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

KENTUCKY COFFEE NUT TREE SEED OIL[1]

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The Kentucky coffee nut tree (*Gymnocladus dioica*) grows over an area extending from central New York westward to Minnesota and southward to the Tennessee line. It is not a common tree and probably grows most abundantly in the State after which it is named. The pods from this tree measure from 8 to 15 cm. in length and have from three to six seeds imbedded in a mucilaginous material. The black seed coating is exceptionally hard and the seed itself is very compact. The average weight of the seeds is about 2.5 g.

The sweet mucilaginous material in the pods is considered by some people to be poisonous, but only brief reports of the poisonous nature could be found in the literature. Cytisine is reported by Chesnut[2] in the leaves and the mucilaginous material of the pods. A saponin and a toxalbumin are reported to be present in the seeds.[3] The same authors report deaths from eating the unroasted seeds but no references are given.

Only very meager reports can be found on the chemical examination of the pods and the seed. Stone and Test[4] examined the mucilaginous material of the pods for carbohydrates and found glucose and sucrose in large quantities. The insoluble part of the material was provisionally called a gluco-araban. Approximate analysis of the seed and some of the constants of the oil from the seeds has been made.[3]

Since very little work has been done on the chemical examination of the seeds and the pod, we are subjecting them to a complete examination. This paper deals with the analysis of the oil from the seeds and includes an approximate analysis of the seeds and the pods.

The pods were collected in Fayette County, Kentucky, in the fall of 1923. The seeds were separated from the pods and the pods were air-dried and ground. The seeds were shelled, ground and extracted at once. Most of the work was done one year after collecting but due to an unavoidable delay the results have not been ready for publication.

Experimental Part

Quantitative extractions were made as shown in Table I.

The analysis was made by the official methods. The sugar by inversion is rather high for both the seed and the pod.

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[1] Read before The Kentucky Academy of Science, May 7, 1927.

[2] Pammel, "Manual of Poisonous Plants," The Torch Press, Cedar Rapids, Ia., **1911**, p. 537.

[3] Watson and Sayre, *J. Am. Pharm. Assoc.*, **6**, 601 (1917).

[4] Stone and Test, *Am. Chem. J.*, **15**, 660 (1893).

TABLE I

QUANTITATIVE EXTRACTIONS

	Seed, %	Pod, %
Petroleum ether (50–60°)	19.27	0.41
Ether	19.92	1.24
Alcohol (95%)	49.00	42.05

TABLE II

APPROXIMATE ANALYSIS

	Seed, %	Pod, %		Seed, %	Pod, %
Moisture	5.98	11.41	Free invert sugar	0.00	3.56
Ash	3.85	3.18	Sugar by inversion	12.06	18.95
Protein (N, 6.25)	32.30	6.50	Pentosans	5.67	17.29
Crude fiber	2.01	21.12	Starch (diastase)	13.32	18.91

Physical and Chemical Examination of the Oil from the Seeds

The oil was obtained by extracting 2360 g. of the shelled, ground seed with absolute ether. The last traces of ether were removed by heating in a vacuum. Four hundred and eighty g. of a clear, light yellow oil with a bland taste was obtained. On standing, the oil deposited a small amount of solid. The oil is practically odorless. The physical and chemical properties are given in Table III.

TABLE III

PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE OIL

d^{20}	0.9219
n^{20}	1.4769
Iodine no. (Hanus)	137.5
Saponification value	191.03
Reichert-Meissl no.	0.44
Acid value	0.39
Acetyl value	11.35
Unsaponifiable matter, %	1.28
Soluble acids (% of butyric acid)	0.83
Insoluble acids, %	93.93 (Iodine no., 132.0)
Unsaturated acids (corr.), %	89.74 (Iodine no., 145.0)
Saturated acids (corr.), %	4.86 (Iodine no., 3.4, before correcting)

The iodine number would indicate a semi-drying oil but only a trace of a film was developed on exposure to the air on a glass plate for a week.

The low Reichert-Meissl number shows that only a trace of glycerides of the lower fatty acids is present, while the low acetyl value indicates a small amount of glycerides of the hydroxylated acids. The oil does not become rancid readily. The saturated and unsaturated acids were obtained by the lead salt-ether method, using the usual precautions and corrections.[5] The percentage of saturated acids is rather low.

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[5] Baughman, Brauns and Jamieson, THIS JOURNAL, **42,** 2398 (1920).

