

PRELIMINARY STUDIES ON THE ESSENTIAL OIL FROM *ARISTOLOCHIA INDICA*

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SUMMARY

The essential oil from the roots of *Aristolochia indica* has been shown to consist chiefly of *d*-camphor, one new azulenic sesquiterpene and ledol.

Aristolochia indica (Sanskrit: *Rudrajata*; Kannada: *Isvariberu*) belongs to the family of Aristolochiaceæ¹ and the essential oil from its root was studied previously by Krishna Rao *et al.*²

The roots of *Aristolochia indica* for the present investigation were procured locally and steam distillation gave the essential oil in a yield of 0.52%. The analytical constants of the present sample are compared with that of Krishna Rao *et al.*, in Table I. The results of preliminary fractionation with a precise fraction assembly are given in Fig. 1. Fractions A to B (Fig. 1) were combined and refractionated from a modified claisen flask. Six fractions were collected and their physical constants are recorded in Table II. No crystalline derivatives (like hydrochloride hydrobromide, bromide or nitrosite) could be prepared from fraction 1 (Table II). Fraction 3 (Table II) gave a crystalline semicarbazone

TABLE I

Analytical constants of the essential oil from Aristolochia indica

Constants	Present sample	Sample worked by Krishna Rao <i>et al.</i> ²
Density	$d_4^{22} = 0.929$	$d_{25}^{25} = 0.9525$
Refractive index	$n_D^{22} = 1.4991$	$n_D^{25} = 1.5023$
Acid value	2.9	2.0
Ester value	11.9	7.9
Ester value after acetylation ..	49.2	22.5
Optical rotation	-9.9 (in CHCl ₃ solution)	-33.11

