TABLE II

Condensation of Glycerides Using Hydrogen Fluoride

Exp. No.	Reactants	Conditions	Conversion %	Remarks
1	26 g. (0.12 equiv.) coconut oil 86 g. (1.1 moles) benzene 330 g. (16.5 moles) HF	Overnight at room temperature and atmospheric pressure	0	
2	47.2 g. (0.22 equiv.) coconut oil *19.5 ml. (0.22 mole) benzene* 414 g. (20.7 moles) HF	*Heat in bomb in steam bath for 3 hrs.*	7[a]	108-216°C./1 mm.
3	47.2 g. (0.22 equiv.) coconut oil 19.5 ml. (0.22 mole) benzene 298 g. (14.9 moles) HF	Heat in bomb at 125°C. for 3 hrs.	19	106-220°C./1 mm.
4	47.2 g. (0.22) equiv.) cocoonut oil 35.8 ml. (0.4 mole) benzene 318 g. (15.9 moles) HF	Heat in bomb at 100°C. for 5.5 hrs.	19	84-216°C./1 mm.

[a] The 2,4-dinitrophenylhydrazone of the mass was prepared and recrystallized several times from methanol. It melted at 99-100°C. and did not depress the melting point of a known sample of laurophenone-2,4-dinitrophenylhydrazone (mp. 99-100°C.). Analysis—Calc'd: N, 12.72. Found: N, 12.40, 12.43.

amount of product was isolable. Ratios of 2.1:1 to 3:1 were effective.

The condensation employing hydrogen fluoride produced only traces of ketones at room temperatures and atmospheric pressure, and only poor yields at temperatures in the range of 70-125°C. and autogenous pressures.

Alkylation with glycerol as a probable side-reaction may account for the low glycerol recoveries and for the residue of unknown materials.

Summary

The direct condensation of glycerides with benzene in the presence of aluminum chloride or hydrogen fluoride to produce aralkyl ketones has been described.

Acknowledgment

This work was supported by the Purex Corporation Ltd., Southgate, Calif.

REFERENCES

1. Bowles, A. F., U. S. Patent 2,144,324 (1939).
2. Cox, E. H., J. Am. Chem. Soc., *52,* 352-358 (1930).
3. Cryer, J., Trans. Roy. Soc. Canada, III (3), *19,* 29 (1925).
4. Englert, R. D., Silverstein, R. M., and Richards, L. M., Paper No. I (in press).
5. I. G. Farbenind, Ger. patent 637,384 (1936).
6. Martin, H., and Hirt, R., U. S. Patent 2,205,728 (1946).
7. Norris, J. F., and Sturgis, B. M., J. Am. Chem. Soc., *61,* 1413-1417 (1939).
8. Robinson, J. D., U. S. Patent 2,061,593 (1936).
9. Siggia, S., "Quantitative Organic Analysis Via Functional Groups," p. 17, New York, John Wiley and Sons Inc. (1949).

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Report of the Spectroscopy Committee—1952-1953

THE Spectroscopy Committee in its November 15, 1948, report recommended a detailed spectrophotometric method for the analysis of fats and oils to the Society for its adoption. As a result, A.O.C.S. Tentative Method Cd 7-48 was issued as a part of A.O.C.S. methods. Following the work done in 1950 and 1951 additional recommendations concerning the method were made in the 1951 report of the Committee. As a result, the method was revised in May, 1951.

Present Work

The committee has done additional work during the past year and a half, following the procedure as revised in May, 1951. The object of this work was to check the precision of the method and to investigate additional details which seemed pertinent on the basis of previous work carried out. Accordingly, six samples were submitted to the committee members and were analyzed. The six samples submitted were:

Oil No.	Kind of oil	Iodine value	% Saturated acids*
1	Unhardened soybean oil	135.0	13.92
2	Hydrogenated soybean oil	106.4	14.87
3	Hydrogenated soybean oil	77.7	16.48
4	Fish oil	177.5	22.85
5	Fish oil+soybean oil (50% No. 1+50% No. 4)	155.3	17.80
6	Linseed oil	188.1	8.45

* Determined by the Southern Regional Research Laboratory, following a modification of the Bertram Oxidation method described by K. A. Pelikan and J. D. Von Mikusch in Oil and Soap *15,* 149-150 (1938).

