# OIL FROM THE SEEDS OF ADENANTHERA PAVONINA. A SOURCE OF LIGNOCERIC ACID.

*By S. M. Mudbidri, P. Ramaswami Ayyar and H. E. Watson.*

The *adenanthera pavonina* (Linn.) is a moderate sized deciduous tree belonging to the order *leguminosæ*. It is sometimes known as the red-wood tree from the colour of its hard heart-wood. Vernacular names are :—Tamil, *ani kundumani* ; Kanarese, *manjetti* ; Malayalam, *manjadi* ; Burmese, *ywetgyi* ; Sanskrit, *tamra.*

It is found in the Eastern sub-Himalayan tract, the Western Ghats, Sylhet, the Andamans and Burma. It bears small, yellow, fragrant flowers ; the pods are 4-9 in. long and about 0·5 in. wide, linear and curved. They burst on the tree and the two sides coil upon drying ; each pod bears 10 to 12 shining lenticular seeds which are yellow before ripening and finally become bright scarlet and hard.

The root, bark and leaves are used in India for application to swellings and the powdered seeds are prescribed for headache, rheumatism and sunstroke. The flowers and unripe seeds are said to be of value in dyeing. The wood is very hard and heavy and is used for building purposes and for making ornaments and furniture. The seeds have long been used as weights. C. S. Brown (*The Coins of India*, p. 57) says, 'The weight of manjadi (*adenanthera pavonina* seed) about 5 to 6 grains, was used as a basis of one of the coins "fanam" in South India long before the sixteenth century.' The actual weight is usually stated to be 4 grains. A trial on 50 seeds some years old gave an average of 0·241 gm. (3·7 grains), but the variation between individual seeds was considerable. The weight of the majority (86 per cent.) was fairly uniformly distributed between the values 0·210 and 0·270 gm. but individuals differed somewhat widely, the extremes noticed being 0·128 and 0·299 gm. It appears that the adoption of the seeds as weights is not, as might be anticipated, owing to their uniformity in size, but because of their hardness and smoothness, the usual practice being to select those which are equal in weight.

## EXPERIMENTAL.

The kernel and the husk are nearly equal in weight and difficult to separate. In a preliminary experiment 175 gms. of husk were found to yield only a trace of oil when extracted with petroleum ether and therefore, subsequently, the whole seeds were crushed and used for extraction. The oil had a slightly reddish colour and a peculiar smell. The constants are given in Table I.

## TABLE I.

### *Oil from the Seeds of* Adenanthera Pavonina.

| | |
|---|---|
| Oil in the kernel | 28 per cent |
| Oil in whole seed | 14 ,, |
| Weight of kernel | 49·7 , |
| Average weight of seed | 0·24 g. |

### *Constants of Oil.*

| | |
|---|---|
| Refractive index at 60° | 1·4570 |
| Specific gravity at 15·5° | 0·9168 |
| Acid value | 0·56 |
| Iodine value | 87·9 |
| Saponification value | 181·4 |
| Unsaponifiable matter | 1·4 per cent |
| Viscosity (Redwood) | 188 sec. |
| Acetyl value | 3·4 |
| Reichert-Polenske value | 1·22 |
| Polenske value | 0·24 |

### *Constants of Mixed Fatty Acids.*

| | |
|---|---|
| Solidifying point (titre) | 58·4° |
| Refractive index at 60° | 1·4541 |
| Mean molecular weight | 301 |
| Unsaturated acids | 64 per cent. |
| Mean molecular weight of unsaturated acids | 286 |
| Saturated acids | 36 per cent. |
| Mean molecular weight of saturated acids | 328 |
| Iodine value of unsaturated acids | 111 |
| Hehner value | 95·5 |

The iodine value shows that it is a non-drying oil. The low saponification value of the oil and the high molecular weight and titre of the mixed fatty acids indicate the presence of an acid with a high molecular weight. A second preparation of the oil had a specific gravity of 0·9157 and an iodine value of only 81.

