...	...	trace
2	100–104°	0·8435	1·4644	+ 59·78°	27·9
3	104–110°	0·8502	1·4667	+ 54·27°	9·2
4	110–115°	0·8570	1·4685	+ 44·83°	4·9
5	115–125°	0·8762	1·4706	+ 18·62°	2·7
6	125–135°	0·9186	1·4733	+ 16·22°	3·4
7	135–160°	0·9465	1·4795	+ 8·45°	6·6
8	160–180°	0·9562	1·4902	− 2·72°	10·9
9	180–200°	0·9779	1·5015	− 10·45°	13·5
10	200–220°	1·0356	1·5142	...	11·4
	Residue and loss				9·5

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

Fractions 2 to 6, which were free from aldehydes and ketones, were repeatedly distilled under diminished pressure, the final fractionation being over sodium, and the results are summarised in Table III.

TABLE III.

No.	B.p. 100 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent.	Terpinene, 2HCl from 5 c.c.	Sabinenic acid from 10 gms.
A	94–96°	0·8367	1·4603	+ 56·01°	1·3	*a*	5
B	96–97°	0·8382	1·4623	+ 65·45°	5·2	1·6	4·9
C	97–98°	0·8388	1·4630	+ 68·84°	9·9	1·6	4·9
D	98–100°	0·8390	1·4655	+ 64·86°	5·4	0·9	3·7
E	100–101°	0·8395	1·4656	+ 61·41°	2·2	0·5	*a*
F	102–103°	0·8398	1·4661	+ 56·81°	4·7	0·3	*a*
G	103–106°	0·8425	1·4686	+ 39·74°	1·1	*a*	1·4
H	106–108°	0·8459	1·4689	+ 35·42°	1·1	*a*	*a*
I	108–110°	0·8492	1·4702	+ 24·75°	0·8	0·9*	Nil
J	110–113°	0·8529	1·4706	+ 18·93°	1·3	*a*	*a*
K	113–116°	0·8605	1·4706	...	0·6	*a*	*a*
L	116–120°	0·8713	1·4706	...	0·3	*a*	*a*
M	120–125°	0·8920	1·4680	...	1·4	0·8*	*a*

(*a*) Not determined. * From 2·5 c.c.

d-*Sabinene*.—Fractions A to D consisted essentially of *d*-sabinene, the constants of fraction C agreeing well with those quoted for this hydrocarbon.

TABLE IV.

	Fraction C.	*d*-Sabinene from Canada oil *
d_{30}^{30}	0·8382	d_{15}^{15} 0·8481
n_D^{30}	1·4630	...
$[\alpha]_D^{30}$	+ 68·8°	+ 68·9°

* Parry, "Essential oils," II, 56.

For a number of the fractions the yields of terpinene dihydrochloride and of *d*-sabinenic acid (Wallach, *Annalen*, 1908, **359**, 268) are given in the table. The *d*-sabinenic acid after recrystallisation from hot water had m.p. 55–57° and in alcoholic solution (*c*. 1·002) $[\alpha]_D^{30}$ + 110·7° (Found: C, 64·9; H, 8·7: calc. C, 65·2; H, 8·7 per cent.). The identity was confirmed by careful comparison with an authentic specimen. The terpinene dihydrochloride after crystallisation from dilute alcohol had m. p. 52° which was not depressed on admixture with a specimen from another source (Found: Cl, 33·8; calc. 33·9 per cent.).

d-Δ^4-*Carene*.—From amongst the products of the oxidation with potassium permanganate of fractions H to L (Table III) a small quantity of an acid, m.p. 172–173°, was separated, which was identified as *cis*-caronic acid. Since this indicated the presence of either Δ^3-or Δ^4- carene a portion of these fractions was redistilled at the ordinary pressure and the fraction of b.p. 163–168°/685 mm. collected separately. This fraction was oxidised in acetone solution with potassium permanganate (*J.C.S.*, 1922, **121**, 2292), when a small quantity of a keto-acid was obtained which yielded a semicarbazone, m.p. 178–180°, not depressed when mixed with the original semicarbazone prepared from *d*-1 : 1-dimethyl-2-γ-ketobutyl*cyclo*propane-3-carboxylic acid.

1 : 4-*Cineole*.—The fractions H to M had a marked camphoraceous odour, which was more intense in the higher-boiling fractions. Analysis of fraction H showed the presence of an oxygenated substance mixed with the hydrocarbon (Found: C, 79·9; H, 11·7; $C_{10}H_{18}O$ requires C, 77·9; H, 11·7 per cent.), whilst fraction M on redistillation (b.p. 109–112°/100 mm.) gave on analysis C, 78·6; H, 11·7 per cent. This fraction, which did not give any of the characteristic reactions of

1 : 8-cineole, yielded on treatment with hydrogen chloride in acetic acid solution terpinene dihydrochloride, m.p. 52°, whilst on oxidation with potassium permanganate on the water bath it gave an acid, which was sparingly soluble in water and had m.p. 157° (cf. Wallach, *loc. cit.*). The aqueous solution from which this acid was separated yielded a small quantity of *cis*-caronic acid, and as has already been mentioned (p. 92) there can be little doubt that this fraction of the oil was a mixture of 1 : 4-cineole and *d*-Δ^4-carene.

