• *Short Communication*

Thermal Decomposition of Methyl Oleate

A RECENT PUBLICATION (1) announces the isolation and identification of five compounds (i.e., 9-octadecene; decanoic acid methyl ester; 9,17-hexacosadiene; 9,17-hexacosadienoic acid methyl ester; and 9-octadecene-1,18-dioic dimethyl ester) as the major decomposition products of methyl oleate when heated in the absence of oxygen. The author proposes a mechanism which involves a preferential splitting at positions *alpha* to the double bond. Furthermore, he speculates that one of the four resulting radicals, i.e., $\cdot CH=CH—(CH_2)_7—COOCH_3$ is capable of abstracting three hydrogen atoms from methyl oleate and also from octadecene to form the radicals: $\cdot CH=CH—(CH_2)_6—CH=CH—(CH_2)_7—COOCH_3$ and $\cdot CH=CH—(CH_2)_6—CH=CH—(CH_2)_7—CH_3$ respectively. Each of these radicals is then to react with the octyl and with the $\cdot CH_2—(CH_2)_6—COOCH_3$ radical to give the compounds with the 26 carbon chains.

Although the compounds isolated and identified by this worker indicate a specific breakdown of the substrate, we have some reservations on the proposed mechanisms.

First, splitting at positions *alpha* to the double bond is less likely than cleavage at *beta* positions. While the average C-C bond strength is approximately 83 kcal/mole, the dissociation energies for the vinylic bond and for the allylic bond are of the order of 109 and 60 kcal/mole respectively (2). Secondly, the probability of a specific abstraction of two hydrogen atoms from the ultimate position and one from the penultimate position to form terminally unsaturated radicals must be extremely low. Primary C-H bonds are relatively strong, and it is difficult to visualize why two such atoms are preferentially abstracted.

In order to account for the formation of the isolated products, we wish to suggest an alternative mechanism which is based on the more likely splitting at positions *beta* to the double bond and which also precludes the three hydrogen atom abstraction proposition. As shown in Fig. 1, homolysis at "a" gives a heptyl radical I and an 11-carbon radical II. Similarly rupture at "b" gives radicals III and IV. Reaction of radicals I and IV would result in the formation of 9-octadecene and addition of radicals II and III would give the octadecenedioic dimethyl ester. Methyl oleate may also decompose to produce CO_2 and a methyl radical (or CO and a methoxy radical) and a 17-carbon alkenyl radical V (Fig. 2). The latter may then form ethene and a 15-carbon alkenyl radical V. Shortening of alkyl radicals by 2-carbon atoms and the formation of ethene has been shown to occur in thermal degradation (3). Now radical V can react with radical IV to give 9,17-hexacosadiene or with radical II to give 9,17-hexacosadienoic acid methyl ester.

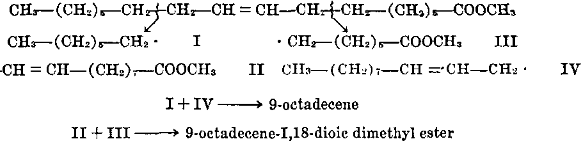

FIG. 1.

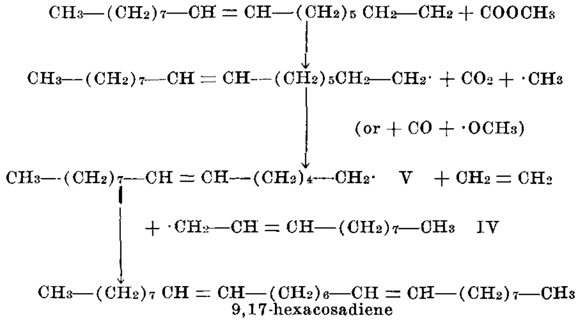

FIG. 2.

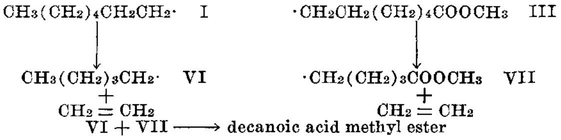

FIG. 3.

Similarly the formation of decanoic acid methyl ester can result from addition of the two 5-carbon radicals VI and VII, as shown in Fig. 3.

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REFERENCES

1. Sen Gupta, A. K., Fette Seifen Anstrichmittel *68*(6), 475–83 (1966).
2. Morrison, R. T., and R. N. Boyd, "Organic Chemistry," Allyn and Bacon Inc., Boston, 1964, p. 39.
3. Markley, K. S., "Fatty Acids," Interscience Publishers Inc., New York, 1961, p. 1030.

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