

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE]

The Composition of the Seeds of *Sapindus Drummondii*<sup>1,2</sup>

BY O. C. DERMER AND L. T. CREWS

The tree *Sapindus drummondii* H. and A., commonly known as Western Soapberry or Wild Chinaberry, is widely distributed in the south-western part of the United States. Its clusters of yellow translucent fruits or "berries" ripen in the fall and remain on the tree during the winter. Each drupe-like fruit contains a round, black, hard-shelled seed which averages 0.4 g. in weight as compared to 1 g. for the whole fruit. The reputedly toxic pericarp is rich in a saponin which has been employed as a soap substitute, while the polished seeds have been used as primitive ornaments.

The only published chemical data on this fruit<sup>3</sup> show that whole fruits from Oklahoma contain 8%, and their seed kernels 43%, of a non-drying oil.

## Experimental

The fruits used in this work were gathered in December and January from trees in the Cimarron River valley near Coyle, Oklahoma. After several months the slightly sticky outer pulp was removed by hand and preserved for an intended investigation of the saponin present. Nearly all the seeds were ground whole, for kernels could be separated from shells only by tedious hand sorting.

Since it is well known that different methods of extraction of an oil remove different kinds and proportions of other substances, some of the meal (1-2 kg.) was percolated with ether, some with petroleum ether, and some was warmed and pressed hydraulically to remove the oil. The oils thus obtained, after the removal of any solvent and filtration, gave substantially the same constants. The seed kernels were found to contain 42.7% of ether-soluble materials,<sup>4</sup> whereas the whole seeds contained 23-24%.

The oil was greenish-brown to yellow-brown in color and had the characteristic but not unpleasant odor and taste of the seed kernels. It did not become rancid readily. The usual physical properties and chemical constants were determined by standard methods<sup>5</sup> unless otherwise specified. The results, in Table I, show the limits of variation of characteristics of the oils extracted by different methods.

(1) This is an abstract of a thesis submitted by Mr. Crews in partial fulfillment of the requirements for the degree of Master of Science at the Oklahoma Agricultural and Mechanical College in 1939.

(2) The authors wish to express their thanks to members of the Department of Botany for help in identifying the plant, and to Dr. J. E. Webster for apparatus and suggestions.

(3) Report of the Chief of the Bureau of Chemistry and Soils, U. S. Department of Agriculture, 1938, p. 7.

(4) Determined by Dr. J. E. Webster.

(5) Jamieson, "Vegetable Fats and Oils," Chemical Catalog Co., Inc. New York, 1932.

TABLE I

## CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE OIL

Specific gravity, 25°/25°	0.903-0.917
Refractive index, $n_{25}^D$	1.4704-1.4722
Acid value	0.3-0.9
Saponification value	213-219
Iodine no. (Hanus)	81.5-83.5
Thiocyanogen no.	63.9-67.2
Unsaponifiable matter, %	1.2
Reichert-Meißl no.	0.0
Polenske no.	0.0
Acetyl value	14.5
Unsaturated acids, %	74-77, <sup>a</sup> 82 <sup>b</sup>
Saturated acids, %	17-20, <sup>a</sup> 13 <sup>b</sup>

<sup>a</sup> Calculated from iodine number and thiocyanogen number. <sup>b</sup> Observed by separation and weighing, and corrected for impurities.

The air-dry exhausted meal was analyzed with the following results: protein 21.3%; crude fiber 18.0%; ash 3.70%; moisture 8.40%. It contained starch (iodine test) but no reducing sugars.

**Fatty Acids.**—Saturated acids were best separated from unsaturated acids by low-temperature crystallization of the free acids from acetone.<sup>7</sup> The unsaturated fraction gave a negative hexabromide test for linolenic acid. The presence of oleic acid was confirmed by its conversion to elaidic acid, but bromination of the unsaturated fraction in petroleum ether at -10° gave no precipitate of linoleic acid tetrabromide, probably owing to the solvent action of the large amount of oleic acid dibromide present. From the iodine number and the thiocyanogen number of the original oil it can be estimated that there were present about 60-65% of oleic acid and 15% of linoleic acid.

Fractional crystallization of portions of the mixed saturated acids (iodine numbers 5.0-28) led to the isolation of palmitic acid, m. p. 61.5-62.5°, and stearic acid, m. p. 68.5-69.5°, identified by melting points and mixture melting points. No others could be found, although average molecular weights obtained by either direct titration or saponification of the saturated fraction from different runs indicated the presence of an acid higher than stearic acid in the series.

When a portion of the saturated acids derived from the oil extracted with petroleum ether was distilled at 1 mm., a few crystals of alkali-insoluble material were isolated from the highest-boiling fraction and about an equal amount from the residue in the still. After recrystallization from alcohol, these waxy crystals melted at 63-64° and about 130° (indefinite), respectively. They were proved to be alkanes by their insolubility in even hot concentrated sulfuric acid. The known occurrence of

(6) Association of Official Agricultural Chemists, "Methods of Analysis," Washington, D. C., fourth edition, 1935, p. 30.

