The Oleo-Resin from Hardwickia Pinnata.

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Hardwickia Pinnata (Tamil—Kolavu, Madeyan, Sampirani; Malayalam—Shurali, Kiyavu, Kolla; Canarese—Yenne mara), otherwise known as the Malabar Mahogany, is a very lofty and handsome tree, found in the evergreen forests of Travancore, Tinnevelly, Coimbatore, Malabar, Mysore and Canara, growing to a height of about 100 feet, with a trunk of about 4 feet in diameter. It belongs to the order of the Leguminosæ and is closely related to the several species of Copaifera of South America from which the oleo-resin known as Balsam of Copaiba is tapped. The wood of the tree gives a valuable timber and is coming into use for cabinet work and furniture, for which its ornamental appearance makes it very suitable. When the tree is bored with an auger a few feet above the ground, a dark oleo-resin exudes from the heart wood. In the Pharmacographia Indica (Vol. I, p. 510) it is stated to be used medicinally in India in the place of Copaiba. This oily resin, which has the smell and taste of Copaiba, but a much darker colour, is being collected only in small quantities in South Canara and Travancore and is sold to the public at auction at an average price of Rs. 2 a gallon. It is ordinarily thinned with turpentine oil and used as a natural wood varnish. Such a varnish takes a very long time to dry and is easily decolourised by weathering. The practice in Travancore is to tap mature trees for their oleo-resin immediately before they are felled for their timber in the dry months, usually from December to May. The yield of resin is about 12 gallons for a tree 8 feet in girth and the maximum amount collected from any single tree is stated to be 40 gallons. In Mysore the trees are tapped every second or third year by cutting a notch in the trunk about 5 feet from the ground and inserting a metal tube or trough to carry the exudation into the receptacle placed at the base of the tree.

Several authorities have examined the oleo-resin and a resume of the results obtained is given by D. Hooper in the *Pharmaceutical Journal* (1907, *78*, 4) who also examined the physical constants of two samples of resin sent to the Indian

Museum, Calcutta. One of the specimens was sent from Tinnevelly and the other from South Canara. The conclusion drawn is that the characteristics of the oleo-resin of Hardwickia Pinnata are sufficiently distinct to prevent any confusion being made between it and Copaiba and Garjun Balsams.

Schimmel & Co. (Reports April 1905 and April 1907) by steam distilling the oleo-resin obtained 44 per cent of a colourless oil with the following constants:—Sp. gr. 15°=0·9062, $\alpha_D = 7° 42'$; acid number 0·85, ester number 2·88, soluble in about 5 and more volumes of 95% alcohol.

G. Weigel (*Pharm. Zentral.*, 1906, *47*, 773) states that the oleo-resin gives 48·3 per cent of resin acid, 3·2 per cent of resene and 48·5 per cent of volatile oil and concludes that the oleo-resin is analagous to Copaiba Balsam.

Experimental.

We have examined two specimens of the oleo-resin. One of these was sent by the Mysore Forest Department from the Ghats of the Hassan District in September 1916, and the other was collected by one of us in the forest near Tenmali Travancore in April 1917.

The Travancore sample was obtained from a tall tree with a girth of 9 feet and the tapping was made by means of an auger giving a bore hole 1½″ diameter and 12″ deep. The flow of oleo-resin was slow and was complete after 5 hours, the amount of resin collected being about 2 gallons.

A. Properties of the Oleo-resins.

Both specimens were thick viscid liquids of a dark brown almost black colour. In thin layers they were transparent and of a greenish yellow colour, but in thick layers the colour was deep wine red when viewed in transmitted light. The odour is not unpleasant. The oleo-resin is soluble in alcohol, ether, light petroleum, glacial acetic acid, carbon disulphide and turpentine. With concentrated sulphuric acid it gives a dark red solution, and in concentrated ammonium hydroxide it dissolves yielding a greenish coloured solution, which becomes turbid when kept. The Travancore specimen when treated with alcohol gave a small amount of green residue which was soluble in light petroleum. The oleo-resin is not completely soluble in sodium hydroxide solution.

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

	Travancore specimen.	Mysore specimen.	Hooper's values.
D 15°	1·008	0·997*	1·007—1·012
Acid value	90·2	84·6	97·2 —99·8
Saponification value ...	112·9	103·7	106 —112
Acetyl value	79·6	83·0	———
Per cent of volatile oil ...	42·7	47·0	39·5 —41·1

The volatile oil was determined by heating 5 grams of the resin* in an air bath at 120° until the weight was constant.

