

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

THE OIL OF THE BITTERSWEET SEED¹

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The bittersweet (*Celastrus scandens*) is a hardy vine growing over a wide area east of the Rocky Mountains and is well known for its fruit, which is widely used in the fall for its decorative value. The fruit consists of clusters of small berries which when ripe break open and expose the brilliant scarlet pulp. Imbedded in the pulp are from four to six seeds which are about the size of a grape seed.

A review of the literature indicated that very little work of a chemical nature had been done on this plant and practically none on the seed. Extracts of the bark have been used in medicine² for the treatment of chronic liver infections and it is said to be an emetic and a diaphoretic. The superficial analyses of the bark which have been made³ showed the presence of the usual constituents that are found in all plants and that no glucoside or alkaloid was present. A study by Keller⁴ of the red coloring matter of the pulp seemed to show that this material was a connecting link between carotin and xanthin. Only one reference could be found concerning the seed. Wells and Reeder⁵ made an alcoholic and an ether extract of the seeds which they said contained palmitic acid, palmitin and olein. At best, our knowledge of the chemical nature of this plant is meager, and since about two pounds of the seed became available⁶ it was thought worth while to subject the oil to a complete chemical analysis. The seeds contained a high percentage of oil and the oil itself was found to be an exceptional mixture for a vegetable oil.

The berries that supplied the seed for this investigation came from the Kentucky river region within a radius of twenty miles of Lexington, Kentucky. They had been gradually collected over a period of four years and were free from pulp. The seeds showed no deterioration and appeared to be the same as some freshly separated. Because of their oily nature the seeds had to be ground in a food chopper and the oily mash was extracted with ether at once.

¹ From a thesis presented by Charles F. Krewson to the Faculty of the Graduate School of the University of Kentucky in partial fulfilment of the requirements for the degree of Master of Science, June, 1932.

² Wood and La Wall, "United States Dispensatory," Lippincott, Phila., 1926, 21st ed., p. 1247.

³ Bernhard, *Am. J. Pharm.*, **54**, 1 (1882); Hoch, *ibid.*, **63**, 523 (1891); Dillingham, *Am. Naturalist*, **51**, 391 (1907).

⁴ Keller, *Am. J. Pharm.*, **68**, 183 (1896).

⁵ Wells and Reeder, *Chem. News*, **96**, 199 (1907).

⁶ We are indebted to Dr. F. E. Tuttle of this department for furnishing us the seed.

Experimental Part

Quantitative extractions were made as shown in Table I.

TABLE I
QUANTITATIVE EXTRACTIONS

	%
Petroleum ether (50–60°)	36.06
Ether	46.72
Ethyl alcohol (95%)	53.22

The seed contains an average percentage of oil and the large difference between the petroleum ether and the ether extracts is noteworthy. The large amount of esters of the lower fatty acids, which was shown to be present later, would account for this difference.

The approximate analysis was run by the official methods, the results being listed in Table II.

TABLE II
APPROXIMATE ANALYSIS OF THE EXTRACTED MEAL OF BITTERSWEET SEED

	%		%
Moisture	3.05	Free invert sugar	0.49
Ash	2.88	Sugar by inversion	1.60
Protein (N × 6.25)	18.94	Pentosans	5.87
Crude fiber	9.14	Starch (diastase)	0.68

The seed is very low in starch and rather high in crude fiber.

The Physical and Chemical Examination of the Oil.—The oil was obtained by extracting 950 g. of the ground seeds with absolute ether. The ether was evaporated and the last traces were removed in a vacuum. Three hundred and ninety-seven grams of a clear medium yellow oil having a slight agreeable odor and a bland taste was obtained. The physical and chemical properties are given in Table III.