*Refining.*—The oil was refined by treatment with 10 per cent. sodium hydroxide solution in slight excess of the amount required to neutralise the free acid at 70°. The small quantity of soap formed was removed by washing with hot water. The oil was dried by heating to 110° and agitated for 15 minutes with 5 per cent. of its weight of fullers' earth at 70°; after filtering it had an acid value of 0·08 and was colourless, but the odour remained.

*Hydrogenation.*—The refined oil was reduced at 180° with 5 per cent. nickel kieselguhr catalyst (Cf. *J. Indian Inst. Sci.*, 1922, 5, 62). At regular intervals samples of oil were removed, filtered from the catalyst and determinations made of the iodine value and refractive index. The last was measured on an Abbé refractometer at a temperature not far removed from 60° and the results calculated to 60° taking 0·00037 as the change per degree. The results are given in Table II.

## TABLE II.

*Relation between Iodine Value and Refractive Index.*

| No. of Sample | Iodine value (Winkler) | $n_D^{60^\circ}$ observed | $n_D^{60^\circ}$ calculated $1{\cdot}4472 + \mathrm{I.V.} \times 10^{-4}$ | Difference | Time of hydrogenation, minutes |
|---|---|---|---|---|---|
| Original | 87·9 | 1·4570 | 1·4560 | 10 | ... |
| 1 | 87·5 | 1·4569 | 1·4560 | 9 | 5 |
| 2 | 82·6 | 1·4560 | 1·4555 | 5 | 10 |
| A.1 | 81·2 | 1·4559 | 1·4553 | 6 | 10 |
| A.2 | 69·9 | 1·4543 | 1·4540 | 3 | 20 |
| 3 | 65·6 | 1·4538 | 1·4538 | 0 | 30 |
| A.3 | 39·2 | 1·4510 | 1·4511 | 1 | 45 |
| 4 | 29·9 | 1·4498 | 1·4502 | 4 | 60 |
| A.4 | 18·4 | 1·4489 | 1·4490 | 1 | 75 |
| 5 | 6·1 | 1·4478 | 1·4478 | 0 | 90 |
| A.5 | 2·5 | 1·4474 | 1·4474 | 0 | 105 |
| 6 | 1·6 | 1·4473 | 1·4474 | 1 | 120 |
| A.6 | 0·2 | 1·4472 | 1·4472 | ... | 135 |

The shape of the curve connecting iodine value and refractive index is very like those for cashew kernel, cotton-seed, mohua and similar oils; the refractive index of the completely hardened oil, 1.4472, is however higher than the value for a normal oil 1·4468, again indicating the presence of an acid of high molecular weight.

*Unsaponifiable Matter.*—50 gms. of the oil were saponified and the soap completely dried and extracted with ether for 12 hours, 0·16 gm. of unsaponifiable matter being obtained. A portion was recrystallised three times and yielded crystals melting at 134·5–135° corresponding to sitosterol, the sterol being estimated by making the insoluble digitonin compound and found to comprise 46 per cent. of the unsaponifiable matter. The acetyl derivative was also prepared and after four crystallisations melted at 125·5–126° corresponding to sitosterol acetate.

*Composition of the Oil.*—The separation of the saturated and the unsaturated acids was effected by a slight variation of Twitchell's method (*Ind. Eng. Chem.*, 1921, **13**, 806). The mixed fatty acids (5 gms.) freed from unsaponifiable matter were dissolved in 40 c.c. of 95 per cent. alcohol and heated to boiling. On adding 1·5 gms. of lead acetate dissolved in 60 c.c. of boiling 95 per cent. alcohol the precipitate did not dissolve even on continued boiling. The solution was cooled at 15° for 6 hours when the precipitate was removed, washed with alcohol and again treated with 100 c.c. of boiling 95 per cent. alcohol containing 5 gms. of acetic acid. Contrary to usual experience the precipitate did not dissolve completely. It was therefore filtered, washed with hot alcohol and decomposed with hydrochloric acid. The liberated acid melted at 80·3° and had a mean molecular weight of 368 showing it to be lignoceric acid.

