THE CHEMICAL CONSTITUENTS OF THE SEEDS OF SAPINDUS DRUMMONDII

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By

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PREFACE

The fruits of Sapindus drummondii H. and A., commonly known as Western Soapberry, Wild China Tree, Drummond's Soapberry, and Indian Soap Plant, are not commercially utilized, but since the tree is widely distributed in the Southwest, there is local interest in its products. The tree in the vicinity of Stillwater grows from 15 to 25 feet high and has a scaly, brown bark. The fruit is a grape-like cluster of yellow berries with black, hard-shelled seeds; these ripen in the fall and stay on the tree all winter. The pericarp, which is reported to contain 37% saponin (19), has been used as a soap substitute and in the manufacture of varnish and floor-wax. The polished seeds have been used as buttons or ornaments in bracelets and necklaces. The wood is easily split into strips suitable for making baskets, pack saddles, frames, etc.

Since no study of the chemical composition of the seeds had been made, the present work was designed to remedy the deficiency. After the seeds were found to be comparatively rich in oil, most of my work was concentrated on the determination of constants of this oil and the separation and identification of the fatty acids present.

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HISTORICAL

An enormous amount of work has been done with vegetable fats and oils. Among the plants studied are the following relatives of Sapindus drummondii H. and A.:

Macassar, Cassum, or Paka Tree oil (Schleichera trijuga) of the Sapindaceae which are found in India, East Indies, and Ceylon has been investigated by Bolton and Jesson (4), Lewkowitsch (13), Poleck (17), and Dhingea, Hilditch, and Vickery (7). The oil is considered unfit for feeding purposes unless properly refined; it can, however, be used as an illuminant and in the manufacture of soap.

Rambutan Tallow (Nephelium lappaceum) of China, Sunda Islands, Malay, and elsewhere has been studied by Georgi (8), Baczenski (3), and Morgan and Holmes (14).

Pulsam Fat (Nephelium mutabile) has also been studied by Georgi (8). The fat can be used for edible purposes or the manufacture of candles and soap.

Soap Tree Oil (Sapindus trifoliatus) is obtained from cultivated trees in Bengal. The properties and constituents of the oil are reported by Paranjpe and Aggar (16).

Mexican Buckeye (Ungnadia speciosa), one of the Sapindaceae of Texas and New Mexico, has been investigated by Cheel and Penford (6) and Schaedler (18).

The fatty oil of the fruits of Sapindus mukurossi is described by Kafuku and Hata (12).

The fruits and seeds of Sapindus marginatus have been analyzed by G. S. Jamieson (11). He has suggested that the

oil would be valuable for the manufacture of soap because of its low content of unsaponifiable matter.

The constants and physical properties of the Sapindaceae just mentioned are to be found in Table I. In addition to the information contained in Table I, Sapindus trifoliatus seeds are reported to contain 3.5% moisture and 2.4% ash. The saturated acids present are palmitic (5.6%), n-eicosanic (21.9%), lignoceric (2.5%), and stearic (8.5%); the only unsaturated acid is oleic (61.5%). The oil from the seeds of Schlichera trijuga is reported to contain the following acids: palmitic (5-8%), arachidic (20-25%), stearic (2-6%), myristic (1%), acetic (small amount), oleic (60-70%), and linolic (2-4%). Nephelium lappaceum also contains n-eicosanic acid.