These oils were analyzed at least in duplicate by all six members of the committee. The oils were analyzed first, following exactly the procedure outlined in the A.O.C.S Tentative Method Cd 7-48 as revised in May, 1951. They were then re-analyzed using a 45-min. isomerization time at 180°C. The composition of the samples was calculated in the former case, using the calculations set down in the A.O.C.S. method. The compositions were also calculated for the 45-min. isomerization, using data submitted by the Eastern Regional Research Laboratory and reported in a paper by Brice, Swain, Herb, Nichols, and Riemenschneider in the Journal of the American Oil Chemists' Society, July, 1952, Volume XXIX, pages 279-287. The data were recalculated for both the 25- and 45-min. isomerizations, making no background corrections when k'_{268} and k'_{315} were greater than one. The composition of samples 2 and 3 was also recalculated, using the debromination constants originally a part of the method as issued in 1948. All of these data are given in the attached five tables.

Conclusions

As a result of the work herein reported, several conclusions can be drawn:

a) Reasonably reproducible results, using A.O.C.S. Tentative Method Cd 7-48, revised May, 1951, can be obtained in the hands of experienced operators.

b) No particular increase in either precision or accuracy is obtained by using a 45-min. isomerization time.

TABLE I

Non-Conjugated Acids
% Arachidonic

Oil No.		Lab 1		Lab 2			Lab 3		Lab 4		Lab 5		Lab 6		Av.
		A	B	A	B	C	A	B	A	B	A	B	A	B	
1	25 min. regular background corrections	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01	0.01	0.00	0.00	0.00
2		0.03	0.02	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.00	0.00	0.02	0.01	0.01
3		0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4		34.1	34.8	37.1	36.4	35.9	38.0	38.3	32.6	34.8	34.5	......	38.8	38.6	36.2
5		17.6	17.1	18.3	18.1	18.3	19.6	19.3	16.1	17.2	20.6	......	20.5	20.2	18.6
6		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00
1	45 min. regular background corrections	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
2		0.01	0.02	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4		23.6	23.3	24.9	24.8	24.9	26.6	26.0	22.1	21.5	23.6	......	26.9	28.0	24.7
5		11.8	12.0	12.5	12.4	12.5	13.4	13.0	11.4	10.7	12.9	......	14.4	13.6	12.6
6		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	25 min. no back cor. when k'_{268} and k'_{315} greater than 1	0.00	0.00	0.00	0.00	0.00	......	......	0.01	0.02	0.00	0.00	0.00	0.00	0.00
2		0.03	0.02	0.01	0.01	0.01	......	......	0.01	0.02	0.00	0.00	0.02	0.01	0.00
3		......	......	......	......	......	......	......	......	......	......	......	......	......	......
4		46.2	46.9	47.4	47.0	46.7	48.0	48.2	44.6	46.3	47.0	......	47.8	47.7	47.0
5		23.7	23.1	24.1	24.1	24.1	24.6	24.5	22.8	23.4	29.7	......	25.6	24.6	24.5
6		0.00	0.00	0.00	0.00	0.00	......	......	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	45 min. no back cor. when k'_{268} and k'_{315} greater than 1	0.00	0.00	0.00	0.00	0.00	......	......	0.01	0.00	0.00	0.00	0.00	0.00	0.00
2		0.00	0.02	0.00	0.00	0.00	......	......	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3		......	......	......	......	......	......	......	......	......	......	......	......	......	......
4		34.1	34.1	34.4	34.3	34.4	35.1	34.5	32.2	31.5	38.9	......	36.5	37.1	34.8
5		17.2	17.2	17.7	17.6	17.5	18.2	17.9	16.5	15.8	20.0	......	18.8	18.8	17.8
6		0.00	0.00	0.00	0.00	0.00	......	......	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	25 min. isom.	0.03	0.02	0.02	0.02	0.00	0.03	0.03	0.00	0.00	0.00	0.00	0.03	0.02	0.01
3	old constants	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.01
2	45 min. isom.	0.01	0.02	......	......	......	0.02	0.02	......	......	0.00	0.01	......	......	0.01
3	old constants	0.00	0.00	......	......	......	0.00	0.00	......	......	0.02	0.03	......	......	0.01

c) Background corrections are unnecessary and probably undesirable when k'_{268} is greater than 1.0 and when k'_{315} is greater than 1.0.

