

SCIENTIFIC SECTION

THE OIL OF PONGAMIA GLABRA.^{1,2}

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Pongamia glabra is a tree which grows in the jungles over the greater part of India. It is known in different vernacular tongues as "pongam," "hongey" and "karanja." The tree, belonging to the *Leguminosæ*, is almost evergreen, the glabrous bright green leaves being replaced in March by new ones as rapidly as they fall. The flowers, appearing in April or May, are white and pale mauve, and are borne in racemes. The seed pod is woody and glabrous, from one-eighth to one-fourth inch thick and one and one-half to two inches in length. It usually contains one abortive and one perfect seed, the latter resembling a lima bean. The seed weighs about 1.4 grams, consists of about 5% husk and 95% kernel and has a red color becoming dark brown on storage.

The seeds contain from 27 to 33% of oil. As expressed the oil is usually thick and reddish-brown, and has been used as a burning oil and for medicinal purposes. Its therapeutic properties have been applied in the treatment of skin diseases, rheumatism and ulcers. It appears to have been used both by native apothecaries and European physicians (1). The early Sanskrit medical literature of India contains frequent references to the use of one part or another of the tree. Not only has the oil been used in medicine but also a paste of the unripe seed pulp, poultices of the leaves and the milky juice of the root bark.

The present uses of the oil are for illumination and for leather dressing. The crude oil has a bitter taste and an unpleasant odor, not removed by common refining operations, which militate against its availability as a food oil, although it can be produced abundantly and cheaply.

Lewkowitsch (2) and Grimme (3) have determined the constants of the oil as follows:

	A.	Lewkowitsch.	B.	Grimme.
Specific gravity.	0.9352	$\frac{40^\circ}{40^\circ}$	0.9240	$\frac{40^\circ}{40^\circ}$
Saponification No.	178.0		183.1	185.1
Iodine No.	94.0		89.4	77.3
Unsaponifiable	9.22		6.96	8.16
Reichert-Meissl No.		1.10
Acid No. (as % oleic acid)	3.05		0.50	21.27
Melting point of fatty acids	44.4°		43.8°

NOTE.—Sample A was prepared in Lewkowitsch's laboratory by extracting the seeds with ether; sample B was obtained from India. Grimme's oil was obtained by ether extraction.

Grimme determined the following constants for the mixed fatty acids:

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² Read before Scientific Section, at the 73rd Annual Meeting, Des Moines, Iowa, August 24-28, 1925.

³ An abstract of a thesis presented by M. C. T. Katti in partial fulfillment of the requirements for the degree of Master of Science in Chemistry in the Graduate School of the University of Illinois, 1924.

Melting point	43.8°
Freezing point	42.5°
n_D^{20}	1.4637
Neutralization value	180.1
Iodine No.	78.8
Mean molecular weight	308.7

Desai (4) by analysis of the mixed acids has determined their composition as follows:

Myristic acid	0.23%	Dihydroxy stearic acid	4.36
Palmitic acid	6.06	Linolenic acid	0.46
Stearic acid	2.19	Linolic acid	9.72
Arachidic acid	4.30	Oleic acid	61.30
Lignoceric acid	3.22	Unsaponifiable	3.56

The unsaponifiable matter was found to contain brasicasterol and sitosterol, together with an oil of high index of refraction.

EXPERIMENTAL.

Having in mind the fact that this oil can be easily produced in large amounts, the authors decided to make a study of the constants of the oil and the possibilities of refining in such a way as to remove the unpleasant odor and bitter taste. The refining operations could not be carried out on a large scale to test the commercial possibilities of the methods, but they served to indicate the direction in which large scale methods might succeed. Some interesting observations were also made on constituents of the oil and the seed.

In determining the constants of the oil two samples were used. Sample A which was obtained through the courtesy of the firm of Brahmappa Tavanappannavar, Davangere, India, was freshly expressed by means of an Anderson "expeller" three months before, and was of a bright yellow color gradually turning to orange. Sample B was from Central India and was a comparatively old sample, dark red in color.

