

# CHEMICAL EXAMINATION OF THE ESSENTIAL OILS DERIVED FROM *ANETHUM SOA* ROXB. OIL FROM THE GREEN HERB AND THE SEEDS

BY BRAJ KISHORE MALAVIYA AND SIKHIBHUSHAN DUTT

(From the Chemical Laboratory, University of Allahabad)

Received July 29, 1940

*Anethum soa* Roxb. is an annual glabrous herb belonging to the Natural Order of Umbelliferae. It is commonly known as "Soa ka sag" in Hindi and "Solfa" in Bengali. It occurs throughout the tropical and subtropical India. It is available in the vegetable market chiefly in the months of January, February and March. For the most part it is used for culinary purposes and as a condiment. To a certain extent it is also used for medicinal purposes.

According to Dymock,<sup>1</sup> the leaves moistened with oil are used as a stimulating poultice or suppurative. Mahometan writers describe it as resolvent and obstriant, carminative, diuretic and emmenagogue.

The herb is strongly scented, but its aroma is not very nice or pleasant. It imparts a good flavour to the vegetables with which it is cooked and it is on this account that it finds a good market. The herb has a height of 6 inches to 3 feet, but the aroma of the plant is most when it is about 6 inches to 1 foot high and is very leafy. The stems do not contain much smell and as the herb grows taller and the proportion of stems increases, the aroma becomes less and consequently its value as an aromatic herb becomes considerably diminished. When the herb flowers, it loses its value as an aromatic herb altogether, and is then not cut down, but retained in the fields for the purpose of getting the seeds. When the seeds begin to appear, the leaves do not remain on the plant except a few here and there and the stems become rather hard.

Although the herb is very common in the Indian markets and is valued only for its aroma, it is rather queer that it has not yet been used for extracting the essential oil even on an experimental scale in India. In Europe there is a similar but not identical variety of herb known as *Anethum graveolens*, growing in Miltitz, which was examined by Schimmel & Co.<sup>2</sup> They obtained from it 0.116 per cent. of a pale green oil, the stale odour of which was entirely different from dill seed oil ( $D_{15}^{\circ} = 0.8752$ ;  $\alpha = +108^{\circ}35'$ ;  $n^{20^{\circ}} = 1.4769$ ). It was soluble in an equal volume of 90 per cent. alcohol, but on the other

hand even 10 volumes of 80 per cent. alcohol were insufficient for solution. The chief constituent of the oil was found to be *d*-phellandrene, whereas carvone appeared to be not present at all. With sodium sulphite about 40 per cent. of the material reacted which when liberated from the sulphite combination had an odour of fatty aldehydes rather than that of carvone.

Dill herb oil which was distilled from the fresh herb of *Anethum graveolens* L. in Russia with an yield of 0.56 to 1.5 per cent. (referred to the dry weight of the material), possessed according to Tschernchin<sup>3</sup>, the following constants :  $D = 0.8724$ ;  $\alpha = +64^{\circ}35'$ ;  $n = 1.481$ ; carvone content = 15 per cent.

As regards the Indian variety known as *Anethum soa*, the oil from the seeds only has been examined by Rao, Sudborough and Watson<sup>4</sup> and they have only determined the physical and chemical constants of the oil.

The fresh green herb examined by us on steam distillation gave a green essential oil with a disagreeable smell having the following constants :

	per cent.
Yield .. .. .	0.062 (referred to the fresh herb).
Specific gravity (20°C.) .. .. .	0.8726
Refractive index (20°C.) .. .. .	1.4867
Optical rotation (28°C.) .. .. .	+286.6°
Acid Value .. .. .	2.10
Ester value .. .. .	6.72
Saponification value .. .. .	8.82
Saponification value after acetylation .. .. .	37.80
Formylation value .. .. .	4.90
Total aldehydes calculated as citral and estimated by the hydroxylamine method .. .. .	1.3
Carvone content .. .. .	Nil
C <sub>10</sub> H <sub>18</sub> O from Sap. Value .. .. .	3.15
Alcohols in the original oil calculated on the basis of Sap. Value after acetylation .. .. .	10.76

A careful examination of the oil showed that it contains a high percentage of *α*-phellandrene and small proportions of eugenol, iso-eugenol, thymol and phellandral.

