

# CHEMICAL EXAMINATION OF THE ESSENTIAL OIL DERIVED FROM THE SEEDS OF *CARUM ROXBURGHIANUM* BENTH.

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*Carum Roxburghianum* Benth. is a low annual herb belonging to the Natural Order of Umbelliferae. It grows abundantly throughout the Gangetic plains and also in the Central Provinces and in Hyderabad in Deccan. It is known in Hindi as "Ajmud" and in Bengali as "Shah Jira" or "Randhuni", and is one of the lesser known spices cultivated in India for the flavouring of food. The seeds are very difficult to distinguish from ordinary *Caraway* or "Jira" seeds except by their very different flavours, so very closely similar are their external appearances. The corresponding plants also look almost identical with each other. The plants grow during the cold season and the seeds are ready for harvesting by the end of March.

Apart from their use as a spice in ordinary food preparations, they are also used as flavouring materials in various Achars, Chutneys and Preserves. They are also one of the constituents of numerous "curry powders" often sold in the market. The seeds are also highly medicinal. According to Kirtikar and Basu,<sup>1</sup> the seeds are useful in hiccup, vomiting and pain in the bladder. They form an ingredient of carminative and stimulant preparations and are very useful in dyspepsia and flatulence.

In view of the great medicinal importance of the seeds and their economic value, it was thought desirable to undertake the chemical examination of the essential oil contained in them which is undoubtedly the active principle of the material. No detailed investigation appears to have been made in this subject upto this time.

The essential oil is very easily obtained from the seeds by steam distillation in an yield of 2.5 per cent. Further examination of the oil resolved it into a number of different constituents, amongst which the major ones have been found to be *d-limonene*, *α-terpinene* and *dl-piperitone*. Amongst the minor constituents, the following have been definitely identified: *d-linalool*, *dl-terpineol*, *thymol*, *thymoquinol*, *p-isopropyl-benzoic acid* and a

*Ketonic acid*  $C_{10}H_{14}O_3$  of unknown constitution. Traces of Cuminol have also been found to be present.

### Experimental

20 Kgs. of the crushed seeds were submitted to distillation in steam from a large copper still fitted with a tinned funnel condenser and an automatic trap for the separation of the essential oil from the aqueous distillate. The oil recovered from the trap was dried with anhydrous magnesium sulphate and filtered. 520 Gms. of the dry essential oil were thus obtained, thereby giving an yield of about 2.5 per cent. on the weight of the seeds. The following table gives the properties of the oil:

Table I

#### Chemical and Physical Properties of the Essential Oil

Colour of the oil .. .. .	Greenish-yellow
Sp. Gr. at 20° C. .. .. .	0.9488
Refractive index at 20° C. .. .. .	1.4880
Optical rotation at 33° C. .. .. .	+25.5°
Acid value .. .. .	4.9
Saponification value .. .. .	49.1
Saponification value after acetylation .. .. .	74.2

300 c.c. of the essential oil were distilled at the ordinary pressure through a Young's column, and the different fractions obtained at various temperatures refractionated through suitable fractionating columns for a number of times until the following ultimate fractions were obtained :

TABLE II

#### Fractionation of the essential oil

Fraction No.	Boiling range (° C.)	Volume of distillate (c.c.)	Sp. Gr. at 20° C.	Refractive index at 20° C.	Optical rotation at 30° C.	Per cent. yield
1	170-80	162	0.8488	1.4716	+92.9	54.0
2	180-90	9	0.8498	1.4726	+65.7	3.0
3	200-10	14	0.8748	1.4716	+26.5	4.7
4	210-20	17	0.9408	1.4836	+ 5.0	5.7
5	220-30	32	0.9405	1.4876	- 1.5	10.7
6	230-40	21	0.9766	1.4906	± 0	7.0
7	240-50	13	0.9691	1.4926	± 0	4.3
8	250-60	14	0.9750	1.4966	± 0	4.7
9	Residue	13	0.9733	1.4966	± 0	4.3
10	Loss by distillations	5	..	..	..	1.7

