ESSENTIAL OIL FROM THE BERRIES OF *JUNIPERUS COMMUNIS* LINN.

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SUMMARY

The essential oil from the berries of *Juniperus communis*, grown in certain parts of the East Punjab, and locally known as 'Hauber', has been found to contain *d*-α-pinene as the major constituent. The present findings, which are in agreement with the composition of normal juniper-berry oil of non-Indian origin, differ from the observations of Simonsen,[1] according to whom this oil consisted mostly of *d*-sabinene.

On one occasion, during the study of some Indian essential oils, the author needed a genuine sample of *d*-sabinene. According to Simonsen[1] a convenient source for this terpene was the essential oil from the berries of Indian *Juniperus communis*. Attempt was, therefore, made to isolate *d*-sabinene from this source. Unfortunately, no sabinene could be isolated from the genuine oil examined by the author. On the contrary, the oil was found to contain *d*-α-pinene, as the major constituent. As Simonsen's results are likely to mislead other workers also, it is thought necessary to put our observations on record. It will be seen, from what follows, that the present oil resembles normal juniper-berry-oil from non-Indian origin.

The berries, used in this investigation, were obtained from certain parts of the Hoshiarpur District of the East Punjab and were identified as the berries of *Juniperus communis* at the Forest Research Institute, Dehra Dun, through the courtesy of Dr. S. V. Puntambekar. These berries were in the semi-dry condition, having a dark-red appearance and a characteristic odour. The essential oil was isolated by distilling the crushed berries with water in an yield of 0·83 per cent. It is a faintly yellowish oil, with a characteristic smell. Its physico-chemical constants are recorded in Table I. Side by side the constants of the oil examined by Simonsen, and those of the European Juniper berry oil[2] are also given for comparison.

The mono-terpene portion of the oil was first separated by distilling the oil under reduced pressure. Thus about 85 per cent. of the oil was obtained between 103–10°/125 mm. This was redistilled under atmospheric pressure when a fraction (*a*) consisting 71 per cent. of the oil was

TABLE I

Constants	Indian Juniper Berry Oil		European Juniper Berry Oil[2]
	Present Oil*	Simonsen's Oil[1]	
Density ..	$D_4^{27°}$, 0·9180	$D^{30°}$, 0·8788	0·865 to 0·890
Refractive Index ..	$n^{25.5}$, 1·4820	$n^{30°}$, 1·4780	1·4750 to 1·4880
Optical Rotation ..	α_D, +20·8°	Could not be determined as the oil was deeply coloured	−3° to −20°
Acid Value ..	4·7	5·9	1 to 4
Ester Value ..	20·5	21·2	2 to 8
Saponification Value after acetylation ..	..	49·1	15 to 25

* The constants recorded in this column are those of a sample of the present oil which remained lying for about two months after the steam distillation.

obtained at 154–55°/750 mm. and the rest (*b*) of this portion boiled in a wide range of 155–80°/750 mm. Fraction (*a*) was distilled over sodium in order to remove any oxygenated impurity. The analysis of the distilled product corresponded to the formula, $C_{10}H_{16}$ of a terpene. It was found to possess the following properties: $D_4^{34°}$, 0·8488; n^{34}, 1·4635, α_D, + 29·72. It forms a nitroso-chloride, m.p. 110° and a nitrol benzyl amine, m.p. 122°. These observations suggested that fraction (*a*) consisted of *d*-α-pinene. This was confirmed by taking the mixed m.p.'s of the above derivatives with the corresponding authentic derivatives of *d*-α-pinene when no depression in their m.p. was observed.

The portion boiling in the range, 155–80°/750 mm. did not give the terpinene hydrochloride indicating the absence of sabinene, reported by Simonsen.

The non-mono terpenic portion of the oil was insufficient for a thorough study and was therefore not examined.

The difference in the composition of the present oil and that examined by Simonsen might possibly be due to the difference in the botanical origins of the two oils.

EXPERIMENTAL

Isolation of the essential oil.—The essential oil was obtained by distilling the crushed berries (1 kilo) with water. The oil (8·3 g.) separated from the aqueous distillate as a light yellowish layer which was removed and dried over anhydrous sodium sulphate. Yield, 0·83 per cent.

Fractionation of the oil.—The oil (28 c.c.) was first separated into two parts: (i) the mono-terpenic portion (24 c.c.), b.p. 103–110°/125 mm.; and (ii) the higher boiling portion (4 c.c.).

The mono terpenic portion (24 c.c.) was then redistilled under atmospheric pressure and the following fractions were collected:

Fraction	B.P.	Yield	Percentage in oil
A	154–55°/750 mm.	20 c.c.	71
B	155–80°/750 mm.	3·4 c.c.	12

Identification of pinene in fraction A.—Found: C, 88·10; H, 11·65; $C_{10}H_{16}$ requires C, 88·23; H, 11·76 per cent.

Formation of nitroso-chloride.—To the fraction (10 c.c.), dissolved in glacial acetic acid (10 c.c.) and cooled to 0°, amyl nitrite (20 c.c.) was added gradually. After cooling the mixture thoroughly in a freezing-bath, hydrochloric acid (40 c.c., 2 parts acid and 1 part water) was added dropwise. On standing, the nitroso chloride separated. This was purified by dissolving in chloroform and then reprecipitating it with methanol. By repeating this operation several times the m.p. of the product rose from 106° to 110° and did not rise further. Mixed m.p. with the nitroso-chloride of pinene (m.p. 110°) was the same.

Formation of nitrol benzyl amine.—The nitroso chloride (·5 g.) was dissolved in the least amount of alcohol and an alcoholic solution of benzyl amine (0·3 g.) was added, and the mixture warmed on the water-bath for five minutes. The reaction product was poured into water and the white solid which separated, was recrystallised from dilute alcohol, m.p. 122° mixed m.p. with α-pinene nitrol benzyl amine m.p. 122°, remained undepressed.

Fraction B.—The fraction (1 c.c.) dissolved in ether (5 c.c.) and chilled in ice, was saturated with dry hydrochloric acid. On removal of the solvent under suction an oily residue was obtained which did not give any solid on cooling.

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REFERENCES

1. Simonsen .. *Indian Forest Records*, 1924, **12**.
2. Parry .. *The Chemistry of Essential Oils and Artificial Perfumes*, 4th Edn., 1921, **1**, 34.