ARGEMONE OIL.

By S. Narayana Iyer, J. J. Sudborough and P. Ramaswami Ayyar.

The plant *Argemone mexicana* Linn. (the Mexican or prickly poppy) is indigenous to Jamaica, the Caribbean Islands and Mexico and from this latter country the Spaniards brought it to Europe under the name of 'Fico del inferno'. It was introduced into India three centuries ago and is now found distributed widely in the fields and waste lands even at altitudes of 5000 feet. It is extremely common in the United Provinces and the Punjab and it is claimed that enormous quantities of seed could be collected.

The Vernacular names are:—Hindi, Bharbhana or Kutaila; Bengali, Shiel Kanta; Marathi, Daruri or Kandew; Canarese, Datturi; Tamil, Birama dandu; Malayalam, Brahma-danti.

The plant is an annual, springing up during the cold season, and is characterised by its yellow flower, prickly leaves with white veining and the yellow juice which exudes when any portion of it is broken.[1] The seeds are small, spherical and black with a rough exterior due to pits and depressions. They are about the size of rape-seed (548 = 1 gram) and are poisonous when taken in quantity. According to Hooper[2] they contain oil 36, carbohydrates, proteins and fibre 49, moisture 9, and ash 6 per cent. Bloemendal[3] gives the oil-content as 35–39 per cent. and according to Lewkowitsch[4] the seeds yield 25–30 per cent. of oil when pressed. Bhaduri,[5] on the other hand, obtained, only 22·3 per cent. of oil by extracting Indian seed with light petroleum. In these laboratories, when local seeds were crushed and extracted respectively with ether and light petroleum, the yields of oil were 34·6 and 29·4 per cent.

The oil is largely used for burning purposes and in medicine for treatment of syphilis and certain skin diseases. Its properties are those of a drying oil and it is used to a certain extent as a substitute for linseed oil in South America. It has a nauseous and acrid taste and when administered causes purging and vomiting and these characteristics preclude its use for edible and culinary purposes.

The cake is unsuitable for cattle fodder, but its composition indicates that it would form an efficient fertilizer.

Analytical data for the oil are given in Table I.

---

[1] For full description of the plant and the uses of different parts, see Kirtikar and Basu's *Indian Medicinal Plants*, p. 79.

[2] *Agric. Ledger*, 1907, 35.

[3] *Pharm. Weekblad*, 1906, 14.

[4] *Chem. Tech. Oils, Fats and Waxes*, 1922, ii. 142.

[5] *Amer. J. Pharm.*, 1914, 49.

TABLE I.

Analytical data for Argemone oil.

—	Ether extraction	Light petrol extraction	K. Bhaduri	Le Sueur and Crossley	
				1	2
Yield of oil	34·6	29·4	22·3	...	...
Solidifying point	...	...	16·17°	...	...
Sp. gr. 25°	0·9396	0·9209	0·9117 at 28°	0·9247 at 153°	0·9259 at 15·5°
Do. 100°	...	...	0·9007	...	...
n_D at 60°	1·4593	1·4601	1·4653 at 32°	1·4675	...
Saponification value ...	189	190	185·5	190·3	187·8
Iodine value	120	121	102·2	122·5	119·9
Acetyl value	...	39	27·9	...	...
Acid value	25·0	12·0	146	6·0	83·9
Reichert-Meisel value ...	...	0·3	0·61	0	0
Polenske value	...	0·2	...	...	...
Unsaponifiable matter ...	...	1·3	...	...	...
Hehner value	...	93·0	94·0	95	...
Maume test	...	...	65°	...	...

The oil obtained by extraction with ether has a reddish-brown colour, whereas that extracted by light petroleum is yellow. Both oils when refined by alkali treatment yield a product with a pale yellow colour but still retaining the characteristic odour of the raw oil.

Fatty acids from the oil.—The oil was saponified with alcoholic sodium hydroxide, the soap extracted with ether to remove unsaponifiable matter and then decomposed by hydrochloric acid (1 : 2) in an atmosphere of carbon dioxide. The analytical data for the mixed fatty acids are given in Table II, together with data for the saturated acids. The separation into saturated and unsaturated acids was accomplished by Twitchell's process [1] using 95 per cent. (by volume) alcohol, and the operation was repeated a second time.

[1] *J. Ind. Eng. Chem.*, 1921, 13, 806.

TABLE II.

Fatty acids from Argemone oil.

—	Mixed Acids	Saturated Acids	Unsaturated Acids	
			i	ii
Percentage	93·0	13·9	48·3	37·8
Titre value	23°	...	...	...
Mean molecular weight	274·1	268	277·4	273·6
Iodine value	127·9	2·6	149	135
n_D^{60}	1·4518	1·4389	1·4527	1·4526

Hydrogenating Argemone oil.—Before hydrogenation the oil was refined by treatment with the requisite amount of 10 per cent. aqueous sodium hydroxide solution in two stages. The soap was removed by filtration through cloth and the oil then well washed with boiling water, heated at 110° and finally treated with 4·5 per cent. of ignited Fuller's earth at 70–80°.

