ESSENTIAL OIL FROM THE LEAVES OF "*ANNONA SQUAMOSA* LINN."

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SUMMARY

The essential oil from the leaves of *Annona squamosa* Linn. has been shown to consist of α-pinene (7%); one unidentified monocyclic terpene (4%); β-caryophyllene (50%) and two bicyclic sesquiterpene hydrocarbons giving cadalene on dehydrogenation (5·0% each).

Annona squamosa Linn., a handsome tree about six metres high, is a native of West Indies and is cultivated throughout India. It is also known as *Sitaphal.*[1]

The green leaves collected locally during the month of May 1952, on steam distillation gave an essential oil in 0·08% yield. The oil was green in colour which did not change on exposure to light, and had a pleasant smell and a bitter taste.

The essential oil (225 g.) on careful and repeated fractionation in a Tower's Distillation Column furnished five main fractions. The physical constants of the various fractions obtained are recorded in Table I.

Fraction I which constituted about 7·3% of the oil has been shown to consist essentially of α-pinene, by the preparation of the characteristic derivatives. The optical rotation is low which may be due to the presence of other optically active isomers.

Fraction II which formed 4·4% of the total oil has been shown to consist of a monocyclic terpene. Perbenzoic acid titration gave the value of 0·1 number of double bonds in one hour and 0·96 number of double bonds in 48 hours indicating the presence of one exocyclic double bond. On ozonolysis formaldehyde was formed which was identified as formaldimethone, m.p. 188°. It did not form any characteristic derivatives of monocyclic terpenes.

Fraction III, as indicated by the physical properties and the ready formation of the blue nitrosite is chiefly composed of β-caryophyllene. This was confirmed by the preparation of other derivatives of β-caryophyllene (Table III).

Fraction IV has been shown to be a sesquiterpene hydrocarbon by an elemental analysis and other properties. Perbenzoic acid titration indicated the presence of two double bonds, 1·990 number of double bonds were obtained after 36 hours. Dehydrogenation with selenium gave cadalene and an unidentified azulene.

Fraction V, from its physical constants and elemental analysis has also been shown to be a sesquiterpene hydrocarbon. It gave cadalene on dehydrogenation with selenium. Titration with perbenzoic acid gave an equivalent of 1·120 number of double bonds after half an hour while after 40 hours the value was 1·9. These results show the presence of two double bonds, one of which may be the easily reacting endocyclic double bond and the other probably exocyclic[2].

EXPERIMENTAL

Essential Oil.—The green leaves, 1,000 lb., were steam distilled in batches in a still with a capacity of 300 lb. of leaves using steam at 30 lb./sq. in., when the essential oil (300 g., 0·08% yield) was obtained. The physical and the other chemical constants of the oil were determined according to the standard methods,[3] after centrifuging and drying the oil over anhydrous sodium sulphate. The constants are as follows:

> $d_{4°}^{26°}$ 0·91104; n^{27} 1·4995; α_D^{25} −2·5; Acid value 1·5; Ester value 45·2; Acetyl value 3·31; Solubility in alcohol 4·0 volumes and Iodine value 205·0.

Fractionation.—A batch of the essential oil (225 g.) was carefully fractionated through a glass helices packed column of the total condensation variable take off type (J. W. Towers & Co., Ltd.). Five fractions were collected with an approximate reflux ratio 1 : 10. The properties of the various fractions are recorded in Table I.

Identification of α-pinene.—This fraction was refractionated thrice in an Emil Greiner's column in order to obtain it free from β-pinene (Found: C, 88·20; H, 11·65. $C_{10}H_{16}$ requires C, 88·24; H, 11·76 per cent.).

The crystalline derivative like nitrosochloride,[4] nitrol-benzylamine and pinonic acid[5] were prepared. The results are summarised below in Table II.

Identification of β-caryophyllene.—The evidences for the identification of β-caryophyllene in *Annona squamosa* oil are summarised in Table III.

The blue nitrosite was prepared according to the standard method. It was further characterised by the preparation of nitrolbenzylamine. The

TABLE I

No.	b.p.	Density	Ref. Index	Optical Rotation	Wt. in gm.	% Yield
I	66–68°/28 mm. ..	d_4^{26} 0·86095	n^{26} 1·4675	α_D^{26} +18·0	12·5	7·3
II	77–78°/28 mm. ..	$d_4^{26\cdot5}$ 0·8655	n^{26} 1·4755	α_D^{26} −29·5	7·5	4·4
III	112–113°/8·5 mm.	d_4^{24} 0·8995	n^{26} 1·49625	α_D^{23} −9·0 to −9·35	85	50·35
IV	105–106°/5·0 mm.	d_4^{24} 0·91304	n^{23} 1·5055	α_D^{20} +4·4	9·2	5·4
V	113–115°/2 mm. ..	d_4^{24} 0·9224	n^{23} 1·506	α_D^{24} +50·0 to +55·6	9·0	5·3
VI	Above 120°/1 mm.	..	..	..	25	..
	Residue ..	..	..	..	30	..

