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The 3020-cm^{-1} Band in the Infrared Absorption Spectra of Methyl Esters of Unsaturated Higher Fatty Acids

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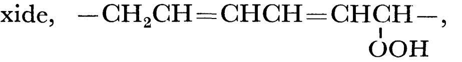
Studies were made of the infrared absorption spectra of methyl esters of oleic, elaidic, linoleic, linoelaidic, *trans*-10, *cis*-12-octadecadienoic, α-eleostearic, stearolic, stearic, 9,10-dideutero-oleic, and 9,10-dideutero-elaidic acids in the C–H stretching region. It was further confirmed that the prominent absorption bands at 3020 cm^{-1} occurring in the infrared absorption spectra of methyl esters of unsaturated higher fatty acids are assignable to the =C–H stretching vibrations of a *cis*-ethylenic double bond. The =C–D stretching vibrations of deutero-ethylenic double bonds (–CD=CD–) in methyl 9,10-dideutero-oleate and -elaidate occurred at 2250 and 2225 cm^{-1} respectively.

It is well known that, in the infrared absorption spectra of some unsaturated higher fatty acid methyl esters such as methyl oleate and methyl linoleate, a prominent absorption band occurs at 3020 cm^{-1}, which is on the higher-frequency side of the absorption bands attributable to the stretching vibrations of carbon-hydrogen bonds in the methylene and methyl groups.

Two explanations have been reported of the assignment of the absorption band at 3020 cm^{-1}. Sinclair *et al.*[1] assigned the absorption band at 3020 cm^{-1} to the =C–H stretching vibrations of an ethylenic double bond in their study of the infrared absorption spectra of oleic, linoleic, linolenic, arachidonic, and elaidic acids, and their methyl esters. On the other hand, Adams and Auxier[2] assigned the absorption band at 3020 cm^{-1} to the C–H stretching vibrations of alpha methylene groups adjacent to an ethylenic double bond on the basis of their observations that the intensity of this band diminished simultaneously with the oxidation of dipentaerythritol linoleate, and that the intensity of this band was very small in oleate, greater in linoleate, and still greater in linolenate. Privett *et al.*[3] supported the latter explanation on the basis of their observations that this band was much weaker in the conjugated peroxide-concentrate from autoxidized methyl linoleate than in oleate or in *cis-trans* conjugated linoleate; this is in accordance with the speculation that the expected structure of the peroxide,  $-\mathrm{CH_2CH{=}CHCH{=}CH}\underset{\substack{|\\ \mathrm{OOH}}}{\mathrm{CH}}-$, would have only one alpha methylene, compared to two for oleate or conjugated linoleate, and three for linoleate, and that this fact agreed best with the assignment of this band to the alpha methylene group. Fukuzumi and his collaborators[4–19] discussed, by employing this explanation, the infrared absorption spectra in liquids, methyl eicosapentaenoate, methyl docosahexaenoate, and methyl octadecatetraenoate, and further confirmed the assignment of the absorption band at 3020 cm^{-1} to the C–H stretching vibrations of alpha methylene groups adjacent to an ethylenic double bond; they did this on the basis of the observation that the intensity of this band was much smaller in conjugated methyl docosahexaenoate(with different *polytrans* conjugated polyene systems) than in non-conjugated methyl docosahexaenoate(with isolated *cis*-ethylenic double bonds only), in spite of the presence of the same number of ethylenic double bonds in both.[13]

Thus, the assignment of the absorption band at 3020 cm^{-1} seems to be not necessarily established in the field of fat and oil chemistry.

This paper will describe a study of the infrared absorption spectra of methyl esters of unsaturated higher fatty acids, such as oleic, elaidic, linoleic, linoelaidic, *trans*-10,*cis*-12-octadecadienoic, α-eleostearic, stearolic, 9,10-dideutero-oleic, and 9,10-dideutero-eladic acids, in the C–H stretching region; some information will be presented to facilitate a choice between these alternative explanations of the assignment of the absorption band at 3020 cm^{-1}.

