The Isomeric Structure of the C_{18} Unsaturated Acids from their Raman and Infra Red Spectra

J. W. McCUTCHEON,* M. F. CRAWFORD,** H. L. WELSH***

ALTHOUGH the cis-trans relationship between oleic and elaidic acids is well known and has been demonstrated beyond doubt by synthetic and analytical methods, the determination as to which is trans and which cis, is not at all clear, although the preponderance of opinion has been to give oleic the cis structure. This conclusion has been based for the most part on the dimensional relationship of oleic and stearic acid from a study of monomolecular layers (1), parachor values (2), reduction of stearolic acid to oleic (3), rates of hydrogenation (4), heats of combustion (5), and the ease of elimination of HBr from the dibromo derivatives (6). This last paper is probably the most conclusive chemical proof to date, that oleic is the cis form, although the exceptions to the above rule are very numerous and one must accept such evidence with caution (7, 8).

That oleic is the trans form, has been vigorously maintained by Bertram (9), on theoretical considerations based on the fact that in the elaidinizing reaction two parts of elaidic and one part of oleic is formed. His conclusions are weakened considerably by the assumptions necessary. From a study of the emulsive powers of the potassium salts of these fatty acids, Bertram and Kipperman (10) concluded that oleic more closely resembles stearic acid than does elaidic, and hence the former must be the trans form. These papers constitute the most powerful argument in favor of a trans structure for oleic, although mention might be made of work by Wildschut (11) on dipole moments, and by Esafov (12) on the relationship between the hydroxy acids.

Linoleic or $\Delta^{9, 12}$ octadecadienoic acid is theoretically capable of existing in four cis-trans modifications. It is generally recognized however, that only one form occurs naturally (13, 14, 15, 16) which is also identical to that produced from the debromination of either solid or liquid tetrabromide (17, 18, 19, 20). Various structures given in the literature, (21, 22) have been found untenable in view of later findings. Two recent papers (15, 19) go no further than to suggest the structure as possibly cis-cis. One of these papers (19) might cause one to feel there is chemical evidence to support a cis-cis structure, by the unintentional use of the word "cis" in two senses, that is, as cis addition, and cis structure. Cis addition can proceed as rapidly with a trans bond as with a cis one.

Linelaidic or $\Delta^{9, 12}$ octadecadienoic acid was first prepared by Kass and Burr (17) and subsequently studied by Hilditch and Jasperson (15). The latter conclude that the elaidinizing reaction reverses both bonds and assign a trans-trans structure to it, although the evidence is extremely weak and depends on a known structure for linoleic.

Linolenic or $\Delta^{9, 12, 15}$ octadecatrienoic acid may exist theoretically in eight cis-trans modifications. From chemical evidence to date (23) it appears probable that only one natural structure occurs, identical to those produced by debromination methods. No cis-trans structure has been suggested for this acid.

In view of the confusion and doubt existing over the structures to be assigned to these acids it was considered advisable to study the problem by means of the Raman and Infra-Red spectra.

Experimental

Preliminary work on the spectra indicated the necessity of working with the esters of the acids which are far more stable. The ethyl esters were used to avoid any tendency toward association. Since esterification and saponification have no effect on the isomerism of the C_{18} acids, the conclusions reached through the esters, is also valid for the free acids.

Fluorescence was extremely troublesome even on highly refined and purified compounds. due to the minute traces of oxidation products formed in handling. By using a closed system whereby the product was distilled directly into the Raman tube in five steps and at the extremely low pressure of 10^{-4} mm., this difficulty was completely overcome.

Ethyl oleate was prepared from pure olive oil by separating the saponified acids with the modified Twitchell method (24). The resulting unsaturated acids were then separated from residual traces of saturated acids and from linoleic acid by crystallizing from acetone solutions according to the method of Brown and Shinowara (25). Final purification was effected by crystallizing the lithium salt five times from 80% alcohol, separating the acids and esterifying in the usual way, using 4 N alcoholic hydrochloric acid. The iodine value (Wijs) was 81.24. Ethyl elaidate was prepared from the unsaturated fatty acids of olive oil. They were thoroughly separated from residual traces of saturated acids by chilling a 10% acetone solution to —20°C. The resulting acids were then elaidinized in the usual manner, using nitric acid and sodium nitrite, and the solid acid recrystallized five times at —20°C from an approximate 10% acetone solution. It was then further purified through the lithium salt and esterified as above. The iodine value (Wijs) was 80.85 and the melting point of the free acid was 43.5°C. Because of the ease of crystallization, the ethyl elaidate was considered the purer of the two, notwithstanding the lower iodine value (26). Ethyl stearate prepared from Eastman stearic acid of m.p. 69.5°C was used as a control to establish the position of the double bond lines in the series. Ethyl linoleate and ethyl linolenate were prepared by debromination methods as previously outlined (20, 23). Beta linoleate, formerly established by chemical means as identical to the alpha or natural linoleate, was included in this series. Its preparation followed the lines previously laid down (20). The elaidinization of the ethyl linoleate is essentially the method of Kass and Burr (17).

