TABLE 2

Spectrophotometric Measurements of Linoleic and Linolenic Acids

Sample No.	Extinction Coefficient $a = E \frac{g./l.}{1\ cm.}$									Conjugated Acids					
	Wave Length mμ														
	232	233	262	268	274	280	310	316	322	Diene[1]	Triene[1]	Tetraene[1]	Diene[2]	Triene[2]	Tetraene[2]
Linoleic No. 1	0.499	0.494	0.328	0.396	0.339	0.332	0.0270	0.0321	0.0261	0.39	0.24	0.013	0.39	0.082	0.0063
Linoleic No. 2	0.121	0.115	0.059	0.063	0.055	0.051	0.0056	0.0046	0.0032	0.092	0.038	0.0016	0.077	0.0078	0.00023
Linoleic No. 3	0.095	0.088	0.025	0.026	0.022	0.020	0.0023	0.0018	0.0016	0.072	0.015	0.0008	0.055	0.0033	0.00
Linoleic No. 4	0.062	0.056	0.015	0.013	0.012	0.010	0.0031	0.0026	0.0024	0.046	0.0069	0.0012	0.027	0.00	0.00
Linolenic No. 1	0.424	0.422	0.581	0.677	0.658	0.650	0.349	0.450	0.328	0.31	0.40	0.16	0.33	0.075	0.13
Linolenic No. 2	0.083	0.078	0.022	0.020	0.018	0.016	0.0058	0.0061	0.0049	0.064	0.011	0.0024	0.045	0.00	0.00085

[1] Calculated according to method of Brode *et al* (3).
[2] Calculated according to method of Brice and Swain (2).

The importance of spectrophotometric measurements as a criterion of purity is emphasized.

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The Fatty Acids of Menhaden Oil.

III. Distillation of the Hydrogenated Methyl Esters and Evaluation of the Carbon Series*

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IN THE first paper (1, 2) of this series the methyl esters of menhaden oil were distilled through an efficient column and the C_{12}, C_{14}, C_{16}, and C_{18} fractions were studied mainly by low temperature crystallization. It was pointed out that not all of the C_{18} esters of the specimen were included in the C_{18} main fraction resulting from this distillation because we did not try to distill the high boiling fractions containing the highly unsaturated esters. In view of the work of Framer and van den Heuvel (3) and of our experience in this laboratory the polyethylenic esters of this oil, especially those of the C_{20} and C_{22} series, are seriously altered by long exposure to the conditions of distillation with the resultant formation of polymerised and cyclized material. In view of these facts the usual ester distillation method for the evaluation of the carbon series cannot be applied to the methyl esters of menhaden oil directly. Accordingly we have attempted to evaluate the composition by analysis of the fractions resulting from distillation of the hydrogenated methyl esters. The results thus obtained are slightly distorted, especially in the higher series, because of their high original unsaturation and of the fact that addition of hydrogen to the C_{20} and C_{22} series results in an appreciable increase in the amounts of these fractions actually reported below.

Experimental

Two gallons of the specimen of menhaden oil used in our previous work was hydrogenated for us in the laboratory of the Procter and Gamble Company through the courtesy of Dr. A. S. Richardson. Fourteen hundred and fifty g. of this fat was esterified in the usual manner. The crude esters were distilled: B.P. 180-238° at 2 mm. The residue from this distillation was transferred to a smaller flask and an additional distillate (14.6 g.) obtained; m.m.w. 456 and I.N. 33.9. The yield of esters was practically quantitative. The main product, not including the 14.6 g., analyzed as follows: m.m.w. 300.9; I.N. 6.9. Six hundred and four g. of these esters was distilled through our packed column. The results of the distillation, analyses of the fractions, and calculations of component carbon series are shown in Table I; 6.8 g. of the original 15 g. residue was apportioned to the residue fraction of this distillation and included as "above C_{26}" material in the table.

