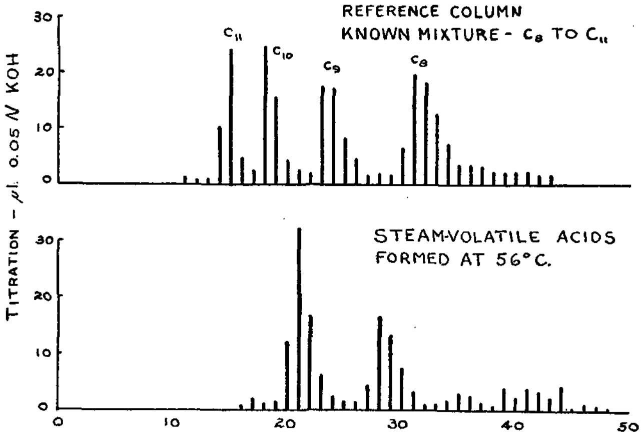

FIG. 3. Monobasic acids formed by autoxidation at 56°C.

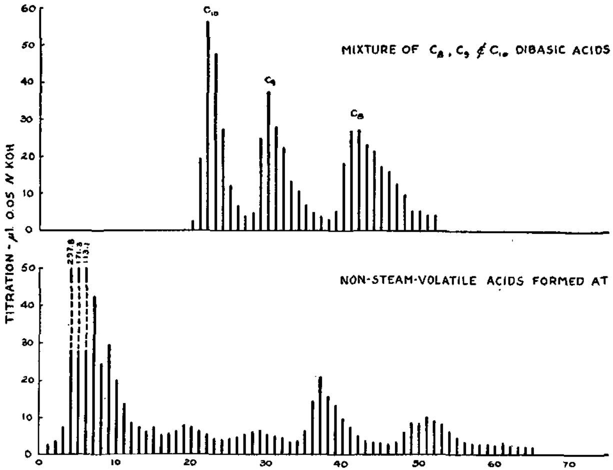

FIG. 4. Non-steam-volatile acids formed by autoxidation at 56°C.

peaks corresponding approximately to nonanoic and octanoic acids. The first of these peaks was shown to be nonanoic by recovery and rechromatographing mixed with known nonanoic acid; both known and unknown came off in one peak. By inference the second peak from the steam-distillation products was assumed to be octanoic acid. When the steam distillate was hydrolyzed and the resulting acids were chromatographed, the same two major peaks came off and, in addition, a much earlier large sharp peak, which could be a long-chain acid whose methyl ester was steam-distillable. Both before and after hydrolysis only 50% of the acid put on the column could be eluted. This could be caused by the presence of some acidic material that was steam-distillable but not eluted by Skellysolve B, perhaps the half-esters of dibasic acids or dibasic-semialdehydes. This will be established by further studies. Both the untreated steam-distillate and its hydrolysate were chromatographed on a column designed to separate dibasic acids. The unhydrolyzed material came off early with no separation. The hydrolysate however contained two minor components, chromatographing in approximately the same positions as nonandioic and octandioic acids, though most of the acids were not held in the column. This would indicate that some dibasic esters had distilled over. The non-volatile material, after hydrolysis, gave a complex chromatogram (Figure 4) when eluted with n-butyl ether. Most of the material was not held; the remainder was separated into a number of as yet unidentified minor components. Two of these correspond approximately to nonandioic and octandioic acids.

The steam-volatile acids from the cobalt-catalyzed autoxidation contained two components that have been tentatively identified as nonanoic and octanoic acids. Two lesser components were also present, in approximately the positions expected for heptanoic and hexanoic acids. The corresponding non-volatile fraction contained only minor and doubtful amounts of dibasic acid. There were several components that were rapidly eluted by n-butyl ether but not so rapidly as the simple mono-basic acids. These may possibly be dibasic semialdehydes, intermediate in polarity between mono- and dibasic acids.

Conclusion

The evidence indicates that γ-radiation at the level used has no specific effect on the products of autoxidation. The initial product, the hydroperoxides, consists of the same four isomers found in non-irradiated autoxidations. An examination of the mono- and dibasic acids, formed by chain scission and complete oxidation, also revealed no products not found in autoxidations energized in other ways.

Summary

1. The hydroperoxides formed by the γ-irradiated autoxidations of methyl oleate at 7.5°C. and 56°C. have been characterized. The mono- and dicarboxylic acids produced by γ-irradiated autoxidation at 56°C. and by cobalt-catalyzed γ-irradiated autoxidation at 73°C. have also been examined.

2. The hydroperoxides were found to be a mixture of the 8-, 9-, 10-, and 11-hydroperoxidoöleates in both samples. They were present in the order $10 > 11 > 9 > 8$.

3. Evidence is presented for the presence of octanoic, nonanoic, octandioic, and nonandioic acids in the 56°C. autoxidation. Octanoic and nonanoic acids were also present in the cobalt-catalyzed autoxidation.

4. No significant departure from non-irradiated autoxidations was found.

REFERENCES

1. Dugan, L. R., and Landis, P. W., J. Am. Oil Chemists' Soc., *33*, 152–154 (1956).
2. Ellis, G. W., Biochem. J., *46*, 129–141 (1950).
3. King, G., J. Chem. Soc., 2114 (1954).
4. Lappin, G. R., and Clark, L. C., Anal. Chem., *23*, 541 (1951).
5. Ross, J., Gebhart, A. I., and Gerecht, J. F., J. Am. Chem. Soc., *71*, 282–286 (1949).
6. Wheeler, D. H., Oil and Soap, *9*, 89 (1932).
7. Zbinovsky, V., Anal. Chem., *27*, 764 (1955).

[Received November 29, 1956]

ADDENDUM

The following reference: Wilson, Glenn R., *31*, 564–568 (1954) should have been cited at the end of the paper on "Fatty Alcohols," by Karl P. Schroeder, in the November 1956 issue of the Journal of the American Oil Chemists' Society (*33*, 565–568).