The yields of refined oil from the ether extracted and light petroleum extracted oils were respectively 55 and 70 per cent. The colour of the refined oil was pale yellow and the acid value 0·1.

The refined oil was hydrogenated in the usual manner[1] at 180° using for each 100 grams of oil 1 gram of nickel in the form of 25 per cent. nickel-kieselguhr catalyst. Samples were removed at given intervals and after filtration the refractive index was determined in an Abbé refractometer at about 60° and the iodine value determined by Winkler's method. The temperature correction for the refractive index was taken at 0·00037 per degree centigrade.

Table III gives the values for the refractive indices and iodine values together with the refractive indices calculated from the formula $n_D^{60°}$ 1·4480 + (I.V) 10^{-4}.

---

[1] *This Journal*, 1922, 5, 62.

TABLE III.

ARGEMONE OIL.

Relation between iodine value and refractive index.

No. of sample	Iodine value. Winkler	$n_D^{60°}$ observed	$n_D^{60°}$ calculated. $1·4480+(I.V.)\times10^{-4}$	Difference	Time of hydrogenation in hours
Original oil.	121·8	1·4614	1·4602	+12	...
2	108·1	1·4612	1·4588	+24	0·25
3	104·7	1·4607	1·4585	+22	0·4
4	100·2	1·4598	1·4580	+18	0·6
5	96·3	1·4593	1·4576	+17	0·75
6	90·5	1·4582	1·4571	+11	1·0
7	84·7	1·4574	1·4565	+ 9	1·25
8	80·2	1·4568	1·4560	+ 8	1·5
9	78·7	1·4565	1·4559	+ 6	1·75
10	66·7	1·4549	1·4547	+ 2	2·0
11	46·3	1·4527	1·4526	+ 1	2·5
12	36·6	1·4514	1·4517	− 3	3·0
13	26·9	1·4506	1·4507	− 1	3·5
14	13·6	1·4497	1·4494	+ 3	4·0
15	8·5	1·4494	1·4489	+ 5	4·5
	0·0		1·4480		

It will be noticed that the refractive indices for hardened samples are almost the same as for hardened samples of rape and mustard oils with the same iodine values.

This similarity of the refractive index–iodine value curves of the hardened samples of the three oils is not due to the presence in all three of glycerides of acids of high molecular weight, e.g., erucic acid, as the examination of the methyl esters derived from the completely hardened argemone oil has shown the absence of any appreciable quantities of esters derived from acids higher than stearic in the series of saturated monobasic acids. The relatively high values for the refractive indices of the original oil and of hardened samples is undoubtedly due to free hydroxyl groups, the presence of which is shown by the relatively high acetyl value of the oil.

Table IV gives the acetyl values of the original oil and of various products prepared from the oil.

TABLE IV.

Acetyl values of the oil and of various products obtained from the oil.

Original oil (crude)	41
Original oil (refined)	39
Completely hardened oil	16·2
Methyl esters of mixed fatty acids from oil	13·9
Methyl esters of liquid acids from oil	18·0
Acids from completely hardened oil	Nil.
Methyl esters of acids from completely hardened oil	Nil.

The acetyl value was determined in each case by Cook's method.[1]

From these values it is clear that rather more than one-third of the total hydroxyl is present in the unsaturated acyl groups and the remainder in the alkyl group, presumably as diglyceride. The results also show that the acyl hydroxyl undergoes complete reduction and the alkyl hydroxyl partial reduction during hydrogenation.

COMPOSITION OF OIL.

The acetyl value of the liquid acids obtained by Twitchell's method of separation indicates that all the hydroxylated acids are present in this portion. An attempt to isolate small amounts of hydroxy-acids from the solid acids by solution in ether and cooling to 0° gave negative results.

Liquid acids.—The precipitation of lead salts in the presence of 95 per cent. (by volume) alcohol was repeated twice and in this way two quantities of liquid acids were obtained. The final solid acids had an iodine value of 2·6 indicating that they were practically free from unsaturated acids. The two portions of liquid acids were examined by Jamieson and Baughman's method[2] and the results obtained are given in Table V.

The hexabromide melted at 178–180° and the tetrabromide at 113–114° and the latter contained 53·1 per cent. of bromine as compared with the theoretical value 53·3. The whole of the tetrabromide did not dissolve when warmed with 250 cc. of light petroleum (b.p. 40–60°) but the melting point and bromine content of the residue proved it to be linolic acid tetrabromide and not linolenic hexabromide.

TABLE V.