The seeds of *Anethum soa* have a high medicinal value, and their therapeutic importance is chiefly due to the essential oil contained in them. According to Dymock,<sup>5</sup> an infusion of the seeds is given as a cordial drink

to women after confinement. Mahometan writers describe it as a resolvent and deobstrient, carminative, diuretic and emmenagogue.

According to Kanny Lal Dey,<sup>6</sup> the oil, essence and water of dill are much esteemed in India as carminative for flatulence in children and in adults.

In his *Pharmacographica Indica*, Dymock<sup>7</sup> describes the chemical composition of the seeds as follows : " Dill fruit yields from 3 to 4 per cent. of an essential oil, a large proportion of which was found by Gladstone (1864-72) to be the hydrocarbon  $C_{10}H_{16}$  to which he gave the name " Anethene ". This substance has a lemon-like odour, Sp. Gr. at 15 C., 0.846 and boils at 172°C. It deviates a ray of polarised light strongly to the right. Nietzki ascertained that there is however present another hydrocarbon. A third constituent of the oil of dill is in all probability identical with carvol.

According to Parry,<sup>8</sup> the Indian dill oil has a much higher specific gravity. The figure for this varies between 0.945 and 0.970. The optical rotation varies between  $+40^{\circ}$  and  $+50^{\circ}$ . This oil contains a body isomeric with ordinary apiol from parsley oil and which has been named dill-apiol.

As a result of two test distillations, Schimmel & Co<sup>9</sup> have found that the oil from the seeds of this variety is not equal to the European oil. They obtained an yield of 3 and 3.5 per cent. respectively and the characters of the oils were as follows :  $D_{15}^{\circ}$  0.9798 and 0.9896;  $\alpha$   $+47.8'$  and  $+45^{\circ}20'$ ;  $n_D$  1.49706 and 1.49903; soluble in 3.8 and 3.2 volumes of 80 per cent. alcohol. Carvone content of both the samples (determined with neutral sodium sulphite) was 22 per cent.

The oil from the seeds of purely Indian origin seems to have been examined by Rao, Sudborough and Watson as has already been mentioned before. They obtained an yield of 3.9 per cent. The oil has the following constants :  $D_{15}^{\circ}$  0.9785;  $\alpha$   $+47.6'$ ;  $n_D$  1.4934. Carvone content by sodium bisulphite method was 19.5 per cent. These authors however did not examine the constituents of the oil and their determination of the carvone content by sodium bisulphite is open to question as carvone is determined best by precipitating the semi-carazone or by neutral sodium sulphite.

The oil obtained in the present investigation came in two lots. In the first fractions a light oil came which floated on the top of the aqueous distillate and was syphoned off from time to time. On continuing the distillation, a heavier oil began to appear which sank to the bottom of the distillate and was removed after the entire distillation process was over. The heavier oil had of course a much higher specific gravity than any hitherto recorded, whereas the average specific gravity of the lighter and the heavier oil taken together was also more than any so far recorded. These two types of oils

that separated automatically, were examined separately. The heavier oil contained a very high proportion of dill-apiol which is the last to distil, and hence the last distillate from the seeds always deposited the oil at the bottom. The yield in this case was rather low on account of the fact that only the oil automatically separating by difference in density was collected and no attempt was made to extract the oil remaining in suspension in the aqueous distillate.

#### *Experimental*

*The essential oil of Anethum soa herb.*—400 kilos of the fresh green herb collected in several lots from a local field was submitted to steam distillation from a large copper still. The green herb was cut from above the roots and the flowering plant or the plant in buds was carefully excluded. The herb was not allowed to remain either in the fields or in the laboratory for any length of time, as otherwise much of the volatile oil is lost. The oil came out entirely in the first distillate, and therefore steam distillation was discontinued after about two hours from the time oil began to appear in the distillate. The oil floating on the top of the aqueous distillate was syphoned off from time to time, and the remaining aqueous liquid returned to the still in the subsequent charge. As only the skimmed oil was collected the yield was comparatively low.