Terpene alcohols: d-1-*methyl*-4-iso*propyl*-Δ^1-cyclo*hexen*-4-*ol*.—Fraction 7 (Table II) was refractionated under diminished pressure with the results given in Table V.

TABLE V.

No.	B.p./100 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent.
i	130—135°	0·9380	1·4696	+18·66°	0·9
ii	135—138°	0·9481	1·4709	...	0·6
iii	138—140°	0·9503	1·4709	...	0·3
iv	140—142°	0·9536	1·4712	+18·72°	1·1
v	142—145°	0·9565	1·4716	+17·02°	0·6
vi	145—150°	0·9582	1·4776	+13·84°	1·5
vii	150—155°	0·9600	1·4812	...	0·6
viii	155—160°	0·9573	1·4844	+ 1·48°	1·2

Attempts to prepare crystalline phenylurethanes from the various fractions were not successful, whilst comparative experiments with phthalic anhyride showed that the percentage of primary alcohols present probably did not exceed 2 per cent. being greatest in fraction viii. The acid phthalate which was formed could not be induced to crystallise. On oxidation of this fraction with chromic acid, evidence was obtained of the formation of an aldehyde, but it could not be obtained pure.

Fractions iv to vi (5 c.c.) were shaken with dilute sulphuric acid (5 per cent.) for a week, and the reaction mixture was exhausted with ether. On removal of the solvent a solid (1·3 gms.) remained which, after crystallisation from methyl alcohol, had m.p. 136–137°, and was identified as *trans*-terpinene-terpin by analysis and by the method of mixed melting point (Found: C, 69·9; H, 12·0; calc. C, 69·8; H, 11·5 per cent.). The acid solution from which the terpinene-terpin had

been removed was saturated with ammonium sulphate and thoroughly extracted with chloroform, when a solid was obtained which had m.p. 113–115°, and on resolidification m.p. 104–105°. No depression was observed on admixture with *cis*-terpin from another source, but, owing to the small quantity of material available, it was not possible to confirm the identity.

The presence of *d*-1-methyl-4-*iso*propyl-Δ^1-*cyclo*hexen-4-ol in fraction vi was supported by its conversion, on treatment with hydrogen chloride in acetic acid solution, into terpinene dihydrochloride. When this fraction of the oil was oxidised with alkaline potassium permanganate at 0° it yielded *d*-1-methyl-4-*iso*propyl-1 : 2 : 4-trihydroxy*cyclo*hexane, which after crystallisation from ether had m.p. 114–116°, anhydrous m.p. 126–128°. In alcoholic solution (*c* 10) $[\alpha]_D^{30}$ + 23·1° was observed (Wallach, *Annalen*, 1906, **350**, 169, gives m.p. 116–117° and 128–129° anhyd., $[\alpha]_D$ + 21·24°). The presence of the unsaturated alcohol was therefore fully established.

Sesquiterpenes.—Fractions 8 and 9 (Table II) were repeatedly redistilled and the residue boiling above 140°/12 mm. was added to fraction 10. The lower-boiling fractions were distilled twice over sodium yielding two main fractions: (*a*) 120–122°/13 mm., d_{30}^{30} 0·9095, n_D^{30} 1·4930, $[\alpha]_D^{30}$ − 10·1°; (*b*) 126–130°/13 mm., d_{30}^{30} 0·9174, n_D^{30} 1·5013, $[\alpha]_D^{30}$ − 3·6°.

From both fractions *l*-cadinene dihydrochloride, m.p. 117–118°, $[\alpha]_D^{30}$ − 38·1° (*c* 0·2546 in alcohol) was obtained (Found: Cl, 25·5; calc. 25·6 per cent.). The identity was confirmed by comparison with an authentic specimen. No other sesquiterpene could be characterised.

Sesquiterpene alcohols.—Fraction 10 (Table II) on redistillation yielded two main fractions (i) b.p. 150–155°/13 mm., d_{30}^{30} 1·0421, n_D^{30} 1·5150; C, 81·8, H, 10·8; (ii) 155–160°/13 mm., d_{30}^{30} 1·2050, n_D^{30} 1·5198, C, 81·6; H, 10·9 ($C_{15}H_{24}O$ requires C, 81·8; H, 10·9 per cent.). Neither of these fractions yielded a crystalline hydrochloride, and the presence of cadinol is therefore improbable. The alcohols did not react with phthalic anhydride at 130°.