Bromides of unsaturated acids.

—	First filtrate	Second filtrate
Percentage of unsaturated acids in total acids	48·3	37·8
Grams taken for bromination	3·05	2·71
Grams of hexabromide	0·093	nil.
Grams of tetrabromide	2·94	2·28
Grams of brominated residue	2·85	2·72
Percentage of bromine in this residue	42·6	39·7

---

[1] *J. Amer. Chem. Soc.*, 1922, 44, 392.
[2] *J. Amer. Chem. Soc.*, 1920, 42, 2398; *cf.* also *This Journal*, 1924, 7, 76.

Acids from the completely hardened oil.—As the amount of saturated acids from the refined oil was so small no attempt was made to fractionate the methyl esters derived from these acids, but the acids from the completely hardened oil (iodine value = 0·5) were converted into methyl esters and these subjected to a process of fractional distillation. The completely hardened oil was saponified with alcoholic potash, the potash soaps dried and extracted with ether in a Soxhlet apparatus in order to remove unsaponifiable matter. The free acids were liberated, dried at 100° and converted into methyl esters by the Fischer-Speier method using a 4 per cent. solution of hydrogen chloride in methyl alcohol. A portion of the methyl alcohol was removed, water added and the liquid extracted twice with ether. The ethereal solution was washed with dilute sodium carbonate solution to remove unesterified acid and dried with anhydrous sodium sulphate. The results of the fractional distillation under a pressure of 10 mm. are given in Table VI.

TABLE VI.

Methyl esters from hardened oil.

Fraction No.	Weight in grams	Boiling point in degrees cent. under 10 mm. pressure
1	7·8	180–187
2	11·5	187–192
3	16·4	192–195
4	5·2	195–200
Residue	2·5	—

Each fraction was separately examined and the following values determined: (*a*) titre of the ester; (*b*) mean molecular weight of ester from the saponification value; (*c*) titre of the acids obtained from the ester; (*d*) mean molecular weight of the acids from their neutralisation value. Table VII gives the values obtained together with the percentage of methyl stearate or stearic acid on the basis that only the two acids are present. For calculating these percentages from the titre values of the esters and acids respectively the solidifying point curves of (*a*) methyl palmitate and methyl stearate and (*b*) palmitic acid and stearic acid previously given [1] were used.

---

[1] *This Journal*, 1923, 6, 126 for esters and Lewkowitsch 1921, I, 118 for acids.

TABLE VII.

Composition of ester fractions.

Fraction No.	1 Titre test	2 Mean mol. weight of ester	3 Melting point of acid	4 Titre of acid	Methyl stearate per cent. from 1	Methyl stearate from 2	Stearic acid per cent. from 3	Stearic acid per cent. from 4
1	30·15	290·1	63·0	62·0	71	72	70	71
2	33·0	293·3	66·3	65·5	84	83	85	84
3	35·2	295·2	67·5	66·5	92	90	90	88
4	36·1	297·1	68·5	67·9	96	96	95	94

The acids obtained from the first fraction were crystallised from 90 per cent. alcohol and after the separation of 2·3 grams of acids a 3rd crop of 0·8 grams was obtained with a mean molecular weight of 258 and a melting point 63·0–63·4°, and was evidently palmitic acid.

A portion of the residue (V) was crystallised three times from methyl alcohol and a product melting at 38–39° and corresponding with methyl stearate (m.p. 38·5°) was obtained. The remainder of the residue was saponified and the resulting acids crystallised twice from 90 per cent. alcohol when an acid with a melting point 68–69° was obtained. This appears to be stearic acid (m.p. 69·3°) and the isolation of this acid in the first batch of crystals indicates the absence in the residue of any appreciable amount of esters derived from acids higher in the series than stearic.

The completely hardened oil is thus a mixture containing only glyceryl palmitate and glyceryl stearate and the amount of the former calculated from the values given in Table VII is 13·9 per cent.

The mean molecular weight of the saturated acids obtained by removing the liquid acids from the total mixed acids by Twitchell's method (cf. p. 31) is 268, which corresponds with the presence of 57·2 per cent. of palmitic acid in the solid acids or 7·95 per cent. in the total mixed acids, whereas the percentage of palmitic acid in the acids from the completely hardened oil is 13·8 per cent. It is clear from these figures that the liquid acids must contain either palmitic acid, which escaped precipitation by the Twitchell process, or some acid such as palmito-oleic or hydroxypalmito-oleic acid.

In order to ascertain whether it is possible for palmitic acid, when present in a mixture of acids corresponding in composition with the mixed fatty acids from argemone oil, to escape precipitation as lead salt by Twitchell's method of separating solid and liquid acids, a mixture having the following composition was subjected to Twitchell's process using about 20 grams: palmitic 13·8, stearic 6·0, ricinoleic 49·0, oleic 14·2 and linolic 57·0 per cent. Two experiments gave concordant results, viz., 19·8 and 19·9 compared with the theoretical 19·8 per cent. It is thus clear that there is present in the liquid acids some unsaturated acid which gives rise to 5·95 per cent. of palmitic acid on reduction.