---

*Technical Supervisor, Lightfoot Schultz Co., Hoboken, N. J., formerly Chief Chemist, Lever Bros., Ltd., Toronto, Can.

**Assistant Professor of Physics, University of Toronto, Toronto, Can.

***Demonstrator in Physics, University of Toronto, Toronto, Can.

Thirty six and seven tenths grams of ethyl linoleate and 0.37 gm. (1%) selenium were mechanically agitated at 190° to 220°C for six hours, under a stream of CO_2. After the first hour a constant rise in refractive index was observed. The product was separated by distillation into ethyl linelaidate, 23.3 gm. and a residue. The distillate was saponified and 3.0026 gm. brominated in the usual manner. No solid precipitate came down even after hours of standing, contrary to the findings of Kass and Burr (17) but confirming those of Hilditch and Jasperson (15). Two liquid bromides were formed, one separating from petroleum ether at room temperature, the other only at temperatures below —60°C. The remaining elaidinized fatty acid was esterified, distilled and refined in the usual manner. Yield 12.1 gm.

Raman Spectra

The usual technique for taking Raman spectra was employed with the exception of an unusually long collimator tube, f = 200 cm. permitting quantities of material down to 2 ml. to be used. Illumination was effected by banks of mercury arc lamps and the tube was cooled by jets of air. A Wollaston double image prism was employed for studying the polarisation of the Raman lines.

The graphical presentation of the lines is given in Fig. 1. Length of line represents intensity, width, broadness. The Raman lines characteristic of the unsaturated esters is given in Table 1, together with polarisation data and intensity.

Infra Red Spectra

From theoretical considerations involving changes in dipole moment during vibration, it can be shown that in the neighborhood of the characteristic double bond frequency, 1,670 cm-¹, corresponding to a wave length of about 6.0 μ, a strong absorption should occur with cis compounds and be absent for trans. Infra-red studies were made in this region using a standard Hilger infra red spectrometer with a rock salt prism. Fig. 2 is the result of plotting the ratio of the transmissions of the unsaturated compounds to the transmission of the saturated stearate.

Fig. 2

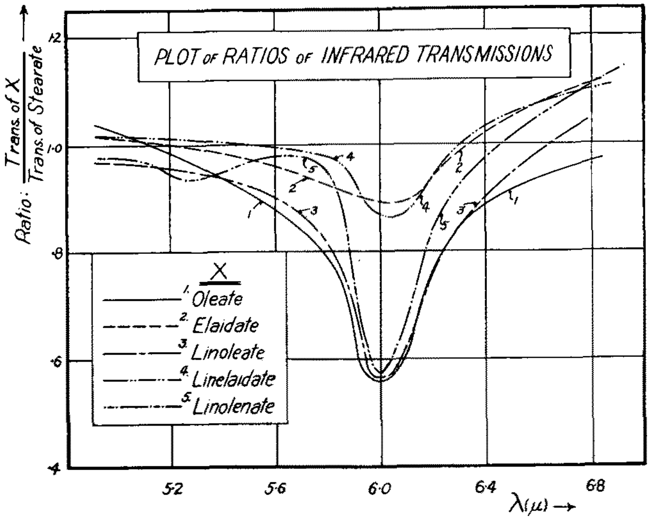

TABLE 1.—RAMAN LINES CHARACTERISTIC OF THE UNSATURATED ETHYL ESTERS

Oleate	Elaidate	Linoleate	β—Linoleate	Linelaidate	Linolenate
		953 1	952 1		954 0
974 3 d	962 1	972 5 d	973 4 d	977 1	971 2
1267 7 d	1269 1	1264 7 d	1264 7 d	1261 2 d	1250 1 1265 6 d
1655 8 p	1669 8 p	1643 6 d 1658 10 p	1643 5 d 1657 10 p	1656 10 p 1668 5 d	1656 9 p
3009 6 p	3008 3 p	3012 5 p	3012 5 p	3009 2 p	3013 8 p

Note: Frequencies, relative intensities (scale 0-10) and polarisations are listed respectively. p—polarised, d—depolarised.