Examination of Sample B (Table I).

A small specimen of the oil remaining from the 1923 distillation was hydrolysed with an alcoholic solution of potassium hydroxide and the terpene and sesquiterpene fractions were examined. The terpene fraction, after distillation over sodium, was separated into two main fractions: (*a*) b.p. 95–98°/100 mm., d_{30}^{30} 0·8302, n_D^{30} 1·4604, $[\alpha]_D^{30}$ + 3·1°: (*b*) 98–100°/100 mm., d_{30}^{30} 0·8322, n_D^{30} 1·4625, $[\alpha]_D^{30}$ + 2·5°. On

oxidation of fraction *b* with potassium permanganate *dl*-sabinenic acid, m.p. 83–84°, was obtained, thus establishing the presence of *dl*-sabinene in this fraction of the oil. The sesquiterpene fraction was found to have a higher rotation, $[\alpha]_D^{30} - 37{\cdot}5°$, than that of sample A. It yielded a specimen of *l*-cadinene dihydrochloride with a rotation identical with that previously obtained. The nature of the other hydrocarbon present was not determined.

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THE CONSTITUENTS OF SOME INDIAN ESSENTIAL OILS. PART XXIV. THE ESSENTIAL OIL FROM THE RHIZOMES OF 'CURCUMA ZEDOARIA,' ROSCOE.*

By B. Sanjiva Rao, Vishnu Purushottam Shintre, and John Lionel Simonsen.

In previous communications in this series (*J. Ind. Inst. Sci.*, 1926, **9A**, 133, 140) the constituents of the essential oils derived from the rhizomes of *Kæmpferia galanga* and *Curcuma aromatica* were described, and we have now examined a third oil belonging to the *Zingiberaceæ*, namely that derived from the rhizomes of *Curcuma zedoaria*, Roscoe.

C. zedoaria grows wild in the Eastern Himalayas, and it is cultivated throughout India and Ceylon; it also grows widely in the Philippine Islands. The oil from the roots grown in the Philippines has been examined by Bacon (*Philippine J. Sci.*, 1910, **5A**, 261), who separated from it a crystalline sesquiterpene alcohol, m.p. 67°, but he does not appear to have characterised any of the remaining constituents. Earlier investigators (*Schimmel's Rep.*, Oct., 1890, 66; Haensel, *Pharm. Ztg.*, 1899, **44**, 752) established the presence in the oil, of cineole and of a crystalline substance, m.p. 142·5°, but nothing further would appear to be known of its composition. A preliminary examination of the oil was made in these laboratories in 1924 (*J. Ind. Inst. Sci.*, 1925, **8A**, 154), but no attempt was made to identify the various constituents present.

The rhizomes, which were greyish-white in appearance and, unlike *C. longa* and *C. aromatica*, seem to contain very little colouring matter, were found to yield on distillation in steam 0·94 per cent. of an oil of which approximately one-third was heavier than water. A thorough examination of this distillate has shown it to have the following composition:—*d*-α-pinene 1·5 per cent., *d*-camphene 3·5 per cent., cineole 9·6 per cent., *d*-camphor 4·2 per cent., *d*-borneol 1·5 per cent., unidentified alcohols trace, sesquiterpenes 10·0 per cent., sesquiterpene alcohols 48 per cent., residue (probably mainly sesquiterpene alcohols) 21 per cent.

The sesquiterpene fraction was found to be a mixture of substances, one of which yielded a small quantity of a crystalline nitrosate,

* Reprinted from the *Journal of the Society of Chemical Industry*, 1928, **47**, 171T.

m.p. 82–83°. This was probably the nitrosate of zingiberene, the nitrosate of which is stated to melt at 86°. When the sesquiterpene fraction of the oil was heated with sulphur resinification took place, but more satisfactory results were obtained with selenium (cf. Diels, *Ber.*, 1927, **60**, 2323). The naphthalene hydrocarbon, cadalene, was separated from the reaction product and characterised by the preparation of the picrate, m.p. 115°.

The bulk of the oil was a complex mixture of sesquiterpene alcohols. These did not react with phthalic anhydride, and the alcohol group was therefore probably tertiary; since attempts to prepare crystalline derivatives were unsuccessful, they were not further examined. No evidence was obtained of the presence of either of the crystalline substances (m.p. 67° and 142·5°) isolated by Bacon and Haensel.

EXPERIMENTAL.

The rhizomes, which were in the form of dry discs, were disintegrated and the grey powder was distilled in steam, when a viscid dark green oil was obtained. From 220 kg. of the rhizomes 1·55 kg. of an oil lighter than water and 0·51 kg. of an oil heavier than water were obtained (yield 0·94 per cent.). The constants of the oil dried over magnesium sulphate are given in column I of Table I, whilst in column II are given the constants of the oil distilled in 1924, and in column III those observed by Bacon (*loc. cit.*).