The oil was dried over anhydrous sodium sulphate and filtered. The filtered and dried oil was submitted to distillation in vacuum under a pressure of 15 mm. and the following fractions were collected:

TABLE I  
*Physical Constants of the Above Fractions*

Fraction No.	Boiling range ° C.	Volume of distillate c.c.	Per cent. yield
1	60- 80	128	78.0
2	80-130	15	9.2
3	130-150	4	2.5
4	150-170	10	6.0
5	170 and above	2	1.2
6	Residue	4	2.5
	Loss	1	0.6

TABLE II

Fraction No.	Specific gravity at 20° C.	Refractive index at 20° C.	Optical rotation at 20° C.
1	0.8595	1.4695	+178.4
2	0.9464	1.4765	+ 39.5
3	1.0140	1.4900	+ 12.4
4	1.1173	1.5115	+ 6.7
5	1.0754	1.5035	..

Fraction No. 1 was refractionated under a vacuum of 15 mm. and the following fractions were collected :

TABLE III

Fraction No.	Boiling range ° C.	Volume of distillate c.c.	Per cent. yield
7	60-80	118	74.6
8	82-84	2	1.7
8a	Residue and loss	2	..

5 c.c. of Fraction No. 7 was dissolved in 10 c.c. of low boiling petroleum ether and 5 g. of sodium nitrite in 8 c.c. of water was added to the solution, 5 c.c. of glacial acetic acid was then added in small instalments and the mixture thoroughly stirred. A white crystalline magma was formed. It was filtered on a force filter and crystallised from acetone. Two fractions were obtained, one easily soluble in acetone and crystallising in colourless prisms melting at 107°C. and the other somewhat difficultly soluble and crystallising in fine colourless needles melting at 114°C. Fraction No. 7 was therefore confirmed to be  $\alpha$ -phellandrene, and the above mentioned crystalline derivatives to be to two isomeric nitrosites.

*Fraction No. 8* gave an oxime M.P. 86°C. On account of the small quantity of the fraction, more derivatives could not be prepared and the oxime already prepared could not be further purified or analysed. But in all probability this fraction was phellandral, as the oxime of phellandral should have according to Gildemeister a M.P. of 87–88°C.

TABLE IV

*Physical Constants of the Above Fractions*

Fraction No.	Specific gravity at 20° C.	Refractive index at 20° C.	Optical rotation at 20° C.
7	0.8529	1.4675	+178.5
8	0.9414	1.4745	..

*Fraction No. 8* had a strong acidic reaction on litmus paper. It partially dissolved in dilute caustic soda solution, and the alkaline liquid on acidification deposited an oily substance. The entire fraction was therefore extracted with dilute caustic soda and the portion insoluble in the liquid separated. The non-phenolic portion was submitted to distillation at the ordinary pressure and the following fractions were collected :

TABLE V

*Physical Constants of the Above Fractions*

Fraction No.	Boiling range ° C.	Volume of distillate c.c.	Per cent. yield
9	194–198	4	3.7
10	210–215	2	1.8
11	Phenolic portion recovered after acidifying the alkaline solution	0.9	0.8

TABLE VI

*Physical Constants of the Above Fractions*

Fraction No.	Specific gravity at 20° C.	Refractive index at 20° C.
9	0.9016	1.4700
10	0.9651	1.4775

*Fraction No. 11* congealed to a mass of radiating needles on cooling in a freezing mixture and gave a benzoyl derivative melting at 104°C. It was thus identified to be iso-eugenol.

*Fraction No. 3* was aldehydic in nature, but could not be identified on account of the small quantity of the liquid available.

