

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNITED STATES GEOLOGICAL SURVEY, DEPARTMENT OF THE INTERIOR]

The Analysis and Composition of Fatty Material Produced by the Decomposition of Herring in Sea Water¹

BY ROGER C. WELLS AND E. THEODORE ERICKSON

The widely accepted theory of the origin of petroleum in sedimentary deposits through the decomposition of organic matter derived from plants or animals, or both, adds special interest and importance to our knowledge of observable changes in such materials under natural conditions. The material described in this paper, found to be calcium and magnesium salts of fatty acids, came from a wrecked boat load of herring, and had apparently resulted from the action of sea water on the herring, though for exactly how long a period is not known.

This material was collected at Mole Harbor, Admiralty Island, Alaska, by Mr. A. Hasselborg, and sent to Dr. David White, of the United States Geological Survey, who turned it over to the Chemical Laboratory of the Survey for study and analysis. It was reported that the wreck had long

ANALYSIS (BY E. T. ERICKSON) OF FATTY MATERIAL DERIVED FROM THE DECOMPOSITION OF HERRING

C.....	63.63
H.....	10.06
N.....	0.43
S.....	0.93
Ca.....	5.00
Mg.....	0.82
K.....	0.03
Na.....	0.26
Fe ₂ O ₃	Trace
Al ₂ O ₃	0.12
PO ₄	0.19
SO ₄ , CO ₃	None
NaCl.....	2.72
SiO ₂	0.20
	<hr/>
	84.39
Undetermined, mainly oxygen, by difference.....	15.61
	<hr/>
	100.00

rested in fifteen fathoms of water. As it finally broke up Mr. Hasselborg observed that pieces of this particular material rose to the surface, broke up, and gradually sank again. The material, as received in Washington, sank in sea water of specific gravity 1.03, unlike free fatty acids, which float. This fact indicates that such material might be deposited directly in sediments. The sample consisted of fairly uniform pieces with a greasy feel, somewhat porous and nearly white in appearance, with some finer broken material. The larger pieces seemed to consist of layers.

This analysis was made with material dried at 105° for one hour, during which the loss was 5.90%. This loss was found to be practically all the water and did not include a significant quantity of

organic matter. Nitrogen was determined by the Dumas method, and sulfur by the Carius method. The difference represents mainly organic oxygen. The most striking features shown by the analysis are the high percentages of calcium and magnesium and low percentage of phosphate:

¹ Published by permission of the Director of the U. S. Geological Survey.

the calcium cannot be present as calcium phosphate or carbonate but must be mainly in an organic compound.

Further tests to determine the identity of the organic material were made by decomposing it with hydrochloric acid. The resulting insoluble fatty acids were filtered off, dried, extracted with benzene, and the unsaturated and saturated acids separated by the Varrentrap method.² The saturated fatty acids probably include palmitic acid, myristic acid, and some acids of lower molecular weight. These conclusions are based on determinations of the melting points of the fractionated material. Three small fractions were separated by adding magnesium acetate to the alcoholic solution of the mixed acids. These fractions, freed from magnesium, had melting and solidifying points of 58 and 56°, 58.5 and 55°, and 57 and 55.5°, respectively. The melting and solidifying points of the original saturated fatty acid material were 53 and 51°; those of material remaining from the fractionation 48 and 47°.

Stearic acid did not seem to be present, although Lexow³ states that its glyceryl ester occurs in Norwegian herring oil, together with the esters of palmitic and myristic acids. On the other hand, Fryer and Weston⁴ state that the "stearine" obtained from Japanese herring and other fishes is chiefly "palmitin." Tsujimoto⁵ isolated palmitic and myristic acids from fatty material obtained from the great herring at Hokkaido (Hokushu) but found the glyceryl ester of stearic acid present in relatively small quantities. Thus the range of saturated fatty acids recovered from the Mole Harbor material is about the same as that in glyceryl ester form in herring oil.

The unsaturated fatty acid portion was amber colored, of an oil-like appearance, and gave an iodine adsorption figure of 70 by the Wijs method. This figure is low compared with that of known herring oils. Lexow,⁶ in 120 Norwegian herring oils collected from different localities and at different seasons of the year, found a high average of 148 during August and a low average of 115 during March.

A summary of the findings in the quantitative work is given in the following table.

The non-saponifiable matter yielded a small quantity of the characteristic cholesterol precipitate with digitonin. This precipitate was converted to acetate, the melting point of which confirmed the presence of cholesterol. Because of lack of material the state of occurrence of the cholesterol was not determined.

² Holde, "The Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes," Trans. by E. Mueller, John Wiley and Sons, Inc., New York, 1922, p. 371.

³ Lexow, *Chem. Umschau Fette, Öle, Wachse, Harze*, **28**, Part 7, 85 (1921).

⁴ Fryer and Weston, "Technical Handbook of Oils, Fats and Waxes," Cambridge Press, 1917, Vol. I, p. 101.

⁵ Tsujimoto, *J. Soc. Chem. Ind. Japan*, **29**, 195-202; *Chem. Abs.*, **20**, 2912 (1926).