Experimental

Materials. Each sample of the methyl esters used for the determinations of the infrared absorption spectra was prepared by the esterification of the corresponding acid (obtained by a process to be described later) with methanol by using *p*-toluenesulfonic acid as a catalyst. Its purity was estimated to be above 99%, except for methyl 9,10-dideutero-

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1) R. G. Sinclair, A. F. McKay, G. S. Myers, and R. N. Jones, *J. Amer. Chem. Soc.*, **74**, 2574 (1952).

2) K. Adams and R. W. Auxier, *Official Digest*, **322**, 669 (1951).

3) O. S. Privett, W. O. Lundberg, N. A. Khan, W. E. Tolberg, and D. H. Wheeler, *J. Amer. Oil Chemists' Soc.*, **30**, 61 (1953).

4) K. Fukuzumi, S. Ito, and S. Nakanishi, *Yukagaku*, **12**, 89 (1963).

5) K. Fukuzumi and Y. Iwata, *ibid.*, **12**, 93 (1963).

6) K. Fukuzumi, Y. Iwata, and K. Kawashima, *ibid.*, **12**, 165 (1963).

7) K. Fukuzumi, S. Ito, and T. Hatachi, *ibid.*, **12**, 348 (1963).

8) K. Fukuzumi and I. Ando, *ibid.*, **12**, 351 (1963).

9) K. Fukuzumi and K. Shibata, *Yukagaku*, **12**, 396 (1963).

10) K. Fukuzumi and T. Miyakawa, *Kogyo Kagaku Zasshi*, **66**, 1320 (1963).

11) K. Fukuzumi and T. Yatsuo, *ibid.*, **66**, 1324 (1963).

12) K. Fukuzumi, Y. Iwata, and M. Takada, *ibid.*, **66**, 1675 (1963).

13) K. Fukuzumi and T. Wakita, *ibid.*, **66**, 1846 (1963).

14) K. Fukuzumi and T. Miyakawa, *ibid.*, **67**, 2065 (1964).

15) K. Fukuzumi, T. Miyakawa, and H. Morohira, *ibid.*, **67**, 2070 (1964).

16) K. Fukuzumi and T. Miyakawa, *ibid.*, **67**, 2074 (1964).

17) K. Fukuzumi and T. Maruyama, *ibid.*, **68**, 308 (1965).

18) K. Fukuzumi, *Fette·Seifen·Anstrichm.*, **71**, 104 (1969).

19) K. Fukuzumi, *ibid.*, **71**, 953 (1969).

oleate. The analysis was made by combinations of gas-liquid chromatography, infrared absorption spectrometry, and ultraviolet absorption spectrometry.

Methyl oleate was prepared from oleic acid ($n_{\mathrm{D}}^{17.0}$ 1.4612) fractionated from olive oil fatty acids by the urea-adduct process: iodine value (I. V.) 85.6; $n_{\mathrm{D}}^{14.4}$ 1.4543. The presence of the *trans*-isomer was not detected by means of the infrared absorption spectrum.

Methyl elaidate was prepared from elaidic acid (mp 44.5—45.0°C), which had itself been isolated by the recrystallization of an elaidinized matter obtained by the nitric acid-potassium nitrite isomerization of oleic acid: I. V. 85.6; $n_{\mathrm{D}}^{16.2}$ 1.4529.

Methyl stearolate[20] was prepared from stearolic acid (mp 47.2—47.3°C), which had itself been isolated by the recrystallization of a crude product obtained by the dehydrobromination of dibromostearic acid (prepared by the bromination of oleic acid in ether) with isoamyl alcohol and potassium hydroxide: I. V. 85.7; $n_{\mathrm{D}}^{17.9}$ 1.4578.

Methyl linoleate[21] was prepared from linoleic acid ($n_{\mathrm{D}}^{16.3}$ 1.4711), which had itself been fractionated, by the urea-adduct process in a nitrogen atmosphere, from safflower-oil fatty acids free from unsaponifiable matter: I. V. 172.3; $n_{\mathrm{D}}^{16.0}$ 1.4629. Its ultraviolet and infrared absorption spectra indicated that it contained trace amounts of the conjugated acid ester and of the *trans*-isomer.

