assumption that mono- and di-esters have the same adduct-forming tendency is also questionable.

Urea fractionation of crude glycerol monolaurate prepared by the method of Basu-Roy-Choudhury et al. (17) also supported these conclusions. The percentages of diglycerides decreased in the successive fractions and the monoglycerides showed a gradual increase (Table XI). The triglycerides appeared in the last fraction. The results obtained in this laboratory are supported by those of Roncero, Fiestas, Mazuelos, and Moreno (9) and by Bradley, Mueller, and Shokal (10).

### Summary

This study of the glycerolysis of linseed, coconut, and sesame oil at 200°C., 225°C., and 250°C. shows that coconut oil, because of its low-average-molecular weight, is esterified more easily than sesame and linseed oils. Comparison of the reactions of sesame and linseed oils indicates that saturated acids are transesterified more easily than the unsaturated ones. The amount of glycerol to be used is determined by its miscibility at the particular reaction temperature.

Results of alcohol extraction of the crude monoglycerides from linseed and coconut oil indicate that the glycerides separate on the basis of degree of esterification rather than on unsaturation.

Urea adduct fractionations of the technical monoglycerides of sesame oil and lauric acid show that diglycerides form urea adducts more easily than do monoglycerides. In this case, also, the fractionation is related to the degree of esterification rather than unsaturation.

### Acknowledgment

The authors wish to express their gratitude to Nagpur University for providing research facilities and for the award of research fellowship to one of them (S. N. Shah).

#### REFERENCES

REFERENCES
1. Mehta, T. N., Rao, C. V. N., Laxmikantan, V., and Shah, S. N., J. Am. Oil Chemists' Soc., 32, 478 (1955).
2. Choudhury, D. K., and Mukherji, B. K., J. Indian Chem. Soc., 31, 116 (1954).
3. Haller, A., Compt. Rend., 143, 657 (1906).
4. Pore, J., Oleagineux, 7, 21-24 (1952); J. Am. Oil Chemists' Soc., 29, 164 (1952).
5. Rossi, C., Bottazi, D., and Croce, G., Chimica e Industria, 37, 356-359 (1955); cf. C. A. 49, 13668 (1955).
6. Feuge, R. O., and Gros, Audrey T., J. Am. Oil Chemists' Soc., 27, 117 (1950).
7. Basu-Roy-Choudhury, R. C., Sarkar, S., Chakrabarty, M. M., and Goswami, M. N., Science and Culture (India), 20(8), 395 (1955).
8. Holman, R. T., Lundberg, W. O., and Malkin, T., "Progress in the Chemistry of Fats and Lipides," vol. 2, p. 253.
9. Roncero, A. V., Fiestas, J., Mazuelos, F., and Moreno, J. M., Fette u. Seifen, 54, 550 (1952).
10. Bradley, T. F., Mueller, A. C., and Shokal, E. C., U. S. Patent 2,700,036, Jan. 18, 1955.
11. Heckles, T. S., and Dunlap, L. H., J. Am. Oil Chemists' Soc., 32, 224 (1955).
12. Pohle, W. D., and Mehlenbacher, V. C., Oil and Soap, 23, 48 (1946).
13. Pohle, W. D., and Mehlenbacher, V. C., J. Am. Oil Chemists' Soc., 37, 54 (1950).
14. Kawai, S., J. Soc. Chem. Ind. (Japan), 44, 705 (1941); Chem. Abs., 42, 2118 (1948).
15. Runk, R. H., Ind. Eng. and Chem. 44, 1124 (1952).
16. Feuge, R. O., and Bailey, A. E., Oil and Soap, 23, 259 (1946).
17. Bau-Roy-Choudhury, R. C., Sarkar, S., Chakrabarty, M. M., and Goswami, M. N., Science and Culture (India), 20(7), 344 (1955).

[Received April 9, 1956]

## International Collaboration on Glycerine Analysis

URING the past four years collaborative analyses have been carried out among laboratories in the United Kingdom, Europe, and the United States under the auspices of the Glycerine Analysis Committee of the American Oil Chemists' Society. The firstyear analyses were made by the International Acetin Method and the new A.O.C.S. Sodium Periodate Method. These analyses and previous collaborative work showed the superior accuracy of the sodium periodate method. This led to the withdrawal of the Acetin Method and the adoption of the Sodium Periodate Method as the Official Method by the A.O.C.S. and the International Union of Pure and Applied Chemistry. Since then some modifications of the sodium periodate method have been proposed. The principal modifications involve using an indicator for determining the titration endpoint in place of the electrometric endpoint, a larger sample so that the titration would be approximately 80 ml. in place of 40 ml., the use of nitrogen to protect the solution during the titration, and the use of a neutral, sodium periodate reagent in place of the acidified sodium periodate. These variations were incorporated in the Sodium Periodate Method adopted by the British. During the past year a collaborative study was undertaken to determine the relative merits of the various modification.