In subsequent separations acetic acid was added with the lead acetate and the lead salt insoluble in hot alcohol filtered and decomposed separately. The filtrate was treated in the usual way to separate the saturated and unsaturated acids, 64 per cent. of the total acids being found unsaturated with an iodine value of 111. The saturated acids had an iodine value of only 0·3 and were thus practically free from unsaturated acids.

*Unsaturated Acids.*—The acids (4 gms.) were treated with slight excess of bromine in 100 c.c. of dry ether and cooled to 0°, but hexabromide was not formed, showing the absence of linolenic acid. Excess of bromine was removed with sodium thiosulphate and the bromides obtained after washing and drying the solution and evaporating the ether. The product was separated into three fractions by treatment with petroleum ether (b.p. 40–60°). The first two fractions were almost pure linoleic tetrabromide as shown in Table III.

## TABLE III.

*Analysis of Unsaturated Acids.*

| | I | II |
|---|---|---|
| Acids brominated, gms. ... ... ... | 4·015 | 3·98 |
| (*a*) Insoluble in hot petrol ... ... ... | 1·005 | 0·875 |
| M. p. after crystallisation ... ... ... | 113·5° | 113° |
| Bromine content... ... ... ... | 53·0 | 52·4 |
| (*b*) Insoluble at 0° ... ... ... ... | 0·855 | 0·77 |
| M. p. after crystallisation ... ... ... | 113° | 113·5° |
| Bromine content ... ... ... ... | 52·7 | 52·5 |
| (*c*) Soluble at 0° ... ... ... ... | 4·995 | 5·13 |
| Bromine content ... ... ... ... | 37·0 | 37·4 |
| Linoleic tetrabromide ... ... ... | 4·5 per cent | 7 per cent. |
| Oleic dibromide ... ... ... ... | 95·5 ,, | 93 ,, |
| Total oleic acid ... ... ... ... | 76·5 ,, | 77·6 ,, |
| Total linoleic acid ... ... ... ... | 23·5 ,, | 22·4 ,, |

The mean percentage of oleic acid is thus 77·0 and linoleic acid 23·0. Calculated from the iodine value of the unsaturated acids these percentages are, 76·7 and 23·3 respectively, a good agreement.

*Saturated Acids.*—A preliminary examination of the saturated acids present was made by reducing 150 gms. of the oil to zero iodine value, liberating the free acids and converting into the methyl esters. These were fractionally distilled at 8 mm. pressure and determinations made of the mean molecular weight, titre of the esters and melting points of the acids for each fraction. From these the composition could be deduced, but owing to the large amount of stearic acid resulting from the reduction of the unsaturated acids, the resolution into definite binary mixtures was somewhat uncertain and consequently the results are not given in detail. A large quantity of mixed acids is now available and this will shortly be examined.

The first fraction of methyl esters after redistilling, cooling to 18° and removal of the solid, gave an ester with a molecular weight of 240, from which an acid was obtained melting at 54°. This corresponds closely with methyl myristate (M.W. 242; acid m.p. 54°).

Fifteen other fractions yielded mixtures of the esters of palmitic, stearic and lignoceric acid in varying proportions, the final percentage composition being as shown in Table IV. This table also gives the calculated composition of the original oil making use of the data in Tables I and III regarding the quantity and composition of the unsaturated acids.

## TABLE IV.

*Composition of Acids from* Adenanthera Pavonina *Oil*

| Acid | Hardened Oil | Original Oil |
|---|---|---|
| Myristic ... ... | 0·4 | 0·4 |
| Palmitic ... ... | 9·0 | 9·0 |
| Stearic ... ... | 65·3 | 1·1 |
| Lignoceric ... ... | 25·3 | 25·5 |
| Oleic ... ... | ... | 49·3 |
| Linoleic ... ... | ... | 14·7 |