TABLE I

	Schlichera trijuga	Nephelium lappaceum	Nephelium mutabile	Sapindus trifoliatus	Ungnadia speciosa	Sapindus mukurossi	Sapindus marginatus
Seed Wt.	0.5-1.0 g.	?.	?.				?.
% Kernel	60			45			57.67
% Oil	60-72	34-40	60	30	50	28 (12)	40.90 (11)
Sap. V.	215-230(13) 227 (4)	193.8 (3) 193 (8)	193 (8)	194 (16)	203 (6) 192 (18)	220.72 (12)	90.4*(11)
Iodine Number	54.5 (4) 48-69 (13)	43.8 (8) 39.4 (3)	41.6 (8)	58.3 (16)	84 (6) 82 (18)	62.45 (12)	89.2 (11)
R. M. V.	16 (4) 9 (13)			1.5 (16)			
Unsap.	1.5-7.2 (7) 3.1 (13)			1.2 (16)	.6 (6)	.43 (12)	.57 (11)
Acid V.	4.8 (8)	.7 (8)				.711	1%*(11)
Titer	52° (4) 52° (13)	51.5 (8) 57 (3)	50.9 (8)				
Refractive Index	n_D^{40} 1.4537 (4)	n_D^{40} 1.4590 (8)	n_D^{40} 1.4579 (8)	n_D^{25} 1.4764 (16)	n_D^{20} 1.4666 (18)	n_D^{30} 1.4690 (12)	n_D^{25} 1.4709 (11)
Sp. G.		99/15.5° .8629 (8)	99/15.5° .8597 (8)	100° .8540 (16)	15° .912(18) 15° .917(6)	30°.9328 (12)	
M. P.		40-42 (8) 42-46 (3)	40-42 (8)			41-42 (12)	

*Probably a typographical error.

EXPERIMENTAL

The fruits used in this experiment were gathered Southeast of Coyle, Oklahoma from trees along the roadside. The pericarps were removed by hand and the seeds were ground in a Wiley mill. A percolator type extractor designed by Dr. J. E. Webster was used to separate the oil from the meal. Sulfuric ether was the solvent used in the first extraction and petroleum ether was used for a second. A third separation was made employing meal from one year old seeds with petroleum ether in a Soxhlet extractor. In each case, after extraction, as much as possible of the solvent was distilled off over a steam bath, at first under ordinary pressure and later under reduced pressure. The residual oil was set away in an ice box until needed. The sulfuric ether extract was a greenish brown oil whereas that from petroleum ether was yellow-brown in color. The extracted meal resembled starch in appearance and taste.

The usual constants and physical properties of the oil were determined by standard methods (10). The crude fiber was determined by the method recommended by A.O.A.C. (1) and the starch and sugar tests were taken from Hawk and Bergeim (9). The results are to be found in Tables II and III.

TABLE II

ANALYSIS OF EXTRACTED MEAL FROM SAPINDUS DRUMMONDII SEEDS

	New Seeds	Old Seeds
Average Fruit Weight	1.01 g.	.68
Percent Seed	42.6	41.0
Protein (% N x 6.25)-Kjeldahl	21.33%	13.43%
Fiber	17.98	
Ash	3.70	
Moisture	8.40	6.20
Starch Test	positive	
Fehling Test	negative	

TABLE III

CONSTANTS AND PHYSICAL PROPERTIES OF THE OIL

	New Seeds		Old Seeds*
Extraction Solvent	Ether	Ligroin	Ligroin
Weight of Meal Extracted	2095 g.	1288 g.	461 g.
Percent Oil	24.0	23.5	8.9
Sap. V.	212.7	219.2	208.3
Iodine No. (Hanus)	83.5	82.5	95.1
R. M. V.	0		
Pol. V.	0		
Unsap. Matter	1.2%		
Acid Value	0.95		
Refractive Index $n_D^{25^\circ}$	1.4722	1.4718	1.4718
Specific Gravity $25/25^\circ$	0.9168	0.9032	0.9155
Acetyl Value	14.5		
Thiocyanogen No.	67.2	65.3	64.8

*The values are probably not reliable due to incomplete extraction of the oil.

The saturated and unsaturated fatty acids were separated from the crude oil by the lead soap-ether method (10). An additional amount of the saturated fraction was prepared by chilling a 20% solution of a new portion of the mixed acids in methyl alcohol and filtering (5). An attempt to separate the saturated and unsaturated fatty acids by the lead soap-alcohol method (15) failed to give satisfactory results. Hartsuch (20) reports similar experiences with the last two methods mentioned.