TABLE III
PHYSICAL AND CHEMICAL CONSTANTS OF BITTERSWEET SEED OIL

d^{20}	0.9772	Acetyl value	147.5
n^{20}	1.4815	Unsaponifiable matter, %	2.96
Iodine No. (Hanus)	121.5	Soluble acids (% butyric acid)	18.98
Thiocyanogen Iodine No.	69.96	Insoluble acids, %	70.94
Saponification value	297.07	Unsaturated acids (corr.), %	57.13
Reichert–Meissl No.	70.86	Insol. saturated acids (corr.), %	9.83
Acid value	3.98	Hexabromide No. of insoluble acids	17.66

The results point to the fact that this oil is different in composition from most vegetable oils. The Reichert–Meissl number is higher than any other we have been able to find recorded in the literature. This would indicate a high per cent. of volatile acids as esters, which is further substantiated by the very high saponification value and the high value for soluble acids. The acetyl value is of very little significance under

these conditions. The saturated and unsaturated acids of the water insoluble mixture were separated by the lead salt-ether method using the usual precautions and corrections.⁷ The results are probably not as accurate as they would be on an ordinary oil due to the high percentage of the soluble acids.

Unsaturated Acids.—Using the iodine number, the thiocyanogen-iodine number, and the percentage of unsaturated acids in the oil one can calculate the percentage of each unsaturated acid present.⁸ Using this method the results in Table IV were obtained.

TABLE IV
PERCENTAGE OF UNSATURATED ACIDS IN THE OIL

Acid	Acids, %	Glycerol esters, %
Oleic	0.23	0.25
Linolic	36.79	38.46
Linolenic	20.11	21.03

The percentage of glycerol linolenate calculated from the hexabromide number⁹ is 4.82%. The large difference between the two methods is probably accounted for by the presence of most of the linolenic acid in the beta form which does not form an insoluble hexabromide. The percentage of oleic acid is so small that it can be safely said that it is absent.

Insoluble Saturated Acids.—The saturated acids, separated by the lead salt-ether method, were esterified and 29.7 g. of methyl esters was obtained. These were fractionally distilled under diminished pressure as shown in Table V.

TABLE V
FRACTIONAL DISTILLATION OF THE METHYL ESTERS OF THE INSOLUBLE SATURATED ACIDS

Fraction	Pressure 4.2 mm.	Temp., °C.	Wt., g.
1		156 -157	3.3
2		157 -157.5	9.6
3		157.5-159	4.3
4		159 -160.5	4.2
5		160.5-163	1.4
6		163 -172	3.0
7		172 -180	2.7
Residue			0.5

The iodine number and the saponification value of each fraction were determined and, using the method of Baughman and Jamieson,¹⁰ the percentage of the various acids present was calculated. The results are given in Table VI.

⁷ Baughman, Brauns and Jamieson, *THIS JOURNAL*, **42**, 2398 (1920).

⁸ Kaufmann and Keller, *Z. angew. Chem.*, **42**, 73 (1929).

⁹ Steele and Washburn, *J. Ind. Eng. Chem.*, **12**, 52 (1920).

¹⁰ Baughman and Jamieson, *THIS JOURNAL*, **42**, 155 (1920).

TABLE VI
ANALYSES OF THE METHYL ESTERS OF THE INSOLUBLE SATURATED ACIDS

Fract.	Iodine number	Saponification value	Esters of unsaturated acids, %	Mean mol. wt. of esters of saturated acids	Palmitic acid		Stearic acid	
					%	g.	%	g.
1	2.49	204.8	1.23	273.8	92.49	3.05	1.14	0.04
2	4.58	204.5	2.26	273.9	91.47	8.78	1.19	0.11
3	7.87	204.1	3.90	274.0	89.92	3.87	1.19	0.05
4	8.76	203.7	4.38	274.6	89.26	3.75	1.39	0.06
5	10.67	199.2	5.28	281.7	53.43	0.75	36.56	0.51
6	18.15	192.9	9.00	290.5	24.26	0.73	62.34	1.87
7	21.24	191.4	11.00	292.9	16.52	0.53	68.21	2.18

The results show that palmitic and stearic acids are the only acids present in the saturated acid mixture. The acids were obtained from fraction 1 and recrystallized several times from alcohol. The main fraction had a constant melting point of 62–62.5° and a molecular weight by titration of 255.79. Fraction 7 was treated in the same way and an acid melting constantly at 69.2° was obtained. This acid had a molecular weight by titration of 283.1. These results indicate the presence of palmitic acid and stearic acid. The residue was examined in the same way for arachidic acid but no acid with a melting point higher than 69° could be isolated.