For this collaborative work we are indebted to the British Group, which provided a specially purified glycerol which was diluted to approximately 90% glycerol and a synthetic crude containing approximately 68% glycerol.

The glycerol content of the C. P. glycerol was based upon the specific gravity tests which are the most precise and accurate means for determining the glycerol content of such solutions. The accuracy of the various procedures and modifications were evaluated by comparing the average analyses on the C. P. glycerine with the percentage of glycerol found by the specific gravity method.

There were eight laboratories in the United Kingdom, eight in Europe, and 14 in the United States which took part in this collaborative work. The results are given in the following tables. Table I gives a comparison of the methods and modifications with respect to accuracy and precision. The individual analyses are given in Tables II, III, and IV. The statistical analysis of the collaborative data by H. P. Andrews follows the tables together with Table V summarizing his data.

### Statistical Analysis of International Collaborative Study

Two samples of glycerine, one C. P. and a made-up crude, were analyzed for percentage of glycerol in duplicate by 29 international collaborating laboratories, each using a number of variations of the A.O.C.S. and British methods. The variations involved acidified and neutral reagent, the use or omission of nitrogen with the acidified reagent, and the use of an indicator or electrometric endpoint.

Statistical analyses have been made to determine the within- and among-laboratories precision of the various modifications of the methods. The means and variance components are summarized in the attached tabulation. Concerning the absolute values obtained, and related to accuracy:

- a) there was no significant difference between values obtained by the A.O.C.S. and British methods, irrespective of the use of acidified or neutral reagents or indicator or electrometric endpoints;
- b) using a neutral reagent gave slightly, and significantly lower values than were obtained with an acidified reagent;
- c) titrating to an electrometric endpoint gave significantly higher values than the indicator endpoint, irrespective of other conditions; and
- d) in the British method, using the acidified reagent, the omission of nitrogen gave significantly higher results than were obtained when nitrogen was used.

With respect to precision of the various methods:

- a) the within-laboratory precision of the British method was somewhat better than that of the A.O.C.S. (average A.O.C.S.  $S^2 = 0.0111$ , British  $S^2 = 0.0049$ ). However the among-laboratory precision was reversed with the variability among laboratories being greater for the British method than for the A.O.C.S (average A.O.C.S.  $S^2 = 0.1101$ , British  $S^2 = 0.1594$ ). Since among-laboratory variation is the major contributor to error, the over-all precision of the A.O.C.S. method ( $S^2 = 0.1212$ ) was superior to that of the British method ( $S^2 = 0.1643$ );
- b) precision was slightly poorer, using the acidified reagent ( $S^2 = 0.1485$ ), than with the neutral reagent ( $S^2 = 0.1364$ ), and this was particularly true with the A.O.C.S. method (the difference was negligible with the British);
- c) there was no significant difference in the precision obtained by using indicator or electrometric endpoints; and
- d) omission of nitrogen with the acidified reagent in the British method very markedly decreased the precision,  $S^2 = 0.2773$  compared to  $S^2 = 0.1631$  for the acidified reagent with nitrogen.

These analytical variations were directly proportional to the magnitude of the measurement and consequently were larger for the C. P. than for the made-up crude sample. For this reason it seems impractical to attempt to calculate probability limits for various analytical situations.

H. P. ANDREWS

The statistical evaluation and comparison of the average analysis with that by the specific gravity method indicate the following:

- a) analysis of the C. P. Glycerine by the A.O.C.S. Method, using acidified and neutral reagent (electrometric endpoint), and the British Method, using acidified reagent (electrometric endpoint), gave results closer to the glycerol content as determined by specific gravity than the other modifications (Table I);
- b) precision obtained with the A.O.C.S. Method among the collaborators was slightly better than with the British Method (Table I); and

c) on the Made-up Crude the most accurate results were obtained by using the electrometric titration in the A.O.C.S. Method and British Method with acidified and neutral reagent. The apparently better precision on the crude is due to using a larger sample, which gave approximately the same titration as for the C. P. Glycerine.

The complete data and statistical report provide the information necessary for any other comparisons that one may wish to make on these methods and modifications.

TABLE I										
Averages and Precision	for the	Methods	and Modifications	Used						

	C.	P. Glycero	al			
Method	Ave	rage	Precision expressed as $95\%$ confidence limits for individ- ual analyses among laborato- ries, standard deviation $\times 2$			
Specific gravity	90	.19	±0	).13		
	Electro- metric endpoint	Indicator endpoint	Electro- metric endpoint	Indicator endpoint		
A.O.C.S. Acidified reagent Neutral reagent British Acidified reagent Neutral reagent	90.17 90.14 90.18 90.07	89.87 89.86 89.96 89.85	$\pm 0.80 \\ \pm 0.72 \\ \pm 0.90 \\ \pm 0.88$	$\pm 0.84 \pm 0.76 \pm 0.92 \pm 0.96$		
Acidified reagent (without N <sub>2</sub> )	90,35	90.11	$\pm 1.18$	$\pm 1.32$		
	Mad	le-Up Crud	le			
A.O.C.S. Acidified reagent Neutral reagent British Acidified reagent Neutral reagent Acidified reagent	68.03 68.03 68.05 68.00	67.85 67.83 67.85 67.87	$\pm 0.64$ $\pm 0.60$ $\pm 0.68$ $\pm 0.72$	$\begin{array}{c} \pm 0.60 \\ \pm 0.54 \\ \pm 0.70 \\ \pm 0.66 \end{array}$		
(without N2)	68.22	68.01	$\pm 0.90$	±0.68		