For comparison the values obtained by Hooper in 1907 are given and the differences between the values obtained by him and by us are small.

The values usually given for Copaiba and Garjun resins are:—

	Copaiba Balsam.†	Garjun Balsam.††
Sp. gr. 15°	0·916 —0·995	0·955—0·965
Acid value	33·1 —81·5	5·0 —10·0
Saponification value ...	49·0 —94·3	10·0 —20·0
Per cent of volatile oil ...	41·8 —62·4	40 —70

From these numbers it is clear that the oleo-resin from *Hardwickia Pinnata* more closely resembles Copaiba than Garjun Balsam.

B. Isolation and Properties of the Volatile Oil.

In the earlier experiments both samples of oleo-resin were subjected to steam distillation in the ordinary way. The removal of the oil by this method was somewhat tedious as the ratio oil steam was only 1: 40. In subsequent experiments the distillation was effected by means of super-heated steam. For this purpose we employed the following apparatus, which we have

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* 0·9926 at 22·3°.

† Umney and Bennet, *Pharm. J.* 1901.

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

used repeatedly for distilling volatile oils on the small scale with super-heated steam. The oil, contained in a round bottom flask, was immersed in a bucket containing mineral lubricating oil which was heated by a large gas burner. The flask was held down in the bath by means of a wire net work to which heavy weights were attached. The super-heating was effected by passing the steam through a coil of compo. tubing surrounding the body of the flask and also immersed in the oil bath. The steam was then led through the oleo-resin in the flask and the distilled oil and water separated in the usual way. When the oil bath was at 165° to 170° the escaping steam and volatile oil were at 135° to 140° and the ratio oil : steam was about 1 : 10 and during a part of the time even 1 : 5.

The distilled oil is practically colourless and has a characteristic resinous odour. It has a feebly acidic re-action and a pungent bitter taste. When distilled under atmospheric pressure it begins to boil at 248° under 684 mm., the greater part passes over at 248—253° and the temperature then rises gradually to 256° and a small amount of a viscid yellow oil remains. Slight decomposition occurs during the distillation and the products have a burnt odour.

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

	Travancore oil	Mysore oil	Different varieties of copaiba oil	Schimmel & Co's. values of copaiba oil	Caryophyllene
Sp. gravity at 15°C	0·931	0·908	0·903-0·908	0·900-0·910	0·903
Refractive Index at 20°C ...	1·500	1·500	1·495-1·500	—	1·4998
Rotation in 100 mm tube at 23°C ...	−1·72°	−7·86°	−7° to 21°	−8·1°	−9°
Range of boiling point at ordinary pressure	257°-271°C	257-271°C	245-275°C	—	259°C
Range of boiling point under reduced pressure	126°-132°C at 13 mm.	126-132°C at 13 mm.	—	—	—
Acid valve ...	trace	trace	nil	nil	nil
Saponification value	nil	nil	nil	nil	nil
Acetyl value ...	12·6	1·4	nil	nil	nil

When distilled under reduced pressure three fractions are obtained, the first quite colourless and the last yellow and a little viscous. The following are the numbers obtained for the different fractions :—

	1st Fraction 126 – 128°/13mm Yield 68 – 70%		2nd Fraction 128 – 132°/13mm Yield 25—27%		Residue above 132° Yield 5—6%
	Rotation at 20°C	Refractive Index at 20°C	Rotation at 20°C	Refractive Index at 20°C	Refractive Index at 20°C
Travancore oil	–4·28	1·4998	+0·79	1·5106	1·5122
Mysore oil	–8·04	1·4993	–6.78	1·4996	1·5093

The acetyl values of the volatile oil indicate the presence of an alcohol and assuming that this is a sesquiterpene alcohol $C_{15}H_{25}.OH$ the amounts present would be 5% in the Travancore oil and 0·6 per cent. in the Mysore oil. So far the alcohol has not been investigated.

The physical constants of the volatile oil closely resemble those of the sesquiterpene, carophyllene, one of the constituents of the oil of clove stems and of copaiba oil. (Compare this Vol. p. 41). The presence of carophyllene in the oil from *Hardwickia Pinnata* has been proved by its conversion into caryophyllene alcohol, $C_{15}H_{25}OH$, m.p. 95-96° by Wallach and Walkers's method (Annalen 1892, *271*, 288.) This is prepared by heating 25 grams of the volatile oil with one kilo of glacial acetic acid, 20 grams of concentrated sulphuric acid and 40 grams of water on the water bath for 12 hours, then adding a further quantity of the oil and continuing the heating. The mass is then steam distilled and the first portion of oil which distils over rejected. The latter oily fractions deposit crystals when kept, these are pressed on porous plate and recrystallised from dilute alcohol From 25 grams of the volatile oil 2 grams of crude caryophyllene alcohol m.p. 94° were obtained and these crystallised from dilute alcohol in silky glistening needles melting at 95-96°.

