

# Communications TO THE EDITOR

## The Synthesis of Methyl *cis*-10, *cis*-12-Octadecadienoate

Sir:

We wish to report the synthesis of methyl *cis*-10, *cis*-12-octadecadienoate. The successful isolation of this compound (the first conjugated *cis,cis*-octadecadienoate reported) adds to the series of known isomers of linoleic acid such as the *trans,trans* and *cis,trans* conjugated dienes described previously.<sup>1</sup>

10,12-Octadecadiynoic acid was prepared by the oxidation of 1-heptyne and 10-undecynoic acid;<sup>2</sup> m.p. 43°, Neut. equiv. 276.5; added 3.95 mols H<sub>2</sub> to give stearic acid, m.p. and mixture m.p. 69.5°. Oxidative cleavage with ozone followed by partition chromatography<sup>3</sup> showed that only caproic and sebacic acids were present. The acid was esterified with methanol to produce methyl 10,12-octadecadienoate, m.p. 14°,  $n_D^{25}$  1.4827.

Semi-hydrogenation of the ester was carried

out with ozone produced 92% sebacic acid with the remaining dibasic acids distributed between the 9, 11, and 12 carbon acids. The infrared spectrum is shown in Fig. 1. The C=C stretching region shows a single band at 1605 cm<sup>-1</sup> which results from the vibrational interaction of the two olefinic bonds.<sup>5</sup> The absence of bands in the 900 to 1000 cm<sup>-1</sup> region is taken as evidence for the absence of any *trans* attachment of hydrogens to the olefinic bonds. A CS<sub>2</sub> solution of the ester containing a small amount of iodine isomerized to the *cis,trans* isomer (bands at 982 and 948 cm<sup>-1</sup>) and then partially to the *trans,trans* (strong band at 988 cm<sup>-1</sup>).

The ultraviolet absorption spectrum showed a single peak at  $\lambda_{max}$  235 m $\mu$ ,  $\epsilon$  24,100 (26,800 on basis of 100% diene). The position of the  $\lambda_{max}$  is consistent with the *cis,cis* structure; the *trans,trans* and *cis,trans* isomers absorb at shorter wavelengths.<sup>6</sup> Iodine isomerization of the ester shifted the  $\lambda_{max}$  to 231.5 m $\mu$  with an increase in  $\epsilon$ .

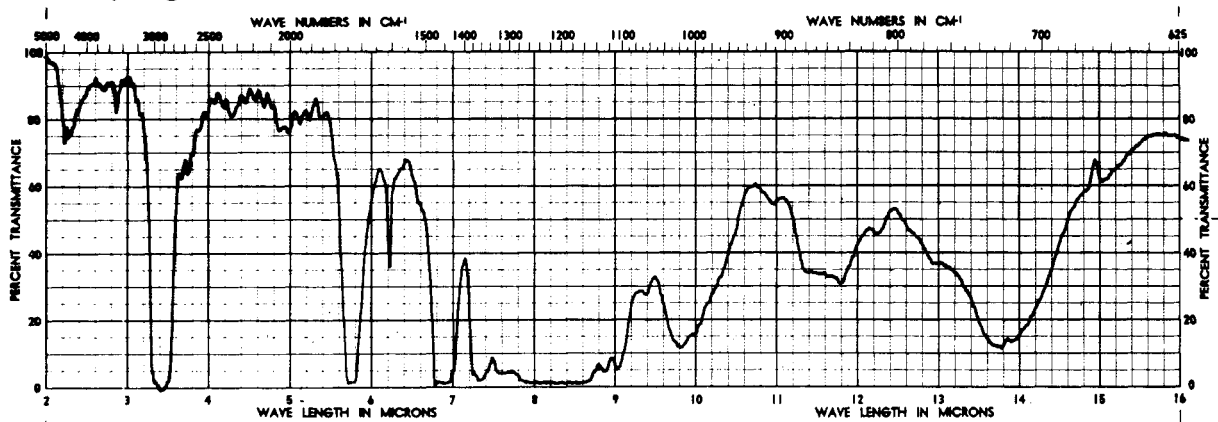


FIG. 1. INFRARED ABSORPTION SPECTRUM OF METHYL *cis*-10, *cis*-12, OCTADECADIENOATE (100% CONC.).

out in ethyl acetate solution in the presence of quinoline using Lindlar<sup>4</sup> catalyst. When 2.0 moles of hydrogen had been absorbed, the reaction was interrupted and the catalyst and solvent removed. The product was fractionally crystallized from acetone (20 ml./g.), and the fraction which crystallized between -35° and -50° was isolated and identified as methyl *cis*-10, *cis*-12-octadecadienoate; m.p. 1.0°,  $n_D^{25}$  1.4690, hydrogen iodine value 163 (theory 172.1). Oxidative cleavage with

The infrared spectrum of this ester lends support to the view that the *cis*-2, *cis*-4-decadienoate described by Crombie<sup>7</sup> contained impurities.

The author wishes to thank C. W. Hoerr for the extensive infrared work during this synthesis and D. H. Wheeler of General Mills, Inc. for checking and confirming the ultraviolet and infrared spectra of this preparation.

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Received December 22, 1955