Methyl linoelaidate[22] was prepared from linoelaidic acid (mp 27.7—28.1°C), which had itself been isolated by the recrystallization of an elaidinized matter obtained from linoleic acid by the selenium (1%) isomerization at 200—210°C for 6 hr in a nitrogen atmosphere: I. V. 172.4; $n_{\mathrm{D}}^{15.0}$ 1.4620.

Methyl trans-10,cis-12-octadecadienoate[23] was prepared from *trans*-10,*cis*-12-octadecadienoic acid (mp 22.0—23.0°C), which had itself been isolated from a crude product obtained by the alkali isomerization of linoleic acid: $n_{\mathrm{D}}^{16.0}$ 1.4750; K_{233} 92.6.

Methyl α-Eleostearate was prepared from α-eleostearic acid (mp 48.1—48.8°C) obtained by the crystallization of tung oil fatty acid: $n_{\mathrm{D}}^{20.0}$ 1.5148.

Methyl 9,10-Dideutero-oleate was prepared by the partial deuteration of methyl stearolate with Lindlar's catalyst[24] in the presence of quinoline. A modified type of Herschberg's apparatus for catalytic hydrogenation was used for the deuteration. In a reduction flask were charged 0.522 g of methyl stearolate, 30 m*l* of cyclohexane, and 0.02 g of quinoline. The air in the apparatus was completely replaced with deuterium (purity: above 99.9 mol%, Showa Denko make). Then, 0.2 g of Lindlar's catalyst was added to the solution, and the deuterium was allowed to be absorbed at 16.5°C under atmospheric pressure with stirring. Deuteration was stopped when the uptake corresponded to one mole of deuterium per mole of methyl stearolate. The catalyst was then filtered off. The cyclohexane solution was washed with dilute hydrochloric acid (1 : 1), and the sample was obtained by distilling away the cyclohexane: I. V. 85.0; $n_{\mathrm{D}}^{8.0}$ 1.4571. The presence of several per cent of *trans*-isomer was detected by studying the infrared absorption spectrum. No other impurities, such as methyl stearolate and methyl 9,9′,10,10′-tetradeutero-stearate, were detected by gas-liquid chromatography or by a study of the infrared absorption spectrum.

Methyl 9,10-Dideutero-elaidate. An elaidinized matter was obtained by the nitric acid-potassium nitrite isomerization of 9,10-dideutero-oleic acid itself prepared by the saponification of methyl 9,10-dideutero-oleate. (The process of the isomerization was the same as that of elaidic acid from oleic acid.) The elaidinized matter was recrystallized from methanol to give 9,10-dideutero-elaidic acid (mp 44.2—44.4°C), from which the sample itself was prepared: $n_{\mathrm{D}}^{18.0}$ 1.4521.

Infrared Absorption Spectra. A JASCO Grating Infrared Spectrophotometer, Model IR-G, with 0.5-mm matched cells was used. The infrared absorption spectrum of each methyl ester was determined in a carbon tetrachloride solution at a concentration of 0.067 mol/*l* (approximately 2%) or in a liquid film at 20°C.

Results and Discussion

Table 1 shows the characteristics of the structural units possibly associated with the absorption at 3020 cm^{-1} of the methyl esters investigated. Figures 1

TABLE 1. INFRARED ABSORPTION OF UNSATURATED HIGHER FATTY ACID METHYL ESTERS AT 3020 cm^{-1}

Methyl esters	Number and configuration of double bond	Number of alpha methylene group adjacent to unsaturated linkage	Absorption at 3020 cm^{-1}
Oleate	*cis* 1	2	○[a]
Elaidate	*trans* 1	2	×
Linoleate	*cis* 2	3	○
Linoelaidate	*trans* 2	3	×*
trans-10,*cis*-12-Octadecadienoate	*cis* 1, *trans* 1	2	○
α-Eleostearate	*cis* 1, *trans* 2	2	○
Stearolate	-C≡C-	2	×
9,10-Dideutero-oleate (d_2-O)	*cis* 1	2	×
9,10-Dideutero-elaidate (d_2-E)	*trans* 1	2	×
Stearate	0	0	×

a) ○: evident. ×: not observed. ×*: the shoulder occurs at about 3030 cm^{-1}, Ref. 26.

