Institute of Malaysia (PORIM). We thank the Director General of PORIM for permission to publish this paper, the Vice-Chancellor of the Malaysia University of Science for encouragement and support, K.G. Berger of PORIM for helpful discussion, Seow Chee Choon from the School of Applied Sciences for use of the wide-line NMR and Fan Yoon Wah for technical assistance.

REFERENCES

1. McFarlane, M., B. Alaka and N. Macfarlane, Oil Palm News, No. 20, 1, 1975.
2. International Developments in Oil Palm, edited by D.A. Earp and W. Newall, The Incorporated Society of Planters, Malaysia, 1977, p. 27.
3. Tan, B.K., F.C.H. Oh, W.L. Siew and K.G. Berger, Paper presented at the International Conference on Palm Oil Product Technology in the Eighties, Kuala Lumpur, 1981.
4. Zobel, H.F., N.N. Hellman and F.R. Senti, JAOCS 32:706 (1955).
5. AOCS Official and Tentative Methods, 3rd Edn., American Oil Chemists' Soc., 1974, Method Cd 10-57.

[Received August 24, 1981]

Preliminary Gas Chromatographic Analysis of Flavor Compounds in Mayonnaise[1]

D.B. MIN and **D.B. TICKNER**, Department of Food Science and Nutrition, Ohio Agricultural Research and Development Center, The Ohio State University, 2121 Fyffe Road, Columbus, OH 43210

ABSTRACT

The flavor compounds in fresh, 3- and 6-month-old mayonnaise at room temperature have been analyzed by a gas chromatographic method. The results indicate that as the storage time of mayonnaise increased, the flavor compounds formed from oil in mayonnaise increased. However, the concentrations of allyl isothiocyanate which is the major flavor compound of mustard, and acetic acid and ethyl acetate which are the major compounds in vinegar did not change during the 6 months' storage at room temperature. The analytical method described has shown good reproducibility in the analysis of mayonnaise flavor compounds and can be used as an instrumental analytical method to evaluate the mayonnaise flavor quality and to complement the sensory evaluation of mayonnaise.

INTRODUCTION

Mayonnaise, which is an emulsified, semisolid food, is one of the most common and popular dressings in America. Over 100 million gal of mayonnaise is produced annually in the U.S. (1).

One of the most important quality parameters of mayonnaise is a consistent good flavor. The flavor quality of mayonnaise changes during storage, but little is known about the chemical changes which are responsible for the undesirable flavor change. This paper reports a simple gas chromatographic method which can measure the changes of flavor compounds in mayonnaise during storage.

EXPERIMENTAL

Samples and Sample Preparation for Flavor Analyses

One of the nationwide commercial brands was selected. The 1-oz mayonnaise jars were stored in light at room temperature for 0, 3 and 6 months. After storage the samples were kept in a freezer at -30 C for 24 hr and then thawed in a refrigerator to break the emulsion. The freeze-broken mayonnaise oil portion was then ready for the analysis of flavor compounds.

Preparation and Procedures of Flavor Isolation Apparatus

The apparatus used for the flavor isolation from the oil of emulsion-broken mayonnaise is a modification of the apparatus reported by Jackson and Giacherio (2) and previously described in detail by Min (3) except that the apparatus used here did not contain K_2CO_3 whereas that described by Min (3) did. One mL of oil from emulsion-broken mayonnaise was introduced by syringe on the top of the glass wool in the isolation apparatus, and the flavor compounds were isolated according to the procedures previously described by Min (3). After volatile flavor isolation, the GC column was disconnected from the U-tube apparatus and then connected to the gas chromatograph to separate the isolated compounds in the GC column.

Gas Chromatography

A Hewlett Packard 5880A gas chromatograph with an electronic integrator for gas chromatographic peak area calculation and a flame ionization detector was used.

A 10-ft × 1/8-in. stainless steel column packed with 80/100 mesh Tenax-GC coated with 10% polymetaphenoxylene (Applied Science Laboratories, State College, PA) was used.

The initial temperature was held at 90 C for 2 min and then the temperature was programmed at 4 C/min to 230 C and held at 230 C for 15 min. The nitrogen flow rate was 40 mL/min.

Identification of Compounds

Pentane, acetic acid, ethyl acetate, allyl isothiocyanate and isomers of 2,4-decadienals were identified by comparing the gas chromatographic retention times to those of authentic compounds. These compounds were purchased from Aldrich Chemical Co., Milwaukee, WI.