Table VII shows the percentage of the two acids in the saturated acids in the oil, and in the oil as glycerides.

TABLE VII
INSOLUBLE SATURATED ACIDS

Acid	Acids in the saturated acids, %	Acids in the oil, %	Glycerides in the oil, %
Palmitic	81.65	8.03	8.42
Stearic	18.35	1.80	1.88

Volatile Acids.—168.5 g. of oil was dissolved in ether and shaken out several times with a dilute solution of sodium carbonate in order to extract the free acids present. This solution will be referred to later under free acids. The ether solution of the oil was evaporated, the remaining oil saponified, made acid with sulfuric acid and steam distilled. The distillate, which was collected in a dilute sodium carbonate solution, was extracted with ether to remove traces of non-acidic material and then concentrated to a volume of 690 cc. This solution was made acid with sulfuric acid, extracted with ether, and then distilled, the distillate being saved. By this means the soluble acids were separated into ether-soluble and water-soluble fractions.

The ether-soluble fraction, which amounted to only 5 g., was dissolved in water, made alkaline with ammonium hydroxide, and silver nitrate added. A small amount of a white solid precipitated and was crystallized. This was analyzed for silver but the material appeared to be a mixture and because of the small amount of the material it could not be further purified. Apparently there is a trace of higher fatty acids present.

The main precipitate came out on concentrating and this with another fraction obtained by further evaporation was analyzed for silver. Fraction 1. Found: Ag,

47.80. Fraction 2. Found: Ag, 49.08. Calcd. for silver caproate: Ag, 48.38. The ether-soluble part of the volatile acids must consist chiefly of caproic acid.

The water solution of the water-soluble fraction of the acids, which amounted to one liter, was made alkaline with ammonium hydroxide and silver nitrate added. No precipitate formed but on concentrating on a water-bath large amounts of free silver kept coming out, which indicated a fairly large amount of formic acid. At a volume of 300 cc., the hot solution was filtered from the silver and on cooling fine white needles crystallized out. Three other fractions of these crystals were obtained by further concentrating the solution. The precipitates were analyzed for silver. The four fractions gave Ag, 64.12, 64.54, 64.54, 64.38%. The percentage of silver in silver acetate is 64.63. This part of the volatile acid mixture must consist of formic and acetic acids.

In conclusion, the volatile acids of the oil which are present as esters consist chiefly of formic and acetic acids with a small amount of caproic acid and a trace of still higher acids. This combination of acids explains the high Reichert-Meissl number and the other abnormal constants.

The Free Acids of the Oil.—The alkaline extract of the ether solution of the oil was treated in the same manner as was the volatile acid solution. The ether-soluble part gave only a trace of material. The water-soluble fraction precipitated silver during the concentration and when a very small amount of solution was left a trace of white needles precipitated. The amount was too small to analyze but was probably silver acetate. The results show that formic acid is the main acid present in the free state in the oil while traces of other acids are also present.

Summary

The oil from the seed of the bittersweet has been analyzed and found to contain an exceptionally large amount of esters of the lower fatty acids. These consist chiefly of esters of formic and acetic acids but a small amount of an ester of caproic acid is also present. The composition of the oil is given in the table.

COMPOSITION OF THE OIL FROM THE BITTERSWEET SEED

Glycerides of	
Linolic acid, %	38.46
Linolenic acid, %	21.03
Palmitic acid, %	8.42
Stearic acid, %	1.88
Soluble acids, calculated as acetic, though about equal amounts of formic and a small amount of caproic are also part of the soluble acids. (It is not known whether these acids occur as glycerides or not.)	15.67
Unsaponifiable material, %	2.96

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