selected combinations of sucrose monostearate and glyceryl monostearate, above some minimum concentration, are capable of producing smaller size droplets and consequently more stable emulsions.

A satisfactory explanation of the behavior of unmilled emulsions containing 0.525% emulsifier, as plotted in Figure 2, is not evident.

Conclusions

The presence of either sucrose distearate or glyceryl monostearate will decrease the stability of preformed mineral oil-in-water emulsions containing sucrose monostearate. With adequate concentrations of emulsifier present the emulsion stability of milled emulsions passes through a maximum as the ratio of glyceryl monostearate to sucrose monostearate is increased. The data suggest that this increased stability results from a decrease in droplet size rather than from the formation of a more tenuous interfacial film.

Acknowledgment

This investigation forms part of a program of research supported by the Sugar Research Foundation Inc., New York, N. Y.

REFERENCES

1. Osipow, L., Birsan, S., and Snell, F. D., J. Am. Oil Chemists' Soc., *34*, 34–8 (1957).
2. Osipow, L., Snell, F. D., and Hickson, J. L., "The Surface Chemistry of Alkyl Esters of Sucrose," presented at the Second International Congress of Surface Activity, London, England, April 8–12, 1957.
3. Osipow, L., Snell, F. D., Marra, D., York, W. C., and Finchler, A., Ind. Eng. Chem., *48*, 1459–64 (1956).

[Received May 27, 1957]

Indian Stillingia Oil and Tallow

S. A. NARANG[1] and SADGOPAL,[2] Forest Research Institute, New Forest, Dehra Dun, India

STILLINGIA OIL AND TALLOW are obtained from the fruits of the tree *Sapium sebiferum* Roxb. (fam. *Euphorbiaceae*). The tree is indigenous to China and has been reported to be growing wild in northern India (24). In India it is known as *tarcharbi* (Dehra Dun) and *pahari-shishim* (Saharanpur) (6). The fruits are borne in small clusters. At maturity the outer brown husks split open and expose three oval seeds about one-half inch in diameter, weighing about 0.15 g. The thick mesocarp contains a fatty substance commonly known as vegetable tallow. The kernel oil is a drying oil known as stillingia oil in English (24) or "Tse-ieene" or "tung-yu" in Chinese (20).

The earliest information on the physico-chemical characteristics of the Chinese stillingia oil were reported by Tortelli and Buggeri (23), Nash (20), Bolton (3), and by the Imperial Institute of London (4). By conventional methods Jamieson *et al.* (15) and Kaufmann *et al.* (17) found 26–29% linolenic, 46–59% linoleic, 9–16% oleic, and 6–9% saturated fatty acids and noted abnormally high saponification values. In 1946 Potts (21) observed that one of the acidic components of the oil had an unusual ultraviolet spectrum. The observation was confirmed by Huang *et al.* (14) in 1949 who however did not reach a conclusion about the structure of the new acid. Only recently Hilditch (8), Hilditch and Crossley (9), and Devine (5) were able to isolate about 5% of a deca-2:4-dienoic acid having a characteristic absorption band at about 260 mμ. This acid has been found to be absent in the Indian stillingia oil which has a saponification value of 205.7. The tallow has been studied by Hilditch *et al.* (13), Jamieson (16), and Armstrong *et al.* (1).

All of these workers studied stillingia oils and tallows from seeds grown in China, Florida, or South Texas. It was therefore of interest to examine Indian varieties also.

Experimental

The external fatty and fibrous coating was easily broken and removed by vigorously stirring the seeds in warm water (50° to 55°C.) for two hours. The decorticated seeds were separated, dried, and extracted with petroleum ether or ethyl ether. Characteristics of the oils extracted by these two solvents were practically identical although yields were not the same (see below). Physico-chemical values are summarized in Table I for comparison with those reported by previous workers.

Fibrous matter and tallow were recovered by filtering off the water and then were dried. Tallow was obtained by extracting the dried, powdered material with benzene. The Indian stillingia tallow has the following characteristics: specific gravity $0.8905^{60°}$, refractive index $1.4560^{60°}$, acid value 0.75, saponification value 203.9, iodine value (Wij's) 24.1, acetyl value 1.9, unsaponifiable matter 1.5%, and Hehner value 93.03.