RESULTS AND DISCUSSION

The flavor compounds in mayonnaise emulsions were first analyzed using the flavor isolation apparatus described by Min (3). The reproducibility of flavor analyses of mayonnaise was not good, which may be due to the combined effects of difficulties of (a) obtaining homogeneous mayonnaise samples for flavor analysis, and (b) accurately transferring 1 mL of mayonnaise sample into the flavor isolation apparatus. Mayonnaise contains a large amount

[1]Ohio Agricultural Research and Development Center Journal Series Article 46-82.

of air, which causes the actual mayonnaise content in a 1-mL sample to vary. That is, the more air content in a 1-mL sample of mayonnaise to be analyzed, the less the amount of other ingredients in mayonnaise. As it is a well known fact that flavor compounds are soluble in oil, the mayonnaise was freeze-broken, as described in Experimental, to analyze flavor compounds. Freeze-broken mayonnaise gave 2 clear layers of oil and water. As mayonnaise is freeze-broken at very low temperatures in a short period of time, it could be assumed that any noticeable flavor compounds would not develop in mayonnaise during the freeze-emulsion breaking process. One mL of freeze-broken oil was analyzed by Min's apparatus (3). The flavor profile of oil was qualitatively the same as the profile of the original mayonnaise without emulsion breakage. To study the reproducibility of flavor analysis in oil, the same emulsion-broken oil sample was analyzed 5 times, and the reproducibility of peak 4 area which was later identified as allyl isothiocyanate (Fig. 1) was analyzed statistically. The coefficient of variation for the reproducibility of the peak 4 area was 2.5% which suggested that the flavor analysis gave good reproducibility. This good reproducibility of analysis may be due to the combined facts that the oil sample is homogeneous, and 1 mL of freeze-broken mayonnaise oil can be accurately transferred into the isolation apparatus using a precise gas chromatographic syringe.

The gas chromatograms of fresh, 3-month and 6-month-old mayonnaises in Figure 1 show that peaks 2, 3 and 4 were present in large quantities in fresh mayonnaise and did not change as storage time increased from 0 to 6 months when the gas chromatographic areas of these peaks determined by an electronic integrator were compared. Dupuy et al. (4), Jackson and Giacherio (2) and Min (3) reported that good, fresh oil does not contain any noticeable gas chromatographic peaks of flavor compounds under similar gas chromatographic conditions. They reported that the amounts of flavor compounds developed in oil increased as storage time increased. Because peaks 2, 3 and 4 were present in large quantity in fresh mayonnaise and did not change as storage time increased, they were assumed to be from ingredients other than oil in mayonnaise. The ingredient labeling showed that mayonnaise contained vinegar and mustard as major ingredients, in addition to oil.

Kahn et al. (5) reported that the major volatile compounds in vinegar are acetic acid and ethyl acetate, and Life Science Research Office (6) reported that allyl isothiocyanate is the major flavor compound in mustard. Therefore, the gas chromatographic retention times of acetic acid, ethyl acetate and allyl isothiocyanate were compared to those of the chromatograms in Figure 1. The retention times of ethyl acetate, acetic acid and allyl isothiocyanate were the same as those of peaks 2, 3 and 4, respectively. The peak areas of ethyl acetate, acetic acid and allyl isothiocyanate did not change as storage time increased, as shown in Figure 1, which indicates that these components of vinegar and mustard oil are stable in mayonnaise during 6 months of storage.

Gas chromatograms showed that peaks 1, 5 and 6, which were almost negligible in fresh mayonnaise, increased greatly along with several other peaks which increased at a lesser degree as storage time increased from 0 to 6 months. Dupuy et al. (4), Jackson and Giacherio (2) and Min (3) reported that the volatile flavor compounds, especially pentane and isomers of 2,4-decadienals in oil, increased as the storage time increased. The gas chromatographic profiles shown in Figure 1 were very similar to those of soybean oil, hydrogenated soybean oil, and corn oil reported by Min (3), except peaks 2, 3 and 4 which are from vinegar and mustard. Therefore, it could be reasonably expected