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[20] K. Kino, *J. Soc. Chem. Ind. Jap.*, **32**, s. b. 187 (1929).

[21] D. Swern and W. E. Parker, *J. Amer. Oil Chemists' Soc.*, **30,** 5 (1953).

[22] Kass and Burr, *J. Amer. Chem. Soc.*, **61**, 1062 (1939).

[23] P. L. Nichols, Jr., S. F. Herb, and R. W. Riemenschneider, *J. Amer. Chem. Soc.*, **73**, 247 (1951).

[24] H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

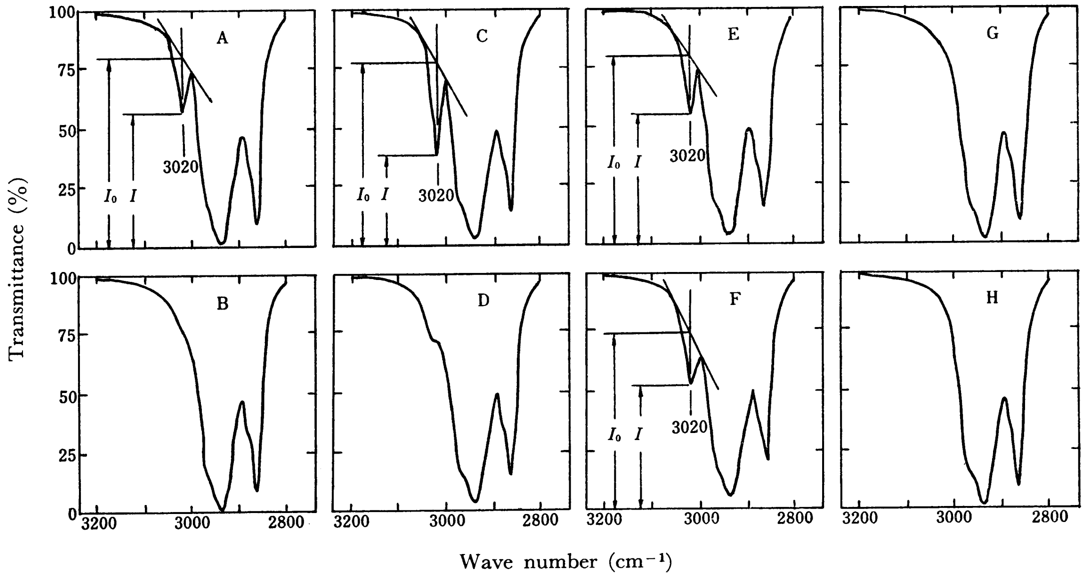

Fig. 1. Infrared spectra of fatty acid methyl esters in the C–H stretching region (in the CCl_4 solution of 0.067 mol/*l* and with the cell of 0.5 mm thickness).
A: methyl oleate. B: methyl elaidate. C: methyl linoleate. D: methyl linoelaidate.
E: methyl *trans*-10,*cis*-12-octadecadienoate. F: methyl α-eleostearate. G: methyl stearolate.
H: methyl stearate.