According to Deussen and Lewinsohn (Annalen 1907, *356*, 2: compare also Annalen 1908, *359*, 254; 1909, *369*, 41; 1910, *374*, 105; 1912, *388*, 136) caryophyllene consists of a mixture of two isomerides termed α and β carophyllenes. α-carophyllene is inactive, yields a nitrosochloride melting at 177°, a nitrosate melting at 161° and a nitrosite melting at 116°, β-carophyllene is optically active, yields a glycol melting at 1 0. 5°, a nitrosochloride melting at 159°, and having α_D =98°, a nitrosite melting at 115° and a dihydrochloride melting at 69—70°. The two isomeric nitrosochlorides can be further distinguished (a) by means of their nitrolbenzlamines melting respectively at 126—128° and 172—175°; (b) by means of the nitrosocarophyllenes formed when hydrogen chloride is removed by the action of sodium ethoxide; the α-nitrosochloride yields an inactive product melting at 128° and the β an isomeric nitrosocarophyllene melting at 120° and having $\alpha_D + 61{\cdot}8^\circ$.

According to Deussen (*ibid.* 388, 140), the presence of β-carophyllene in a sesquiterpene mixture is readily detected and the amount estimated by passing nitrous fumes (from white arsenic and nitric acid) into a 10% ethereal solution of the oil. The absorption lasts for 2—3 hours and the precipitated β-carophyllene nitrosite is removed, washed with ether, dried and weighed. This method has been employed for estimating β-carophyllene in the volatile oil from *Hardwickia Pinnata* but no insoluble nitrosite was obtained.

The nitrosochloride has been prepared from the fraction of the volatile oil boiling at 126—128° under 13 mm. pressure. The yield varied from 7—11 per cent. and the crude product melting at 156. By using Deussen's process of isolating the pure nitrosochloride (*cf.* this Vol. p. 43) and subsequent crystallisation from benzene a product melting at 161° was obtained.

The nitrosate was also prepared and after crystallisation from benzene was obtained as feathery needles melting at 153—154° (Deussen 162°).

From these results it is clear that appreciable amounts of α-carophyllene are present in the volatile oil but that the presence of β carophyllene cannot be detected.

C. The Resin.

When the oleo-resin was distilled with saturated steam the residual resin had a pasty consistency and did not set to a brittle mass unless subsequently heated in an open vessel for several hours at 160°. When superheated steam was used at a temperature of about 180° the residue on cooling set to a hard, brittle resin with a greenish yellow colour in thin layers or dark brown colour in lumps. It dissolved readily in acetone, petroleum ether, benzene, turpentine and linseed oil. The Mysore resin dissolved completely in 90 per cent. alcohol, but the Travancore resin gave a small residue.

The following values were obtained for the two specimens of resins. The values for the resins from copaiba and from chir-pines and also for ordinary colophony are also given.

	Travancore resin	Mysore resin	Resin from different varieties of copaiba	Resin from chir pines	Different varieties of colophony French or American
Acid value	162·2	160·0	68·9 to 136·3	174	173 to 186
Saponification value	193·9	200·0	130·0 to 180·8	184	179 to 193
Moisture	nil	nil	...	0.8%	...
Ash	0·05%	0·02%	...	0·15%	...
Sp. gravity	1·088	...	...	...	1·061 to 1.080
Solubility in alcohol 90%	99·2%	complete	...	...	...
M. P. of the resin	53°—56°C	53°—56°C	...	74°C	...

The usefulness of the brittle resin from *Hardwickia Pinnata* for varnish making has been examined. When mixed with 2—3 times its weight of ethyl alcohol or of wood spirits it yields a good quality spirit varnish. In dry weather this sets readily and after a short time ceases to be sticky.

A good quality oil varnish can also be obtained by heating the resin to 160—180° adding 25—30 per cent. raw linseed oil and a little manganese borate also heated to the same temperature and thinning with turpentine. When used on wood the varnish sets within 24 hours, the colour is light yellow, the lustre is good and it shows no tendency to crack.