The Oleo-resin from Dipterocarpus Indicus.

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In a previous paper (K. Sitaram Iyer and J. J. Sudborough this Vol. p. 29) attention has been drawn to the fact that when the oleo-resin derived from the common S. Indian tree, *Hardwickia Pinnata*, is steam distilled a volatile oil is obtained which contains appreciable amounts of caryophyllene. The properties of the oil are almost identical with those of Copaiba oil and the suggestion was made that the oil might be used in medicine as a substitute for Copaiba oil.

In August 1917 two samples of the oleo-resin obtained by tapping the tree known locally as Dhuma *(Dipterocarpus Indicus)* was submitted to us by the Conservator of Forests, Mysore, for examination. *Dipterocarpus Indicus* is a lofty evergreen tree which occurs in the forests of Konkan, Kanara, Malabar and Travancore and is the wood-oil tree of Western and Southern India.

The oleo-resin is obtained by a process of tapping and when mixed with white dammar (the resin from *Valeria Indica* and known as Piney Varnish, Indian Copal or Malabar tallow) is sold as a crude varnish.

The ordinary wood-oil or Garjan balsam of India is obtained from different species of Dipterocarpus, chiefly in Burma and the Andaman islands. The species mainly used for this purpose appear to be *D. laevis*, *D. tuberculatus* and *D. turbinatus*. This oleo-resin has been examined at various times; Hooper (Report Lab. Ind. Mus. 1906-07 :) has pointed out that different samples differ appreciably as regards both specific gravity and per centage of volatile oil.

The chief characteristics of the wood oils from Burma and the Andamans appear to be :—

(a) When steam distilled they yield a volatile oil consisting mainly of sesquiterpenes and thus resembling the volatile oil from *Hardwickia Pinnata*. The volatile oil is, however, free from caryophyllene, one of the chief constituents of the oil from *Hardwickia Pinnata*, and consists essentially of two isomeric hydrocarbons termed α & β gurjunenes. (Deussen, *Liebig's Annalen* 1910, *374*, 105).

The α-gurjunene is a bicyclic hydrocarbon, boils at 119°/12 mm. and is strongly laevo-rotatory. β-Gurjunene is tricyclic, has b. p. 122.5—123.5°/12 mm. and is feebly dextro-rotatory.

According to Schimmel & Co. (Report Apl. 1913 p. 68) the oleo-resins obtained from *D. turbinatus* and *D. tuberculatus*, Roxb. are quite different and yield volatile oils with somewhat different properties, *e. g.* the oil from *D. turbinatus* has D 15°=0·9271 and $\alpha_D = -37$ whereas the oil from *D. tuberculatus* has D 15°=0·9001 and $\alpha_D = -99{\cdot}5^\circ$.

(b) The oleo-resin has the property of coagulating or setting when heated for sometime at about 100—150° C.

Our examination of the Dhuma oleo-resin shows that the product is intermediate between the oleo-resins from Hardwickia Pinnata and from the ordinary species of Dipterocarpus. It yields a volatile oil with constants very similar to those for the Hardwickia volatile oil and this oil, like the Hardwickia oil, contains α-caryophyllene. The oleo-resin on the other hand, coagulates when heated, and on removal of the volatile oil gives a much harder resin than does Hardwickia Pinnata. The low acid value of the resin indicates its relationship to that derived from Burmese species of Dipterocarpus rather than to Hardwickia.

A. Properties of the Oleo-resin.

The oleo-resin is an opaque, grey fluid, which when left to stand for some time, separates into two distinct layers, the upper of which is a thick, viscid fluid of a dark reddish brown colour, and transparent when placed between the eye and the light. The lower stratum consists of a thick, dirty white substance. The former has a feeble copaiba odour, and a bitter aromatic taste. The oleo-resin is readily soluble in all the ordinary organic solvents, is almost insoluble in concentrated ammonium hydroxide and is only sparingly soluble in dilute sodium hydroxide solution ; with concentrated sulphuric acid it gives a deep red solution and with nitric acid yields a brown resin. When heated on a water bath, it changes its appearance from a dirty yellow, opaque to a clear brownish yellow transparent liquid; on continued heating on the water bath, it gelatinises and does not recover its fluidity when cold.