In order to obtain evidence as to the nature of this acid, i.e., whether it is palmito-oleic or hydroxypalmito-oleic, the following procedure was adopted. The liquid or unsaturated acids with an acetyl value of 16·0 were converted into their methyl esters, the latter acetylated and the product fractionally distilled. The distillation was stopped when about 60 per cent. of the esters had passed over, leaving a residue of about 40 per cent., the object being to avoid decomposition of the higher boiling esters. The following values were determined for the three fractions and the residue:—(*a*) saponification value, (*b*) neutralisation value of the acids obtained on saponification, (*c*) the calculated saponification value of the methyl ester of this acid, (*d*) acetyl value of the fraction calculated from *a* and *c* by Cook's formula, and (*e*) Calculated mean molecular weight of the acids from the saponified fraction.

TABLE VIII.

Acetylated methyl esters of unsaturated acids.

Total weight = 43·9 gram. Pressure = 7-8 mm.

1 Fraction No.	2 Boiling point in degrees C.	3 Grams	*a* Saponification value	*b* Neutralisation value of acids	*c* Calculated saponification value of methyl esters of these acids	*d* Acetyl value	*e* Mean molecular weight of acids
	190–215	1·9	195·7	204·0	194·0	nil	275
	215–220	10·0	192·5	201·7	192·0	nil	278
3	220–225	16·0	196·5	201·0	191·4	5·9	279
Residue	—	15·5	219·2	198·5	189·1	35·1	283

Fractions 1 and 2 contain no acetylated esters and fraction 1 has a mean molecular weight below that of oleic or linolic acid and since it cannot contain palmitic acid must contain palmito-oleic acid. All the acetylated esters are found in the last fractions mainly in the residue and are hence presumably acetylated methyl ricinoleate. This is clearly indicated by the high molecular weight 283 which is higher than that of linolic acid, 280, the chief constituent and much higher than that of hydroxypalmito-oleic acid, viz., 270.

Table IX gives the percentage composition of the mixed fatty acids derived from the oil. The ricinoleic acid has been calculated on the basis that the acetyl value, viz., 18, of the methyl esters of the liquid acids is due entirely to the presence of methyl ricinoleate, and the amount of palmito-oleic acid has been calculated on the basis that the difference between the palmitic acid present in the hardened acids and in the original mixed acids is due to the reduction of palmito-oleic acid.

TABLE IX.

Percentage composition of mixed acids.

Palmitic acid...	7·95.
Stearic acid	5·95.
Palmito-oleic acid	5·87.
Oleic acid	21·79.
Linolic acid	48·02.
Linolenic acid	0·58.
Ricinoleic acid	9·84.

UNSAPONIFIABLE MATTER.

The oil gave 1·3 per cent. of unsaponifiable matter when the dry potassium salts of the mixed acids were extracted with ether, and 42 per cent. of this could be precipitated as the insoluble sterol-digitonin additive compound from alcoholic solution. On crystallising a portion of the unsaponifiable matter from alcohol about 5 per cent. of a substance melting at 191–192° was obtained and from the mother liquor a sterol was deposited which, after crystallisation, melted at 137–138° and yielded an acetyl derivative melting at 125–127° and thus corresponding with sitosterol. The amount was equivalent to 35 per cent. of the unsaponifiable matter.

SUMMARY.

1. The seeds of *Argemone mexicana* (Linn.) yield 29·4 per cent. of a pale-yellow oil on extraction with light petroleum (b.p. 40–60°).

2. The curve showing the relation between the refractive indices and iodine values of hardened samples of oil is characteristic and resembles those for the rape-oils. This is not due to the presence of acids of high molecular weight such as behenic, lignoceric or erucic, but to a certain quantity of hydroxy-acids.

3. The acetyl value of the oil is about 39 and this is partly due to the presence of glycerides of hydroxyoleic acid and partly to diglycerides. The completely hardened oil still retains an acetyl value, whereas the acids or methyl esters from the hardened oil have no acetyl value.

4. The acids from the completely hardened oil are palmitic and stearic, and the mixed acids from the original oil contain palmitic, stearic, palmito-oleic, oleic, linolic, linolenic and ricinoleic acids.

In conclusion we have much pleasure in thanking Dr. H. E. Watson for valuable suggestions during the course of the work.

Department of General and Organic Chemistry,
Indian Institute of Science,
Bangalore.

[Accepted, 9-2-25.]

Printed and published by George Kenneth at the Diocesan Press, Post Box 455, Madras—1925 C7814