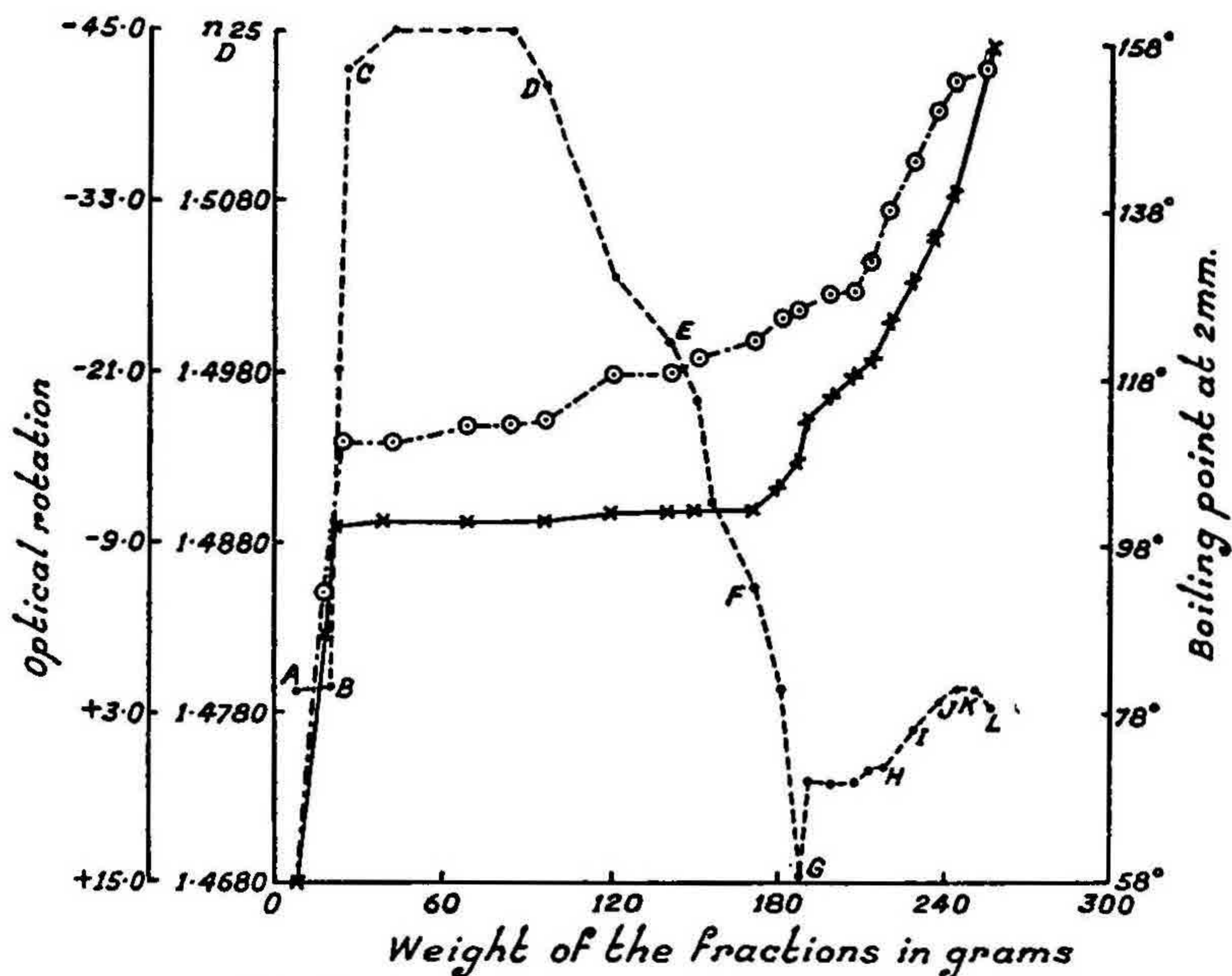


Fig. 1. FRACTIONATION OF 308G. OF ISVARIBERU OIL.

--- Optical rotation *---* Boiling point
 o---o Refractive index

TABLE II

Refractionation of fractions A to B (Fig. 1)

Frn. No.	Wt. of the Frn. g.	Boiling point	Refractive index at 30°	Density
1	1.2	68- 70°/53 mm.	1.4729	0.894 (d_4^{27})
2	2.1	70-105°/53 mm.	1.4710	0.896 (d_4^{27})
3	2.2	105-107°/53 mm.	1.4668	0.904 (d_4^{31})
4	4.9	85- 87°/12 mm.	1.4704	0.909
5	2.4	87-110°/12 mm.	1.4842	..
6	1.9	110-112°/12 mm.	1.4915	..

m.p. 245–47° in 32% yield. The regenerated ketone from the semicarbazone melted at 177° and was identified as *d*-camphor. The non-ketonic portion was not investigated.

Fractions C to D (Fig. 1) were combined together and refractionated using the precise fractionation assembly. The results of this fractionation are given in Table III. Fractions 2, 3 and 4 (Table III) were mixed together and refractionated when six fractions were collected. The middle four fractions which had almost identical physical properties were mixed and distilled twice over sodium when a colourless mobile liquid with physical constants recorded in Table IV was obtained. Its physical and chemical properties appear to indicate it to be a new sesquiterpene, indicated below as 'sesquiterpene A'.

TABLE III
Refractionation of fractions C to D (Fig. 1)

Frn. No.	B.p. at 6 mm.	Volume of fraction in c.c.	Refractive index at 21°	Optical rotation
1	112°	10	1.4945	−40.3°
2	112–112.5°	25	1.4960	−46.2°
3	112–112.5°	25	1.4961	−46.4°
4	112.5–113°	5	1.4962	−46.8°
5	112.5–113°	8	1.4964	−45.2°
		Residue = 7 g.		

TABLE IV
Physical constants of 'sesquiterpene A', 'sesquiterpene B' and Ishwarene

	Sesquiterpene 'A'	Sesquiterpene 'B'	Ishwarene ²
Boiling point	.. 112–12.5°/6 mm.	113°/6 mm.	130–32°/10 mm. 104–05°/1 mm.
Density	.. 0.898 (d_4^{22})	0.905 (d_4^{21})	0.9227 (d_{25}^{26})
Refractive index	.. 1.4956 (n_D^{22})	1.5002 (n_D^{21})	1.5035
Optical rotation (α_D)	−46.4°	−15.8°	−42.37°

The molecular refractivity of 'sesquiterpene A' (66.3)³ is in agreement with that of a bicyclic sesquiterpene with two double bonds. The absence of optical exaltation indicates that the two double bonds are not conjugated. This is supported by the observation that 'sesquiterpene A' is unaffected by sodium and alcohol treatment. The application of Kolthoff and Lee's⁴ method shows that only one of the double bonds is endocyclic. 'Sesquiterpene A' on dehydrogenation with sulphur gives S-guaiazulene.

Fractions D to E (Fig. 1) were mixed and refractionated using the precise fractionation assembly. A small forerun with considerably different physical constants from the rest was obtained. The rest of the distillate was combined with fractions E to F (Fig. 1) and refractionated thrice. The products obtained at the end of the third fractionation are shown in Table V. Fractions 2, 3 and 4 (Table V) were mixed and distilled twice over sodium to give a fraction which is a sesquiterpene and is designated as 'sesquiterpene B'. Its physical constants are given in Table IV, which are different from that of 'sesquiterpene A', but it behaves just like 'sesquiterpene A' in the reactions carried out.