The unsaturated acids were converted to their methyl esters and fractionally distilled under 4 mm. pressure from a modified Hempel flask. From Hanus numbers and saponification equivalents the esters were shown to be a mixture of methyl oleate and methyl linoleate. Since the hexabromide test (10) gave negative results with all four ester fractions linolenic acid was assumed to be absent. An attempt to precipitate linoleic tetrabromide likewise failed, probably owing to the great amount of oleic acid dibromide present (21). The free acid from the first ester fraction formed elaidic acid (M.P. 43°, literature value 44-51.5°) when treated with sodium nitrite and sulfuric acid, confirming the presence of oleic acid. By use of the Kaufmann equation (10) the percentages of oleic, linoleic, and saturated acids were calculated. The ratio of the two unsaturated acids was also calculated from the average Hanus number of the ester fractions. The results are to be found in Tables IV and V. The unsaturated acid fraction from the methyl alcohol separation gave a neutral equivalent of 304.

This material was saponified, acidified, and extracted with petroleum ether. After distillation from a Hickman still, the neutral equivalent was found to be 288.5 which is reasonable for a mixture of oleic and linoleic acid.

TABLE IV

PERCENTAGES OF FREE ACIDS AND GLYCERIDES AS CALCULATED BY THE KAUFMANN EQUATION

	New Seeds		Old Seeds
Extraction Solvent	Ether	Ligroin	Ligroin
% Free Oleic Acid	56.8	53.5	38.4
% Oleic Acid as Glyceride	59.2	55.9	40.1
% Free Linoleic Acid	18.0	19.0	33.5
% Linoleic Acid as Glyceride	18.8	19.9	35.0
% Free Saturated Acids	20.9	23.0	23.6
% Saturated Acids as Glycerides	22.0	24.3	24.9
% Free Unsaturated Acids	74.8	72.5	71.9
% Unsaturated Acids as Glycerides	78.0	75.7	75.1

TABLE V

RESULTS OF FRACTIONAL DISTILLATION OF UNSATURATED ESTERS UNDER 4 mm. PRESSURE

Fraction	Boiling Range	% of Total By Volume	Sap. Equiv.	Hanus No.
1	up to 170°	13.2	292.2	88.0
2	170-2	36.6	289.0	93.5
3	172-7	28.3	296.4	89.0
4	177 up	21.9	263.6	84.0

The average Hanus Number of the mixed unsaturated methyl esters was calculated to be 89.4. This value indicates that the unsaturated fraction consists of 4.3% linoleic acid and 95.7% oleic acid.

The saturated acids from the lead soap-ether extraction were fractionally crystallized and two substances of melting points 61.5-62.5° and 68.5-69.5° were isolated. The lower fraction showed no deviation in melting point when mixed with pure palmitic acid and the melting point of the higher was lowered less than one degree when mixed with pure stearic acid. No substance was found with a melting point lower than 61.5° or higher than 69.5° so it was assumed that only the two acids were present in the saturated fraction. The mixed saturated acids obtained by chilling from methyl alcohol also failed to give a substance of melting point above 69.5° on recrystallization from absolute alcohol. The neutral equivalent of the mixture was found to be 306.0. An attempt was made to purify this fraction by converting to the lead soaps in the presence of chloroform, filtering off the liquid, and reliberating the fatty acids. The neutral equivalent of this substance was 294.0. Distillation of the mixture from a Hickman still gave material with a neutral equivalent of 313.5, but recrystallization of the last drops failed to give a substance with a melting point higher than 69.5°. The distillate was again placed in the still and redistilled into 4 approximately equal fractions which gave neutral equivalents of 283.9, 300.5, 312.8, and 331.1 (in order of increasing

boiling points of the fractions). The last fraction contained a small amount of an unknown substance which was soluble in hot alcohol but insoluble in dilute potassium hydroxide solution and warm concentrated sulfuric acid. It melted at 83-4° after one recrystallization from hot alcohol. The residue was washed from the still with hot alcohol, neutralized with dilute potassium hydroxide, and the soap solution filtered. The residue was dissolved in hot absolute alcohol and allowed to recrystallize. This material was insoluble in warm concentrated sulfuric acid, gave a negative sterol test, and melted indefinitely at about 130°.