By the above procedure the percentage yields from the seeds were tallow 19.3, fibrous matter 12.5, hulls 37.45, and kernels 30.75. Based on the weight of seeds, extraction with petroleum ether (40–60°) gave an oil yield of 18.27% as compared with 16.91% obtained with ether. Based on the weight of kernels, the oil yields were 59.4 and 55.0%, respectively. The oil had a pale yellow color with pleasant odor.

Characterization of Fatty Acids

Fatty acids were isolated in the usual manner by saponification of the oil or tallow. The yield of fatty acids from the oil was 91.2% and from the tallow 93.0%. The fatty acids were resolved into solid and liquid fractions by Twitchell's lead-salt-alcohol method (10). Results of these separations are shown in Table II.

The liquid and solid fatty acid fractions were separately converted into their methyl esters, which were then systematically fractionated by distillation under vacuum. The percentage of saturated acids in each ester fraction was calculated by means of Charnley's formula (11). The amounts of C_{18} mono-, di-, and trienoic acids and unsaponifiable matter were estimated on the basis of iodine and thiocyanogen values according to the equations of Baughman and Jamieson (2). The results of the ester fractionations are given in Table III.

[1] Now Research Fellow, Indian Association for the Cultivation of Science, Calcutta.
[2] Now Deputy Director (Chemicals), Indian Standards Institution, Delhi.

TABLE I
Characteristics of Stillingia Oils

Source of seed	India[a]	India[b]	China (23)	China (20)	China (3)	China (4)	N. America (15)	China (12)	Hong Kong (9)	S. Texas (9)
Refractive index	$1.4790^{30°}$	$1.4791^{30°}$	.....	$1.4835^{23°}$	.....	$1.4783^{40°}$	1.4830	.....	$1.4817^{25°}$	$1.4838^{25°}$
Specific gravity	$0.9539^{30°}$	$0.9541^{30°}$	$0.9370^{15°}$	$0.9395^{15.6°}$	$0.9430^{15°}$	$0.9419^{15°}$	.....	.....	.....	.....
Specific rotation $[\alpha]_D^{30°}$	−6.1°	−6.0°	.....	−4.0°	.....	.....	.....	.....	.....	.....
Saponification value	196.0	196.1	210.4	.....	205.0	205.7	211.7	205.2	205.8	205.5
Acid value	1.5	1.9	12.2	6.2	.....	.....	3.7	2.4	.....	.....
Iodine value (Hanus)	146.0	147.0	.....	.....	.....	.....	.....	.....	.....	.....
Iodine value (Wij's), 30 min.	178.0	179.1	160.6	160.7	187.6	188.8	176.1	176.4	172.0	173.0
Iodine value (Woburn's B)	178.0	179.0	.....	.....	.....	.....	.....	.....	.....	.....
Acetyl value	7.8	7.9	.....	.....	.....	.....	8.5	.....	.....	.....
Diene value	nil	nil	.....	.....	.....	.....	.....	.....	.....	.....
Thiocyanogen value	104.0	103.0	.....	.....	.....	.....	102.7	101.4	.....	.....
Hexabromide value	27.5	27.0	.....	.....	.....	.....	.....	.....	.....	.....
Tetrabromide value	48.3	49.0	.....	.....	.....	.....	.....	.....	.....	.....
Saturated acids by modified Bertram's method, %	7.0	7.1	.....	.....	.....	.....	.....	5.7	.....	.....
Unsaponifiable matter, %	1.2	1.1	1.45	0.44	.....	.....	0.16	3.0	0.8	0.3

[a] Extracted with petroleum ether.
[b] Extracted with ethyl ether.

Fatty acids from the ester fractions were identified conclusively by isolation or by the following chemical means: a) oxidation with permanganate (18) and characterization of the resultant hydroxy acids; b) bromination by the method of Eibner and Muggenthaler (19), and characterization of the bromo-derivatives; and c) fractionation with urea followed by the preparation and characterization of phenylhydrazine derivatives.