TABLE V
Refractionation of fractions D to F (Fig. 1)

Frn. No.	B.p. at 6 mm.	Refractive index at 21°	Optical rotation (α_D)
1	112.5-13°	1.5000	-16.6°
2	do.	1.5002	-16.2°
3	do.	1.5001	-15.8°
4	do.	1.5001	-15.2°

Refractionation of fractions G to H (Fig. 1) furnished some solid which after repeated recrystallisations from petroleum ether melted at 103-04°. This solid is found to have the formula $C_{15}H_{26}O$ or $C_{15}H_{24}O$. It easily undergoes dehydration when heated with potassium bisulphate to give a hydrocarbon whose physical properties are in agreement with those of ledene (see Table VI). This hydrocarbon

TABLE VI
Physical constants of the dehydrated solid m.p. 103-04° isolated from Iswariberu oil

	Dehydrated solid from <i>Iswariberu</i> oil	Ledene ⁶
Boiling point	113-15°/5 mm.	116-18°/6 mm.
Density	0.924 (d_{25}^{26})	0.923 (d_{20})
Refractive index	1.5024 (n_D^{25})	1.50273 (n_D^{20})

on sulphur dehydrogenation gives S-guaiazulene. These observations indicate that the solid m.p. 103–04° is ledol.

Fraction H to I (Fig. 1) is light blue. The other fractions I to L (Fig. 1) are quite dark coloured. The blue colouring matter of fraction H to I is sensitive to syrupy phosphoric acid. It could not be isolated in a pure form. When Fractions I to L (Fig. 1) were mixed and refractionated it was not possible to isolate any appreciable quantity of a constant boiling fraction. Hence the distillate was not further examined.

EXPERIMENTAL*

170 lb. of the root of *Aristolochia indica* was cut into small pieces and steam distilled. The pressure, initially was slightly above the atmospheric pressure. After six hours, the pressure of the steam was raised to 35 lb./sq. inch. The steam distillation was continued for six more hours. After this stage no essential oil distilled over. The floating oil (398 g.) was separated, dried over anhydrous sodium sulphate and filtered. There were some suspended impurities which were removed by centrifuging. The oil was greenish yellow. It has a pungent bitter taste and a characteristic odour. Its analytical constants were determined by standard methods and are given in Table I. 'Sesquiterpene A' (Found: C, 87.3; H, 11.7, $C_{15}H_{24}$ requires C, 88.24; H, 11.76 per cent.).

Attempts to characterise 'sesquiterpene A'.—Attempts to prepare crystalline hydrochloride, nitrosite or tetrabromide proved futile.

Sulphur dehydrogenation of 'sesquiterpene A'.—A mixture of 1 g. of 'sesquiterpene A' and 0.5 g. of sulphur was heated at 190–210° for 30 minutes and then distilled when a blue distillate was obtained. From this a deep blue azulene (80 mg.) was isolated by using the phosphoric acid extraction method⁷ followed by chromatography on alumina. It gave a T.N.B. adduct m.p. 151–51.5°, whose melting point was undepressed when mixed with an authentic sample of S-guaiazulene *s*-trinitrobenzene adduct.

Epoxide of 'Sesquiterpene A'.—10 g. of the 'sesquiterpene A' was dissolved in 400 c.c. of chloroform and treated under stirring at 0° with enough of N/15 perbenzoic acid solution to convert it to the monoxide. On working out 4 g. epoxide was obtained as a light yellow liquid (b.p. 125–28°/2 mm.) $n_D^{25} = 1.5055$ (Found: C, 81.19; H, 10.6, $C_{15}H_{24}O$ requires C, 81.8, H, 10.9 per cent.).

Dihydrosesquiterpene A.—15 g. of 'sesquiterpene A' was shaken with 200 mg. of platinum oxide (Adam's catalyst)⁵ in 70 c.c. of absolute alcohol. Hydrogenation virtually stopped when one mole of hydrogen was absorbed. The product had b.p. 106–08°/5 mm. $n_D^{31} = 1.4808$; $d_4^{31} = 0.891$; MR_D found 65.8 $C_{15}H_{26} = 1$ requires $MR_D = 66.6$ (Found: C, 87.8; H, 12.0; $C_{15}H_{26}$ requires C, 87.4; H, 12.6 per cent.).

* Melting points and boiling points are uncorrected; carbon and hydrogen analysis by B. R. Seetharamiah.

'Sesquiterpene B'.—(Found: C, 87.93; H, 11.28, $C_{15}H_{24}$ requires C, 88.24; H, 11.76 per cent.).

Reactions of the solid m.p. 103–04° isolated from Iswariberu oil.—(Found: C, 82.1%, H, 11.9, $C_{15}H_{26}O$ requires C, 81.1; H, 11.7 per cent.).

Dehydration.—3 g. of the above solid was thoroughly mixed with 2 g. of fused potassium bisulphate and heated at 180–90° for 30 minutes. The reaction mixture was taken up in water and extracted with ether. It was then worked up in the usual way. The product obtained was purified by distilling twice over sodium. The physical constants of the hydrocarbon (Yield, 1.2 g.) thus obtained are given in Table VI (Found: C, 87.84; H, 11.04, $C_{15}H_{24}$ requires C, 88.24; H, 11.76 per cent.). 0.6 g. of the hydrocarbon on sulphur dehydrogenation for one hour at 195–200° gave 51 mg. of a deep blue azulene which gave a T.N.B. adduct m.p. 150–51°.

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