(7) Brown and Stoner, THIS JOURNAL, 59, 3 (1937); cf. Hartsuch *ibid.*, 61, 1142 (1939).

saturated hydrocarbons in seed coats and the ability of seeds of *Sapindus drummondii* to take a high polish suggest that these alkanes came from the unremoved seed coats rather than from the kernels. Such complications in fat chemistry have been remarked before.<sup>8</sup>

The seed oils of the following relatives of *Sapindus drummondii* have been studied: *Schlichera trijuga*,<sup>6</sup> *Naphelium lappaceum*,<sup>5</sup> *Naphelium mutabile*,<sup>5</sup> *Sapindus trifoliatus*,<sup>5</sup> *Ungnadia speciosa*,<sup>5</sup> *Sapindus mukurossi*,<sup>9</sup> and *Sapindus marginatus*.<sup>10</sup> The iodine number of the seed oil of *Sapindus drummondii* is higher than that of any of the others except *S. marginatus*; this is in agreement with

(8) Schuette, Cowley and Chang, *THIS JOURNAL*, **56**, 2085 (1934).

(9) Kafuku and Hata, *J. Chem. Soc. Japan*, **55**, 369 (1934).

(10) G. S. Jamieson, unpublished work.

the observation that, among related plants, growth in a cooler climate connotes greater unsaturation of the oil. The principal difference between the oil of *S. drummondii* and that of any of its relatives, however, appears to be its lack of *n*-eicosanic (arachidic?) acid.

### Summary

1. The physical and chemical characteristics of the seed oil of *Sapindus drummondii* have been determined.

2. The fatty acids present consist chiefly of oleic acid, accompanied by smaller amounts of linoleic, palmitic and stearic acids.

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## Studies on Lignin and Related Compounds. XLVI. The Action of Ozone on Isolated Lignins<sup>1</sup>

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The action of ozone on lignin preparations has been studied by a number of workers but the identifiable fragments split off by this treatment have been too small to be of any real value in the elucidation of the structure of lignin. Thus Phillips and Goss<sup>2</sup> isolated anisic acid in small yield by the action of ozone on methylated alkali lignin obtained from corn cobs. Bell, Hawkins, Wright and Hibbert<sup>3</sup> have noted the formation of acetone in the ozonization of birch formic acid lignin. In general it may be said that, when a lignin is subjected to the action of ozone, there results, after treating the resulting product with water, a water-insoluble lignin and an aqueous solution. This latter solution contains mainly a water-soluble, lignin-like material and oxalic acid. The more prolonged the treatment with ozone, the smaller is the resulting water-insoluble and the greater the water-soluble fraction. This action is accompanied by a decrease in the methoxyl content of the ozonized lignin.

In connection with studies being carried out in these Laboratories on the mechanism of the solubilization of lignins by means of aqueous bisulfite solution, it was observed that formic<sup>4a</sup> and

acetic acid<sup>4b</sup> lignins are insoluble in aqueous bisulfites but that after a carefully controlled ozonization in formic acid solution they become completely soluble.

The increase in the solubility in sulfite "cooking liquor" and the decrease in the methoxyl content of the lignin with increasing degree of ozonization were studied by carrying out a series of ozonizations on identical samples of birch formic acid lignin using increasing amounts of ozone. The resulting ozonized samples were then analyzed for methoxyl and the quantitative solubility in sulfite "cooking liquor" was determined (Table I).

TABLE I

THE ACTION OF OZONE ON BIRCH FORMIC ACID LIGNIN

G. of O <sub>3</sub> reacting per 2 g. of lignin	Water-insoluble fraction		Original minus final OCH <sub>3</sub>	% solubility in sulfite liquor of ozonized lignin
	% yield	% OCH <sub>3</sub>		
0.167	95	15.9	2.7	36
.290	88	13.9	4.7	61
.368	68	11.7	6.9	88
.404	72	12.5	6.1	78
.396	73	12.6	6.0	73
.405	65	11.5	7.1	82
.463	60	11.8	6.8	80
.544	53	10.9	7.7	93

These results expressed graphically (Fig. 1) show that both the loss in methoxyl and the increased solubility in sulfite liquor vary directly with the amount of ozone employed. From these data it was possible to calculate the approximate amount

(1) From a thesis submitted to the Faculty of Graduate Studies and Research, McGill University, by Rodger M. Dorland in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, May, 1939. Paper XLV, *THIS JOURNAL*, **61**, 2204 (1939).

(2) Phillips and Goss, *THIS JOURNAL*, **55**, 3466 (1933).

(3) Bell, Hawkins, Wright and Hibbert, *ibid.*, **59**, 598 (1937).

(4) (a) Lief, Wright and Hibbert, *ibid.*, **61**, 1477 (1939); (b) A. Bell, Ph. D. Thesis, McGill University, 1937.