*Fraction No. 4* was also acidic, and 5 c.c. of this fraction was treated with dilute caustic soda solution. 3 c.c. of the liquid did not dissolve and was separated. The non-phenolic portion (Sp. Gr. at 20°C. = 1.1126; Refractive Index at 20°C. = 1.5185) could not be identified, but the phenolic portion isolated from the alkaline liquid on acidification gave two benzoyl derivatives. One of them remained liquid, but the other separated in fine crystals. The solid portion was filtered and recrystallised. It melted at 69°C. and was identical with benzoyl-eugenol. The liquid derivative solidified on cooling in a freezing mixture and then melted at 30-32°C. It was identified to be benzoyl-thymol. The phenolic portion in *Fraction No. 4* was therefore identified to be a mixture of eugenol and thymol.

*Fraction No. 5* solidified on cooling in fine needles. It gave a benzoyl derivative 104°C. and was phenolic in character. It was identified to be iso-eugenol.

Thus the essential oil from the green herb of *Anethum soa* was found to have the following composition:

	per cent.
<i>d-a</i> -phellandrene .. ..	74.6
Eugenol and thymol .. ..	2.4
Iso-eugenol .. ..	2.0

				per cent.
Phellandral ..	..	..	..	1.7
Unidentified ..	..	..	..	11.6
Residue and loss ..	..	..	..	7.7

*Essential oil from Anethum soa seeds.*—60 kilos of the crushed seeds were distilled in steam from a large copper still. In the beginning a light oil came over and accumulated on top of the aqueous distillate. This was removed from time to time and it constituted the 'light oil' described further on. On continuing the distillation, a heavy oil was deposited at the bottom of the aqueous distillate and this was also collected separately. The aqueous distillate freed from the two types of essential oils was returned to the still in a subsequent charge. The oils were dried over anhydrous sodium sulphate and filtered. The physical constants of the oils were determined and are given in the following table :

TABLE VII

	Light oil	Heavy oil
1. Specific Gravity at 20° C.	0.9719	1.0573
2. Refractive Index at 20° C.	1.4905	1.5385
3. Specific Rotation at 30° C. .. ..	+38.5°	+23.6°
4. Percentage of Carvone estimated by neutral soda sulphite ..	28.0	20.6
5. Percentage of carvone determined by semi-carbazide method ..	68.1	47.5
6. Acid value .. ..	..	..
7. Saponification value ..	32.8	..

*Examination of the Light Oil*

260 c.c. of the oil was distilled under a press. of 15 mm. and the following fractions were collected:



*Chemical Examination of the Essential Oils*

TABLE VIII

Fraction No.	Boiling range ° C.	Volume of distillate c.c.	Per cent. yield
1	upto 80	10	3.9
2	80- 90	30	11.5
3	90-100	18	6.9
4	100-110 (const. 104)	50	19.2
5	110-120 (const. 114)	69	26.5
6	120-130 (const. 125)	..	..
7	130-140	9	3.5
8	140-160	39	15.9
9	above 160	2	0.8
10	Residue and loss	3	1.2

TABLE IX

*Physical Constants of the Above Fractions*

Fraction No.	Specific gravity at 20° C.	Refractive index at 20° C.	Optical rotation at 36° C.
1	0.81635	1.4695	+102.4
2	0.87675	1.4715	+ 86.2
3	0.89285	1.4750	+ 71.0
4	0.92885	1.4835	+ 54.9
5	0.97905	1.4915	+ 46.3
6	0.99345	1.4965	+ 38.2
7	1.03375	1.5035	+ 29.3
8	1.13035	1.5235	+ 45.0
9	1.18875	1.5195	+ 45.3

The various fractions obtained above were refractionated several times under ordinary pressure and the fractions distilling between the same boiling range were collected together. The following set of fractions were thus obtained :

TABLE X

Fraction No.	Boiling range °C.	Volume of distillate c.c.	Per cent. yield
11	upto 170	1	0.6
12	170-180 (const. 173-175)	22	12.6
13	180-190	5	2.9
14	200-210	11	6.2
15	210-220	24	13.7
16	220-230	77	4.0
17	230-250	7	4.0
18	250-286 (const. 285)	3	1.7
19	274-284 (const. 284)	11	6.3
20	284-290 (const. 285)	8	4.6
21	Residue and loss	6	3.4