The constants of the oil as determined by the authors for Sample A are:

Saponification No.	189.1
Iodine No. (Hanus)	89.1
Reichert-Meissl No.	1.04
Unsaponifiable matter	2.4%
Acid No. (calculated as oleic)	8.36%
Soluble acids (calculated as butyric)	1.95%
Insoluble acids (with unsaponifiable matter)	93.25%
Neutralization value of insoluble acids	196.1
Mean molecular weight of insoluble acids	286.0
Iodine No. of insoluble acids (Hanus)	92.6
Saturated acids (lead salt-ether method)	20.16% of oil
Unsaturated acids (lead salt-ether method)	69.92% of oil
Saturated acids (combination of barium salt-benzene and lead salt-ether methods)	21.30%
Unsaturated acids (combination of barium salt-benzene and lead salt-ether methods)	72.70%

For determination of the unsaponifiable matter the oil was saponified with alcoholic potassium hydroxide, and after boiling off the alcohol the soap was dissolved in water and this solution

shaken out repeatedly with ether in a separatory funnel. The ether extracts were combined and washed several times with water, finally distilling off the ether and weighing the residue.

The Acid Number was determined by shaking 20 grams of the oil with 100 cc. of neutral 95% alcohol and titrating the dissolved acid with 0.1 normal potassium hydroxide, using phenol phthalein as the indicator.

The saturated and unsaturated acids were separated according to the lead salt-ether method of Gusserow and Varrentrapp as modified by Muter and de Koningh (5). In this method the separation is not sharp due to the mutual solubilities of the two groups of lead salts, one in the other.

Farnsteiner (6) has shown that when the barium salts of fatty acids are treated with moist benzene (95% benzene, 5% alcohol of 95%) the salts of the less saturated acids dissolve while those of the saturated acids and of the oleic acid are insoluble. The second separation of the saturated and unsaturated acids was made by Farnsteiner's method. The saturated acids, including the oleic acid, were then treated by the lead salt-ether method, and the oleic acid added to the less saturated acids. During the benzene separation it was found that some of the barium oleate was dissolving in the benzene with the salts of the less saturated acids. The Iodine Number of the oleic acid was determined and found to be 86.5 (theory 90.07).

Preliminary Bleaching Experiments.—1. The oil was shaken with Lloyd's reagent, as a substitute for Fuller's earth, and filtered through paper.

2. The oil was treated with bone ash, using the same procedure as with Lloyd's reagent.

3. The oil was saturated with sulphur dioxide and allowed to stand for 24 hours, then filtered from a spongy precipitate.

4. The oil was shaken with a slightly greater volume of strong sodium hydroxide solution than was required to combine with the free acids. The residual oil was washed with water and dried with calcium chloride.

5. The oil was shaken for 90 minutes with coarsely powdered calcium chloride and filtered cold.

6. Live steam under pressure was admitted into the oil for 10 minutes, the water separated and the oil filtered.

7. The oil was mixed with cobalt oxalate, heated to 80° and oxygen bubbled through for 15 hours, then filtered.

8. Five grams of oil, 2.002 Gm. of potassium dichromate and 1 cc. of dilute sulphuric acid were shaken together in a test-tube and the oil separated.

Samples A and B were subjected to these treatments, with the following results, sample A being originally orange yellow, while sample B was dark brownish red.

	A.	B.
Experiment 1	No color change	No color change
Experiment 2	No change	No change
Experiment 3	Bright yellow	Bright yellow
Experiment 4	No change	Bright red
Experiment 5	Bright yellow	Bright yellow
Experiment 6	No change	No change
Experiment 7	No change	Bright red
Experiment 8	Light yellow	Bright yellow

Further Attempts at Refining.—The three things to be accomplished in refining this oil are, the removal of the bitter substance, the removal of the odorous principle and bleaching. The procedures attempted on a larger scale were extraction

with ethyl alcohol, treatment with alkali, blowing with superheated steam and the use of "Norit" vegetable carbon. The oil used in these experiments was freshly received from India in cans, was turbid and of a dark red color. The oil was filtered to remove suspended matter before any of the treatments mentioned were used.

A. Four hundred and fifty grams of the oil was blown with superheated steam in a 2-liter flask for 2½ hours. After separating as much water as possible from the oil 25 cc. of a 20% solution of sodium hydroxide was added with vigorous shaking and the oil filtered from the soap by means of fine cheese cloth. The filtered oil was washed with water until free from soap.

Neither the color nor taste of the oil had undergone any change, but the odor was much improved. The residual oil was then shaken with four 250-cc. portions of cold 76% alcohol. Some difficulty was met with in separating the oil and alcohol. The separated oil was somewhat lighter in color and was nearly free from the bitter principle.

The oil was then mixed with 3 grams of Norit and warmed on the steam-bath for 90 minutes with frequent shaking. After standing over night it was filtered, when no further change in color could be observed and only a slight bitter taste remained. The oil was finally shaken with three successive portions of cold 95% alcohol, 15 cc. each. The alcohol did not separate completely but left a turbid oil, which was cleared by heating on the steam-bath under a pressure of 30 mm. of mercury until the alcohol was removed. The final yield was 287 grams of orange-colored oil free from bitter taste and unpleasant odor.