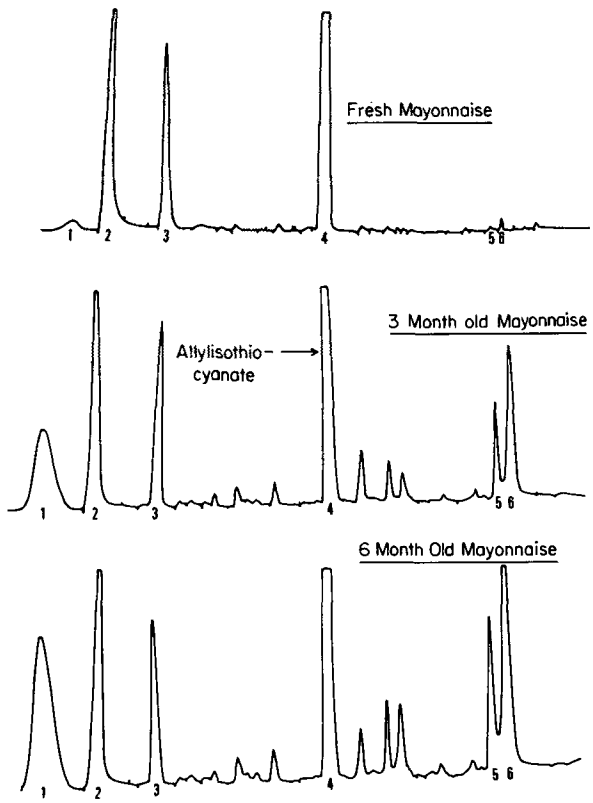

FIG. 1. The gas chromatograms of fresh, 3-month and 6-month-old mayonnaises. 1: pentane; 2: ethyl acetate; 3: acetic acid; 4: allyl isothiocyanate; 5 and 6: isomers of 2,4-decadienals.

that flavor compounds can be formed from oil in mayonnaise where oil is the major component, representing more than 65% of mayonnaise.

The gas chromatographic retention times of pentane and isomers of 2,4-decadienals which were reported as the major volatile compounds formed in pure oils during storage were determined and indicated that pentane, *cis,cis*-2,4-decadienal and *trans,trans*-2,4-decadienal had the same retention times as peaks 1, 5 and 6 in Figure 1, respectively.

The comparisons of gas chromatograms of fresh, 3- and 6-month-old mayonnaises indicates that, qualitatively, the 3 samples have the same types of flavor compounds, but quantitatively, the gas chromatograms of these 3 samples are quite different. As the storage time increased, the amounts of pentane and isomers of 2,4-decadienals, which are flavor compounds formed from oil in mayonnaise by oxidation, increased. Dupuy et al. (4), Jackson and Giacherio (2) and Min (3) reported that the amounts of pentane and isomers of 2,4-decadienals increased as the flavor quality of oil decreased. The increase of pentane and isomers of 2,4-decadienals clearly indicates that the oil in mayonnaise produces flavor compounds which could affect the flavor quality of mayonnaise and that the undesirable flavor changes in mayonnaise during storage could be at least partly due to the oxidation of oil in mayonnaise, as was expected. The minimization of oil oxidation in mayonnaise during storage could increase the flavor stability of mayonnaise. This study also shows that the content of acetic acid and ethyl acetate from vinegar and allyl isothiocyanate from mustard in mayonnaise do not change during the 6-month periods of storage at room temperature.

As the contents of ethyl acetate, acetic acid and allyl isothiocyanate can be measured with good reproducibility, this analytical method could also be used to determine the

uniformity of mayonnaise as a quality control method by measuring ethyl acetate and acetic acid for vinegar content and allyl isothiocyanate for mustard content in mayonnaises.

This report is mainly concerned with the development of an analytical method which can measure the changes of flavor compounds of mayonnaise during storage periods. It will be necessary to analyze numerous mayonnaises with a wide range of sensory scores to determine how well the instrumental gas chromatographic analyses can be correlated with sensory scores.

REFERENCES

1. Mayonnaise, Salad Dressing, and Related Products, U.S. Domestic and International Business Administration, U.S. Govt. Printing Office, 4, 1973.
2. Jackson, H.W., and D.J. Giacherio, JAOCS 54:458 (1977).
3. Min, D.B., J. Food Sci. 56:1453 (1981).
4. Dupuy, H.P., E.T. Rayner, J.I. Wadsworth and M.G. Legendre, JAOCS 54:445 (1977).
5. Kahn, J.H., G.B. Nikol and H.A. Conner, J. Agric. Food Chem. 14:460 (1966).
6. Evaluation of the Health Aspects of Mustard and Oil, If Mustard is a Food Ingredient, Life Science Research Office, Federation of American Societies for Experimental Biology, Bethesda, MD, 1975.