d) The present method is valueless for determining the composition of oils such as fish oils containing unsaturated acids of higher unsaturation than tetraene.

e) Because of the presence of cis- and trans-isomers in all hydrogenated oils and the presence of iso-acids (position isomers) in hydrogenated oils which contained higher unsaturation than diene, *i.e.*, linolenic or arachidonic acids, the present method is not satisfactory for the analysis of hydrogenated oils.

f) As hydrogenated oils contain a mixture of cis- and trans-isomers, analysis of such samples by the techniques of the present method followed by calculations, using constants obtained from acids prepared by bromination-debromination methods (which have been shown to consist of cis- and trans-mixtures) might afford more satisfactory results than use of the constants prepared from the natural acids (the all cis-isomers). The results of these collaborative studies show that use of the debromination constants for the calculation on hydrogenated soybean oil instead of the recommended natural-acid constants did not give much more satisfactory results.

Recommendations

It is recommended that A.O.C.S. Tentative Method Cd 7-48, revised May, 1951, be changed as follows:

E Calculations, page 8 add under c-3, "When k'_{268} is greater than one, no correction for background need be made and $k'_3 = k'_{268} - k_3$." Under c-4, add "When k'_{315} is greater than one, no correction for background need be made and $k'_4 = k'_{315} - k_4$.

TABLE II

Non-Conjugated Acids
% Linolenic

Oil No.		Lab 1		Lab 2			Lab 3		Lab 4		Lab 5		Lab 6		Av.
		A	B	A	B	C	A	B	A	B	A	B	A	B	
1	25 min. regular background corrections	6.9	6.8	7.5	7.6	7.6	7.4	7.4	6.5	7.1	7.2	8.0	7.5	7.4	7.3
2		1.9	1.9	2.1	2.1	2.1	2.0	2.1	2.1	2.0	2.1	2.1	2.1	1.3	2.0
3		0.02	0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.04	0.04	0.03	0.02	0.02
4		−17.7	−18.0	−21.2	−20.1	−19.8	......	......	−19.4	−22.2	−18.3	......	−21.5	−20.4	−19.9
5		−5.6	−5.4	−6.4	−6.2	−6.4	......	......	−6.2	−7.5	−10.2	......	−7.0	−7.8	−6.9
6		45.4	45.7	49.4	49.4	48.3	46.6	47.7	47.0	48.4	49.8	49.4	45.2	52.1	48.0
1	45 min. regular background corrections	6.9	6.5	7.6	7.4	7.4	7.4	7.5	6.0	5.6	8.0	8.2	7.5	7.5	7.2
2		1.9	1.8	2.0	2.0	2.0	2.0	2.0	2.0	1.9	2.0	2.1	2.1	2.1	2.0
3		0.02	0.02	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.04	0.04	0.00	0.02	0.01
4		−8.9	−8.8	−10.3	−10.3	−10.1	......	......	−9.4	−9.9	−11.5	......	−11.8	−12.7	−10.4
5		−1.4	−1.6	−1.7	−1.7	−2.1	......	......	−0.95	−1.3	−2.2	......	−2.2	−2.0	−1.7
6		45.9	44.4	48.9	48.7	49.1	47.4	48.0	47.5	45.6	50.1	50.4	48.7	47.1	47.8
1	25 min. no back cor. when k'_{268} and k'_{315} greater than 1	7.8	7.9	8.2	8.2	8.3	8.2	8.2	8.2	8.0	8.2	9.1	8.1	7.9	8.2
2		2.2	2.3	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.5	2.5	2.3	2.3	2.4
3		......	......	......	......	......	......	......	......	......	......	......	......	......	......
4		−17.6	−17.5	−18.9	−18.3	−18.2	......	......	−19.7	−20.7	−18.0	......	−17.3	−17.5	−18.4
5		−5.2	−4.4	−5.5	−5.4	−5.5	......	......	−6.2	−6.6	−10.5	......	−5.4	−6.1	−6.1
6		48.5	49.5	50.9	50.8	50.2	50.4	51.0	48.1	50.2	55.9	56.4	48.6	47.7	50.6
1	45 min. no back cor. when k'_{268} and k'_{315} greater than 1	7.9	7.8	8.1	8.2	8.2	8.2	8.3	8.1	7.1	9.3	9.1	8.3	8.3	8.2
2		2.4	2.2	2.4	2.4	2.4	2.3	2.3	2.4	2.3	2.6	2.6	2.5	2.5	2.4
3		......	......	......	......	......	......	......	......	......	......	......	......	......	......
4		−6.3	−6.6	−6.5	−6.4	−6.4	......	......	−14.5	−13.5	−11.4	......	−7.7	−8.3	−8.8
5		0.29	0.38	0.1	0.3	0.2	......	......	−3.4	−2.9	−1.7	......	0.1	0.0	−0.7
6		49.0	48.7	49.9	50.0	50.6	51.0	51.3	49.7	50.6	55.9	55.8	50.1	48.6	50.9
2	25 min. isom.	1.7	1.8	2.0	2.0	2.0	1.9	2.0	1.1	1.0	2.0	2.2	2.0	1.3	1.8
3	old constants	0.01	0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.04	0.03	0.02	0.02
2	45 min. isom.	1.8	1.7	......	......	......	1.9	1.9	......	......	2.0	1.8	......	......	1.8
3	old constants	0.02	0.02	......	......	......	0.01	0.01	......	......	0.01	0.01	......	......	0.01