 TABLE II

 Specific Gravity and Fischer Moisture Analyses of C. P. Glycerol

				-	
Collabo- rator	Glycerol by specific gravity	Moisture by Fischer volumetric method	Collabo- rator	Glycerol by specific gravity	Moisture by Fischer volumetric method
	%	%		%	%
1	90,15	9.1	16	90.18	10.0
<b>2</b>	90.12	9.8		90.19	10.1
3	90.17	9.8	17	90.30	9.8
4	90.26	10.0			9.8
-	90.26	10.0	18	90.18	9.8
5	90.17	9.8 .	19	90.15	9.8
	90.17	9.8	20	90.23	-
6	90.15	10.0	21	90.21	
7	90.28	10.3	22	90.21	
	90.29	10.3	23		i —
8	90.23	9.8	24	90.17	9.8
	90.26	9.8	25	90.17	
9	90.23	8.4	26	90.21	10.1
10	$90.13 \\ 90.15$	$\begin{array}{c} 10.1 \\ 10.2 \end{array}$	27	90.18	
11	90.13 90.17	9.4	28		9.5
		9.9	29		
12	90.21	9.9 9.8			
13	90.27	_			
14	90.14	9.9			
-	90.16	9.8			
15	90.10	9.9			
1	90.10	9.9			