TABLE I.

—	No. I	No. II	No. III
d_{30}^{30}	0·9724	d_{15}^{15} 0·9863	d_{4}^{30} 0·933–0·993
n_{D}^{30}	1·5002	n_{D}^{30} 1·5024	1·4922–1·507
Acid value	1·3	2·1	...
Saponification value ...	3·0	9·8	0–2·0
Do. after acetylation.	66·6	73·8	...
Yield, per cent.	0·94	1·01	0·065–0·25

A quantity of the oil was treated with an alcoholic solution of potassium hydroxide to hydrolyse any esters present and fractionated under diminished pressure using a four-pear Young still-head, with the results summarised in Table II.

TABLE II.

No.	B.p./100 mm.	d_{30}^{30}	n_{D}^{30}	$[\alpha]_{D}^{30}$	Yield, per cent.
1	55–100°	...	...	...	Trace
2	100–110°	0·9026	1·4606	+ 17·8°	2·1
3	110–120°	0·9026	1·4618	+ 15·7°	4·1
4	120–130°	0·9117	1·4628	+ 12·0°	5·6
5	130–140°	0·9200	1·4656	+ 10·5°	3·8
6	140–160°	0·9322	1·4742	+ 10·3°	9·9
7	160–180°	0·9307	1·4886	+ 3·5°	9·1
8	180–200°	0·9402	1·5034	*	14·6
9	200–230°	1·010	1·5225	*	30·8
10	230–250°	1·027	*	*	9·9
11	Residue	...	...	...	18·8

* These fractions were too deeply coloured for determination of the rotation.

Fractions 1 to 4, which were free from aldehydes and ketones, were systematically fractionated under diminished pressure, the final distillation being over sodium, when the following fractions were obtained.

TABLE III.

No	B.p./100 mm.	d_{30}^{30}	n_{D}^{30}	$[\alpha]_{D}^{30}$
i	96—98°	0·8821	1·4601	+ 25·3°
ii	98—100°	0·8849	1·4608	+ 26·0°
iii	100—101°	0·8892	1·4608	+ 20·0°
iv	102—106°	0·8985	1·4595	+ 10·3°
v	106—107°	0·9061	1·4563	+ 3·0°
vi	107—110°	0·9095	1·4565	+ 1·8°

Fractions i, ii, and iii were redistilled at the ordinary pressure and yielded two main fractions (*a*) 152–156°/684 mm., d_{30}^{30} 0·8787, n_{D}^{30} 1·4598, and (*b*) 156–162°/684 mm., d_{30}^{30} 0·8849, n_{D}^{30} 1·4605. These two fractions consisted of a mixture of *d*-α-pinene and *d*-camphene. The former hydrocarbon was identified by the preparation of the nitrosochloride, m.p. 104–105°, which yielded on treatment with benzylamine a nitrolbenzylamine, m.p. 122–123°, whilst the latter was characterised by conversion into *d*-*iso*borneol, m.p. 208°, the m.p. of

which was not depressed on admixture with an authentic specimen. Fraction iv was a mixture of *d*-camphene and 1 : 8-cineole. The presence of the hydrocarbon was confirmed by the formation from it of *d-iso*borneol, whilst the cineole was characterised by the preparation of its compounds with phosphoric acid and hydrobromic acid. The percentage of cineole in this fraction as determined by the method of Baker and Smith was 71·5 per cent. Fractions v and vi consisted of nearly pure cineole ; limonene and dipentene could not be detected.

Fractions 5 and 6 (*Table II*).—These two fractions on careful fractionation yielded a crystalline solid (5·7 per cent.) which melted at 186–188°. When the solid (5 gms.) was heated with an excess of phthalic anhydride at 130° for some hours, *d*-camphor (3·7 gms.) was separated. This had m.p. 173–174° and $[\alpha]_D^{30}$ + 43·7° in alcohol solution. Its identity was confirmed by the preparation of the semicarbazone, m.p. 235–237°. The acid phthalate, from which the camphor had been removed, had m.p. 164°, and on hydrolysis gave an alcohol which after crystallisation from light petroleum had m.p. 203-204°, $[\alpha]_D^{30}$ + 38·6° in alcohol solution. The presence of *d*-borneol was confirmed by the preparation of the phenylurethane, m.p. 138°.

The oil (1·5 per cent.), from which the mixture of *d*-camphor and *d*-borneol had been separated, gave on treatment with phthalic anhydride in benzene solution a small quantity of an acid phthalate, m.p. 130–132°, which yielded a silver salt, m. p. 90–93°. These constants do not appear to be identical with those of the corresponding derivatives of any known primary alcohol, but, owing to the small amount of material available, no further examination was possible.