TABLE III
Non-Conjugated Acids
% Linoleic

Oil No.		Lab 1		Lab 2			Lab 3		Lab 4		Lab 5		Lab 6		Av.
		A	B	A	B	C	A	B	A	B	A	B	A	B	
1	25 min. regular background corrections	51.7	51.2	51.0	51.0	51.0	49.8	49.5	51.7	49.9	51.0	51.7	51.0	50.0	50.8
2		22.8	23.2	23.3	23.5	23.7	23.1	23.2	24.7	23.8	25.7	25.3	23.1	22.9	23.7
3		0.64	0.59	0.63	0.63	0.63	0.76*	0.80*	0.77	0.71	0.79	0.66	0.66	0.59	0.68
4		14.7	15.0	15.2	15.3	15.2	11.6	12.1	16.1	15.9	15.4	......	14.8	13.3	14.6
5		32.6	32.6	32.7	33.0	33.2	31.4	31.1	32.5	33.9	35.9	......	30.3	28.4	32.3
6		18.4	19.0	17.3	17.4	17.7	17.4	17.1	15.4	15.6	16.8	17.0	17.5	12.3	16.8
1	45 min. regular background corrections	52.7	51.7	51.9	51.5	52.2	50.3	50.9	51.8	50.3	50.5	50.4	51.8	50.7	51.3
2		25.1	25.8	25.1	25.4	25.1	25.2	25.3	25.6	25.3	28.0	28.1	24.9	24.6	25.7
3		0.84	0.82	0.77	0.79	0.79	0.92*	0.92*	0.74	0.79	0.69	0.61	0.81	0.76	0.79
4		14.0	14.8	14.2	14.1	13.9	13.2	13.3	14.3	14.9	15.6	......	14.5	13.3	14.2
5		31.6	33.2	33.0	33.1	33.1	31.8	31.7	30.8	31.5	35.4	......	34.3	33.7	32.8
6		17.1	20.1	17.2	17.7	18.2	17.9	17.7	18.3	18.1	16.7	17.6	16.1	16.8	17.6
1	25 min. no back cor. when k'_{268} and k'_{315} greater than 1	50.9	50.4	50.5	50.6	50.6	49.3	49.0	50.7	49.3	50.6	51.2	50.6	49.6	50.3
2		22.5	23.0	23.1	23.2	23.4	22.8	23.0	24.5	24.6	27.9	28.3	23.0	22.2	24.0
3		......	......	......	......	......	......	......	......	......	......	......	......	......	......
4		7.1	7.2	7.4	7.6	7.5	2.9	3.4	8.9	7.8	8.3	......	6.4	5.8	6.7
5		28.6	28.2	28.6	28.8	29.1	26.2	26.4	28.0	28.0	28.6	......	26.1	24.5	27.6
6		16.3	16.5	16.4	16.5	16.4	14.9	14.9	14.8	14.4	12.8	13.1	15.2	15.3	15.2
1	45 min. no back cor. when k'_{268} and k'_{315} greater than 1	51.9	50.9	51.6	51.0	51.8	49.8	50.5	50.5	48.8	49.7	49.7	51.4	50.2	50.6
2		24.7	25.5	24.9	25.1	25.0	25.0	25.1	25.3	24.9	27.8	27.6	24.7	24.4	25.4
3		......	......	......	......	......	......	......	......	......	......	......	......	......	......
4		5.8	6.7	6.4	6.2	6.1	5.9	5.9	7.0	6.9	5.6	......	6.4	5.3	6.2
5		27.2	28.6	28.8	28.9	28.8	27.7	27.7	28.2	28.4	27.4	......	30.3	29.4	28.4
6		14.8	17.2	16.6	16.9	17.3	15.7	15.6	15.9	15.0	15.6	14.5	15.2	15.9	15.9
2	25 min. isom.	24.4	24.9	25.0	25.2	25.4	24.6	24.8	26.4	25.5	27.5	27.8	24.7	24.4	25.4
3	old constants	0.64	0.58	0.68	0.68	0.68	0.81*	0.85*	0.78	0.71	0.86	0.72	0.66	0.59	0.71
2	45 min. isom.	27.2	27.8	......	......	......	27.2	27.3	......	......	28.8	28.6	......	......	27.8
3	old constants	0.87	0.84	......	......	......	1.4*	1.4*	......	......	0.96	0.96	......	......	1.1