TABLE II
Properties of Fatty-Acid Fractions

Acid fraction	Oil			Tallow		
	Total	*Liquid*	*Solid*	*Total*	*Liquid*	*Solid*
Yield, %	91.2	76.2	23.1	93.0	17.0	83.0
Iodine value	187.0	200.8	137.9	25.2	82.9	12.3
Thiocyanogen value	111.0	116.7	80.0	....	....	....
Mean molecular weight	273.0	274.0	269.0	262.0	270.0	260.0
Neutralization value	205.3	204.9	209.0	214.1	207.8	215.8
Optical rotation	0	0	0	0	0	0

Thus the presence of oleic acid in both the oil and the tallow was demonstrated by the formation of dihydroxy-stearic acid, m.p. 130°C. and a phenylhydrazide, m.p. 72–3°C., which showed no melting point depressions when mixed with authentic samples. The linoleic and linolenic acids were identified in the form of their oxidation products, tetrahydroxy-stearic acid, m.p. 173–74°C., and hexahydroxy-stearic acid, m.p. 204–205°C., respectively. Further evidence of the presence of linoleic and linolenic acids was obtained by the isolation of tetra-bromide, m.p. 113–114°C., and hexabromide, m.p. 178–79°C. The following saturated acids were isolated and identified by their mixed melting points with authentic samples: myristic acid, m.p. 53–54°C.; palmitic acid, m.p. 60–61°C.; phenylhydrazide, m.p. 110–11°C., and anilide, m.p. 92–93°C.; stearic acid, m.p. 69–71°C.

The unsaponifiable fractions from the oil and from the tallow were recrystallized from absolute alcohol.

TABLE III
Composition of Fatty Acid Fractions as Determined by Methyl Ester Distillations

Acid fraction	Oil		Tallow	
	Solid	*Liquid*	*Solid*	*Liquid*
Saturated acids, %				
C_8	0.3	1.2	....	....
C_{10}	0.8	0.2	....	....
C_{12}	....	....	....	0.3
C_{14}	0.7	0.2	3.5	0.7
C_{16}	1.3	1.5	61.9	0.3
C_{18}	1.0	....	5.8	0.1
Unsaturated acids, %				
Oleic	5.5	3.9	11.8	15.6
Linoleic	10.6	42.8	....	....
Linolenic	3.1	26.9	....	....

In each case the resultant white crystals had a melting point of 139–40°C. and formed an acetate, m.p. 129–30°C. The principal unsaponifiable component thus appears to be a sitosterol.

Glyceride Structure of the Oil

A solution of 40.0 g. of the neutral oil in six times its weight of pure, dry acetone deposited no crystals when stored in a refrigerator for one week. This observation showed the absence of trisaturated glycerides. This conclusion was confirmed when no residue remained after repeated oxidations of 40.0 g. of the neutral oil with four times its weight of powdered potassium permanganate dissolved in 400 ml. of dry acetone (12).

A solution of 56.6 g. of neutral oil in 566.0 g. of petroleum ether was brominated according to the method of Suzuki *et al.* (22), also reported by Hashi (7), allowing the mixture to stand in a refrigerator over-night. Excess of bromine was then destroyed with sodium thiosulphate. The solution was washed and dried. The solvent was distilled off. The viscous residue was successively extracted with absolute alcohol, mixtures of alcohol and acetone, and acetone according to the scheme shown in Figure 1.

Neutral Oil 56.6 g.
Brominated in Light Petroleum Ether

Insoluble Extracted with absolute alcohol			Soluble Extracted with absolute alcohol		
(1) Soluble viscous liquid	Insoluble (absolute alcohol and acetone [1:1])		Insoluble (absolute alcohol and acetone [1:1])	Soluble viscous liquid	(5)
(2) Soluble viscous liquid	Insoluble (acetone)		Insoluble (acetone)	Soluble viscous liquid	(6)
(3) Soluble viscous liquid	Insoluble White crystalline solid	(4)	Insoluble (nil)	Soluble viscous liquid	(7)

FIG. 1.

Each fraction was debrominated by saturating its dry methyl alcohol solution with hydrogen chloride, adding an equimolecular amount of zinc dust and refluxing the mixture for eight hours. The debrominated products were taken up in petroleum ether and

saponified. The concentration of the individual fatty acid in each fraction was estimated from thiocyanogen and iodine values (2). Results are summarized in Table IV. These data were used for the calculation of the glyceride compositions, which are presented in Table V.