Sesquiterpenes and sesquiterpene alcohols.—Fractions 7–10 (Table II) were repeatedly distilled under diminished pressure when ultimately the following fractions were obtained :—

TABLE IV.

No.	B.p./100 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield, per cent.
a	160–161°	0·9014	1·4942	−8·2°	0·5
b	170–180°	0·9111	1·4958	−6·8°	13·1
c	180–185°	0·9234	1·5027	*	0·6
d	185–190°	0·9398	1·5068	*	0·7
e	190–200°	0·9813	1·5150	*	6·9
f	200–210°	1·0104	1·5218	*	9·6
g	210–220°	1·021	1·5358	*	9·9
h	220–230°	1·029	1·5442	*	7·3
i	230–240°	1·034	...	*	12·1

* These fractions were too deeply coloured for the determination of the rotation.

Fractions (*a*) and (*b*) on redistillation over sodium were separated into three main fractions.

TABLE V.

No.	B.p./9 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	$[R_L]_D$	Yield, per cent.
x	112–114°	0·8903	1·4902	−7·7°	...	0·7
y	116–118°	0·8898	1·4922	−8·4°	66·6	2·6
z	120–121°	0·8947	1·4960	− 8·8°	66·0	6·6

Fractions (*x*) and (*y*) were analysed (Found: for (*x*) C, 87·9 ; H, 11·9; for (*y*) C, 87·9 ; H, 11·8 ; $C_{15}H_{24}$ requires C, 88·2 ; H, 11·8 per cent.). None of the fractions yielded crystalline hydrochlorides or nitrosites, but from fraction (*z*) a small quantity of a crystalline (see above) nitrosate, m.p. 82–83°, was separated; as already mentioned, this was probably the nitrosate of the monocyclic sesquiterpene zingiberene. Unfortunately it was not possible to confirm the presence of this hydrocarbon.

When fractions (*y*) and (*z*) were treated with selenium under the conditions used by Diels (*loc. cit.*) a hydrocarbon, b.p. 135–140°/10 mm., n_D^{30} 1·5334, was obtained. There can be little doubt that this hydrocarbon consisted essentially of cadalene, since it yielded a picrate melting as stated by Ruzicka (*Helv. Chim. Acta*, 1921, 4, 508) at 115° (Found : C, 58·9 ; H, 5·1 ; N, 9·9. $C_{21}H_{21}O_7N_3$ requires C, 59·0 ; H, 4·9 ; N, 9·8 per cent.).

Fractions (*c*) to (*i*) consisted essentially of sesquiterpene alcohols, as is indicated by the analyses of fractions (*c*) and (*d*) (Found : for (*c*) C, 84·4 ; H, 10·8 ; for (*d*) C, 81·6 ; H, 10·9. $C_{15}H_{24}O$ requires C, 81·8 ; H, 10·9 per cent.).

Attempts to prepare crystalline derivatives of these alcohols or to dehydrogenate them with sulphur were not successful.

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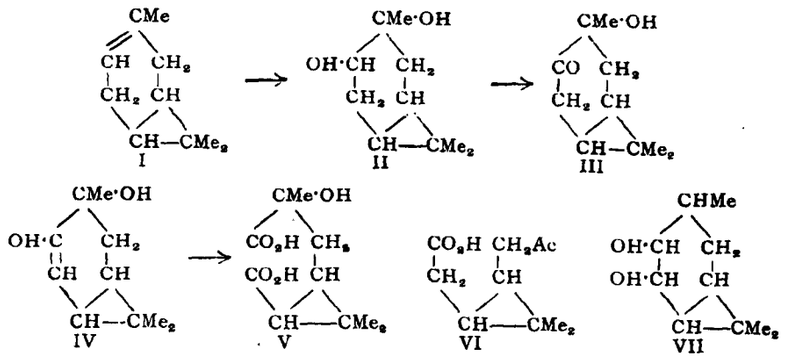
II.—THE CONSTITUENTS OF INDIAN TURPENTINE FROM 'PINUS LONGIFOLIA', ROXB. PART IV.*

By P. Parameswaran Pillay and John Lionel Simonsen.

In Part II of this series (*J. C. S.*, 1923, **123**, 550) attention was directed to the fact that, although the oxidation of *d*-Δ^4-carene with potassium permanganate in acetone solution proceeded smoothly with formation of *d*-1 : 1-dimethyl-2-γ-ketobutyl*cyclo*propane-3-carboxylic acid, the oxidation of *d*-Δ^3-carene(I)under analogous conditions did not yield the isomeric keto-acid, $C_{10}H_{16}O_3$ (VI), but proceeded in a more complex manner. The main products of the latter oxidation were two hydroxy-acids (V), the suggested mechanism of their formation being represented by the following scheme :



It appeared to us of interest to attempt (i) the preparation of the keto-acid (VI) and (ii) to determine whether the scheme outlined above actually represents the mechanism of the oxidation of the hydrocarbon.