Fig. 1

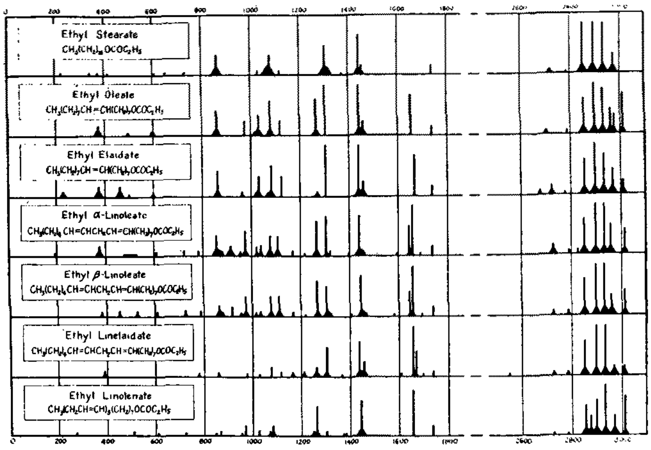

CHART OF RAMAN FREQUENCIES

Conclusions

From the work of Bourguel, Gredy, Piaux and associates (27, 28, 29) and others it has been established that for all molecules of the type RCH = CHR′ the ethylenic bond gives rise to a frequency in the neighborhood of 1,650 cm-¹ and that for cis compounds this frequency is 10 to 20 cm-¹ lower than in the corresponding trans compound. It is also characteristic of ethylenic compounds that a Raman line occurs at approximately 3,010 cm-¹ frequency units which has about twice the intensity in a cis compound than in a trans.

Examining the data for ethyl oleate and ethyl elaidate, we see at once from Table 1, that the double bond frequency of ethyl oleate is 14 units lower than that for ethyl elaidate and hence oleic acid is a cis isomer while elaidic is a trans. This conclusion is supported by the intensity of the 3,009 line in the oleate and by the strong infra red absorption in the neighborhood of 6.0 μ Fig. 2. Although Bertram (9) arrived at the oposite conclusion from a study of equilibrium data in the elaidinizing reaction, it appears that the basic argument used was a sound one. He eliminated the possibility of two hydrogen atoms falling close to one another, on the ground that they repel. It appears likely here that he overlooked the possibility that the CH_3-$(CH_2)_7$- and the -$(CH_2)_7$-COOH groups might also repel, and overshadow the natural repelling action of the two hydrogens to such an extent as to actually reverse the process. The data of this paper supports such a view. In addition it is possible to reconcile the work of Bertram and Kiperman (10) if we recall that the acids, and possibly the potassium salts as well, associate in pairs (30). The resemblance between stearic and the cis isomer oleic, then becomes clear, a condition not existing were oleic the trans compound.

An examination of the Raman data on the α and β linoleates shows them to be identical, a conclusion reached by one of us (20) on purely chemical grounds and since supported by the work of Riemenschneider, Wheeler and Sando, (19) and by Kass and Burr (17).

The Raman lines for ethyl linoleate and ethyl linelaidate, Table 1, show a heavy intense polarised line at approximately 1,657 cm^{-1} in both compounds and a weaker depolarised line 15 units lower than the main frequency line for the linoleate and 12 units higher for the linelaidate. This symmetrical structure leads one to believe that the elaidic reaction reverses not one, but both bonds. From chemical considerations, it would be hard to conceive of only one bond being isomerized under the drastic conditons of the reaction, a point of view supported by the work of Hilditch and Jasperson (15). Therefore if lineoleic were cis-trans or trans-cis, the elaidic form would also be trans-cis or cis-trans. However, it can be demonstrated that all four of these compounds should exhibit infra red absorption at wave length 6.0 μ. From Fig. 2, it is seen that ethyl linoleate is strongly absorbing, while ethyl linelaidate does not absorb infra red radiation to any extent. It is concluded therefore that these compounds are not cis-trans or trans-cis isomers but must be cis-cis and trans-trans. From the strength of the infra red absorption in the two cases, it is concluded that ethyl linoleate is cis-cis while the linelaidate is trans-trans. The intensity of the Raman line at frequency 3,012 and 3,009 cm^{-1} lends additional support to the above conclusion.

Ethyl linolenate is strongly absorbing in the infra-red, Fig. 2, has a single strong polarised frequency at 1,656 cm^{-1} and an intense line at frequency 3,013 cm^{-1}. It is concluded therefore that this compound is undoubtedly cis-cis-cis. The fact that it has no dopolarised lines may be attributed to its symmetrical character.

Summary

Infra-Red and Raman spectroscopic examination of the unsaturated C_{18} fatty acids leads to the conclusion that the naturally occurring acids such as oleic, linoleic and linolenic contain only cis double bond linkages, while the artificial elaidic and linelaidic acids contain only the trans linkages.