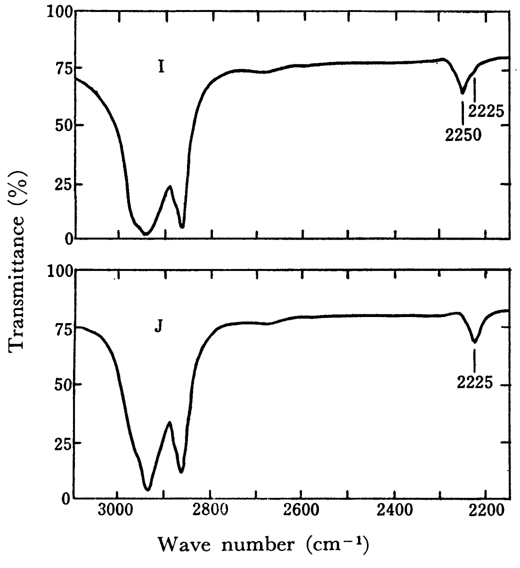

Fig. 2. Infrared spectra of methyl 9,10-dideutero-oleate (I) and methyl 9,10-dideutero-elaidate (J) in the C–H and C–D stretching regions (liquid films).

and 2 show the infrared absorption spectra of the methyl esters in the C–H stretching region.

Among the methyl esters investigated, oleate, linoleate, *trans*-10,*cis*-12-octadecadienoate, and α-eleostearate possess prominent absorption bands at 3020 cm^{-1}.[25] The accurate determination of the optical densities of these esters at the 3020-cm^{-1} bands is difficult because the bands overlap with the C–H stretching bands of the methylene and methyl groups. However, the approximate values of the optical densities, as calculated from the transmittances obtained by the base-line method at the absorption maximum at 3020 cm^{-1} (I/I_0, see Fig. 1), were as follows (in the CCl_4 solution of 0.067 mol/*l* and with the cell of 0.5-mm thickness): oleate, 0.156; linoleate, 0.315; *trans*-10,*cis*-12-octadecadienoate, 0.160; α-eleostearate, 0.158.

The ratio between the optical densities, 1.00 : 2.02 : 1.03 : 1.01, is almost equal to the ratio of the numbers of the *cis*-ethylenic double bonds present in the molecules, 1 : 2 : 1 : 1; there is thus no difference between isolated and conjugated systems.

On the other hand, elaidate and linoelaidate,[26] in which the ethylenic double bonds are of the *trans*-structure, do not possess prominent absorption bands at 3020 cm^{-1}, though they, like oleate and linoleate, have alpha methylene groups adjacent to the ethylenic double bonds. In addition, stearolate, methyl 9,10-dideutero-oleate (d_2-O), and methyl 9,10-dideutero-elaidate (d_2-E), which all have alpha methylene groups adjacent to a triple bond or dideutero–ethylenic double bonds (–CD=CD–), do not possess an absorption band at 3020 cm^{-1}.

From the above facts, it seems most reasonable to conclude that the absorption bands at 3020 cm^{-1} evident in the absorption spectra of methyl esters of unsaturated higher fatty acids are attributable to the =C–H stretching vibrations of *cis*-ethylenic double bonds, and not to the C–H stretching vibrations of alpha methylene groups adjacent to ethylenic double bonds.

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[25] Sinclair *et al.*[1] reported that similar bands were observed in oleic, linoleic, linolenic, and arachidonic acids, and proposed the spectrographic method for the determination of the degree of the *cis*-unsaturated acids, basing the procedure on the optical densities of the absorption bands at 3020 and 2920 cm^{-1}.

[26] Linoelaidate possesses only a very weak absorption band at about 3030 cm^{-1}; this absorption is not attributable to the trace of the *cis*-isomer in the sample methyl ester. At any rate, its intensity is much lower than that of the absorption band at 3020 cm^{-1} in linoleate.

The propriety of the above view can be more clearly explained by the following results.

Both d_2-O and d_2-E have two alpha methylene groups adjacent to a deutero-ethylenic double bond. The deutero-ethylenic double bond in d_2-O has the *cis*-structure, while that in d_2-E has the *trans*-structure. None of them shows an absorption band at 3020 cm^{-1}. However, the absorption band attributable to the =C-D stretching vibrations of the deutero-ethylenic double bond occurs at 2250 cm^{-1} in d_2-O and at 2225 cm^{-1} in d_2-E. A slight shoulder at 2225 cm^{-1} in d_2-O indicates the formation and mixing of several per cent of the *trans*-isomer after methyl stearolate was subjected to the partial deuteration with Lindlar's catalyst in the presence of quinoline.