*Physical Constants of the Above Fractions*

TABLE XI

Fraction No.	Specific gravity at 20° C.	Refractive index at 20° C.	Optical rotation at 36° C.
11	..	1.46738	..
12	0.8572	1.4683	+102.0
13	..	1.4733	..
14	0.9186	1.4823	+ 68.3
15	0.9484	1.4873	+ 65.8
16	0.9985	1.4928	+ 50.0
17	1.0477	1.5043	+ 33.3
18	1.1357	1.5203	+ 11.0
19	1.1562	1.5263	± 0.0
20	1.1720	1.5283	± 0.0

*Fraction No. 11* could not be identified on account of the small quantity of the substance in hand. *Fraction Nos. 12 and 13* were identified to be *d-limonene*. They gave tetrabromides having m.p. 104°C. *Fraction Nos. 14 to 17* were found to be *d-carvone*. *Fraction Nos. 14 and 15* were digested with neutral sodium sulphite. The residual oils were very small in quantity and no definite tests could be made but the non-ketonic fraction from *fraction No. 14* had a characteristic smell of anisic aldehyde and that from *15* had a distinct smell of anethol. It was kept in a freezing mixture and fine crystals got deposited in *15* but the quantity was insufficient to admit melting point determination even. *Fraction No. 16* was almost entirely pure *d-carvone*. It gave an oxime m.p. 72°C. ; a semi-carbazone m.p. 162°C. and a hydrogen sulphide compound m.p. 210°C. Similar compounds were obtained from *fractions 14, 15 and 17* as well. *Fraction No. 17* was also digested with neutral sodium sulphite and the non-ketonic fraction was found to be pure dill-apiol on examination. *Fraction Nos. 18, 19 and 20* were identified to be dill-apiol. Each of them gave a tribromide having a m.p. 110°C.

Dill-apiol was freed from associated phenolic bodies which are present in the fractions containing this fraction by extraction with caustic soda in which dill-apiol is insoluble. This treatment is necessary in order to get the dill-apiol in a perfectly pure state. All the fractions, viz., 18, 19 and 20 were found to contain very small proportions of phenolic bodies. The quantities of phenolic bodies were too small to admit of any detailed examination. However the three phenolic bodies obtained from the three fractions mentioned above were benzoylated. *Fraction No. 18* gave a solid benzoyl derivative and the other two fractions gave liquid benzoyl derivatives. Nothing further could be done with these fractions but on account of the fact that the liquid derivatives solidified on cooling they were very likely benzoyl derivatives of Thymol. *Fraction No. 18* was most probably eugenol.

The residue dissolved easily in chloroform and with difficulty in alcohol. No. solid substance could be isolated. The whole thing remained a sticky mass even after repeated solution and concentration.

#### *Examination of the Heavy Fraction*

112 c.c. of the heavy fraction was submitted to fractional distillation under a pressure of 15 mm. and the following fractions were collected :

TABLE XII

Fraction No.	Boiling range °C.	Volume of distillate c.c.	Per cent. yield
1	upto 80	3	2.7
2	80 -90	6	5.4
3	90-100	18	16.1
4	120-130	12	10.7
5	130-150	14	12.5
6	150-160	46	41.1
7	above 160	1	0.8
8	Residue and loss	12	10.7

TABLE XIII

*Physical Properties of the Above Fractions*

Fraction No.	Specific gravity at 20° C.	Refractive index at 20° C.	Optical rotation at 34° C.
1	0.8685	1.4733	+94.9
2	0.8821	1.4763	+93.5
3	0.9386	1.4873	+66.5
4	0.9830	1.5023	+38.1
5	1.0774	1.5113	+23.2
6	1.1694	1.5263	± 0.0
7	1.1694	1.5263	± 0.0

The various fractions mentioned above were refractionated under ordinary pressure and the fractions boiling within the same boiling range were collected together. The following fractions were thus obtained.