### Collaborators

Country Canada Names and Addresses

Denmark

K. H. Russell Swift and Company Toronto, Ontario K. Helholt Aarhus Oliafabrik Aarhus, Denmark

TABLE III C. P. Glycerine—Percentage of Glycerol by

	C. P. Glycerine- A.O.C.S. Method					Percentage of Glycerol by British Method						
	A.	0.0.8.1	vietnoa				british	method	Ació	lified		
		lified gent		itral gent		tral gent		lified gent	rea	gent nitted		
	Ind.	Elect.										
1	$90.4 \\ 90.4$	$90.7 \\ 90.8$	$90.0 \\ 90.0$	$90.6 \\ 90.5$	$89.6 \\ 89.7$	$89.7 \\ 89.8$	$\substack{90.1\\90.2}$	$90.3 \\ 90.4$	$\substack{90.2\\90.4}$	$90.4 \\ 90.5$		
2	$90.4 \\ 90.4$	$\frac{90.5}{90.5}$	$\begin{array}{c} 90.1 \\ 90.1 \end{array}$	$90.4 \\ 90.4$	89.8 89.8	$89.9 \\ 89.9$	$\begin{array}{c} 90.1 \\ 90.1 \end{array}$	$90.2 \\ 90.2$	$\substack{90.1\\90.1}$	$\substack{90.2\\90.2}$		
3	$90.1 \\ 90.1$	90.3 90.3	90.0 90.0	$90.1 \\ 90.0$	90.0 90.0	$90.1 \\ 90.0$	$90.1 \\ 90.1$	$90.3 \\ 90.3$	$\substack{90.1\\90.1}$	$90.2 \\ 90.3$		
4	89.2	89.4	89.0	89.0	88.6	88.7	89.1	$     89.1 \\     89.1 $	89.1	89.1		
5	$89.3 \\ 89.8$	$\begin{array}{c} 89.4 \\ 90.0 \end{array}$	$\begin{array}{c} 88.9 \\ 89.7 \end{array}$	89.0 89.9	88.7 89.8	$\begin{array}{c} 88.7 \\ 89.9 \end{array}$	89.0 89.9	90.0	$\begin{array}{c} 89.1 \\ 89.7 \end{array}$	89.1 89.8		
6	$89.8 \\ 90.0$	90.0 90.2	$\begin{array}{c} 89.8 \\ 90.1 \end{array}$	$89.9 \\ 90.3$	89.8 90.1	$\begin{array}{c} 90.0 \\ 90.3 \end{array}$	$89.9 \\ 90.1$	$\begin{array}{c} 90.0 \\ 90.2 \end{array}$	$\begin{array}{c} 89.8 \\ 90.0 \end{array}$	90.0 90.1		
7	$90.1 \\ 89.3$	$90.2 \\ 89.4$	$90.2 \\ 89.2$	90.4 89.4	90.3 89.1	$\begin{array}{c} 90.4 \\ 89.5 \end{array}$	$90.1 \\ 89.0$	$90.2 \\ 89.4$	$\begin{array}{c} 90.1 \\ 89.1 \end{array}$	$90.2 \\ 89.6$		
8	89.3 89.8	89.4	89.1	89.3 90.0	89.3	89.6	89.0	89.3 90.0	89.1 89.9	89.6 90.0		
	89.8	90.0 90.0	$89.8 \\ 89.7$	90.1		90.0 90.0	89.9 89.9	90.1	90.0	90.1		
9	$89.5 \\ 89.6$	$\substack{90.1\\90.0}$	_	$\begin{array}{c} 90.1\\90.1\end{array}$	$89.4 \\ 89.4$	$\begin{array}{c} 91.3 \\ 91.3 \end{array}$	$89.5 \\ 89.5$	-90.7 90.7	=			
10	$89.6 \\ 89.6$	$90.0 \\ 90.0$	$89.7 \\ 89.7$	90.0 90.0	$\frac{89.7}{89.7}$	$89.6 \\ 89.6$	$89.6 \\ 89.6$	$\begin{array}{c} 90.0\\90.0\end{array}$	$89.9 \\ 89.9$	$\begin{array}{c} 90.0\\ 90.0\end{array}$		
11	$\frac{88.7}{88.7}$	$89.5 \\ 89.5$	$89.0 \\ 89.0$	89.8 89.8	$89.0 \\ 89.0$	$89.4 \\ 89.4$	$\frac{88.9}{89.3}$	$89.4 \\ 89.8$	$89.7 \\ 89.7$	$89.9 \\ 89.9$		
12	90.5	91.1	90.1	$90.1 \\ 90.2$	90.1	90.1 90.6	$91.3 \\ 91.2$	$91.6 \\ 91.5$	$91.5 \\ 91.5$	$91.8 \\ 91.8$		
13	90.5 90.1	91.0 90.3	90.2 89.9	90.0	90.6 89.6	89.8	89.6	90.0	90.0	89.9		
14	90.1 90.0	$90.2 \\ 90.2$	$\begin{array}{c} 89.9 \\ 90.0 \end{array}$	$\begin{array}{c} 90.0\\ 90.2 \end{array}$	$\begin{array}{c} 89.7\\ 89.9\end{array}$	$\begin{array}{c} 89.9 \\ 90.0 \end{array}$	$89.7 \\ 90.0$	$89.8 \\ 90.1$	$87.9 \\ 90.1$	$\begin{array}{c} 90.1 \\ 90.3 \end{array}$		
15	$90.0 \\ 90.1$	$90.3 \\ 90.3$	$\begin{array}{c} 90.0 \\ 90.1 \end{array}$	$\begin{array}{c} 90.2 \\ 90.4 \end{array}$	89.9 90.0	$90.0 \\ 90.0$	$\begin{array}{c} 90.0\\ 90.0\end{array}$	$90.1 \\ 90.1$	$90.1 \\ 90.2$	$90.3 \\ 90.3$		
