fore be more suitable to use this value rather than the 6-hour value in future work. Total non-conjugated linoleate could be calculated directly from this value. The value for sp. a at 232 m μ at $4\frac{1}{2}$ hours is estimated graphically to be 86.0. The formulae for calculating x, y, and z, taking k₃ as 86.0 for all isomers at 285 minutes are as follows:

 $x = 0.04568k_1 - 0.04353k_2 + 0.01020k_3$ $y = 0.00941k_1 - 0.03378k_2 + 0.02530k_3$ $z = -0.05509k_1 + 0.07730k_2 - 0.02388k_3$

It is obvious that the method is only an approximation since it involves values of sp. a taken at times when it is changing rapidly and involves differences between values determined at different times of reaction. All values reported are averages of at least two determinations. Duplicate determinations occasionally varied as much as two units. Any modification of technique which would give better reproducibility would certainly improve the accuracy of the method.

This method is based on the assumption that the isomers used to establish the constants are of known purity and that cis, trans isomers with one cis and one trans double bond would behave identically whether the trans double bond were at the 9, or 12 position. The purity of the cis-9, trans-12 lineleate is probably the one most subject to suspicion. An independent method of checking its purity and of preparing other pure cis, trans or trans, cis isomers would be desirable.

The observed values and calculated equations are. of course, specific for the conditions of temperature, reagents and conditions used: KOH, glycol, 180°C. (9), and the use of methyl esters.

Compound IV, the non-conjugated fraction of dehydrated castor oil esters, showed 32.5% cis. cis. 41.5% cis, trans and 2.7% trans, trans nonconjugated lineleate. Infrared data approximately checked with this amount of trans double bonds. This shows that the new double bond formed in dehydration is about equally cis and trans.

Monomers recovered from the progressive thermal polymerization of non-conjugated linoleate isomers have also been examined. Those from normal cis, cis, linoleate showed rapid formation of cis, trans isomers with very little trans, trans isomer, and rapid disappearance of cis, cis isomer as the cis, trans isomer is formed. Monomers from linolelaidate also showed formation of appreciable amounts of cis, trans isomer, but very little cis, cis isomer. The thermal isomerization of trans, trans to cis, trans linoleate is apparently less extensive than that of cis, cis to cis, trans linoleate. A monomer from polymerization of cis, trans linoleate (V) showed almost no cis, cis, or trans, trans isomer. It thus appears that the cis, trans nonconjugated linoleate isomer is the form which most readily forms and accumulates during thermal polymerization.

Thus, although the present work does not greatly affect the interpretation of spectral analyses for linoleate in natural oils, it does point out that materials which have been subjected to conditions of heat or catalysis which could cause cis-trans shifts, require special conditions for spectral analysis if gross errors are to be avoided. It will be interesting to compare the alkali isomerization of normal cis, cis, cis linolenate with the known trans, trans, trans elaidolinolenic acid, and the unknown cis, trans isomers if, and when, they become known. The extension of infrared and ultraviolet studies to the non-conjugated and conjugated linolenates is under way by us now. It is hoped that the present work and extensions of it will provide useful tools of research for following the isomeric changes involved in operations on unsaturated oils such as heat-bodying, distillation, and resin formation, where conditions prevail which undoubtedly lead to cis-trans and position isomerization of the polyene acid present.

REFERENCES

- 1. Beadle and Kraybill, J. Am. Chem. Soc., 66, 1232 (1944).
- 2. Brice and Swain, J. Opt. Soc., 35, 532 (1945).
- 3. Frankel and Brown, J. Am. Chem. Soc., 65, 415 (1943).
- 4. Kass and Burr, J. Am. Chem. Soc., 61, 1062 (1939).
- 5. Kimura, Fettchem Umschan, 43, 78 (1935).
- 6. Mangold, Monatsh., 15, 309 (1894).
- 7. Mathews, Brode, and Brown, J. Am. Chem. Soc., 63, 1064 (1941).
- 8. McKay and Bader, J. Org. Chem., 13, 75 (1948).
- 9. Mitchell, Kraybill, and Zscheille, Ind. Eng. Chem., Anal. Ed., 15, 1, (1943).
- 10. Nichols, Riemenschneider, and Herb, J. Am. Oil Chem. Soc., 27, 329 (1950).
- 11. Nichols, Herb, and Riemenschneider, J. Am. Chem. Soc., 73, 247
- 12. Paschke and Wheeler, J. Am. Oil Chem. Soc., 26, 278 (1949). 13. Riemenschneider, Herb, and Nichols, J. Am. Oil Chem. Soc., 26, 371 (1949).
- 14. Swern, Knight, Shreeve, and Heether, J. Am. Oil Chem. Soc., 7, 17 (1950).
- 15. Terry and Wheeler, Oil and Soap, 23, 88 (1946).
- 16. Tolberg and Boyd, Anal, Chem. (in press).
- 17. von Mikusch, J. Am. Chem. Soc., 64, 1580 (1942).
- 18. von Mikusch, Angrew Chem., 62, 475 (1950).

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Correction

The second paragraph of the section under Conclusions for the paper entitled "The Deposition of Lime Soap on Fabrics During Washing," by Knowles, Berch, and Schwartz, which appeared on page 161 of the April 1952 issue of the Journal of the American Oil Chemists' Society, should have read as follows:

1. Peptizing power, as exemplified by the Nessler tube test, is not a realistic index of the extent to which a surfactant will prevent firm deposition. A good peptizing agent will however minimize the loose deposition resulting from a filtration effect, and this is of importance in many practical situations.