

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

LEXINGTON, KENTUCKY

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]
**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

Description	M. p., °C.	Formula	N, %			Soluble in 100 cc. of 95% alc. at 25°, g.
			Calcd.	Found		
5-Butyl-	183	C ₇ H ₁₂ ON ₂ S	16.27	16.38, 16.25	...	
5-Decyl-	182.5	C ₁₃ H ₂₄ ON ₂ S	10.93	11.08, 11.10	0.452	
5-Duodecyl-	180.5	C ₁₅ H ₂₈ ON ₂ S	9.75	9.83, 9.91	.267	
5-Tetradecyl-	176.5	C ₁₇ H ₃₂ ON ₂ S	8.96	8.97, 9.01	.082	
5-Hexadecyl-	175	C ₁₉ H ₃₆ ON ₂ S	8.23	8.33, 8.37	.007	

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.

While the substances obtained are easily formed in excellent yields, they are not at all suitable for the intended use, as they show little or no melting-point depression when mixed, and thus presumably form solid solutions to an unusual extent. A similar product prepared from commercial "stearic acid," containing about equimolecular proportions of palmitic and stearic acids, melted at 175°. It is to be noted that the melting points obtained for the various members of the series are rather close together, and tend to fall as the length of the side chain increases.

As their structure suggests, these pseudo-thiohydantoin can be hydrolyzed to give the corresponding mercapto acids. The method adopted after several trials was to boil a solution of the hydantoin with an equal weight of sodium hydroxide in 10 parts of 85% alcohol. The hydrolysis usually required about 20 hours. At the end of this time, the solution was diluted and acidified, and the acid which separated was decolorized and crystallized from alcohol. The data are summarized in Table II.

TABLE II
α-MERCAPTO ACIDS

Description	M. p., °C.	Formula	S, %	Calcd.	Found	
				Equiv. wt.	S, % ^a	Equiv. wt. ^b
Caproic ^c	b. 234	C ₆ H ₁₂ O ₂ S		148.1		148.2
Lauric	59	C ₁₂ H ₂₄ O ₂ S	13.8	232.2	13.65	233
					13.71	
Myristic	66	C ₁₄ H ₂₈ O ₂ S	12.31	260.2	12.42	259.7
					12.44	
Palmitic	72-73	C ₁₆ H ₃₂ O ₂ S	11.12	288.3	10.81	290
					10.71	
Stearic	80	C ₁₈ H ₃₆ O ₂ S	10.13	316.3	10.27	316
					10.32	

^a Carius method.

^b By titration in alcohol.

^c The α-mercaptocaproic acid was prepared by hydrolysis with barium hydroxide in much more dilute alcohol and isolated as the barium salt, which was readily soluble in water and melted at 192°.

Anal. Calcd. for C₁₂H₂₂O₄S₂Ba: Ba, 31.8. Found: 31.74, 31.88.

The relative ease of oxidation of mercaptans to the corresponding disulfides makes it difficult to predict whether products obtained by the procedure described would be the mercapto acids or their oxidation products. The sulfur content and the equivalent weight are scarcely sufficient to decide this question. Accordingly, the substance described as mercapto-lauric acid was dissolved in acetic acid containing sodium acetate in excess, and one equivalent of iodine, also in acetic acid, was added to the warm solution. The iodine was reduced, and from the solution lauric acid α-disulfide was obtained, melting at 48°.

Anal. (Carius). Calcd. for C₂₄H₄₆O₄S₂: S, 13.86. Found: 13.61, 13.55. Equiv. wt. Calcd. (dibasic): 231.3. Found: 233.

The original product was thus evidently the mercapto acid.

A number of the simpler pseudo-thiohydantoina have been oxidized to the corresponding sulfonic acids, usually with potassium chlorate and hydrochloric acid in water solution. This method seemed of doubtful applicability to such insoluble substances as those described in this paper. A number of attempts under rather varied conditions were made to obtain the sulfonic acids in question by oxidation of the mercapto acids, but no products of even approximate purity were isolated except in the case of mercaptocaproic acid.

α -Carboxy-*n*-amylsulfonic Acid.—Barium mercaptocaproate was oxidized in water solution with the calculated amount of barium permanganate. The barium salt of the sulfonic acid was readily soluble in hot water, and melted at 196°.

Anal. Calcd. for $C_8H_{16}O_3S\text{Ba}$: Ba, 41.43. Found: 41.31.

The free sulfonic acid could not be obtained crystalline.

Summary

1. The pseudo-thiohydantoina corresponding to caproic, lauric, myristic, palmitic and stearic acids have been described, together with the α -mercapto acids obtained from them by hydrolysis.

2. The pseudo-thiohydantoina, while easily obtainable, offer no promise as derivatives for the separation or identification of the higher fatty acids.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

A SUGGESTED MECHANISM OF THE SPLITTING OF THE CYCLOPROPANE RING BY BROMINE

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The splitting that occurs when bromine acts on cyclopropane derivatives has usually been considered to take place by the addition of bromine at the bond broken. Cyclopropane carboxylic acid, for example, gives with bromine both the 1-bromo-substitution product and α,γ -dibromobutyric acid. It seems customary to regard these two substances as products of simultaneous and independent reactions.² Bruylants³ remarks that in

¹ The material here presented was used by Louis Sattler in partial satisfaction of the requirements for the degree of Doctor of Philosophy, University of Chicago, 1925.

² After this paper had been prepared for publication, a translation of a rather inaccessible article by Kischner [*J. Russ. Phys.-Chem. Soc.*, **41**, 659 (1909)] was obtained. Kischner remarks: "The described results of the bromination of the chloride of trimethylene carboxylic acid, as well as of the acid itself, may be formulated as the addition of one molecule of bromine. It might be more accurate, however, to describe the production of the end product as the result of two successive stages: (a) the formation of the normal substitution product; (b) the addition of hydrogen bromide, which is accompanied by the rupture of the trimethylene ring." He did not test the action of