TABLE IV
Characteristics and Compositions of Fatty Acids from Fractions of Brominated Stillingia Oil

Brominated glyceride fractions	1	2	3	4	5	6	7
Weight of bromo-glyceride, grams	2.7	1.2	75.2	18.7	1.1	1.0	20.0
Weight of total fatty acids, grams [a, b]		31.7		8.2		10.8	
Properties of fatty acids							
Saponification equivalent		279.9		278.9		277.6	
Iodine value		197.7		188.9		161.0	
Thiocyanogen value		112.6		125.4		117.8	
Saturated fatty acids, grams		1.2		nil		2.4	
Saponification equivalent		250.0		....		251.0	
Unsaponifiable matter, grams		0.3		0.1		0.2	
Fatty acid composition, % of total acids		62.5		16.2		21.3	
Saturated		2.4		....		4.7	
Oleic		2.0		5.2		2.1	
Linoleic		40.3		4.1		7.9	
Linolenic		17.8		6.9		6.6	

[a] Excluding non-saponifiable matter.
[b] Because of their small size, Fractions 1 and 2 were combined with 3, and Fractions 5 and 6 were combined with 7.

TABLE V
Probable Composition of Stillingia Oil Glycerides

Glyceride	Mol Percentage
Di-saturated-mono-linolein	7.9
Mono-saturated-di-linolein	7.9
Mono-oleo-di-linolein	6.1
Mono-linoleno-di-linolein	45.7
Mono-linoleo-di-linolenin	10.7
Mono-oleo-di-linolenin	3.3
Oleo-linoleo-linolenin	18.4

Glyceride Structure of Tallow

In contrast to the oil the tallow was easily fractionated by crystallization from acetone at low temperatures, according to the scheme shown in Figure 2. Each fraction was then converted to its methyl esters, which were fractionally distilled. From the distillates, fatty acids were recovered by saponification in the usual manner and identified by means of iodine values. Results are summarized in Table VI.

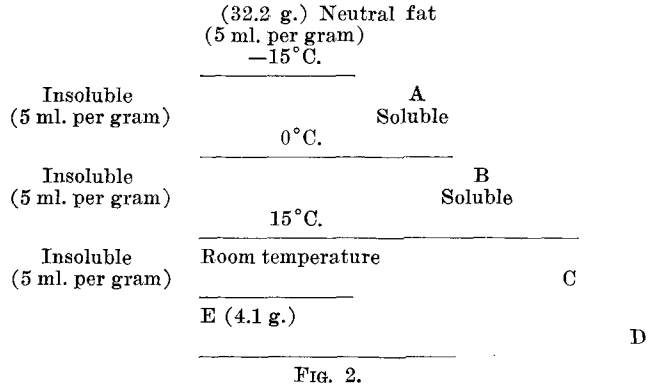

FIG. 2.

The occurrence of tripalmitin in the tallow was conclusively proved by its isolation. A solution of 50.0 g. of the tallow in 500.0 ml. of dry acetone was treated with 150.0 g. of finely powdered potassium permanganate (12). The fully saturated product was isolated in the customary manner in a yield of 16.1 g. The crude product had an acid value of 1.2, saponification equivalent of 266.5, and iodine value of 1.0.

TABLE VI
Characteristics and Compositions of Fatty Acids from Glyceride Fractions of Stillingia Tallow

	A	B	C	D	E
Weight grams	10.0	8.0	7.9	2.2	4.1
Iodine value	35.7	26.0	18.1	7.7	0
Component acids, mol %	31.7	25.1	24.9	5.8	12.5
Fatty acids composition, mol % of total acids					
Myristic	.....	1.6	1.1	.....	.....
Palmitic	19.5	14.4	16.5	5.3	12.5
Stearic	.....	2.1	2.4	0.1	.....
Oleic	12.2	7.0	4.9	0.4	.....

After recrystallization from acetone the melting point was 64.5°C. From these properties it follows that the fully saturated glycerides were primarily tripalmitin and formed 32.2% of the original tallow.

TABLE VII
Probable Glyceride Composition of Stillingia Tallow

Glyceride	Mol Percentage
Tripalmitin	16.6
Dipalmito-mono-stearin	7.4
Dipalmito-mono-myristin	3.3
Dimyristo-mono-palmitin	0.6
Distearo-mono-palmitin	3.3
Dipalmito-mono-olein	64.0
Mono-palmito-di-olein	4.8

Summary

The stillingia oil and tallow from the seeds of *Sapium sebiferum* Roxb., have been studied for their component fatty acids and component glycerides. The fatty acids composition was determined by Twitchell's lead-salt-alcohol method followed by systematic fractionation of the methyl esters under high vacuum. The glyceridic composition of the stillingia oil has been examined by permanganate-oxidation and bromination methods whereas the composition of the glycerides of the stillingia tallow was arrived at by using the low-temperature crystallization technique.