TABLE II

Properties	α-Pinene		Fraction I
	Hawkins, Fuguitt[6]	Dupont, Desalbers[7]	
B.p.	52·2°/20 mm.	156°/760 mm.	66–68°/28 mm.
Density	d_4^{15} 0·8542	$d^{15°}$ 0·8620	d_{26}^{26} 0·86095
Ref. Index	n_D^{12} 1·4631	$n_D^{12°}$ 1·4650	n^{26} 1·4675
Optical Rotation	α_D^{25} +34·07	α_D+48·85	α_D^{26} +18·0°
Molecular Refractivity ..	43·86 calc.	..	43·9
M.p. of nitrosochloride ..	110°	..	108° C.
M.p. of nitrolbenzylamine ..	122–123°	..	122°
M.p. of pinonic acid ..	68°	..	67–68° C.

TABLE III

Properties	β-Caryophyllene	Fraction IV
B.p.	103–103·5°/4 mm.[8]	112–112·5°/8·5 mm.
Density	$d^{20°}$ 0·9075[8]	$d_{4°}^{24°}$ 0·8995
Ref. Index	$n_D^{20°}$ 1·4995[8]	$n^{25°}$ 1·49625
Optical Rotation	$[\alpha]_D -8\cdot16$[8]	α^{23} −9·35
Molar Ref.	66·16[8]	66·42
M.p. of nitrosite	110°[9]	110°
M.p. of nitrosochloride	175°[10]	174°
M.p. of nitrolbenzylamine	172°[11]	172°
M.p. of β-caryophyllene alcohol	94–96°[10]	95°
M.p. of iodonitrosite	126°[9]	125°

caryophyllene alcohol was prepared according to the method of Asahina and Tsukamoto.

Fraction IV.—This fraction was twice refractionated in an Emil Greiner's column. (Found: C, 88.2; H, 12·1. $C_{15}H_{24}$ requires C, 88.16; H, 11.84 per cent.). It did not form nitrosochloride and nitrosite derivatives.

Dehydrogenation.—The hydrocarbon (1 g.) was heated with selenium (2 g.) in a long necked distillation flask (5 c.c.) with side tube plugged and carrying an air condenser for 20 hours at 290-300° and for another 15 hours at 300–310°. The product was then distilled off under reduced pressure when a deep violet liquid (0·65 g.) was obtained.

The azulene and cadalene were separated according to the method of Sukh Dev and Guha.[12] The cadalene was identified as cadalene picrate m.p. 114° and azulene could not be identified.

Fraction V : Presence of a cadinenic sesquiterpene.—The fraction V (1·0 g.) and selenium (2·0 g.) were heated together for 36 hours at 300–310° C. when no more hydrogen selenide was evolved. The product was worked up in the usual way. The cadalene was identified as its picrate, m.p. 114° C. Mixed melting point with an authentic sample remained undepressed.

Further studies towards the structure of this hydrocarbon are in progress.

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REFERENCES

1. Kirtikar and Basu .. *Indian Medicinal Plants*, 1933 Ed., **1**, 66.
2. Kolthoff and Lee .. *J. Polymer Sci.*, 1947, **2**, 206.
3. Guenther .. *The Essential Oils*, 1948, **1**.
4. Wallach and Otto .. *Liebigs Ann.*, 1888, **245**, 251; *Ibid.*, 1889, **253**, 251.
5. Thurber and Roll .. *Ind. Eng. Chem.*, 1927, **19**, 739.
6. Hawkins, Fuguitt, Stallcup .. *J.Am.C.S.*, 1942, **64**, 2928.
7. Dupont and Desalbers .. *Bull. Soc. Chem.*, 1923, IV, **33**, 1252.
8. Naves and Perrottet .. *Helv. Chem. Acta.*, 1941, **24**, 789.
9. Sukh Dev and Guha .. *J.I.C.S.*, 1949, **26**, 319.
10. Wallach and Walker .. *Annalen*, 1892, **272**, 288 ; *Chem. Abst.*, 1922, **16**, 3312.

    Asahina and Tsukamoto .. *J. Pharm. Soc. Japan*, 1922, 463.
11. Deussen and Lewisohn .. *Ann.*, 1908, **359**, 245.
12. Sukh Dev and Guha .. *J.I.C.S.*, 1949, **26**, 269.