B. Five hundred grams of oil was blown for five hours with steam from a line carrying 40 pounds pressure. After separating the water the oil was shaken with 20 cc. of 40% sodium hydroxide solution, then allowed to stand for eight hours, after which the oil was filtered from the soap by means of paper. The filtered oil had undergone no appreciable change in color, so was shaken six times with 350 cc. portions of cold 95% alcohol. The suspended alcohol was removed as above, and the residual oil mixed with 3 grams of Norit and warmed for one hour at 27-28° under a pressure of 20 mm. of mercury. The oil was filtered at once, obtaining 348 grams of a clear, light orange colored oil.

C. Eight hundred grams of the oil was gently shaken with 15 cc. of 40% sodium hydroxide. The yellow foots were allowed to settle and the oil filtered through cotton. In order to obtain complete recovery the foots were washed with low boiling petroleum ether from which the oil was recovered by distillation of the solvent. The oil was next shaken six times with 750-cc. portions of 95% alcohol, then treated with superheated steam for three hours, dried under diminished pressure and treated with 7 grams of "Norit." In all 709 grams of oil was recovered. The oil was bright lemon yellow in color and neither the bitter taste nor the unpleasant odor were apparent.

D. Seven hundred and fifty grams of oil was shaken six times with 750 cc. of cold 95% alcohol and the oil then blown with superheated steam for four hours. The oil was finally dried under diminished pressure and filtered. The yield of clear yellow oil was 653 grams, in which neither unpleasant taste nor odor were apparent.

E. Eight hundred grams of oil was placed in a 3-liter round bottom flask having a two-hole stopper. The stopper carried a reflux condenser and a tube reaching to the bottom of the flask and connected with a second flask containing 1500 cc. of 95% alcohol. The alcohol was distilled, the vapors bubbling through the oil and the condensed alcohol running back into the flask. After cooling the alcohol was returned to the alcohol flask and the distillation repeated, this time leaving about 200 cc. of alcohol undistilled. This residue was removed and the process repeated, making in all six extractions. The oil was finally treated with superheated steam and filtered as in D with a yield of 643 grams of oil free from objectionable odor and taste.

Where alkali refining was attempted the foots were removed with difficulty and with a potential loss of oil. The odor was most effectively improved by superheated steam. Norit treatments were of little value. When the alcoholic washings were concentrated some oil separates, but as the alcohol is largely removed the mixture again becomes homogeneous. The oil separates again on adding a little alcohol, and contains the bitter principle.

The effect of the various treatments upon the appearance of the oil and its chemical constants is as follows:

Sample.	Yield.	Color.	Taste.	Odor.	Acid No.	Iodine No.
Original		Dark Red	Bitter	Objectionable	8.06	88.3
A	63.8%	Orange	Free from bitter material	Free from objectionable odor	0.30	87.7
B	69.6%	Bright orange	"	"	0.27	88.2
C	88.6%	Lemon yellow	"	"	0.19	87.8
D	87.0%	Yellow	"	"	0.55	85.4
E	80.0%	"	"	"	0.26	86.9

The Odorous Principle of the Oil.—Since the odor of the oil was improved by treatment with superheated steam, the distillate obtained with superheated steam from 500 grams of oil was examined for a volatile oil to which the characteristic odor and taste might be attributed. About 800 cc. of distillate having the odor of the oil was obtained. This distillate was concentrated by cohobation under diminished pressure, as shown by the following table.

No.	Volume of liquid.	Temperature.	Pressure mm. Mercury.	Volume distillate.
I	800 cc.	26–29°	22–23	500 cc.
II	500 cc.	24–27°	19–20	260 cc.
III	260 cc.	24–27°	19–20	125 cc.

Residue I was turbid, yielding its turbidity to ether. On evaporating the ether 2–3 drops of oil were obtained having a pronounced odor, but not that of the oil. Distillates I, II and III were all clear, and in each the odor of the oil was intensified. Residues II and III were clear and without odor.

Thirty cc. of residues II and III and of distillate III were each titrated with 0.0999 *N* sodium hydroxide. Residue II consumed 0.27 cc., residue III 0.23 cc. and distillate III 0.17 cc.