16	90.0 90.1	90.2 90.4	90.2 90.1	90.4 90.1	90.0 89.9	90.1 90.0	90.1 90.0	$90.2 \\ 90.2$	$90.3 \\ 90.1$	$90.4 \\ 90.2$		
	90.0	90.4	90.3	90.5	90.0	90.1	90.0	90.1	90.1	90.2		
17	$\begin{array}{c} 90.0\\ 89.9 \end{array}$	$\substack{90.1\\90.0}$	$89.9 \\ 90.0$	90.1 90.1	$\substack{90.1\\90.1}$	$\substack{90.2\\90.2}$	$\substack{90.1\\90.1}$	$\begin{array}{c} 90.2 \\ 90.2 \end{array}$	$\begin{array}{c} 90.2 \\ 90.2 \end{array}$	$\begin{array}{c} 90.3 \\ 90.3 \end{array}$		
18	$89.9 \\ 89.7$	$90.3 \\ 90.2$	$89.4 \\ 89.3$	90.0 89.9	$\substack{90.1\\90.1}$	$\begin{array}{c} 90.4 \\ 90.6 \end{array}$	$90.0 \\ 89.9$	$\substack{90.1\\90.2}$	$89.7 \\ 89.6$	$\substack{90.1\\90.2}$		
19	$89.6 \\ 89.4$	$90.1 \\ 89.9$	$89.8 \\ 89.9$	90.2 90.4	$\substack{90.1\\90.1}$	${00.2 \\ 90.2 }$	$\substack{90.1\\90.1}$	$\begin{array}{c} 90.2 \\ 90.2 \end{array}$	$90.4 \\ 90.3$	$90.5 \\ 90.4$		
<b>20</b>	$89.8 \\ 89.9$	$\begin{array}{c} 90.0\\ 90.0\end{array}$	$89.8 \\ 89.9$	$\substack{90.2\\90.2}$	$\substack{90.1\\90.1}$	$\begin{array}{c} 90.3\\90.3\end{array}$	_	_	$\substack{90.1\\90.2}$	90.3 90.4		
<b>21</b>	89.3	89.6	89.3	89.6			—					
<b>22</b>	$\begin{array}{c} 89.3 \\ 89.5 \end{array}$	89.7 90.0	$\begin{array}{c} 89.4 \\ 90.0 \end{array}$	89.6 90.3	90.2	90.3	90.1	90.4	90.5	_		
23	$\begin{array}{c} 90.4 \\ 90.5 \end{array}$	$\begin{array}{c} 90.8 \\ 90.7 \end{array}$	$\begin{array}{c} 90.1 \\ 90.3 \end{array}$	90.3 90.4	$\begin{array}{c} 90.3 \\ 90.3 \end{array}$	$\begin{array}{c} 90.4 \\ 90.5 \end{array}$	$\begin{array}{c} 90.2 \\ 90.1 \end{array}$	$\begin{array}{c} 90.3 \\ 90.4 \end{array}$	90.4 90.4			
24	$90.4 \\ 90.2$	$90.6 \\ 90.5$	$\begin{array}{c} 90.4 \\ 90.0 \end{array}$	90.5 90.3	$90.3 \\ 90.3$	90.5 90.4	90.3	90.5	90.5 90.4	90.6		
25	$90.2 \\ 89.7$	90.4 89.9	90.1 90.0	90.4 90.2	$90.2 \\ 89.8$	$\begin{array}{c} 90.4 \\ 90.0 \end{array}$	90.4 89.8	90.6 90.0	90.4 89.8	90.6 90.0		
	89.8	90.0	90.0	90.2	89.7	89.9	89.7	89.9	89.8	90.0		
26	$\substack{90.2\\90.2}$	$\begin{array}{c} 90.5 \\ 90.5 \end{array}$	$\substack{90.1\\90.1}$	$90.5 \\ 90.5$	$\substack{90.2\\90.2}$	$\substack{90.2\\90.2}$	$\substack{90.2\\90.2}$	$\substack{90.2\\90.2}$	$\begin{array}{c} 90.2 \\ 90.2 \end{array}$	$90.2 \\ 90.7$		
27	$90.3 \\ 90.3$	$90.7 \\ 90.7$	$90.3 \\ 90.3$	$90.5 \\ 90.5$	$90.6 \\ 90.5$	$90.8 \\ 90.7$	$90.6 \\ 90.6$	$90.7 \\ 90.8$	$\begin{array}{c} 90.5\\90.6\end{array}$	$90.7 \\ 90.7$		
<b>28</b>	$89.6 \\ 89.4$	$90.0 \\ 89.7$	$\substack{90.1\\90.0}$	90.5 90.4	$\substack{89.2\\89.2}$	$89.5 \\ 89.6$	$\substack{90.1\\90.0}$	$\frac{90.2}{90.2}$	$\begin{array}{c} 91.0\\ 91.0\end{array}$	$92.5 \\ 92.5$		
29	89.9 90.0	$\begin{array}{c} 90.2 \\ 90.3 \end{array}$	89.9 90.0	90.5 90.5	89 <b>.9</b> 90.0	$\begin{array}{c} 90.2\\90.2\end{array}$	90.0 90.0	90.3 90.3	90.8 90.8	91.0 91.0		
Uı	nited H	Kingdo		Unileve Port S				atory				
			•	Lever 1	Bros.	Port S	unligh	t Ltd.				
			1	Port S Colgate Manak	e-Palm							
			1	Manch Thoma Newca:	s Hed		d Com	pany				
				Joseph Warrir	Crosf	ield ar		s Ltd.				
				Hehner Londor	r and	Cox L						
				Imperi Nobel	al Che Divisi	mical on		tries L	td.			
				Steven:			е					