The simplest method for the preparation of the keto-acid is the oxidation of the terpene with ozone and in preliminary experiments, made over 2 years ago, evidence of its formation was obtained. Unfortunately, owing to a breakdown in our apparatus, those experiments had to be temporarily abandoned and in the meantime Semmler (*Ber.*, 1927, **60**, 1591) has described the result of his experiments on the oxidation of Δ^3-carene with this reagent and has rendered unnecessary a resumption of our work.

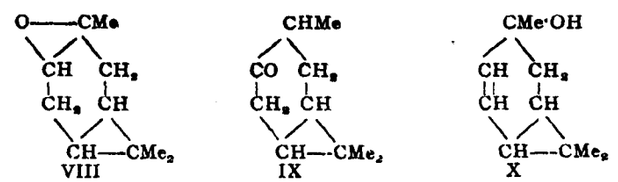
To solve the second part of our problem it was necessary to devise a convenient method for the preparation of the glycol (II).

* Reprinted from the *Journal of the Chemical Society*, 1928, 359.

This substance is formed in small yield when *d*-Δ^3-carene is oxidised with potassium permanganate in alkaline solution (*J. C. S.*, 1920, **117**, 576), but the process is quite unsuited to its preparation in quantity. A good yield of a glycol was obtained by using hydrogen peroxide ; although in the case of pinene fission of the dicyclic structure occurs (Henderson and collaborators, *J. C. S.*, 1912, **101**, 2288 *et seq.*), the main product from *d*-Δ^3-carene is carene glycol. The glycol, however, is not identical with the one previously described. When anhydrous, it has m. p. 90–91° and is optically inactive both in ethyl-alcoholic and in chloroform solution, whereas the latter has m. p. 69–70° and in chloroform solution $[\alpha]_D$ + 16·05°. The glycols may represent *cis*- and *trans*-modifications ; optical isomerism, however, is not impossible, since two new asymmetric centres are formed in the oxidation. In the absence of definite evidence, we propose to call the glycol of m. p. 69–70°, *d*-carene-α-glycol and that of m.p. 90–91°, *d*-carene-β-glycol. The prefix '*d*' is retained, since the β-glycol yields optically active derivatives and the optical inactivity therefore only ' apparent.'

d-carene-β-glycol is stable to potassium permanganate in cold acetone and is only very slowly attacked on warming. Attempts to oxidise it to the hydroxy-ketone (III) were unsuccessful. It contains, however, a secondary alcohol group, since, when heated with phthalic anhydride at 110° for some hours, it yields an *acid phthalate*. The formation of this monoacid phthalate furnishes strong evidence against the glycol having formula (VII) (compare *loc. cit.*, p. 551).

When the glycol is treated with dilute sulphuric acid it yields a mixture of *p*-cymene and an oil, b. p. 152°/100 mm., which is strongly lævorotatory. This oil appears to be l-*carene oxide* (VIII) and although it was not obtained quite pure (see p. 204) there can be little doubt as to its constitution, since when it is heated with phthalic anhydride to 160° it yields the β-glycol acid phthalate.



The formation of the oxide in this way was somewhat unexpected, since it was anticipated, in view of the instability of *cyclo*hexene oxide (Brunel, *Compt. rend.*, 1903, **137**, 62), that either the isomeric ketone (IX) or the unsaturated alcohol (X) would be formed. Evidence of the formation of the ketone (IX) was, however, obtained, since the

impure oxide in contact with semicarbazide acetate for some months gave a *semicarbazone*, $C_{11}H_{19}ON_3$; the quantity obtained was insufficient for the isolation of the ketone. The oxide is remarkably stable and does not undergo hydration even when shaken with sulphuric acid for some days. This stability is probably connected with the dicyclic structure containing the *gem*-dimethyl group, the marked influence of this group on ring formation having been frequently commented upon, especially by Ingold and Thorpe.

In addition to *d*-carene-β-glycol, an oil having the same composition was separated from the oxidation products of *d*-Δ³-carene. This oil was slightly lævorotatory in chloroform solution and gave on treatment with dilute sulphuric acid, in addition to *p*-cymene, an oil consisting essentially of *l*-carene oxide. The liquid glycol was therefore probably a mixture of stereoisomerides.

l-Carene oxide is much more readily attacked by potassium permanagante in acetone solution than the glycol. The product of the reaction is a complex mixture of acids showing no tendency to crystallise. From the mixture a small quantity of a keto-acid, $C_9H_{14}O_3$, was separated in the form of its well-crystallised *semicarbazone*, m.p. 165–166°. This semicarbazone was not identical with either of the two semicarbazones of 1 : 1-dimethyl-2-β-ketopropyl-*cyclo*propane-2-carboxylic acid previously described (*loc. cit.*, p. 559), but since the semicarbazone can exist in twelve isomeric forms, this is not remarkable. The quantity of semicarbazone available was insufficient to allow of a detailed examination of the keto-acid, but the presence of the $CO\cdot CH_3$ group was proved by the formation of bromoform when the keto-acid was oxidised with sodium hypobromite solution.