Two drops of 0.1 *N* potassium permanganate were added to 10 cc. of each of the three solutions mentioned above, in order to test for unsaturation. Residues II and III showed no immediate reaction but in 15–20 minutes the color of the reagent was changed. Distillate III, however, instantly decolorized the permanganate. Distillate III also decolorized bromine water.

Fifty cc. of distillate III was shaken with 70 cc. of ether. The odor was completely removed from the aqueous solution. The ether layer was dried over calcium chloride, when the odor was so pronounced as to almost entirely mask the odor of the ether. The ether was evaporated in a gentle current of air but no visible residue was obtained. The pronounced odor of the oil was apparent for about four hours, but disappeared entirely.

Apparently the odorous principle of the oil is very volatile with steam and in the absence of the oil evaporates rapidly and spontaneously. It is apparently unsaturated and soluble in both water and ether, but can be completely extracted by ether from the water.

The Bitter Principle of the Oil—Preliminary Examination.—Five grams of the residue obtained by evaporating the alcoholic extract from Method A above was dissolved in 40 cc. of ether and the solution extracted with three successive portions of normal sulphuric acid. This extract did not become turbid when rendered neutral or alkaline, and yielded no precipitate with alkaloidal reagents.

The alcoholic solution from Method B, measuring about 1400 cc. was concentrated to 200 cc., 5 grams of oil separating at this time. After removing the separated oil the extract was saponified with potassium hydroxide, and after evaporating the alcohol and dissolving the soap in water the solution was extracted with eight successive portions of ether, 50 cc. at a time. The

extract obtained upon evaporation of the ether was a thick, orange-brown colored syrupy mass, which was very bitter.

The residual soap solution was acidified with hydrochloric acid, obtaining a flocculent precipitate above an oily liquid at the bottom of the beaker and an oily layer of fatty acids floating on the water. The bottom oil was dark red and the precipitate light yellow. The oil was apparently more of the unsaponifiable matter mentioned in the previous paragraph which had escaped the ether extraction.

The flocculent precipitate after being washed free from hydrochloric acid could not be crystallized from alcohol, it being apparently too soluble. Petroleum ether of 30–50° boiling point dissolved very little. Benzene dissolved about 30–35%, the remainder being entirely insoluble in this solvent. Evaporation of the benzene left a gummy residue too small for further study. The benzene insoluble portion was light gray in color and distinctly acidic. After drying it melted at 205–207°. 0.1100 gram dissolved in alcohol required 5.77 cc. of 0.0999 *N* sodium hydroxide for neutralization, giving a neutral equivalent of 192.6.

When Extracts C, D and E were treated in the same fashion the same unsaponifiable bitter oil was obtained, but no trace of the acidic precipitate. The precipitate was obtained in a preliminary test on the extract in Method A. In Methods A and B the oil was treated with steam before the alcohol extraction, in C, D and E after the alcohol extraction.

Examination of the Bitter Matter.—This, a thick dark red syrup, could not be crystallized directly after distillation of the ether, but after standing about three weeks it became turbid due to the separation of an amorphous yellow solid. When washed with 95% alcohol the bitter gummy material dissolved leaving a yellow amorphous powder. The alcoholic extracts from Method E on concentration and standing over night gave a similar amorphous deposit. Very little of this material was obtained by the third and subsequent extractions. Sixteen hundred grams of oil by Method E gave 15.6 grams of the solid in this way. The unsaponifiable matter obtained from the residual alcoholic extracts yielded additional solid material.

The bitter material was fused with phthalic anhydride in an attempt to form a half phthalic ester of any hydroxy compound which might be present. The fusion mixture was taken up with benzene and extracted with sodium carbonate solution, but this solution, after saponification and acidification, yielded nothing to ether extraction. Apparently no alcoholic grouping was present.

Five grams of the bitter material was refluxed with 6 grams of potassium permanganate and 2 cc. of 15% sodium hydroxide in 100 cc. of water for one hour. Upon filtration a light brown filtrate appeared which became turbid when acidified. Extraction with ether yielded a brownish red amorphous solid from which low boiling petroleum ether extracted a whitish granular product soluble in hot water. The residue from the hot water treatment was a brown gum. This material, weighing about 0.01 Gm. was dissolved in neutral alcohol, when 4.8 cc. of 0.0999 *N* sodium hydroxide was required for its neutralization.

The whitish granular material was acidic, softened at 103° and melted at 113°. Its solution in hot water gave upon cooling tiny white crystals which softened at 111° and melted at 114°. This substance was possibly slightly impure dihydroxystearic acid, from oleic acid present in the oil. The quantity available was too small for further work.