The component fatty acids of the stillingia oil have been found to consist of caprylic (1.5%), capric (1.0%), myristic (0.97%), palmitic (2.8%), stearic (1.0%), oleic (9.4%), linoleic (53.4%), and linolenic (30.0%); the latter two are the major constituents.

The glycerides of the oil were found to consist of disaturated-mono-linolein (7.9%), mono-saturated-di-linolein (7.9%), mono-oleo-di-linolein (6.1%), mono-linoleno-di-linolein (45.7%), mono-linoleo-di-linolenin (10.7%), mono-oleo-di-linolenin (3.3%), and oleo-linoleo-linolenin (18.4%).

The fatty acids composition of the stillingia tallow was found to be lauric (0.3%), myristic (4.2%), palmitic (62.3%), stearic (5.9%), and oleic (27.4%). The component glycerides were found to be trisaturated (31.2%), disaturated monounsaturated (64.0%) and monsaturated, diunsaturated (4.8%).

Acknowledgment

The authors wish to express their grateful thanks to the Scientific Research Committee (U.P.) for an award of a research scholarship to one of them (Narang). Grateful acknowledgment is made of the laboratory facilities granted for the work by the president, Forest Research Institute and Colleges, Dehra Dun. Sincere thanks are also due to D. F. O. Kangra (Punjab), who supplied us with the seeds of *Sapium sebiferum* Roxb.

REFERENCES

1. Armstrong, E. F., and Allan, John, J. Soc. Chem. Ind., *43*, 216T (1924).

2. Baughman, W. F., and Jamieson, G. S., J. Am. Oil Chemists' Soc., *42*, 152 (1920).
3. Bolton, E. R., "Oils, Fats, and Fatty Foods," p. 239, P. Blakiston's Sons and Company, Philadelphia, Pa., 1928.
4. Bull. Imper. Inst., vol. 28, p. 429, Imperial Mineral Resources Bureau, London (1930).
5. Devine, J., J. Sci. Food Agr., *1*, 88 (1950).
6. Gamble, J. S., "A Manual of Indian Timbers," p. 624. S. Low, Marston, and Company, Ltd., London, 1902.
7. Hashi, K., J. Soc. Chem. Ind., Japan, *30*, 849, 856, (1927): *31*, 117 (1928).
8. Hilditch, T. P., J. Oil Col. Chem. Assoc., *32*, 5 (1949).
9. Hilditch, T. P., and Crossley, A., J. Sci. Food Agr., *1*, 292 (1950).
10. Hilditch, T. P., "The Chemical Constitution of the Natural Fats," p. 468, Chapman and Hall Ltd., London, 1949.
11. Ibid., p. 505.
12. Ibid., p. 513.
13. Hilditch, T. P., and Priestman, J., J. Soc. Chem. Ind., *49*, 397T (1930).
14. Huang, P. T., Holman, R. T., and Potts, W. M., J. Am. Oil Chemists' Soc., *26*, 405 (1949).
15. Jamieson, G. S., and McKinney, R. S., Oil and Soap, *15*, 295 (1938).
16. Jamieson, G. S., "Vegetable Oils and Fats," p. 57, Reinhold Publishing Corporation, New York, 1943.
17. Kaufmann, H. P., and King, B. W., Fette u. Seifen, *46*, 388 (1939).
18. Lewkowitsch, J., "Chemical Technology and Analysis of Oils, Fats, and Waxes," vol. 1, p. 575, Macmillan and Company, London, 1921.
19. Ibid., p. 585.
20. Nash, L. M., Analyst, *29*, 110 (1904).
21. Potts, W. M., Paint Oil Chem. Rev., *109*, 16 (1946).
22. Suzuki, B., and Yokoyama, Y., Proc. Imp. Acad., Tokyo, *3*, 526 529 (1927); Suzuki, B., ibid.,*5*, 265 (1929).
23. Tortelli and Buggeri, Chem. Ztg., *21*, 5 (1927).
24. Watt, G., "A Dictionary of the Economic Products of India," Part 11, p. 449, Government of India, Department of Revenue and Agriculture, London, 1891.