If it is true that the absorption band at 3020 cm^{-1} is due to the =C–H stretching vibrations of the *cis*-ethylenic double bond, the absorption at 3020 cm^{-1} will not occur in d_2-O, but the absorption band attributable to the =C–D stretching vibrations of the *cis*-deutero-ethylenic double bond corresponding to the above band must occur in d_2-O. Fortunately, spectroscopic data by Hoffmann[27] are available in this case.

The =C–D stretching frequency of a *cis*-deutero-ethylenic double bond corresponding to 3020 cm^{-1} was calculated to be 2247 cm^{-1} from the ratio of 1.344 : 1 between the stretching frequencies of the =C–H(νC–H) and the =C–D(νC–D) of Hoffmann's data; this value agrees very well with the value of 2250 cm^{-1} for that of d_2-O.

Furthermore, the =C–H stretching frequency corresponding to the 2225 cm^{-1} in d_2-E was calculated in the same way to be 2990 cm^{-1}. Sinclair *et al.*[1] reported that weak bands appeared at 2995, 3015, and 3033 cm^{-1} in the infrared absorption spectrum of elaidic acid. According to the results of the present experiments, the absorption band at 2995 cm^{-1}, among the three bands, corresponds to the =C–H stretching band of a *trans*-ethylenic double bond.

It was, thus, further confirmed that the 3020 cm^{-1} absorption band occurring in the infrared absorption spectra of methyl esters of unsaturated higher fatty acids is due to the =C–H stretching vibrations of *cis*-ethylenic double bonds in the isolated or the conjugated system, and not to the C–H stretching vibrations of alpha methylene groups (including the group existing between the two double bonds, of course) adjacent to the ethylenic double bonds.

Some reports, mentioned in the preface of this paper, have stated that the diminution in intensity of the 3020 cm^{-1} absorption band coinciding with the oxidation of methyl esters of unsaturated higher fatty acids is to be attributed to the loss of alpha methylene groups adjacent to an ethylenic double bond as a result of the formation of a hydroperoxide ($-\mathrm{CH}{=}\mathrm{CH}\text{-}\mathrm{CH_2}\text{-} \rightarrow -\mathrm{CH}{=}\mathrm{CH}-\underset{\mathrm{OOH}}{\underset{|}{\mathrm{CH}}}-$),[5–8,12,13,15] as a result of the formation of a conjugated system ($-\mathrm{CH}{=}\mathrm{CH}-\mathrm{CH_2}-\mathrm{CH}{=}\mathrm{CH}- \rightarrow -\mathrm{CH}{=}\mathrm{CH}-\mathrm{CH}{=}\mathrm{CH}-\mathrm{CH_2}-$),[9,12,14,15] or as a result of consumption for polymerization,[10] indicating that the expected structure of the hydroperoxide obtained has the $-\mathrm{CH}{=}\mathrm{CH}-\mathrm{CH}{=}\mathrm{CH}-\underset{\mathrm{OOH}}{\underset{|}{\mathrm{CH}}}-$ or the $-\mathrm{CH}{=}\mathrm{CH}-\underset{\mathrm{OOH}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH}{=}\mathrm{CH}-$ group.[3,4,12] However, it seems to be important to consider that the decrease in this band is due to the loss of *cis*-ethylenic double bonds, including that by isomerization to the *trans*-form coinciding with the maintenance of the intact position, with migration to a new position, or with the formation of a conjugated system.

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[27] E. G. Hoffmann, *Ann.*, **618**, 276 (1958).

	νC-H, cm^{-1}	νC-D, cm^{-1}
cis- $C_2H_5CH{=}CHC_2H_5$	3010	—
cis- $C_2H_5CD{=}CHC_2H_5$	3010	2240
cis- $C_2H_5CD{=}CDC_2H_5$	—	2240