Fifty grams of the bitter material was distilled under a pressure of 5–6 mm. of mercury and the distillate collected between 150° and 180°. The portion weighed 9.6 Gm. and was a light orange-brown oil of a peculiar smell and very unpleasant taste. Its refractive index was 1.4764 at 25°. The residue in the distilling flask solidified on cooling to a sticky varnish. The iodine number of the original bitter material by Hanus' method was 67.91, of the distillate 86.21 and of the residue 45.00.

The unsaponifiable bitter material was soluble in ether, chloroform, benzene and ethyl alcohol, but only very slightly so in petroleum ether. Its odor was similar to but not identical with that of the crude oil. One drop of this substance mixed with 2 cc. of acetic anhydride gave a bright red color upon the addition of one drop of 1:1 sulphuric acid. The color was changed to yellow upon the further addition of acid. This reaction is apparently characteristic for pongam oil, since it was given by both the crude and refined oil, and the hydrogenated crude fat. It was not obtained with the hydrogenated refined fat. A comparison of the reaction obtained with various oils follows:

Common name.	Botanical Source.	Reaction.
Cotton seed oil	<i>Gossypium hirsutum</i>	Pale pink
Margosa or neem oil	<i>Melia azadirachta</i>	Moderate dark yellow
Mahua fat	<i>Bassia latifolia</i>	Pink
Safflower oil	<i>Carthamus tinctoria</i>	Apple green
Nigerseed oil	<i>Guizotia abyssynica</i>	Light bluish green
Coconut oil	<i>Cocos nucifera</i>	Greenish
Castor oil	<i>Ricinus communis</i>	Yellowish
Peanut oil	<i>Arachis hypogaea</i>	Pale pink
Sesame oil	<i>Sesamum indicum</i>	Peacock blue
Linseed oil	<i>Linum usitatissimum</i>	Light yellow green
Pongam oil	<i>Pongamia glabra</i>	Bright red
Refined pongam oil	<i>Pongamia glabra</i>	Orange-red
Hydrogenated pongam oil	<i>Pongamia glabra</i>	Orange-red
Hydrogenated refined pongam oil	<i>Pongamia glabra</i>	Colorless

Examination of the Crystalline Material.—The yellow amorphous powder previously mentioned crystallized from ether in small pale yellow needles softening at 151° and melting completely at 153.5°. Repeated recrystallizations from 95% alcohol finally yielded white shining needles softening at 157.5° and melting completely at 159°. A small amount of gummy semi-solid material was obtained as residue upon evaporation of the final mother liquors.

All of the solid material obtained from the alcohol extracts in refining method (E) was combined and treated with alcoholic potash to saponify any fat present, the solution evaporated to dryness and extracted with ether in a Soxhlet apparatus. After washing the extract with distilled water to remove any soap the solvent was evaporated and the residue repeatedly crystallized from absolute methyl alcohol. All of the crops of crystals obtained were in the form of white needles and melted at 157.5–159°.

That the material evidently existed in the oil and, therefore, in the seed and was not a product of hydrolysis was shown by the fact that the crude oil (which was turbid) on standing to clarify deposited a mucilaginous substance mixed with yellow granules of the size of poppy or mustard seed. The material was separated by filtration and the mucilage washed off mechanically by means of ether. The granules upon solution in methyl alcohol yielded crystals identical with the above. Similar material was obtained from the press cake.

The mucilage washed from the nodular deposit by means of ether was separated by filtration and washed repeatedly with ether. The material remaining on the paper was viscous and as bitter in taste as the unsaponified bitter substance previously mentioned. While insoluble in ether it dissolved in chloroform and gave a similar reaction with acetic anhydride and sulphuric acid.

Desai and others (4) claim to have isolated from the unsaponifiable matter of pongam oil two phytosterols, brassicasterol, m. p. 147° and sitosterol, m. p. 137°. An exhaustive fractional crystallization of the solid material from the unsaponifiable matter failed to yield a trace of either of these substances.

Supposing this material to be a phytosterol a small portion was warmed with acetic anhydride. The product obtained melted at 157.5–159° after being twice crystallized and upon admixture with the original substance no depression of the melting point was noted. We conclude that the material was not acetylated. Fig. 1.

Another portion was boiled with acetic anhydride for two hours. The material recovered by crystallization had undergone no change in its physical properties. Substitution of acetyl chloride for acetic anhydride in the attempted acetylation was without result. Fig. 2.