Bibliography

1. Langmuir, I. Proc. Nat. Acad. Sci. 3:251-7. 1917.
2. Semeria, G. B. and Ribotti-Lissone, G. Gazz. chim. ital. 60:862-6. 1930.
3. Robinson, G. M. and Robinson. R. J. Chem. Soc. 127:175. 1925.
4. Plisov, A. K. and Golendeev, V. P. Rep. U.S.S.R. Fat & Margarine Inst. 2:12-21. 1935.
5. Keffler, L. J. P. Rec. trav. chim. 49:415-424. 1930.
6. Maruyama, T. and Suzuki, B. Proc. Imp. Acad (Tokyo) 7: 379-382. 1931.
7. Bernthsen. A. Organic Chemistry, 1922 Ed. revised by J. J. Sudborough, Blackie and Son. Ltd., London. Page 255.
8. Whitmore, F. C., Organic Chemistry, D. VanNostrand, New York, 1937. Page 470.
9. Bertram, S. H. Chem. Weekblad. 33:3-5. 1936.
10. Bertram, S. H. and Kipperman. E.C.S. Chem. Weekblad. 32:624-627. 1935.
11. Wildschut, A. J. Physica 12:194-210. 1932.
12. Esofov, V. I. J. Gen. Chem. U.S.S.R. 7:1403-1412. 1937.
13. Hilditch, T. P. and Green. T. G. Biochem. J. 29:1552-1563. 1935.
14. Smit, W. C. Rec. trav. chim. 49:539-551. 1930.
15. Hilditch, T. P. and Jasperson, H. J. Soc. Chem. Ind. 58:233-241. 1939.
16. Haworth, R. H. J. Chem. Soc. 1456-61. 1929.
17. Kass, J. P. and Burr, G. O. J. Am. Chem Soc. 61:1062-66 1939.
18. Kass, J. P., Lundberg, W. O., and Burr, G. O. Oil and Soap 17: 50-53. 1940.
19. Riemenschneider, R. W., Wheeler, D. H., and Sando, C. E. J. Biol. Chem. 127:391-402. 1939.
20. McCutcheon, J. W. Can. J. Research B: 16:158-175. 1938.
21. Smith, F. L., and West, A. P. Philippine J. Sci. 32:297-316. 1927.
22. Nicolet, B. H. and Cox, H. L. J. Am. Chem. Soc. 44:144-152. 1922.
23. McCutcheon. J. W. Can. J. Research B; 18:231-239. 1940.
24. Modified Twitchell Separation, Oil and Soap 12:287. 1935.
25. Brown, J. B. and Shinowara, G. Y. J. Am. Chem. Soc. 59:6-8. 1937.
26. McCutcheon. J. W. Ind. and Eng. Chem. Anal. Ed. 12:465. 1940.
27. Bourguel, M., Gredy, B., and Piaux, L. Compt. rend. 195:129-131. 1932.
28. Delaby, R., Piaux, L., and Guillemonat, A. Compt. rend. 205:609-611. 1937.
29. Gredy, B. Bull. soc. chim. 2:1029-1037 and 1951-1958. 1935; 3:1101-1107. 1936; 4: 415-422. 1937.
30. King, A. M. and Garner, W. E. J. Chem. Soc. 1449-1456. 1934.

The Insecticidal Properties of Some Fatty Acid Derivatives

A. W. RALSTON, J. P. BARRETT and E. W. HOPKINS

RESEARCH LABORATORY, ARMOUR AND CO., CHICAGO, ILL.

Introduction

The high cost of pyrethrum, uncertainty of supplies, and unsuccessful attempts to grow the crop commercially in this country have given considerable impetus to the search for new insecticidal compounds. The fatty acid derivatives present a logical and promising field for such an investigation. The fats themselves, such as whale oil, fish oil, peanut oil, palm oil or cottonseed oil, have been employed for the control of scale insects on plants and have been used in a number of cases as fungicides. The latter use has been rather extensively investigated by Martin and Salmon (1). The soaps are frequently used as the emulsifying and spreading agents for insecticides and less generally as the toxic principle. The activity varies somewhat with the particular type of insect used in the test; however, it is generally found to be at a maximum with the soaps of capric, lauric, and myristic acids. Tattersfield and Gimingham (2) stated that the toxicity of soap is due to the free acid liberated by hydrolysis. Fleming and Baker (3) found potassium myristate to be effective against the Japanese beetle. Ginsburg and Hunt (4) observed that certain fatty acids are injurious to plant tissues. Soaps and oleic acid are generally more toxic to insects than those of stearic acid. Metallic soaps, such as copper oleate, have been frequently used for the control of various fungus diseases, and since the soaps of the heavy metals are oil soluble, they are generally applied in a hydrocarbon solvent.

While the simpler fatty derivatives, such as the soaps of fatty esters, have been extensively employed, either as the toxic agent or as the wetting and spreading