*Chemical Examination of the Various Fractions*

*Fraction No. 1.*—This was found to be an unsaturated hydrocarbon with a strong smell resembling limonene. On further examination it was found to be a mixture of *d*-limonene and  $\alpha$ -terpinene in the proportion of approximately 65:35. It gave a brilliant green coloration on treatment with nitrous acid in accordance with Gildemeister's<sup>2</sup> directions, and the reaction product on standing for a long time yielded only relatively small proportions of colourless needles melting at 155° C., which were found to be  $\alpha$ -terpinene nitrosite. The comparatively small yield of the nitrosite and also the fact that on treatment with bromine in glacial acetic acid the fraction gave only liquid bromine addition products and both hydrogen chloride and nitrosyl chloride failed to give any crystalline derivative, led to the suspicion that the fraction in question must naturally be a mixture of  $\alpha$ -terpinene with a much larger proportion of some other hydrocarbon having a similar boiling point, which could evidently be limonene or dipentene. On account of the impossibility of separating the two products by physical methods, the  $\alpha$ -terpinene in the mixture had to be destroyed by treatment with cold chromic acid in accordance with Beckmann's<sup>3</sup> method, and the remaining hydrocarbon after purification was found to be *d*-limonene (b.p. 176–78° C.,  $D_{20}^{\circ} = 0.8495$ ,  $n_D^{20} = 1.4760$ ,  $D^{30} = +120.5^{\circ}$ ). It readily gave a tetrabromide with bromine in glacial acetic acid melting at 104° C.

*Fraction No. 2.*—This was found to be mainly *d*-limonene mixed with dipentene and  $\alpha$ -terpinene. With bromine in acetic acid, it readily yielded the tetrabromide melting at 104° C. and with nitrous acid it gave the bright green colour reaction of terpinene, but the yield of the crystalline nitrosite was very little. On destruction of the  $\alpha$ -terpinene in the mixture with cold chromic acid, the residue was found to be a mixture of dipentene and limonene only. The proportion of  $\alpha$ -terpinene in the mixture was approximately 15 per cent. but that of the other two components could not be determined.

*Fraction No. 3.*—This was found to be *d*-linalool. The phenylurethane derivative prepared in the usual manner melted at 65° C.

*Fraction No. 4.*—This was identified to be terpineol. The nitroso-chloride prepared by the usual methods melted at 110–12° C., and the nitrol-piperidide obtained by the action of piperidine on the former melted at 155–56° C.

*Fraction No. 5.*—There was considerable difficulty in the identification of this fraction which was found to be ketonic in nature. It gave an oxime

melting at 117–18° C. and a semicarbazone melting at 228–29° C. It had a strong smell resembling old eucalyptus oil. A crystalline potassium bisulphite compound was obtained by the action of potassium metabisulphite in hot water. The substance was ultimately identified to be *dl*-piperitone. It gave thymol on oxidation with ferric chloride in glacial acetic acid. (Oxime: Found N = 8.0 ;  $C_{10}H_{14}NOH$  requires N = 8.3 per cent. Semicarbazone: Found N = 20.5 ;  $C_{10}H_{14}NNHCONH_2$  requires N = 20.09 per cent.)

*Fraction No. 6.*—This was found to be acidic in reaction. It was extracted with 5 per cent. aqueous sodium hydroxide solution and the aqueous layer after saturation with carbon dioxide, extracted with ether. The ethereal extract on complete evaporation of the solvent yielded an oil smelling strongly of thymol and on standing for three days in the refrigerator deposited a small quantity of colourless woolly needles. These were separated from the oily mother-liquor on a porous plate and on recrystallisation from hot water melted at 140° C. These were identified to be thymoquinol by direct comparison with a synthetic specimen. The yield was 0.7 g.