* Corrected to av. preconjugated.

TABLE IV
Conjugated Acids

Lab. No.	Conjugated Diene						Conjugated Triene					
	Oil 1	Oil 2	Oil 3	Oil 4	Oil 5	Oil 6	Oil 1	Oil 2	Oil 3	Oil 4	Oil 5	Oil 6
1	0.13	1.2	0.49	0.78	0.49	0.24	0.03	0.02	0.00	0.00	0.02	0.02
2	0.12	1.2	0.49	0.78	0.45	0.23	0.03	0.02	0.01	0.00	0.02	0.02
3	0.13	1.2	(0.00)	0.76	0.47	0.22	0.03	0.02	0.01	0.00	0.02	0.02
4	0.15	1.3	0.50	0.85	0.55	0.25	0.03	0.02	0.00	0.00	0.02	0.02
5	0.17	1.2	0.50	0.77	0.55	0.25	0.03	0.02	0.01	0.01	0.01	0.02
6	0.13	1.2	0.48	0.76	0.49	0.23	0.03	0.02	0.01	0.00	0.02	0.02
Average	0.14	1.2	0.49	0.78	0.50	0.24	0.03	0.02	0.00	0.00	0.02	0.02
	Conjugated Tetraene						Total Conjugated					
1	0.01	0.00	0.00	0.00	0.00	0.04	0.17	1.2	0.49	0.78	0.51	0.30
2	0.01	0.00	0.00	0.00	0.01	0.04	0.16	1.2	0.50	0.79	0.47	0.29
3	0.01	0.00	0.00	0.00	0.00	0.04	0.17	1.2	(0.01)	0.76	0.49	0.28
4	0.00	0.00	0.00	0.00	0.00	0.04	0.18	1.3	0.51	0.86	0.56	0.31
5	0.00	0.00	0.00	0.01	0.00	0.06	0.20	1.3	0.51	0.79	0.57	0.32
6	0.01	0.00	0.00	0.00	0.01	0.05	0.17	1.2	0.49	0.76	0.52	0.30
Average	0.01	0.00	0.00	0.00	0.00	0.04	0.17	1.2	0.50	0.79	0.52	0.30

( ) Omitted from average.