The following values have been obtained for the two specimens of the oleo-resin :—

	Smaller	Larger	Larger*
Acid value ...	12·6	12·3	11 6
Saponification value ...	16 3	15 8	14·9
Saponification value after acetylation	48 2	48·5	50·4

The percentage of volatile oil present in the oleo-resin was determined by heating five gms. in an air bath at 120°C until the weight was constant. The total volatile matter thus determined from the first sample was 67·85%.

For comparison the values usually given for Garjan resin and Copaiba balsam are mentioned below :—

	Garjan†	Copaiba††
Acid value	5·0—10·0	33·1 -81 5
Saponification value. ...	10·0—20·0	49·0—94 3
% of volatile oil .	40·—70	41·8—62·4

From these results it is clear that the oleo-resin from *Dipterocarpus Indicus* more closely resembles Garjan than Copaiba balsam.

B. Isolation and properties of the Volatile oil.

The volatile oil was isolated both by ordinary steam distillation and also by means of super-heated steam; in both cases the oil was obtained in the form of an emulsion from which the oil gradually separated. The portion still emulsified was cleared partly by heating and partly by filtration.

When super-heated steam was used the oil which distilled over towards the end had a faint bluish tinge.

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* These constants were determined without heating the oleo-resin on the water bath, while the former two are after heating it on a water-bath.

† K. Dieterich Analyse der Harze, 1900, p. 68.

†† Umney and Bennet, *Pharm. J.* 1901.

The volatile oil is colourless, has a characteristic resinous odour resembling that of the oil from *Hardwickia Pinnata*. It has a faintly acidic reaction and a pungent taste. When distilled under atmospheric pressure it begins to boil at 247°/682 mm. the greater part passes over at 250°—254° and the temperature then rises gradually to 256° after which slight decomposition occurs as the distillate acquires a burnt odour, and a small amount of viscid yellow oil remains in the flask.

The following constants were obtained for the two samples of volatile oil :—

	Small quantity.	Large quantity.	Caryophyllene
Sp. gr. at 20°C*	0·9071	0·9041	0·9034
Refr. Ind. at 20 C°†	1·5003	1·5005	1·4998
Rotation in 100 mm. Tube	10·9° at 27·7°	10·9° at 26·1°	9·0°
Range of b. p. at ordinary pressure...	247-266°/682 mm.	247-266°/682 mm.	258-259°/752 mm.
Range of b. p. at reduced pressure ...	146-161°/42 mm.	143-160°/33 mm.	136-137°/20 mm.
Acid value ..	2·00	1·93	Nil.
Saponification value	2·6	2·0	Nil.
Saponification value after acetylation ...	55·5	9·5	Nil.

When distilled under ordinary pressure, four to five fractions were collected. The following are the values obtained for two of the main fractions which were almost colourless :—

Fraction	%	D 20°	$N_D 20°$	α_D (100mm. tube)
250-252°/682	57	0·9051	1·4998	9·8° at 27°
252-254°/682	16	0·9058	1·4999	8·9° at 27°

When distilled under reduced pressure 90-93 % of the oil comes over within 6° namely 146-153°/33 mm.

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* ·0005 is the correction per degree for sp. gr.

† ·00036 Do Do refr. index.

The following values were obtained as the result of one distillation :—

Fraction No.	b. p.	%
1.	143—147°/33 mm.	2·0
2.	147—150°/33 mm.	13·0
3.	150—152°/33 mm.	73·0
4.	152—153°/33 mm.	6·0
5.	153—160°/33 mm.	4·0
Residue in the flask		1·5
Loss		0·5
		100·0

When the first fraction was distilled under atmospheric pressure 72% passed over at 251—253°/685 mm. The last fraction when redistilled under reduced pressure gave 63% boiling at 146—152°/30 mm.

The following are the numbers for the above two redistilled fractions from Nos 1 and 5 and for the main fraction No. 3.