E. R. Bolton London E. C. 1

H. W. Knol Jan Dekker N. V. Wormerveer

G. Carriere Lever's Zeep Moatschappij N. V. Parallelweg, Vlaardingen

	J. A. Reddingius Chemische Fabriek ''Naarden'' Naarden A. P. van der Vet Unilever Research Laboratorium Veersingel Vlaardingen
	J. C. van der Weel N. V. Koninklijke Stearinekaarsenfabrieken ''Gouda-Apollo'' Gouda C. van Rede N. V. Mij. tot Exploitatie der Verenigde Odiefabricken-Zwijndrecht Zwijndrecht
United States	T. C. Bond Swift and Company Los Angeles, Calif.
	Hugo de Bussieres Curtis and Tompkins Ltd. San Francisco, Calif.
	H. S. Mumford Colgate-Palmolive Company Berkeley, Calif.

TABLE IV	
----------	--

Made-Up	Crude-	-Percentage	$\mathbf{of}$	Glycerol	by

	A.	0.C.S. 1	fethod		British Method							
		lified gent		itral gent		utral gent		lified gent	rea	Acidified reagent N2 omitted		
	Ind.	Elect.	Ind.	Elect.	Ind.	Elect.	Ind.	Elect.	Ind.	Elect.		
1	68.1 68.0	$68.3 \\ 68.2$	67.9 67.8	$\begin{array}{c} 68.1 \\ 68.0 \end{array}$	68.0 68.0	$\begin{array}{c} 68.1 \\ 68.1 \end{array}$	68.3 68.1	68.4 68.2	68.3 68.3	$68.4 \\ 68.4$		
<b>2</b>	$\begin{array}{c} 68.3 \\ 68.3 \end{array}$	$     68.4 \\     68.4 $	$67.9 \\ 67.9$	${}^{68.2}_{68.2}$	$67.8 \\ 67.8$	$67.9 \\ 67.9$	$67.9 \\ 67.9$	$68.0 \\ 67.9$	$67.9 \\ 67.9$	68.0 68.0		
3	${068.1 \\ 68.1}$	$68.2 \\ 68.2$		$\begin{array}{c} 68.1 \\ 68.1 \end{array}$	$\begin{array}{c} 68.0\\ 68.0\end{array}$	$\substack{68.1\\68.1}$	68.0 68.1		$68.0 \\ 68.1$	$68.2 \\ 68.2$		
4	$67.5 \\ 67.4$	$67.6 \\ 67.5$	$67.2 \\ 67.2$	$67.2 \\ 67.2$	$66.9 \\ 67.0$	$\begin{array}{c} 67.0 \\ 67.0 \end{array}$	$67.1 \\ 67.2$	$67.3 \\ 67.3$	$67.2 \\ 67.2$	$67.3 \\ 67.3$		
5	$67.8 \\ 67.7$	$67.9 \\ 67.9$	$67.6 \\ 67.6$	$\begin{array}{c} 67.8 \\ 67.8 \end{array}$	$\begin{array}{c} 67.8 \\ 67.8 \end{array}$	$67.9 \\ 68.0$	$67.8 \\ 67.8$	68.0 68.0	67.7 67.7	$67.9 \\ 67.9$		
6	$67.8 \\ 67.8$	67.9 67.9	$68.0 \\ 68.1$	$68.2 \\ 68.2$	$\substack{68.1\\68.2}$	$68.2 \\ 68.4$	67.7 67.7	67.9 67.9	67.8 67.7	68.0 67.9		
7	$67.0 \\ 67.1$	$\begin{array}{c} 67.1 \\ 67.3 \end{array}$	$67.5 \\ 67.5$	$67.7 \\ 67.6$	$67.3 \\ 67.4$	$\begin{array}{c} 67.6\\ 67.6\end{array}$	67.0 67.1	67.5 67.5	$67.2 \\ 67.2$	67.7 67.8		
8	$67.8 \\ 67.9$	68.0 68.1	$67.8 \\ 67.7$	$68.0 \\ 67.9$	$67.9 \\ 67.7$	68.0 67.9	67.8 67.9	68.0 68.1	67.8 67.8	68.0 67.9		
9	$\begin{array}{c} 67.7 \\ 67.6 \end{array}$	$67.9 \\ 67.9$	_	Ξ	$67.5 \\ 67.5$	68.0 68.0	$67.6 \\ 67.6$	$\begin{array}{c} 68.0 \\ 68.0 \end{array}$	Ξ	=		
10	$67.6 \\ 67.6$	67.8 67.8	$67.7 \\ 67.8$	$67.9 \\ 67.0$	67.8 67.8	$67.8 \\ 67.7$	$67.7 \\ 67.7$	68.0 68.0	$67.9 \\ 67.9$			
11	$67.1 \\ 67.1$	$67.7 \\ 67.7$	$67.4 \\ 67.4$	$67.9 \\ 67.9$	67.0 67.0	$67.1 \\ 67.1$	67.0 67.0	$67.2 \\ 67.2$	67.8 67.6	$67.7 \\ 67.8$		
<b>12</b>		$68.5 \\ 68.7$	68.0 67.9	$\substack{\textbf{68.1}\\\textbf{67.9}}$	67.7 67.8	$67.7 \\ 67.8$	$68.3 \\ 68.5$		$68.6 \\ 68.4$			