The quantity of stearic acid thus found is very small and may well be due to experimental error. This acid has not so far been identified in the original oil. The most remarkable property of the oil is however, the high proportion of lignoceric acid it contains, an amount far greater than any hitherto recorded in an oil. Ground-nut oil contains only 3 per cent. and beechwood tar paraffin 10 per cent. (Hell, *Ber.*, 1880, **13**, 1713). Other substances with a high content of lignoceric acid are sphingomyelin and cerebrosides (13 per cent., Levene, *J. Biol. Chem.*, 1913, **15**, 362); the acid oxidation product of Galician paraffin wax (30 per cent., Bergmann, *Z. angew. Chem.*, 1918, **31**, 69) and carnaubon from ox-kidneys (25 per cent., Rosenheim and Maclean, *Biochem. J.*, 1915, **9**, 103).

These are not however, readily obtainable in quantity and thus the oil under consideration is perhaps the most convenient known source of the acid. The separation is readily performed and it is now possible to obtain this formerly somewhat rare material in large quantities.

*Isolation of Lignoceric Acid.*—The seeds (25 kgms.) were extracted with petrol (b.p. 100–120°) and the thick, dirty-red oil saponified with sodium hydroxide. The soap was decomposed with hydrochloric acid and the mixed fatty acids thoroughly washed. These were either filtered directly or after mixing with a small quantity of 88 per cent. alcohol.

After washing with alcohol and one digestion with the same solvent hot, almost pure lignoceric acid melting at 80° was obtained, the yield from 50 kgms. of seeds being 1·12 kgms., or 2·24 per cent. on the weight of seeds and 82 per cent. of the total acid present.

*Purification.*—The crude acid began to boil at 235° under 3 mm. pressure, but distillation was not easy to conduct owing to the blocking of the side tube by the solid acid. On converting the acid into its methyl ester with methyl alcohol containing 3 per cent. of hydrochloric acid and distilling at 3 mm. pressure, the following fractions were obtained.

| Fraction | B. p. 3 mm. | M. p. | Weight, gms. |
|---|---|---|---|
| 1 | 235-240° | 53-54·2° | 2·4 |
| 2 | 249-245 | 54-54·6 | 11·3 |
| 3 | 245-246 | 56-57 | 30·1 |
| 4 | 246-250 | 56·5-57 | 22·4 |
| residue | | 56-58 | 12·9 |

On hydrolysis, fractions 3 and 4 gave pure lignoceric acid melting at 80·5–81° after one crystallisation from 95 per cent. alcohol in which it is sparingly soluble (7·5 gms. per 100 c.c. at the boiling point), but it may be recrystallised from this solvent. A fairly pure specimen melting at 80–81° was obtained in 85 per cent. yield from the crude acid by one crystallisation. The lead salt is only slightly soluble in 95 per cent. alcohol and this property is useful in separating it from the lead salts of acids lower in the series.

*Stearin.*—On cooling at 15° for some days the oil deposited about 10 per cent. of its weight of a solid. It was thought that this might be a glyceride of lignoceric acid and consequently attempts were made to purify it.

After pressing on a porous plate a solid was obtained melting at 34° and with an iodine value of 66. It was insoluble in cold 95 per cent. alcohol and readily soluble in ether, petroleum ether, carbon tetrachloride, carbon disulphide, chloroform, ethyl acetate and warm acetone. By solution in acetone and precipitation with alcohol a small quantity of a tallow-like mass melting at 47–53° was obtained. The iodine value was 33 but the saponification value 234 did not appear to correspond with that of a glyceride. It is probable that the substance is a mixed glyceride containing oleic acid but further identification has not so far been possible.

In conclusion we wish to express our best thanks to Dr. J. J. Sudborough for advice and assistance.

## SUMMARY.

1. The seeds of *Adenanthera pavonina* yield about 14 per cent. of an oil which contains 25 per cent. of lignoceric acid.

2. The physical constants of the oil, the unsaponifiable matter and the approximate composition of the fatty acids have been determined.

*Departments of General and Organic Chemistry,*
*Indian Institute of Science,*
*Bangalore.*

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