The oily mother-liquor from the thymoquinol was extracted from the porous plate by ether and on evaporation of the solvent a light yellow liquid was obtained which did not crystallise even on prolonged standing at the ordinary temperature. On distillation however, the major fraction which boiled at 230–35° C. solidified in the condenser as a colourless crystalline mass which melted at 49° C. This was identified to be thymol by the preparation of the nitroso derivative which melted at 164° C. The yield was 4.5 gm.

The aqueous mother-liquor from the ethereal extract mentioned above on acidification with dilute hydrochloric acid gave a colourless crystalline precipitate which on recrystallisation from dilute alcohol was obtained in the form of long glistening needles melting at 114–15° C. This was identified to be *p*-isopropylbenzoic acid or cumic acid by direct comparison with an authentic specimen. Apparently this acid must have been produced by the oxidation of the corresponding aldehyde or *cuminol*, traces of which were found to be present in the original essential oil. The yield obtained was 1.2 gm.

The residue of the original fraction No. 6 remaining behind after extraction with aqueous alkali (9.5 c.c.) was washed with water, dried and distilled. The major fraction which passed over at 232°–35° C. was found to be piperitone by formation of the oxime and the semicarbazone already described. Traces of *cuminol* could also be detected in the tail fractions, but it could not be isolated either as such or in the form of its derivatives.

*Fraction No. 7.*—This had already partially solidified with formation of a few thick prismatic crystals. The crystals were separated from the mother-liquor and recrystallised from dilute alcohol, when they were obtained in the form of glistening prisms melting at 105–06° C. They could not be definitely identified, but they appear to be those of the ketonic acid  $C_{10}H_{14}O_3$  described by Wallach and Hallstein<sup>4</sup> and obtained by the oxidation of piperitone. These authors have also recorded the melting point of 105–06° C. (Found : C = 65·53 ; H = 7·92 ;  $C_{10}H_{14}O_3$  requires C = 65·93 ; H = 7·69 per cent.)

The mother-liquor from the above crystalline deposit was found to be acidic in reaction and on extraction with aqueous caustic soda and proceeding as already described under *Fraction No. 6*, a small quantity of thymol and a further small quantity of the above-mentioned acid melting at 105·06° C. were obtained. The neutral oil after removal of the acidic constituents was found to be an ester or a mixture of esters with a saponification value of 210, but it could not be definitely identified. Traces of cuminol were also found in the substance.

*Fraction No. 8.*—This was also found to be acidic in reaction and from this also by extraction with alkali, small quantities of thymol and the previously mentioned ketonic acid could be isolated. But the major fraction of the substance consisted of esters together with high boiling hydrocarbons which could not be identified.

*Fraction No. 9.*—This was found to be a dark brown viscous liquid with a few crystals embedded in the sticky medium. It could not be worked up or identified.

#### *Summary and Conclusions*

1. The essential oil of *Carum Roxburghianum* Benth. seeds was obtained in an yield of 2·5 per cent. by steam distillation.

2. Further examination of the oil revealed that it contained the following constituents :

<i>d</i> -limonene	..	..	..	..	35·1 per cent.
<i>d</i> -limonene and dipentene mixture	..	..	..	..	2·5 „
$\alpha$ -terpinene	..	..	..	..	19·4 „
<i>d</i> -linalool	..	..	..	..	4·7 „
<i>dl</i> -terpineol	..	..	..	..	5·7 „
thymoquinol	..	..	..	..	0·2 „
thymol	..	..	..	..	1·7 „
<i>dl</i> -piperitone	..	..	..	..	13·6 „

<i>p</i> -Isopropylbenzoic acid	.. ..	0.4 per cent.
Cuminol	.. ..	traces
Unidentified ketonic acid $C_{10}H_{14}O_3$	.. ..	1.0 „
Unidentified esters	.. ..	5.9 „
Unidentified	.. ..	9.8 „

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## REFERENCES

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