Unsaturated Acids

The bromine addition compounds of the unsaturated acids were made.[6] No hexabromide was obtained, showing the absence of linolenic acid. The precipitate of the bromides obtained melted at 113–114°. This, with the iodine number, indicates that oleic acid and linolic acid are the two acids present. The percentage composition of the unsaturated acids calculated from the iodine number (145.0) is oleic acid, 39.9%, and linolic acid, 60.1%. These results, calculated to percentage of glycerides in the oil, give 37.41% of oleic acid glyceride and 56.37% of linolic acid glyceride. The molecular weight of the unsaturated acids (280.5) would indicate such a mixture; this was obtained by heating the acids with an excess of alkali and then titrating the excess. The usual method of direct titration gave results much higher (300.5). Repeated attempts to isolate the unsaturated acids under conditions that would eliminate oxidation or polymerization always led to the same results. This has been observed by others.[7]

Saturated Acids

Due to the small amount of saturated acids in the oil (4.86%) we were unable to obtain a quantity large enough to warrant an extended separation by fractional distillation of the methyl esters. The molecular weight by titration was 279.3; m. p. 52–53°. This would indicate that stearic acid was the chief acid present. By repeated fractional crystallization from alcohol a very small top fraction was obtained, melting at 76–77°, showing the presence of arachidic acid. The next fraction melted at 58–60° and had a molecular weight by titration of 275.7. A mixture of 40% palmitic acid and 60% stearic acid would give these results. The lower fractions did not vary much from the second fraction. Although these data are incomplete they do indicate that stearic acid and palmitic acid are the main components of the saturated acids and that arachidic acid is present in small amounts.

Unsaponifiable Material

This material which was obtained in small amounts was subjected to an extended fractional crystallization. A very small phytosterol fraction was finally obtained which had a constant melting point of 165–166°.

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.9; H, 11.9. Found: C, 83.47; H, 11.61.

Summary

Approximate analysis of the seeds and pods of the Kentucky coffee nut tree has been made. The physical and chemical characteristics of

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[6] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," The Macmillan Co., London, 1913, 5th ed., vol. 1, pp. 568–578.

[7] Ref. 5, pp. 517–521.

the oil from the seeds have been determined and a phytosterol having a melting point of 165–166° has been isolated. A study of the composition of the oil from the seeds has been made, the results of which are given in the following table.

COMPOSITION OF KENTUCKY COFFEE NUT TREE SEED OIL

Glycerides of	
Oleic acid, %	37.41
Linolic acid, %	56.37
Saturated acids (probably stearic and palmitic acids with a small amount of arachidic acid)	5.08
Unsaponifiable material	1.28

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SOME PSEUDO-THIOHYDANTOINS AND ALPHA-MERCAPTO ACIDS FROM HIGHER FATTY ACIDS

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α-Halogeno derivatives of the simpler fatty acids or their esters condense readily with thio-urea to give 5-substituted pseudo-thiohydantoins. Acids of longer chain than butyric do not seem to have been used for this reaction, and it was thought worth while to extend it to some of the higher homologs, primarily with the hope that the derivatives might be of service in the separation or identification of the higher fatty acids.

Caproic,[2] lauric, myristic, palmitic and stearic acids were converted by standard methods into the α-bromo acids or esters (these react equally well). When the products, dissolved in five parts of alcohol, were warmed for an hour on the water-bath with slightly more than one molecular equivalent of thio-urea, practically quantitative yields of the crude pseudo-thiohydantoins were obtained. Several crystallizations from alcohol were usually necessary before a constant melting point was reached. The results are summarized in Table I.

TABLE I

PSEUDO-THIOHYDANTOINS

			N, %		Soluble in 100 cc. of 95% alc. at 25°, g.
Description	M. p., °C.	Formula	Calcd.	Found	
5-Butyl-	183	$C_7H_{12}ON_2S$	16.27	16.38, 16.25	...
5-Decyl-	182.5	$C_{13}H_{24}ON_2S$	10.93	11.08, 11.10	0.452
5-Duodecyl-	180.5	$C_{15}H_{28}ON_2S$	9.75	9.83, 9.91	.267
5-Tetradecyl-	176.5	$C_{17}H_{32}ON_2S$	8.96	8.97, 9.01	.082
5-Hexadecyl-	175	$C_{19}H_{36}ON_2S$	8.23	8.33, 8.37	.007

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[1] The material here presented is from the Doctor's Dissertation of Langston Fairchild Bate, University of Chicago, August, 1926.

[2] The work on caproic acid was done by Mr. Sik-Chew Lui.