On solution in chloroform and addition of Hanus' solution there was some reaction with iodine indicated by the titration of the iodine with sodium thiosulphate. However, upon separat-

ing the chloroformic solution after the titration and removing the solvent by evaporation, the residue after one recrystallization melted at 157.5–159°. Fig. 3. Figures 4 and 5 represent the crystals of the compound as generally obtained from concentrated solutions, Figure 6 as obtained from dilute solution.

The material dissolved in chloroform did not rotate polarized light. An alcoholic solution yielded no precipitate with an alcoholic solution of digitonin. The substance was very sensitive to sunlight. The white color changed through light yellow to bright yellow and finally to bright orange-red within 4–5 hours.

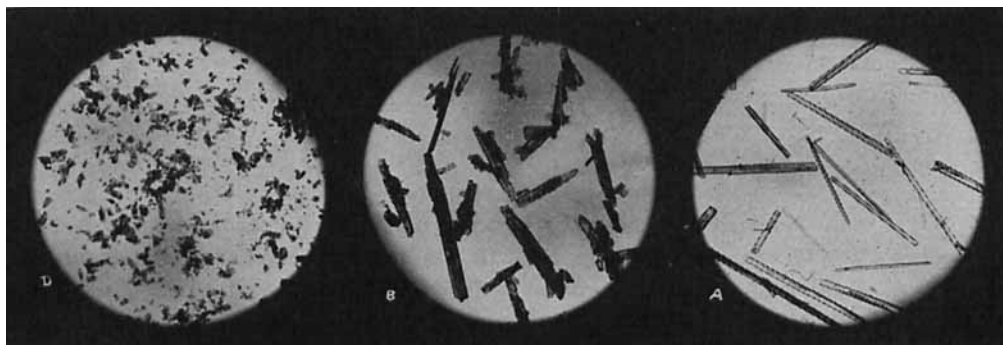


Fig. 1.—Crystallization from Acetic Anhydride. Fig. 2.—Crystallization from Acetyl Chloride. Fig. 3.—Recovered from Chloroform after attempted detn. of Iodine no.

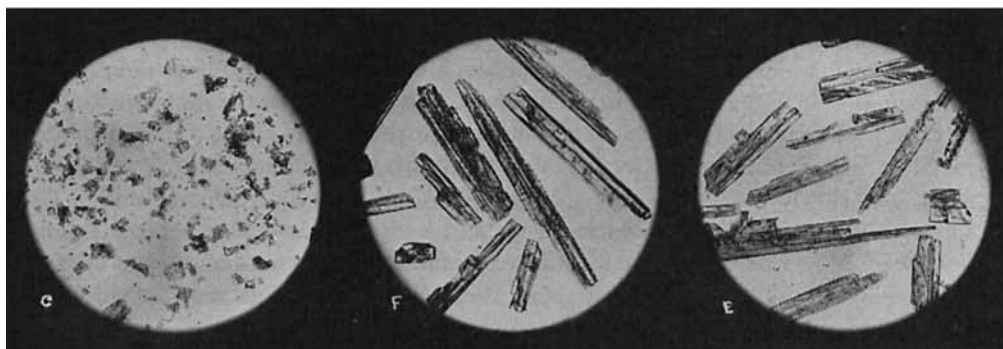


Fig. 4.—Crystallization from Concentrated Solutions. Fig. 5.—Crystallization from Concentrated Solutions. Fig. 6.—Crystallization from Dilute Solutions.

Further exposure was without effect. No depression of the melting point was observed and a single recrystallization from methyl or ethyl alcohol gave the original white substance. Artificial light had no effect on the color of the substance.

A small amount of the substance was dissolved in glacial acetic acid and bromine added in slight excess. An amorphous precipitate was obtained which became crystalline on standing. When dried on a porous plate the crystals melted at 155–156°, but when mixed with the original substance the melting point was lowered to 144–145°. Another portion dissolved in ether was brominated with a glacial acetic acid solution of bromine. No precipitate was formed, so after shaking with sodium sulfite to remove the excess bromine the ether was removed by distillation. Some solid material separated from the remaining acetic acid. This when crystallized twice from

methyl alcohol melted at 146–148°. When mixed with the original it melted at 149° with charring.

Qualitative analysis showed the presence only of carbon, hydrogen and oxygen. Analysis by combustion gave the following results:—

Sample.	CO ₂ .	H ₂ O.	% C.	% H.	% O (difference).
0.2045 Gm.	0.5518 Gm.	0.0752 Gm.	73.60	4.11	22.29
0.1514 Gm.	0.4092 Gm.	0.0520 Gm.	73.72	3.84	22.44
0.1582 Gm.	0.4252 Gm.	0.0568 Gm.	73.30	4.01	22.69
0.1601 Gm.	0.4328 Gm.	0.0538 Gm.	73.73	3.76	22.51

An attempt was made to determine the molecular weight of the compound by the cryoscopic method, using benzene as the solvent.