Some preliminary experiments have been made on the action of hypochlorous acid on *d*-Δ³-carene: the reaction does not proceed smoothly and the products tend to decompose on attempted purification.

EXPERIMENTAL.

Oxidation of d-Δ³-*Carene with Hydrogen Peroxide.* d-*Carene-β-glycol.*—A mixture of the hydrocarbon (1 mol.), dissolved in twice its volume of acetic acid, and hydrogen peroxide (30 per cent., 2 mols.) was kept at 40° for some days and finally at 60° until the oxidation was complete (about 148 hours). The yellowish-brown solution was distilled in steam to remove volatile products (acetic acid and unchanged hydrocarbon), the residue, which deposited a viscid oil on cooling, was repeatedly extracted with ether, the ethereal extracts were washed with sodium carbonate solution until free from acid (A), and

the ether was evaporated. The residual oil was digested with an aqueous-alcoholic solution of potassium hydroxide* to hydrolyse any acetyl derivative present and, after addition of water, the solution was extracted with ether. From the dried ethereal extract, a viscid, brown oil was obtained which gradually crystallised in the ice-chest after addition of water. The d-*carene-β-glycol* thus obtained was washed with light petroleum (b. p. 40—60°) drained, on porous porcelain to remove adhering oil (the filtrate, B, was reserved) and crystallised from much water, separating in flat prisms, frequently twinned; from light petroleum it crystallised in feathery prisms. It was readily soluble in hot water, methyl alcohol, ethyl alcohol, and benzene, and more sparingly soluble in cold water and light petroleum. The air-dried product had m. p. 75°; after drying in a vacuum over phosphoric acid, it was anhydrous and had m. p. 90–91° and b. p. 147–150/18 mm. (Found for air-dried material: loss on drying over P_2O_5, 9·0. $C_{10}H_{18}O_2,H_2O$ requires H_2O, 9·5 per cent. Found for anhydrous material: C, 70·4; H, 10·9. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·6 per cent.). The glycol was optically inactive in ethyl-alcoholic and in chloroform solutions. When treated with chromic acid in acetic acid solution, it underwent complete degradation and did not appear to yield a trace of the hydroxy-ketone; it was not attacked by hydrogen peroxide in the presence of ferrous sulphate (compare Fenton, *J.C.S.*, 1896, **69**, 224).

The *hydrogen phthalate*, obtained by treating the glycol with phthalic anhydride at 110°, crystallised from dilute methyl alcohol in glistening prisms, m. p. 191–192° (Found: C, 67·7; H, 7·3. $C_{18}H_{22}O_5$ requires C, 67·9; H, 6·9 per cent.).

The filtrate (B) from which *d*-carene-β-glycol had been removed was distilled under diminished pressure; the main fraction passed over at 150–160°/29 mm., leaving a considerable resinous residue. On addition of a little water to the distillate and keeping in the ice-chest, a further quantity of the β-glycol crystallised. This was removed, and the filtrate redistilled; it then passed over at 155–157°/28 mm. This oil had the composition of the glycol (Found: C, 70·3; H, 10·8. Calc.: C, 70·6; H, 10·6 per cent.) and was optically active in chloroform $[\alpha]_D$ − 0·69° (c = 6·942). When treated with dilute sulphuric acid under the conditions described below, it yielded *l*-carene oxide and *p*-cymene.

The sodium carbonate solution (A) gave on acidification a mixture of acids which, after conversion into their ethyl esters, distilled irregularly from 90–180°/10 mm. and no homogeneous acid could be isolated.

* The alkaline solution contained a small quantity of a phenol which was not examined.

l-*Carene Oxide.*—The glycol (60 gms.) was mixed with sulphuric acid (5 per cent., 200 c.c.) and heated on the water-bath for 48 hours; steam was passed through the solution, the volatile oil extracted with ether, the ether dried and evaporated, and the residual oil distilled under diminished pressure (100 mm.), the following fractions being obtained; (i) 110–120° (10·5 gms.), (ii) 120–140° (3 gms.), (iii) 140–160° (13 gms.), (iv) above 160° (5 gms.).