Fraction No.	b. p.	$D^{20°}$	$N_D^{20°}$	D (100 mm. tube)
1.	251-253°/685 mm.	0·9051	1·4996	—9°·64 at 29°
3.	150-152°/33 mm.	0·9017	1·5002	—11°·03 at 27°·5
5.	146-152°/30 mm.	0·9147	1 5003	—11°·96 at 28°·C

The fractions Nos. 2 and 3 boiling respectively at 147-150° and 150-152°/33 mm. were refractioned and a distillate boiling at 147-149°/33 mm. obtained. This amounted to 50% of the original volatile oil and had the following properties :—

B. P.	D^{20}	N_D^{20}	$D^{26\cdot5}$
148-149°/34 mm or 252-253°/687	0·90539	1·50005	—10·94°

These values are almost identical with those given for caryophyllene obtained from various sources and more especially for a fraction obtained from the oil of clove stems by differnet authorities, who give the following numbers :—

	B. P.	D	N_D^{20}	α_D
Wallach[1]	258—260°	0·9085 (15°)	1.50094	—
Erdmaun[2]	119—120° (9 mm) or 258—259° (752 mm)	0·9038 (15°)	—	—
Kremers[3]	—	0·9032	1·50019	8·74°
Deussen[4]	132-134° (16 mm.)	0·90346	1·49973	[illegible]·67

The presence of caryophyllenes in the volatile oil has been proved by the formation of caryophyllene alcohol, $C_{25}H_{25}OH$ by Wallach and Walker's method (Annalen, 1892, *271*, 288). The volatile oil (12·5 grams.) was heated with a mixture of glacial acetic acid (500 gram) and concentrated sulphuric acid (10 gram) for 12 hours in the water bath and a further quantity of the oil then added and the heating continued at the end of the reaction.

The mass was then steam-distilled and the later oily fractions after solidifying were pressed on a porous plate and crystallised from dilute alchol. The compound crystallised in colourless silky needless melting at 95-96° which corresponds with the melting point given by Wallach and Walker.

The presence of caryophyllene was also proved by the preparation of a nitrosate by Wallach's method (*Annalen* 1894, *279*, 391). This crude product melted at 148° and crystallised from benzene in slender needles melting at 154°, the yield being 13·5 %.

According to Deussen (*ibid* 1909, *369*, 42) the compound is the nitrosate derived from ∝-caryophyllene and its correct melting point is 162°.

As the result of an examination of the nitroso-chlorides obtained from the caryophyllene of clove-stalks, Deussen and Lewinsohn *ibid.* 1907, *356*, 2) have drawn the conclusion that the caryophyllene is a mixture of at least two isomeric hydrocarbons termed ∝ and β caryophyllene.

Estimation of β caryophyllene.

Deussen (*ibid*, 1912, *388*, 138) has described the following method for estimating the amount of β caryophyllene in

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[1] *Annalen*, 1892, *271*, 298.

[2] *Journ Prak. Chem.*, 1897, [ii], *56*, 146.

[3] *Pharm. Arch.* 1898, *1*, 211.

[4] Annalen, 1908, *359*, 246.

sesquiterpene mixtures. In a vessel protected from light but not cooled externally and containing a 10% ethereal solution of the oil nitrous fumes are passed for 2—3 hours. The voluminous precipitate of β caryophyllene nitrosite is collected, washed with ether, dried and weighed.

The caryophyllene fractions b. p. 126-127°/14 mm. and 127-128·5°/14 mm. from clove-stalks were found to contain respectively 25-27·4% of β caryophyliene. S. American copaiba oil was found to contain 2-5 per cent. and a fraction from African copaiba oil boiling at 128-129·5°/12 mm. 1 ·2 % of β caryophyllene.

We have used this method for detecting the presence of β caryophyllene in the volatile oil from D. *indicus*, but without success. No trace of precipitate was obtained and the ethereal solution when evaporated gave a yellow gum-like mass.

∼ and β-*Caryophyllene nitrosochlorides.*

According to Wallach (*Annalen*, 1892 *271*, 295) the caryophyllene from cloves stalks yields a nitrosochloride, $C_{15}H_{24}NOCl$, melting at 161-163°. Kremers and Schrimer obtained the same nitrosochloride by a slightly different method and give the melting point as 158-160°. By the action of benzylamine on the nitrosochloride these chemists obtained two isomeric nitrolbenzylamines melting respectively at 167° and 128° and hence concluded that the nitrosochloride was a mixture of two isomerides.