TABLE V
Summary of Average Data

Oil No.		Conjugated Acids				Non-Conjugated Acids			% Total Acids—Spectrophotometer					Bertram Oxida.* % Sat.
		% Diene	% Triene	% Tetraene	% Total	% Arach.	% Linolenic	% Linoleic	Total Tetraene	Total Triene	Total Diene	% Oleic	% Sat.	
1	25 min. regular background corrections	0.14	0.03	0.01	0.18	0.00	7.3	50.8	0.01	7.3	50.9	25.3	12.1	13.9
2		1.2	0.02	0.00	1.2	0.01	2.0	23.7	0.01	2.0	24.9	62.1	6.6	14.9
3		0.49	0.00	0.00	0.49	0.00	0.02	0.68	0.00	0.02	1.2	84.0	10.4	16.5
4		0.78	0.00	0.00	0.78	36.2	−19.9	14.6	36.2	−19.9	15.4	32.0	12.0	22.9
5		0.50	0.02	0.00	0.52	18.6	−6.9	32.3	18.6	−6.9	32.8	37.6	6.6	17.8
6		0.24	0.02	0.04	0.30	0.00	48.0	16.8	0.04	48.0	17.0	28.7	1.9	8.5
1	45 min. regular background corrections	0.14	0.03	0.01	0.18	0.00	7.2	51.3	0.01	7.2	51.4	24.6	12.4	13.9
2		1.2	0.02	0.00	1.2	0.00	2.0	25.7	0.00	2.0	26.9	58.1	8.6	14.9
3		0.49	0.00	0.00	0.49	0.00	0.01	0.79	0.00	0.01	1.3	83.8	10.5	16.5
4		0.78	0.00	0.00	0.78	24.7	−10.4	14.2	24.7	−10.4	15.0	75.5	−19.6	22.9
5		0.50	0.02	0.00	0.52	12.6	−1.7	32.8	12.6	−1.7	33.3	58.9	−9.2	17.8
6		0.24	0.02	0.04	0.30	0.00	47.8	17.6	0.04	47.8	17.8	27.7	2.3	8.5
1	25 min. no back cor. when k'_{268} and k'_{315} greater than 1	0.14	0.03	0.01	0.18	0.00	8.2	50.3	0.01	8.2	50.4	23.6	13.4	13.9
2		1.2	0.02	0.00	1.2	0.00	2.4	24.0	0.00	2.4	25.2	60.3	7.7	14.9
3		0.49	0.00	0.00	0.49	0.00	0.02	0.68	0.00	0.02	1.2	84.0	10.4	16.5
4		0.78	0.00	0.00	0.78	47.0	−18.4	6.7	47.0	−18.4	7.5	8.0	33.2	22.9
5		0.50	0.02	0.00	0.52	24.5	−6.1	27.6	24.5	−6.1	28.1	25.2	17.8	17.8
6		0.24	0.02	0.04	0.30	0.00	50.6	15.2	0.04	50.6	15.4	24.0	5.6	8.5
1	45 min. no back cor. when k'_{268} and k'_{315} greater than 1	0.14	0.03	0.01	0.18	0.00	8.2	50.6	0.01	8.3	50.7	22.9	13.7	13.9
2		1.2	0.02	0.00	1.2	0.00	2.4	25.4	0.00	2.4	26.6	57.4	9.2	14.9
3		0.49	0.00	0.00	0.49	0.00	0.01	0.79	0.00	0.01	1.3	83.8	10.5	16.5
4		0.78	0.00	0.00	0.78	34.8	−8.8	6.2	34.8	−8.8	7.0	54.2	−0.4	22.9
5		0.50	0.02	0.00	0.52	17.8	−0.66	28.4	17.8	−0.64	28.9	48.5	0.4	17.8
6		0.24	0.02	0.04	0.30	0.00	50.9	15.9	0.04	50.9	16.1	21.7	6.9	8.5
2	25 min. isom.	1.2	0.02	0.00	1.2	0.01	1.8	25.4	0.01	1.8	26.6	59.3	7.9	14.9
3	old constants	0.49	0.00	0.00	0.49	0.01	0.01	0.71	0.01	0.01	1.2	83.9	10.5	16.5
2	45 min. isom.	1.2	0.02	0.00	1.2	0.01	1.8	27.8	0.01	1.9	29.0	54.3	10.4	14.9
3	old constants	0.49	0.00	0.00	0.49	0.01	0.01	1.1	0.01	0.01	1.6	83.2	10.8	16.5

*Southern Regional Research Laboratory.

Projected Committee Work

As a result of a recent publication, "Influence of Alkali Concentration and Other Factors on the Conjugation of Natural Polyunsaturated Acids as Determined by Ultraviolet Absorption Measurements," by S. F. Herb and R. W. Riemenschneider, Eastern Regional Research Laboratory, Philadelphia, Pa., Journal of the American Oil Chemists' Society, November, 1952, Vol. XXIX, pages 456-461, the committee should investigate isomerization of fatty acids with 21% KOH, comparing the results obtained against those using the present A.O.C.S. method. The possibility of extending the method to the analysis of fats containing pentaene acids should be investigated.