The carbon series of menhaden oil as shown in Table I include acids from C_{14} through and above C_{26}. The 0.1% of C_{12} esters found in our former work (1) is not apparent from the distillation of this comparatively small amount of esters but must be considered as present. Since the saturated and monoethylenic

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TABLE I

Fraction al Distillation of Methyl Esters of Hydrogenated Menhaden Oil

Fraction	°C.	Wt.	Mol. Wt.	I.N.	Composition g.							Above
					C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{26}
Original			300.9	6.9	....	....	....	....	....	....	....	....
1	97-113	14.7	245.2	0.6	13.1	1.6	....	....	....	....	....	
2	113-17	33.7	246.2	0.9	28.7	5.0	....	....	....	....	....	
3	117-34	12.4	268.4	2.6	0.8	11.6	....	....	....	....	....	
4	134-37	135.1	272.2	1.2	....	124.5	10.6	....	....	....	....	
5	137-54	48.1	277.4	3.3	....	35.1	13.0	....	....	....	....	
6	154-56	133.1	296.9	4.8	....	6.1	127.0	....	....	....	....	
7	156-73	15.8	307.1	14.4	....	....	10.7	5.1	....	....	....	
8	173-77	92.9	326.1	9.0	....	....	....	92.9	....	....	....	
9	177-93	16.5	341.3	16.9	....	....	....	7.5	9.0	....	....	
10	193-95	66.5	361.6	0.9	....	....	....	....	48.9	17.6	....	
11	195-215	14.0	367.2	0.9	....	....	....	....	7.3	6.7	....	
Column hold-up		7.0	411.0		....	....	....	....	....		7.0	
Residue		14.6	....		....	....	....	....	....		....	14.6
Totals, grams		604.4			42.6	183.9	161.3	105.5	65.2	24.3	7.0	14.6
Wt. percent					6.9	30.4	26.8	17.5	10.8	4.0	1.2	2.4

esters (2) did not include series above C_{24}, and further since the amounts of C_{24} acids recovered in the saturated and monoethylenic esters were appreciably less than shown in the present work, it is concluded that the C_{24}, C_{26}, and above C_{26} esters include unsaturated esters of these series. Thus it is correct to say that the unsaturated acids of menhaden oil embrace all carbon series from C_{12} to C_{26}, inclusive and probably series still higher.

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Summary

Analysis of the fractions obtained as a result of distillation of the methyl esters of the hydrogenated acids of menhaden oil show the amounts indicated (wt. %): C_{14}, 6.9; C_{16}, 30.4; C_{18}, 26.8; C_{20}, 17.5; C_{22}, 10.8; C_{24}, 4.0; C_{26}, 1.2; above C_{26}, 2.4. In addition, about 0.1% of C_{12} acids was demonstrated previously.

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Spectroscopic Changes in Fats During Rancidification*

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IN connection with studies that were conducted at the University of Minnesota several years ago concerning natural antioxidants in lards some spectroscopic measurements were made on lards which had been oxidized to various degrees by exposure to air in an oven at 63°C. It was found that in the ultraviolet region there occurred increases in the absorption of light that were approximately proportional to the peroxide values of the samples, at least in the earlier stages of rancidification.

In later measurements, illustrated in Figure I, similar increases in absorption were found in samples oxidized at 100°C. However, in common with the observations of many others who have examined various peroxides spectroscopically, it was observed that the increases in absorption were not due to peroxides. When the peroxide values of the oxidized samples were reduced to a low value by treatment with superheated steam, the absorption increased still further (compare curves 6 and 8), suggesting that the chromophores may result directly from molecular rearrangement, decomposition, and polymerization reactions of the peroxides. Spectrophotometric studies of other oxidized fats have led other investigators to the same general conclusions (1).

The present report is a condensed summary of subsequent spectroscopic studies which were initiated for the purpose of obtaining additional insight on the course and mechanism of the autoxidation reaction in fats, the detailed data of which have been presented elsewhere (2, 3). It must be emphasized from the outset that the measurements to be reported were preliminary in character and that no complete studies, and only tentative interpretations, can be given. The experiments were designed primarily to develop techniques and to suggest lines of attack for the more complete studies that are contemplated.

Experimental

The purest available preparations of oleic, linoleic, and linolenic acids in their common natural isomeric forms, some of their conjugated forms and unnatural stereoisomers, and some of their esters, were oxidized individually by exposure to air at constant temperatures. The temperature selected in each case depended

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