13	$\substack{68.1\\68.1}$	$68.3 \\ 68.3$	$68.0 \\ 67.9$	$\substack{\textbf{68.0}\\\textbf{68.1}}$	$\begin{array}{c} 68.1\\ 68.0\end{array}$	$67.8 \\ 67.8$	$67.9 \\ 67.9$	$67.8 \\ 68.1$	$67.9 \\ 67.9$			
14	$68.0 \\ 67.9$	$68.1 \\ 68.1$	68.0 68.0	$\begin{array}{c} 68.1 \\ 68.1 \end{array}$	68.0 67.9	68.0 68.0	$67.9 \\ 67.9$	$\substack{\textbf{68.1}\\\textbf{68.0}}$	68.0 68.0			
15		${}^{68.2}_{68.1}$	${}^{68.2}_{68.2}$	$68.4 \\ 68.5$	67.8 67.9	$67.9 \\ 67.9$	$\begin{array}{c} 68.1 \\ 68.0 \end{array}$	$\substack{\textbf{68.1}\\\textbf{68.1}}$	$\substack{68.1\\68.2}$			
16	$67.9 \\ 67.8$	$\substack{\textbf{68.2}\\\textbf{68.2}}$	$67.8 \\ 68.1$	$\begin{array}{c} 68.1 \\ 68.4 \end{array}$	68.0 68.0	$68.0 \\ 68.0$	$68.0 \\ 67.9$	$\substack{68.1\\68.1}$	$68.1 \\ 68.0$	$\substack{\textbf{68.2}\\\textbf{68.2}}$		
17	$\begin{array}{c} 67.9 \\ 67.8 \end{array}$		$67.8 \\ 67.9$	68.0 68.0	68.1 68.1	${000}{68.1}{68.1}$	${0.1 \\ 68.1 \\ 68.1 }$	${}^{68.2}_{68.2}$	${}^{68.2}_{68.1}$	$\begin{array}{c} 68.2 \\ 68.2 \end{array}$		
18	$\begin{array}{c} 68.0 \\ 67.9 \end{array}$	$68.2 \\ 68.4$	$67.8 \\ 67.8$	$\begin{array}{c} 68.1 \\ 68.1 \end{array}$	67.8 67.9		$68.0 \\ 68.0$	$\begin{array}{c} 68.4 \\ 68.5 \end{array}$	$67.7 \\ 67.7$			
19		$68.2 \\ 68.3$	$67.8 \\ 67.8$	$\substack{68.2\\68.3}$	68.1 68.1		67.8 67.8	$67.7 \\ 67.8$	68.1 68.0	$68.1 \\ 68.0$		
20	$\begin{array}{c} 67.9 \\ 67.8 \end{array}$	$67.9 \\ 68.0$	67.8 67.8	68.0 68.0	$68.1 \\ 68.2$	$68.3 \\ 68.4$	_	_	68.3 68.4			
21	$67.9 \\ 67.8$	$67.4 \\ 67.3$	$67.4 \\ 67.4$	$67.7 \\ 67.6$	_	=	_	Ξ.	_	=		
22	<u>68.0</u>	68.0	$68.0 \\ 68.1$	${}^{68.2}_{68.2}$	$\begin{array}{c} 68.1 \\ 68.1 \end{array}$	${}^{68.2}_{68.2}$	$68.0 \\ 67.9$	$\substack{\textbf{68.1}\\\textbf{68.1}}$	$\begin{array}{c} 68.3 \\ 68.3 \end{array}$	_		
23	$\substack{68.2\\68.2}$	$68.3 \\ 68.3$	${0.0}{68.3}{68.2}$	$\begin{array}{c} 68.3 \\ 68.3 \end{array}$	68.2 68.1		68.0 68.0	${68.2 \atop 68.3}$	$\begin{array}{c} 68.4 \\ 68.4 \end{array}$	_		
24	68.0 68.0	${}^{68.2}_{68.2}$	$67.8 \\ 67.9$	$\substack{\textbf{68.1}\\\textbf{68.1}}$	$68.1 \\ 68.1$	${08.3 \\ 68.2}$	$     \begin{array}{r}       68.2 \\       68.3     \end{array} $		$\substack{68.2\\68.2}$			
<b>25</b>	$67.5 \\ 67.5$	67.7 67.7	_	$\substack{\textbf{68.1}\\\textbf{68.1}}$	67.7 67.7		$67.7 \\ 67.7$	_	67.8 67.8	<u> </u>		
26	${}^{68.1}_{68.2}$	$\begin{array}{c} 68.3 \\ 68.3 \end{array}$	${0.1 \\ 68.1 }$	${}^{68.2}_{68.2}$	68.2 68.2	$68.3 \\ 68.4$	$68.3 \\ 68.2$	68.3 68.2	$68.3 \\ 68.2$	$68.3 \\ 68.2$		
27	$\substack{68.1\\68.1}$	$68.4 \\ 68.4$	$\substack{68.1\\68.1}$	$\begin{array}{c} 68.3 \\ 68.3 \end{array}$			68.3 68.3	68.5 68.5	$68.3 \\ 68.3$	68.5 68.5		
28	67.8 67.8	$\substack{\textbf{68.1}\\\textbf{68.2}}$	$^{67.5}_{68.2}$	$67.9 \\ 68.6$	67.8 67.9	68.0 68.1	$67.6 \\ 67.6$	68.0 68.0	68.3 68.3	$69.6 \\ 69.8$		
29	$67.7 \\ 67.7$	$67.9 \\ 67.9$	$67.6 \\ 67.5$	68.0 68.0	$67.9 \\ 67.9$	68.1 68.1	67.9 67.9		68.5 68.5	68.7 68.7		