A study should be made of the effect of cis-trans isomers present in hydrogenated oils on the results obtained, using the spectrophotometric method. Such a program would involve cooperative work in the infrared region to establish trans-isomer contents.

Cooperative work should be extended to encompass oils containing large quantities of preconjugated constituents. This work should probably be a joint effort with the A.S.T.M. Committee already studying the problem.

The exact program to be followed must, of course, be left to the 1953-54 Committee. The projected committee work proposed is to be considered only as a suggestion in the event that the committee should decide to embark upon an entirely different program.

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chairman

Acetylenic Compounds. I. The Dehydrohalogenation Reactions by Sodamide in Liquid Ammonia and Preparation of Some Mono-Acetylenic Substances and Their Derivatives[1,2]

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IN a previous publication Khan *et al.* (1) described the preparation of stearolic acid by dehydrobromination of dibromostearic acid with sodamide in liquid ammonia. In view of the consistently higher yields obtained by this procedure than with the alcoholic KOH reagent of Adkins (2) and others (3) (17), it seemed desirable to see if this reaction could be applied to the preparation of other acetylenic compounds. The sodamide and alcoholic KOH methods have been compared. The effect of the presence of dienoic acids was shown by using oleic acid, free of such compounds as starting material. Large-scale preparation from 3.2 moles of oleic was also accomplished with some additional precautions.

Purified tetrabromostearic acid was subjected to dehydrohalogenation by sodamide in liquid ammonia. Stearolic acid was then prepared directly from crude olive oil acids in yields of 25-30%.

Diketostearic acid has been prepared by $KMnO_4$ oxidation of the crude stearolic acid obtained from olive oil acids. Stearolic acid was qualitatively detected in mixtures by formation of diketostearic acid. Oleic acid was also detected in mixtures through the formation of stearolic acid and diketostearic acid.

The sodamide dehydrohalogenation method was successfully applied to the preparation of 6-octadecynoic acid from petroselinic acid, phenyl acetylene from styrene, and 10-undecynoic acid from 10-undecelenic acid. The yields of 6-octadecynoic acid were very high compared to those of the latter compounds.

The infrared absorption spectrum of stearolic acid was studied in order to observe absorption due to the triple bond. The freezing point curve was used to determine the absolute purity of stearolic acid.

Some suggestions have been made as to the reasons for the low yields of acetylenic compounds obtained from the unsymmetrical and short chain dibromides.

Experimental

Preparation of Stearolic Acid by Dehydrobromination of Methyl Dibromostearic Acid with Alcoholic KOH. The procedure of Adkins *et al.* (2) was followed, with five separate portions of methyl oleate (35 g., 95-97% pure). Stearolic acid was obtained only twice and in yields of 29 and 34% respectively. In addition, four batches of methyl dibromostearate, each from 35 g. of methyl oleate, were treated separately with 80 g. 85% KOH pellets and 300 ml. of one of the following alcohols: butyl, isobutyl, isoamyl, and amyl. No stearolic acid was obtained in these four experiments.

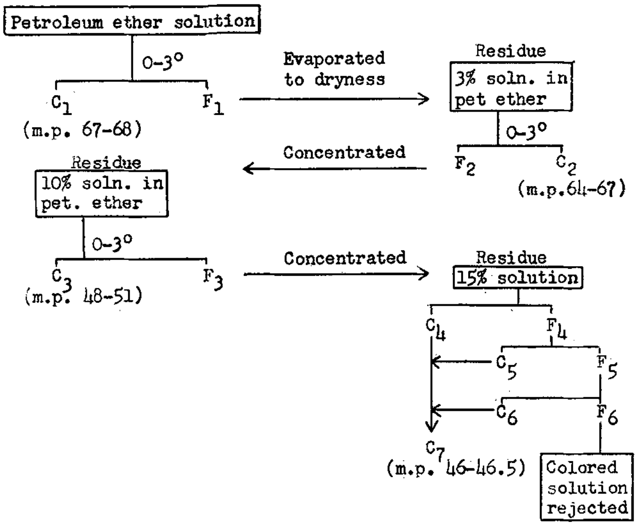

FIG. 1. Isolation of stearolic acid from dehydrobromination of olive oil fatty acids.

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[1] Presented at the 26th fall meeting of the American Oil Chemists' Society, Oct. 20-22, 1952, Cincinnati, O.

[2] Hormel Institute Publication No. 85.

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