DISCUSSION OF RESULTS

In general, this problem has given satisfactory results. The physical properties and constants of the oil examined, as well as the fatty acids present therein, show similarity to those of other Sapindaceae.

The Hanus Number of the oil in question is higher than six of the seven oils described on page 3. This is in agreement with the climatic influence on unsaturation, Sapindus drummondii H. and A. being from a cooler area than the others just mentioned.

The constants and physical properties of the oil extracted from one year old seeds differ slightly from the extract of the new. This may be due to seasonal influences, type of soil on which the trees grew, aging, and/or incomplete extraction.

The acetyl value indicates the presence of free hydroxyl groups. Sterols, which probably make up most of the 1.2% unsaponifiable matter, could account for only a small portion of the acetyl value found; therefore, part of the oil must exist in the form of diglycerides.

Arachidic acid (reported by some to be the same as n-eicosanic acid), which is a usual constituent of the oil from related plants, was not found in the material used for this study.

The high neutral equivalents found for both the saturated and unsaturated acid fractions from the methanol separation might be due to the presence of either an unknown branched-

chain fatty acid of high molecular weight or some inert material, such as sterols or hydrocarbons. Failure to remove this substance by crystallization, resaponification, and distillation could be explained by its sorption by the soaps and its resemblance in melting point and boiling point to the acids known to be present. The solubility behaviors of the materials isolated from the higher boiling fraction of solid acids classify them as paraffin hydrocarbons. Since such hydrocarbons are known to occur in seed coats (11) and since the whole seed takes a high polish suggestive of the presence of a wax, it is believed that the interfering hydrocarbons were derived from these outer coats. Future investigation should be made to test this hypothesis.

Differences in the percentages of the unsaturated acids as calculated by the Kaufmann equation and from the average iodine number are partly due to the fact that Kaufmann assumes the oil to be 100% triglycerides. Experimental errors in the determination of the iodine number and thiocyanogen number may account for part of the discrepancy. Iodine numbers might also be lowered by the prior addition of some foreign substance at the double bond of the unsaturated acids during handling of the material. The results do indicate oleic acid to be more abundant in the oil than linoleic acid.

The low percentage of unsaponifiable matter suggests the possibility of using the oil of soapberries for the manufacture of soap. The fat, protein, and starchy material

present would indicate a possible use as a stock feed, assuming the absence of poisons. The cost of preparing the seeds for commercial uses would be prohibitive at the present time.

A further study of the fruits of this plant as to saponins present in the pericarp, starch, and the amounts of fatty acids present would be of interest and value.

SUMMARY

1. A study has been made of the chemical constituents of the seeds of *Sapindus drummondii* H. and A.
2. The oil is very similar to that of related plants.
3. The fatty acids present are oleic, linoleic, palmitic, and stearic.
4. Oleic acid is more abundant than the other fatty acids present.
5. n-Eicosanic acid is absent.
6. Traces of paraffin hydrocarbons of high molecular weight are present in the oil extracted with petroleum ether.
7. The seeds of *Sapindus drummondii* H. and A. are of no commercial importance at the present time.

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AUTOBIOGRAPHY

I, Lowell T. Crews, was born at St. Louis, Missouri, October 18, 1915. In 1918 I moved to Fairfield, Illinois where I attended public school, graduating from Fairfield Community High School in 1933.

I attended Southern Illinois Normal University, Carbondale, Illinois, from September, 1933 until June, 1937, receiving a Bachelor of Education degree.

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