Solute.	Solvent.	p.p.	M. wt.
0.2947 Gm.	43.92 Gm.	0.100° C.	336
0.3859 Gm.	43.92 Gm.	0.133° C.	332
0.7835 Gm.	43.92 Gm.	0.324° C.	276
1.2963 Gm.	43.92 Gm.	0.500° C.	296

The only similarity to a phytosterol was found in its reaction towards the Hager-Salkowski reagent. As applied, 4 to 5 milligrams of material was dissolved in 3 cc. of chloroform and 2 cc. of concentrated sulphuric acid added down the side of the test-tube. At the contact zone between the acid and chloroform a yellow ring at once appeared. On standing there appeared below this in the acid successive rings of grass green, red, fuchsin and blue. With a phytosterol the color changes appear in the chloroform layer and the acid assumes a green fluorescence. The compound gave a negative reaction for phytosterol with Liebermann's reagent, acetic anhydride and concentrated sulphuric acid.

The compound is tasteless and odorless. It is readily soluble in chloroform, benzene and 95% methyl and ethyl alcohols. It is slowly but completely soluble in ether but practically insoluble in low boiling petroleum ether. It is insoluble in dilute mineral acids, readily soluble in concentrated sulphuric, nitric and acetic acids, and slowly but completely soluble in concentrated hydrochloric acid. The solution in concentrated sulphuric, nitric and hydrochloric acids becomes yellow, but on dilution with water the solutions become colorless and deposit the original substance unchanged. The solution in glacial acetic acid does not change color, and the original material is precipitated on the addition of water.

Hydrogenation of the Oil.—Both the crude and refined oils were hydrogenated with the aid of a nickel catalyst in a small apparatus devised for the purpose and shown in Figure 7. The catalyst was prepared by dissolving 50 grams of nickel sulphate, NiSO₄·6H₂O in water, adding 30 grams of kieselguhr, 100 mesh, and then adding, with constant stirring, a solution containing 25 grams of sodium carbonate. The mixture of nickel carbonate and kieselguhr was filtered on a Buchner funnel and washed with water until the washings were free from sulphate and carbonate ions. It was then dried at 105° in a vacuum oven, powdered finely and preserved in a glass-stoppered bottle.

The nickel carbonate was reduced to the metal in the hydrogenating flask by placing 38 grams of material in the flask, heating the flask to 270°, admitting hydrogen at a pressure of 8–9 mm. above atmospheric and maintaining a temperature of 270–290° for six hours while keeping up the supply of hydrogen. The flask was cooled to room temperature while filled with hydrogen, 350 grams of oil added as rapidly as possible, the current of hydrogen admitted again and the oil constantly stirred. The temperature was brought to 185–195° as rapidly as possible and held at that point for five hours, then allowed to fall to 90° and the fat filtered through paper in a hot water jacketed funnel. The melted fat was practically colorless, having only the slight-

est yellow tint, and on cooling became perfectly white. The solidified fat was hard, brittle and odorless. Its melting point, by Twitchells (7) method, was 64.5° . The Iodine number, by Hanus' method, was 0.89. The crude oil, treated in a similar fashion for ten hours, gave a yellowish brown fat of lower melting point and having an iodine number of 32.2 (Hanus).

Examination of the Seed-cake.—Six hundred grams of the press cake as received was ground fine and percolated with 95% alcohol. Evaporation of the solvent left a thick syrupy liquid from which 10–12 grams of the bitter oil separated. The syrupy mass was first washed with petroleum ether, then with ether. These washings were combined and evaporated, leaving a bitter residue which on standing for four weeks deposited yellow granules. These upon crystallization from methyl alcohol melted at $157\text{--}159^{\circ}$ and were found to be identical with the crystalline matter previously described.