TABLE XIV

Fraction No.	Boiling range °C.	Volume of distillate c.c.	Per cent. yield
9	180-190	1.5	2.5
10	190-220	4.0	6.7
11	220-230	4.0	6.7
12	230-250	7.0	11.7
13	250-280	15.0	25.0
14	285	25.0	41.6
	Residue and loss	3.5	5.8

*Physical Properties of the Above Fractions*

TABLE XV

Fraction No.	Specific gravity at 20° C.	Refractive index at 20° C.	Optical rotation at 31° C.
9	0.8821	1.4758	+90.6
10	0.9184	1.4813	+70.7
11	0.9870	1.4948	+48.6
12	1.0330	1.5033	+43.5
13	1.1575	1.5203	± 0.0
14	1.1696	1.5273	± 0.0

*Fraction No. 9* was identified to be *d*-limonene. It gave a tetrabromide m.p. 104°C. *Fraction Nos. 10, 11 and 12* were identified to be *d*-carvone. They gave hydrogen sulphide compounds having a m.p. 210°C. ; semi-carbazone m.p. 162°C. As the fractions were small in quantities no attempt could

be made to separate the carvone by neutral soda sulphite to study the non-ketonic fraction if any. Fraction Nos. 13 and 14 were identified to be dill-apiol. Both of them gave a tri-bromide m.p. 110°C. Fractions containing dill-apiol were well shaken with caustic soda solution to extract out phenols if any present. Very small quantities were obtained on acidifying the caustic soda extracts and extracting the acidified solution with ether and evaporating off the ethereal extract. These liquids were however benzoylated. The benzoyl derivatives were liquids at ordinary temperature (39°C.) but on cooling they solidified. They were not sufficient even for melting point determination. The phenolic portions were most probably thymol.

Taking both the light and heavy oils together the main constituents of the oil can be recorded as follows :

	Per cent
<i>d</i> -limonene .. .. .	9.0
<i>d</i> -carvone .. .. .	46.5
dill-apiol .. .. .	39.6
Anethol .. .. .	} in traces
Anisic aldehyde .. .. .	
Eugenol .. .. .	
Thymol .. .. .	
Residue and loss .. .. .	4.9

#### Summary

1. On steam distillation Soa herb gives a green oil, yield 0.062 per cent. referred to the green herb.

2. The oil has a Sp. Gr. at 20°C. 0.8726, Ref. index at 20°C. 1.4867 Opt. rot. at 28°C. + 286°.6; acid value 2.10; saponification value 8.82; saponification value after acet. 37.80; formylation value 4.90; total aldehydes estimated by hydroxylamine method 1.3 per cent.

3. The oil consists of  $\alpha$ -phellandrene, eugenol, iso-eugenol, thymol and phellandral.

4. As the oil contains a high percentage of  $\alpha$ -phellandrene it will form a very good source for the extraction of  $\alpha$ -phellandrene. The oil itself is very valuable.

5. The seeds of *Anethum soa* of Indian origin give on steam distillation two types of oil, one heavier and the other lighter than water, yield of the automatically separating oil being 0.474 and the other 0.825 per cent.

6. Physical constants of the seed oils are :—

Sp. Gr. at 20°C. 0.9719 and 1.0573; Ref. index at 20°C. 1.4905 and 1.5385; Opt. rot. +38.5 and +23.6 respectively.

7. The oil contains 9 per cent. *d*-limonene; 46.5 per cent. *d*-carvone; 39.6 per cent. dill-apiol and probably traces of anethol, anisic aldehyde, eugenol and thymol.

REFERENCES

1. Dymock .. .. *Pharmacographica Indica*, 1893, 2, 128-29.
2. Schimmel & Co. .. .. *Annual Report*, 1928, 27-28.
3. A. Tschernchin .. .. *Oil and Fat Industry*, 1927, No. 6, 13.
4. Rao, Watson and  
Sudborough .. .. *Jr. Ind. Inst. Sci.*, 1925, 8A, 183.
5. Dymock .. .. *Pharmacographica Indica*, 1893, 2, 128-29.
6. Kanny Lal Dey .. .. *Indigenous Drugs of India*, 1896, 233.
7. Dymock .. .. *Pharmacographica India*, 1893, 2, 128-29.
8. Parry .. .. *Encyclopedia of Perfumery*, 1925, 234.
9. Schimmel & Co. .. .. *Annual Report*, 1927, 36.