[Received November 16, 1981]

Functionalization at the Double Bond Region of Jojoba Oil: II. Diels-Alder Adducts of Jojobatetraene

A. SHANI, Department of Chemistry, Ben-Gurion University of the Negev, Be'er Sheva 84120, Israel

ABSTRACT

Diels-Alder products derived from jojobatetraene and several dienophiles are synthesized and described. Singlet oxygen forms a cyclic peroxide. The adducts introduce a new line of chemicals derived from jojoba oil.

INTRODUCTION

Increasing unsaturation in the form of conjugated double bonds along the chain of jojoba oil can serve several purposes such as enhancing oxidation capability, and enabling the chemist to widen and diversify a host of chemical reactions, as a result of increased polarizability of the π electrons. We report here on the chemical reactivity of jojobatetraene (III), which is readily available from jojoba oil (I) by NBS bromination and subsequent HBr elimination (1) (see scheme in Fig. 1). We report on the Diels-Alder reaction of several dienophiles whose products introduce a new line of chemicals derived from jojoba oil.

EXPERIMENTAL PROCEDURES

General

The crude product after each chemical transformation was used without further purification for the next step. The usual work-up consisted of pouring the reaction mixture into H_2O, extraction with petroleum ether (60-80), washing with saturated NaCl solution, and drying over anhyd Na_2SO_4. Infrared (IR) and nuclear magnetic resonance (NMR) spectra provided monitors for the chemical change occurring in each reaction. Purity was determined by NMR (2,3). All NMR spectra gave the following: terminal CH_3 at δ 0.92-0.94; an intense signal at 1.2-1.4 for all aliphatic hydrogens; a signal at 1.98-2.05 for allylic hydrogens. Other signals are mentioned later. Integration curves were consistent with the assignment of the different hydrogens. The NMR spectra were determined on a Varian XL-100 in CCl_4 or $CDCl_3$ solution. The IR spectra were determined with a Perkin Elmer 377, usually neat or in $CHCl_3$ solution.

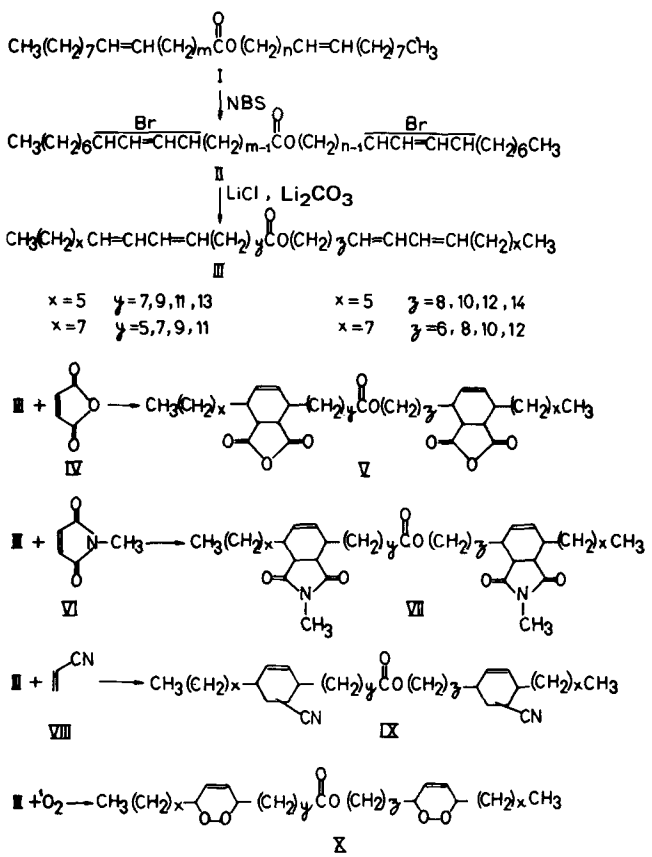

FIG. 1.

Analytical thin layer chromatography (TLC) plates (20 x 20 or 20 x 10 cm and 0.1 mm thickness) were prepared with Silica Gel KGS-254. Preparative thick layer chromatography (PLC) plates (20 x 20 cm and 1 mm thickness)