The Netherlands Members of the Dutch National Glycerine Committee

TABLE V A.O.C.S. Glycerine Analysis-International Collaborative Study-Summary of Means and Variances (% Glycerine)

	Mean		Components of Variance								
	Indica-	Electro-	Within			Between			Total		
	tor	metric	Ind.	Elect.	Avg.	Ind.	Elect.	Avg.	Ind.	Elect.	Avg.
C. P. Glycerine											
A.O.C.S. method											
Acidified reagent	89.87	90.17	0.0176	0.0155	.0166	0.1633	0.1460	.1546	0.1809	0.1615	.1712
Neutral reagent	89.86	90.14	0.0039	0.0052	.0046	0.1373	0.1240	.1306	0.1412	0.1292	.1302
British method									ĺ		
Acidified reagent	89.96	90,18	0.0048	0.0056	.0052	0.2080	0.1956	.2018	0.2128	0.2012	.2070
Neutral reagent	89.85	90.07	0.0079	0.0075	.0077	0.1872	0.2228	.2050	0.1951	0.2303	.2127
Acidified reagent (without N2)	90.11	90.35	0.0841	0.0084	.0462	0.2622	0.4329	.3476	0.3463	0.4413	.3938
Made-Up Crude Glycerine											
A.O.C.S. method									1		
Acidified reagent	67.85	68.03	0.0038	0.0034	.0036	0.0862	0.0996	.0929	0.0900	0.1030	.0965
Neutral reagent	67.83	68.03	0.0126	0.0268	.0197	0.0587	0.0606	.0596	0.0713	0.0874	.0794
British method	01100										
Acidified reagent	67.85	68.05	0.0033	0.0050	.0042	0.1218	0.1083	.1150	0.1241	0.1133	.1192
Neutral reagent	67.87	68.00	0.0025	0.0026	.0026	0.1066	0.1248	.1157	0.1091	0.1274	.1183
Acidified reagent (without N2)	68.01	68.22	0.0030	0.0033	.0032	0.1144	0.2010	.1577	0.1174	0.2043	.1609

W. R. Trent Colgate-Palmolive Company Jersey City, N. J. L. K. White Colgate-Palmolive Company Kansas City, Kans.

Members of the Analysis Committee Cincinnati, Ohio

T. J. Baldwin A.O.C.S. Glycerine Procter and Gamble Company H. C. Bennett Los Angeles Soap Company Los Angeles, Calif. E. L. Bolev Armour and Company Chicago, Illinois W. C. Clark Emery Industries Inc. Cincinnati, Ohio

R. J. Houle Lever Brothers Company Edgewater, N. J. W. A. Peterson Colgate-Palmolive Co. Jersey City, N. J. W. D. Pohle Swift and Company Chicago, Illinois J. B. Segur Arthur D. Little Inc. Chicago, Illinois Arnold Troy E. F. Drew and Company Boston, Mass.

W. D. POHLE, chairman

[Received August 19, 1957]

# Studies on the Nutritional and Physiological **Effects of Thermally Oxidized Oils**

O. C. JOHNSON, E. PERKINS, M. SUGAI, and F. A. KUMMEROW, Department of Food Technology, University of Illinois, Urbana, Illinois

¬DIBLE OILS which had been heated to 200°C. in the  $\Box$  presence of air were shown to have less nutritive value than the comparative fresh oils (1). It has been shown that the polyunsaturated fatty acids in these oils were attacked and the viscosity and oxygen content of the oil were increased. Crampton et al. have suggested that polymeric or cyclic products were formed in heat-polymerized oils and that these products caused at least some of the results observed when diets containing the polymerized oils were fed to rats (2, 3). When oils were aerated at  $90^{\circ}-100^{\circ}$ C., the nutritive value of the oils also decreased (4). Kaunitz et al. have suggested that this growth depression was related to polymeric products since the residue which remained after molecular distillation of these oils proved to be more growth-depressing than the whole oil (5).

The studies to date therefore suggest that polymeric products formed during oxidation of edible oils cause at least part of the growth depression. It was also implied that these polymers were formed from the polyunsaturated fatty acids. Several mechanisms have been suggested which would lead to polymeric or cyclic materials from unsaturated fatty acid esters. Sunderland has proposed a direct reaction between a double bond in one molecule and a methylene group of a second molecule to give a carbon-tocarbon linkage (6). Other workers have suggested that 1:4 addition reactions lead to the polymeric products (7). Paschke and Wheeler found that cyclic products were produced in polymerization of methyl eleostearate (8, 9, 10). Since it has been shown that linoleic acid can undergo these polymerizing reactions, an attempt was made in the present study to relate the linoleic acid content of a fat to thermal oxidative damage as measured by comparative growthrates in rats.

The physiological effects of oxidized oils are not known, but studies have shown that organ-body weight-ratios are affected by these products (4, 11). Other workers have found some loss in the coefficient of digestibility, but most heated oils retain a high coefficient of digestibility (12). In the present work the rate of absorption and the in vitro rate of hydrolysis of thermally oxidized corn oil and the effect of thermally oxidized corn oil on the livers of rats fed