⁶ Lexow, *Chem. Umschau Fette, Öle, Wachse, Harze*, **29**, Part 9, 110-113 (1922).

SUMMARY OF CHEMICAL SEPARATIONS ON SAMPLE FROM MOLE HARBOR

	Per cent.
Loss on heating for one hour at 105°.....	5.90
Organic matter extracted with benzene	{
after treatment of the sample with	
hydrochloric acid	
	Unsaturated fatty acids.... 8.20
	Saturated fatty acids..... 64.50
	Non-saponifiable matter... 0.60
Protein calculated from nitrogen (N × 6.25).....	2.80
Inorganic matter, including sulfur and 2.72 NaCl.....	10.27
Undetermined, including possibly some carbohydrate substance and oxygen required by sulfur compounds, less replaceable hydrogen of fatty acids (0.33).....	7.73
	100.00

The material insoluble in benzene was found on ignition to contain some organic matter. At the beginning of the ignition carbonization was noted, followed by the characteristic odor of burning protein. The material extracted with benzene gave no evidence of undecomposed glyceryl ester. Most of the fatty acids in the original sample must have been combined with the inorganic bases, though some free acids may have been present.

Geochemical Features.—The well-known Engler-Höfer theory of the origin of petroleum from fatty materials in sediments⁷ seems to assume that the fatty substances are isolated in some way from the saline constituents of the water of the sediments during the stage of microbiological decomposition, so that calcium and magnesium compounds of the liberated fatty acids are not formed. According to this theory the fatty substances first change into free fatty acids and glycerin, either by hydrolysis or by microbiological fermentation, or both. Eventually, the fatty acids are assumed to split off carbon dioxide and the hydrocarbons to polymerize into petroleum. It is impossible here to go into the many details of this theory. The present writers wish to emphasize a possibility not heretofore considered—that calcium and magnesium salts may be formed even before or as the material is inclosed in sediments, and that such compounds deposited with the sediments can then yield petroleum under proper environmental conditions, whether by heat, base exchange or otherwise.

The experiments described below were made to find out whether the material from Mole Harbor would show any marked disinclination to form oil upon thermal decomposition in sealed glass tubes. They indicate that such material requires but a slightly higher temperature than free fatty acid material to form oil.

The free fatty acid, palmitic acid, some calcium palmitate and the herring residue from Mole Harbor were each subjected to successive heat treatments in sealed glass tubes during eighteen-hour intervals at 200, 300 and 350° and then finally for seven days at 350°, and any effects that might indicate decomposition noted.

⁷ "Das Erdöl," Leipzig, 1909, II Band, 114-128. E. Engler, *Petroleum Zeitschrift*, 7, 399-403 (1912); "Das Erdöl und seine Verwandten," Braunschweig, 1922, p. 329.

At 200° the palmitic acid and the herring residue darkened slightly and each of the materials melted into a mass that solidified on cooling.

At 300° the palmitic acid darkened further in color and still solidified on cooling. The calcium palmitate and the herring residue remained apparently unchanged from the previous heat treatment.

Under the initial heat treatment at 350° for eighteen hours the palmitic acid yielded a still darker brownish product that remained fluid at ordinary room temperatures. The calcium palmitate and herring residue changed but slightly in color and gave but little appearance of having undergone any further decomposition.

In the further heating for seven days at 350° all the materials yielded a greenish fluorescent petroleum-like product. The yield was similar in each experiment and appeared relatively high compared to the quantity of original material taken. When the tube which had held the calcium palmitate was opened considerable pressure was shown. The odor resembled gasolene. The residue consisted of carbonaceous matter, a little naphthenic-like oil, and calcium carbonate.

Summary

This paper describes the analysis of calcium and magnesium salts of fatty acids derived from herring buried under sea water, and discusses some geochemical possibilities related to the origin of petroleum in sedimentary deposits.

WASHINGTON, D. C.

RECEIVED JULY 18, 1932
PUBLISHED JANUARY 11, 1933

[CONTRIBUTION FROM THE FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

The Preparation and Optical Resolution of Ammonium *dl*-Alpha-Bromocamphor-Pi-Sulfonate

BY A. W. INGERSOLL AND S. H. BABCOCK

The preparation of many asymmetric acids and bases is necessary for a comprehensive study of optically isomeric salts.¹ Obviously those acids and bases whose racemic forms are capable of resolution and whose active forms are useful resolving agents are especially valuable. Also the racemic forms are as necessary for this type of study as the active forms. Bases suitable for resolution work and available in both the racemic and active forms are fairly numerous, but there are relatively few acids of this description. Thus *d*-tartaric, *l*-malic, *d*-camphor-10-sulfonic and *d*- α -bromocamphor- π -sulfonic acids are the only ones that have been much used. The optical antipodes and the racemic forms of these, though known in

¹ (a) Ingersoll and White, THIS JOURNAL, 54, 274 (1932); (b) Ingersoll and Burns, *ibid.*, 54, 4712 (1932).