

melted at 283°-284°C. were finally recovered. These crystals gave a deep blue color on treatment with 10% potassium hydroxide solution, which indicated the DNPH of a dicarbonyl (12). *Anal.* calcd. for di-DNPH of hexene-3-dial-1,6, $C_{18}H_{16}N_8O_8$: C, 45.75; H, 3.41; N, 23.72. Found: C, 45.0; H, 3.48; N, 23.4.

The absorption spectrum of the dihydrazones of dicarbonyls has been shown to differ significantly from that of the monohydrazone (9) and the absorption spectrum of the present preparation, as given in Figure 3, is characteristic of a dicarbonyl dihydrazone.

A schematic summary of the fractionation, isolation, and characterization data is given in Table I.

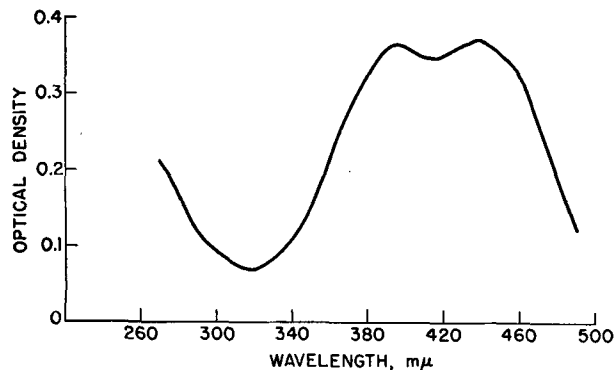


FIG. 3. Absorption spectrum of the dihydrazone of the dicarbonyl in dioxane.

Discussion

Volatile aldehydes isolated from autoxidizing methyl linolenate differ from those isolated from soybean oil autoxidized under the same conditions in the absence of hexanal and in the presence of appreciable amounts of a C_6 dial. It may therefore be assumed that acetaldehyde, propionaldehyde, and α -pentenal isolated from autoxidizing soybean oil could have arisen from linolenic acid.

The formation of acetaldehyde, propionaldehyde, crotonaldehyde, and α -pentenal can be rationalized according to present concepts of the mechanism of oxidation (3, 7). Rationalization of the occurrence of a C_6 dial can be made by postulating the decomposition of a 10,15-dihydroperoxide to give hexene-3-dial-1,6. Ultimate analysis, absorption spectrum, and color reactions are compatible with this postulate.

It seems surprising at the outset that the linolenate radical which comprises 6 to 9% of soybean oil should be the precursor of the principal aldehydes isolated. However studies on the isolated compounds have shown that linolenate oxidizes 1½ to 2 times faster than linoleate and 16 to 25 times faster than oleate (6, 11). Moreover recent studies have shown a marked difference in the course of linolenate oxidation compared to that of oleate or linoleate. Whereas monohydroperoxides of the latter two radicals are relatively stable, polymerization and scission occur immediately upon oxidation of linolenate (4, 5).

Hexanal was isolated from soybean oil but not from methyl linolenate. The presence of hexanal in reverted soybean oil can best be rationalized by considering oxidative reactions of linoleic acid. Hexanal has, in fact, been isolated from autoxidized cottonseed oil (13).

The relationship of the isolated aldehydes to the reversion flavors of soybean oil are the subject of present investigations.

Summary

Volatile cleavage products of autoxidizing methyl linolenate have chromatographically separated and the aldehydes have been isolated as 2,4-dinitrophenylhydrazones. Acetaldehyde, propionaldehyde, and α -pentenal have been identified. A six-carbon atom dialdehyde has been isolated as its hydrazone and is postulated to be hexene-3-dial-1,6.

REFERENCES

1. Delaby, M. R., and Guillot-Allegré, S., *Bull. soc. chim. France*, 53, 301 (1933).
2. Dutton, H. J., Lancaster, Catherine R., Evans, C. D., and Cowan, J. C., *J. Am. Oil Chem. Soc.*, 28, 115-118 (1951).
3. Farmer, E. H., Koch, H. P., and Sutton, D. A., *J. Chem. Soc.*, 1943, 541-547.
4. Fugger, J., Cannon, J. C., Zilch, K. T., and Dutton, H. J., *J. Am. Oil Chem. Soc.*, 28, 285-289 (1951).
5. Fugger, J., Zilch, K. T., Cannon, J. A., and Dutton, H. J., *J. Am. Chem. Soc.*, 73, 2861-2864 (1951).
6. Gunstone, F. D., and Hilditch, T. P., *J. Chem. Soc.*, 1945, 836-841.
7. Kawahara, F. K., and Dutton, H. J., *J. Am. Oil Chem. Soc.*, 29, 372-377 (1952).
8. Martin, C. J., Schepartz, A. I., and Daubert, B. F., *J. Am. Chem. Soc.*, 70, 2601-2602 (1948).
9. Schepartz, A. I., and Daubert, B. F., *J. Am. Oil Chem. Soc.*, 27, 367-373 (1950).
10. Staff, R. J., and Daubert, B. F., *J. Am. Oil Chem. Soc.*, 27, 374-377 (1950).
11. Stirton, A. J., Turer, J., and Riemenschneider, R. W., *Oil and Soap*, 22, 81-83 (1945).
12. Strain, H. H., *J. Am. Chem. Soc.*, 57, 758-761 (1935).
13. Swift, C. E., O'Connor, R. T., Brown, L. E., and Dollear, F. G., *J. Am. Oil Chem. Soc.*, 26, 297-300 (1949).

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CORRECTION

In reference to the article (pp. 582-586) in the November 1952 issue of the Journal entitled "Detergency Evaluation" by Jay C. Harris, the Atlas Electric Devices Company of Chicago, Ill., has asked to have the correct spelling of Launder-Ometer published and some information provided on the size of the jars for the machine. The standard size handles one-pint glass jars or the new metal containers, which are 3½ in. by 8 in. with a capacity of 2½ pints. The company also manufactures a large Launder-Ometer which handles one pint, one quart, or two-quart glass jars or the new metal containers. A few larger metal containers have been made for this model.