Fraction (i) was distilled over sodium and then had b.p. 170–170·5°/685 mm., D_{30}^{30} 0·8627, and $n_D^{30°}$ 1·4869. These figures indicated that the hydrocarbon consisted essentially of *p*-cymene and this was confirmed by analysis (Found: C, 88·9; H, 10·7. Calc.: C, 89·6; H, 10·4 per cent.) and by oxidation to *p*-α-hydroxy*iso*propylbenzoic acid, m. p. 156–157°. Fraction (iii) on redistillation boiled at 150–160°/100 mm. and a portion, b. p. 152°/100 mm., was analysed (Found: C, 79·2; H, 10·5. $C_{10}H_{16}O$ requires C, 79·0; H, 10·5 per cent.). This fraction, which had a pleasant smell reminiscent of linalool, was evidently not quite homogeneous, as was shown by the determination of the constants of two fractions: (*a*) b. p. 150–153°/99 mm., $D_{30°}^{30°}$ 0·961, $n_D^{30°}$ 1·4740, (*b*) b. p. 155–159°/99 mm., $D_{30°}^{30°}$ 0·9794, $n_D^{30°}$ 1·4768, $[\alpha]^{30°}$ —39·16°. There can be no doubt that this substance consisted essentially of l-*carene oxide*; it did not react with the usual ketonic reagents, although, when it was kept for some months with semicarbazide acetate, a small amount of a *semicarbazone* gradually separated. It crystallised from methyl alcohol in lustrous plates, m. p. 193–193·5°, and was probably the semicarbazone of the ketone (IX) (Found: C, 63·1; H, 9·4; N, 20·4. $C_{11}H_{19}ON_3$ requires C, 63·1; H, 9·1; N, 20·1 per cent.). When the oxide was heated for 6 hours at 160° with phthalic anhydride, *d*-carene-*β*-glycol acid phthalate was obtained in excellent yield. It had m. p. 191° and was identical in every way with the phthalate described above. The oxide was stable to bromine in chloroform solution, and to dilute sulphuric acid at the ordinary temperature.

Oxidation of l-*carene oxide.*—The oxide (10 gms.) was dissolved in actone (100 c. c.) and to the solution, well cooled in ice, finely powdered and sieved potassium permanganate (27·7 gms.) was added gradually, oxidation being complete in about 7 hours. The manganese dioxide sludge was collected, washed with acetone, and then repeatedly extracted with boiling water. The brown, aqueous extract was concentrated in a current of carbon dioxide, acidified, and repeatedly extracted with ether, the viscid oil remaining on removal of the solvent was esterified in the usual manner, and the esters were distilled under diminished pressure. The main fraction, b. p. 140–160°/46 mm., was hydrolysed with methyl-alcoholic potassium hydroxide solution; the acid, isolated in the usual manner, was then obtained as a viscid oil. It was dissolved in a slight excess of ammonia and the solution was treated with calcium chloride and boiled; a small quantity of a sparingly soluble resinous salt then separated. This was removed, the solution acidified, and the acid extracted with ether. The pale yellow oil which remained on removal of the solvent yielded on treatment with semicarbazide acetate a *semicarbazone* (0·9 gm.) which, after repeated crystallisation from hot water, was obtained in well formed prisms, decomp. 165–166° (Found: C, 53·1; H, 7·9. $C_{10}H_{17}O_3N_3$ requires C, 52·9; H, 7·5 per cent.). On hydrolysis with dilute sulphuric acid, the keto-acid was obtained as a viscid oil which showed no tendency to crystallise; when it was dissolved in sodium hydroxide solution and treated with sodium hypobromite, bromoform was precipitated, but the dibasic acid formed was insufficient in quantity for examination.

Action of Hypochlorous Acid on d-Δ³-*Carene.*—After a large number of experiments, the method briefly described below was found to be the only one to give satisfactory results.

The hydrocarbon (1 mol.) was mixed with freshly prepared sodium hypochlorite solution (2 mols.), and after the addition of an excess of boric acid the mixture was shaken mechanically until free from hypochlorous acid. The reaction product was separated by ether and purified by distillation under diminished pressure (10 mm.); two fractions were separated, (*a*) b. p. 90–93°, (*b*) 110–113°.

Fraction (*a*), which had $D_{30°}^{30°}$ 1·0123 and $n_D^{30°}$ 1·4992, was the pure monochlorohydrin (Found: Cl, 18·5. $C_{10}H_{17}OCl$, requires Cl, 18·8 per cent.). *Hydroxychlorocarene* was a colourless oil with a fairly pungent smell. It was an extremely stable substance and was unaltered on treatment with silver oxide at the ordinary temperature. Attempts to prepare crystalline derivatives were unsuccessful.

Fraction (*b*), $D_{30°}^{30°}$ 1·0821, $n_D^{30°}$ 1·5060, consisted of somewhat impure dichlorodihydroxymethyl*iso*propyl*cyclo*hexane (Found: Cl, 25·5. $C_{10}H_{18}O_2Cl_2$ requires Cl, 29·5 per cent.) It was a viscid oil which yielded no crystalline derivatives and was probably a mixture of isomerides derived from 1-methyl-4-*iso*propyl- and 1-methyl-3-*iso*propyl-*cyclo*hexane.

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