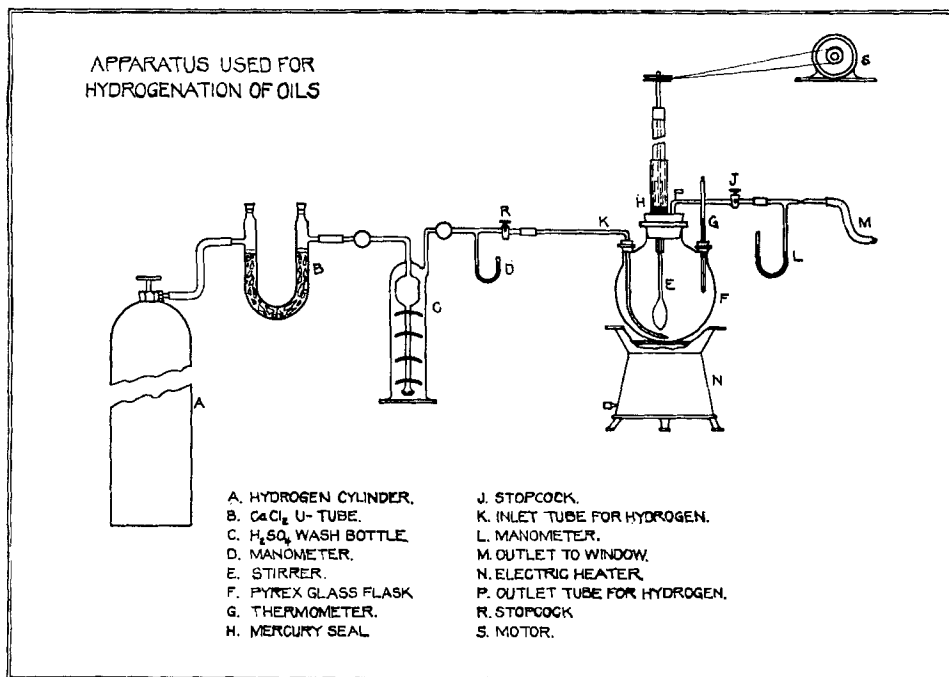


Fig. 7.—Set-up of Apparatus used in Hydrogenation.

SUMMARY.

The expressed oil from the seeds of *Pongamia glabra* has been examined and its chemical and physical constants determined.

A number of experiments for refining the oil are described by which the color, odor and taste are improved. None of these methods have been tested on a commercial scale.

The substance to which the oil owes its bitter taste is found in the unsaponifiable fraction. It is apparently dissolved from the seed by the oil.

The unsaponifiable matter also contains a crystalline substance, melting at 159° , which is apparently not a phytosterol. This crystalline substance is being more thoroughly investigated.

The refined oil was hydrogenated, using nickel as a catalyst. The product was hard, brittle, colorless and odorless.

A specific test for the Pongam oil has been suggested.

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THE VOLATILE OIL OF COLLINSONIA ANISATA.

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Collinsonia anisata Sims, *Micheliella Anisata* (Sims) Briq. is an herbaceous plant of the Labiatae or mint family growing in sandy pine or oak woods from South Carolina to Florida and Alabama.

The plant has a ligneous, knotted root-stock and grows generally from one to two feet high. Usually it blooms about the first of September, the flowering period extending over several weeks. The corollas are cream-colored. The anise-scented leaves have at times been used medicinally as a carminative and stomachic under the name of "citronella tea".

The odor of the plant suggests that it contains either anethol or its isomer, methyl chavicol, or both. These are respectively the *p*-propenyl and *p*-allyl derivatives of anisol.

It is known that anethol has been identified less frequently in plants than methyl chavicol. In some cases they seem to occur together, but always one or the other predominates. The present work was undertaken to determine which one is the characteristic constituent of this plant.

The oil used in this investigation was obtained by steam distillation in October 1909, from fresh material collected near Auburn, Alabama. The above-ground portions of the plants were used. Some of the plants were still in bloom but most had entered the fruiting stage. The yield of oil based on the weight of fresh green plant material was 0.138%. No doubt the yield would have been larger if the plants had been collected and distilled a few weeks earlier.

PHYSICAL CONSTANTS OF THE OIL.

Three samples of oil were obtained, the total volume being about 170 cubic centimeters. The optical activity of one of these was determined soon after distillation. The rotation in a 100-mm. tube was -2.34° at 21° C. The rotation of all three samples determined in 1914 was -0.4° , -2.3° , -1.65° , respectively, in a 100-mm. tube. Since the rotation of sample No. 2 was -2.34° , determined soon after the oil was distilled, it will be seen that practically no change in rotation had occurred by standing five years.

The index of refraction as determined in 1914 by means of an Abbé refractometer was 1.5225, 1.5185, 1.5195, respectively, at 19.2° C.

CHEMICAL EXAMINATION.

Test for Phenol.—When shaken with 5% sodium hydroxide solution in a