In 1907 Deussen (*ibid* 1907, *356*, 2) succeeded in separating the nitrosochloride prepared from the caryophyllene of clove stems and melting at 160° into two isomerides by the following process. The mixed nitrosochloride is warmed with twice its weight of absolute alcohol containing 10% of ethyl acetate for 10 minutes in a bath kept at 70°. When cold the crystals are removed and the process repeated 5 times. In this way the sparingly soluble ∼ nitrosochloride melting at 177° (corr.) is obtained as a residue, and the more soluble β compound can be isolated from the liquors as colourless crystals melting at 159°.

(For summary of the derivatives of ∼ and β caryophyllenes see Deussen, *Annalen*, 1912, *388*, 137).

We have prepared the nitrosochloride from the volatile oil of *D. indicus* by Wallach's method using amyl nitrite and also by Kremers and Schrimer's method using ethyl nitrite (Pharm. Arch. 1899, 2, 293). The yield of nitrosochloride in the different experiments varied from 10·6—11·6 per cent. of the weigat of the volatile oil. These yields are higher than those obtained obtained from the volatile oil of *Hardwickia Pinnata*, namely 7-10 per cent. The crude nitrosochloride melting at 156-158° was treated by Deussen's method and gave the following results —

	M. P.	Weight
Original	155·6—155·8	12·10
After 1st extraction	157·4—157·6	11·61
,, 2nd ,,	128·0—158·1	11·32
,, 3rd ,,	159·2—159·4	11·13
,, 4th ,,	160·4—162·6	10·94
,, 5th ,,	161·4—161·6	10·76
,, 6th ,,	162·6—162·8	10·59

The results indicate that the isolation of pure α nitrosochloride was not so successful as in Deussen's experiments As we found that the nitrosochloride was sparingly soluble in benzene the product from the 6th treatment was twice crystallised from hot benzene and was then obtained in well developed glistening rhomboidal crystals melting at 171·2°.

The 1 per benzene solution was found to be optically inactive, its identity with α caryophyllene nitrosochloride was established by its conversion into α nitrosocaryophyllene (Deussen, *ibid* 1907, *356*, 11, and 1909, *369*, 47) by the eliminatin of hydrogen chloride with the aid of sodium ethoxide. The crude product melted at 124·5-127·5° and after crystallisation from dilute alcohol it was obtained as colourless glistening plate melting at 127-128·5°.

According to Deussen the α compound melts at 128 and the β compound at 12 °.

C. *The Resin obtained after removal of the volatile oil.*

The resin is much harder than that obtained from Hardwickia Pinnata and does not soften so readily. It has a yellwish brown colour in thin sections but in the mass is dark brown. It is very brittle and dissolves readily in most organic solvents with the exception of light petroleum.

The following values were obtained.

		Hardwickia Pinnata.
Acid value	27·2	160-161
Saponification number	39·3	194-200
do after acetylation	90·2	

A comparison of these numbers with those for the resin from *Hardwickia Pinnata* indicates that there is a considerable difference in the acid and saponification numbers of the two resins. The Dipterocarpus resin also differs from that from Copaiba. (*Cf.* this vol. p. 36)

Varnishes have been made from the resin:

(a) A spirit varnish from one part of the resin and two parts of wood spirit or of ethyl alcohol.

(b) An oil varnish by using resin 2 parts, raw linseed oil 1 part, turpentine 3 parts and a little manganese borate as dryer.

The varnishes appear to be of quite good quality and to be durable.

D. *Technical uses of Oleo-resin and its products.*

The oleo-resin itself can be used as a crude varnish, but suffers from the fact that it remains sticky for some time.

The essential oil resembles Copaiba oil, and according to experiments made in the Campbell Hospital, Calcutta, the oleo-resins from both *D. indicus* and *Hardwickia pinnata* may possibly be used successfully in medicine as substitutes for Copaiba oil. The therapeutic values of the two oleo-resin are also being investigated.

The resin obtained after removal of the oil produces both spirit and oil varnishes of good quality.

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