by the other two methods while the k_{315} and k_{346} values lie in between those by the other methods. In the absence of the constants for pure arachidonic and pentaenoic acids at the different maxima it is not possible to calculate the proportions of diene, triene, tetraene, etc., present in the final isomerized product. From the high k values in all these regions by the proposed method, it can be concluded that the extent of conjugation is fairly high. The high k values in all these regions by all the methods confirms again the point made earlier that isomerization with the polyunsaturated acids occurs stepwise.

That isomerization of such polyenoic acids as linolenic, arachidonic, and pentaenoic is still proceeding even after long periods of reaction, holds forth the promise that it is possible to reach a steady state of maximum isomerization with these acids with suitable modifications of the proposed method.[3] Further studies are under way in this laboratory both towards such an ideal state and toward reducing the time required for isomerization.

With the samples of oils analyzed,[3] the proportions of linoleic and linolenic acids as estimated by the three methods lie in the same range. Duplicate values are presented in order that the reproducibility and accuracy of the three methods can better be appreciated. In general, the values obtained by the proposed method are slightly high, which is probably because the extent of conjugation is better with the tertiary butoxide reagent. The proposed method has the advantages that the isomerization is conducted at a lower temperature (90°) when such side reactions as polymerization are not likely to occur and the estimation is done at such a time when at least with one acid, linoleic acid, the isomerization has reached a steady state. With linolenic acid it is still occurring as against the decline in conjugation with the latter acid, in particular, at the times of reaction by the other methods. Thus it is possible that the values by the proposed method are likely to be nearer the truth.

Summary

It has been shown that potassium tertiary butoxide isomerizes such unsaturated fatty acids as linoleic, linolenic, arachidonic, and pentaenoic at a temperature of 90°. With 5% potassium-t-butanol reagent conjugation of linoleic acid attains a maximum at the end of 2 hrs. and remains steady thereafter even up to 10 hrs. while with linolenic, arachidonic, and pentaenoic acids it is still occurring at the end of such long times of reaction as 48 and 10 hrs., respectively. This continuance of reaction at the end of such long periods with these higher unsaturated acids demonstrates that the isomerization with the tertiary butoxide reagent at 90° is not complicated by side reactions, such as polymerization and deisomerization. All the methods studied give high absorption coefficients in the lower regions of maxima—233 mμ with linolenic, 233 mμ and 268 mμ with arachidonic acids—showing thereby that isomerizations of these acids occur stepwise. Based on this study, a method using 5% potassium-t-butanol as reagent, at 90° with a time of reaction of 4 hrs., has been proposed for the estimation of linoleic and linolenic acids. The k_{233} value for linoleic acid (94.0) obtained by this method compares very well with those by the 6.6% KOH-glycol and 21% KOH-glycol methods while with linolenic acid the k_{233} value (63.2) is higher and k_{268} value (74.2) lies intermediate between those by the other methods. The proposed method is shown to estimate the linoleic and linolenic acid contents of several typical oils with about the same degree of accuracy as either the 6.6% KOH-glycol or 21% KOH-glycol methods.

Appendix. When this paper was ready to be submitted, a note (27) describing the use of tertiary butoxide reagent on the kinetic study of isomerization of linoleic and linolenic acids came to our attention. Extinction coefficients at 235 mμ and 268 mμ are reported for linolenic acid and the values (61.4, 74.2) obtained by isomerization with a molar solution of the reagent at 99.5° and 180 minutes' time of reaction are about the same order as those reported in this paper. It is of interest to note that these authors have also noted that no destruction of the product occurs at this temperature and time of heating.

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[3] It may be pointed out that the proposed method does not require a costly, thermostatically-controlled heating bath as the temperature of isomerization is the same as the boiling point of the reagent, which stays practically constant at 89°.

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22nd Annual Review of the Literature on Fats, Oils, and Detergents. I., M. M. Piskur. This journal, vol. 33, p. 206, 1st column, second paragraph: remove complete reference to Steinacker.