[Received April 16, 1956]

Periodate-Permanganate Oxidations for Determining Location and Amount of Unsaturation in Monounsaturated Fatty Acids[1]

E. P. JONES and J. A. STOLP, Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Peoria, Illinois

A MODIFIED METHOD is described for determining accurately the position of unsaturation in monounsaturated acids by oxidative cleavage. By combining Lemieux and von Rudloff's (11) periodate-permanganate oxidative cleavage method with Begemann's (3) chromatographic identification procedure, with slight modifications in technique, we have been able to obtain reproducible yields of the dibasic acids liberated on oxidative cleavage. Oleic acid and elaidic acid of high purity were employed in most of the experimental work. Over-all recovery of dibasic acids was about 92%, and control tests using high-purity azelaic acid instead of oleic acid indicate the quantitative reliability of the procedure employed by us. Isomeric impurities amounting to about 1% have been consistently detected. By replacing potassium carbonate with potassium hydroxide in the oxidation and by careful attention to experimental technique, we have been able to obtain a maximum of 92% dibasic acids from high-purity, monounsaturated fatty acid. Because of the importance of the determination of double-bond position in fat chemistry we have given more than the usual experimental detail in this paper so that anyone wishing to use the modified method will have necessary experimental details and yield data available.

Research in the field of isomerization, reduction, and conjugation of unsaturated fats, fatty acids, and esters has shown double-bond shift and has made it difficult to interpret the findings of various workers. Thus an accurate method for determining the position of unsaturation would be useful in research in this general field.

Armstrong and Hilditch (2) were among the first to employ potassium permanganate in dry acetone or acetic acid to oxidize unsaturated esters. After separation and identification of the acidic end-products they could fix the position of major unsaturation, but the exact amount of total unsaturation and the position of minor unsaturation remained doubtful, principally because of low yield, fragmentary products, and inadequate methods of separation of the acids formed.

Begemann in 1950 introduced partition chromatography for quantitative identification of the acids produced on oxidation with permanganate as well as by the ozonization technique (7). In 1953 Boelhower (4) employed Begemann's technique in an investigation of the catalytic hydrogenation of mono- and diunsaturated esters. He reported that partial reduction with nickel catalysts caused a predominant shift of double bonds away from the carboxyl group, but over-all yields were not given. Oxidation of the unreduced acids and the same acids processed with the catalyst in the absence of hydrogen rounded out a significant contribution.

Allen (1) employed ozonization to fix the position of unsaturation after partial hydrogenation of unsaturated fatty acids, coupled with the chromatographic separation techniques of Higuchi (8) and Corcoran (6). He found equal double-bond migration in both directions, explainable by partial hydrogenation and subsequent dehydrogenation. Lemieux and coworkers (11, 12, 14, 15) in 1955 proposed a novel method of oxidation applicable to mono- and diunsaturated fatty acids and esters in which a mixture of permanganate and sodium meta-periodate oxidizes the soaps in aqueous medium at room temperature. The novel feature of the method centers around the continuous regeneration of permanganate by the periodate under alkaline conditions (pH 7.5 to 9.0). After partial reduction of permanganate to manganate the latter is oxidized back to permanganate as shown by the following reaction:

$$2K_2MnO_4+NaIO_4+H_2O \rightleftarrows 2KMnO_4+NaIO_3+2KOH$$

The acidic products of oxidation were separated by Begemann's chromatographic method. Quantitative yields were reported for oleic acid, elaidic acid, 10-undecenoic acid, 9-eicosenoic acid, and linoleic acid. Less than quantitative yields were reported for methyl oleate, methyl linoleate, triolein, and erucic acid (13-docosenoic) by the addition of pyridine to the aqueous medium.

Experimental

A. Optimum Oxidizing Conditions. Oleic Acid. Upon duplicating the reaction conditions recommended by Lemieux and von Rudloff, the maximum recovery of azelaic acid was approximately 75%. Subsequently all experimental variables were investigated, but the indicated optimum conditions for oxidation did not materially increase the yield of

[1] Presented at meeting of American Oil Chemists' Society, Chicago, Ill., September 24–26, 1956.