A Study of Odor Stability of Commercial Stearic Acid through Isolation and Identification of its Volatile Odoriferous Compounds[1]

HSIUNG CHENG[2] and **STEPHEN S. CHANG**, Department of Food Science, Rutgers, The State University, New Brunswick, New Jersey 08903

ABSTRACT

Commercial stearic acid may have an iodine value of less than 0.5. However, it develops a characteristic objectionable odor quite rapidly, sometimes before a shipment has reached its destination. The present investigation is an identification of the volatile odoriferous compounds which are responsible for this undesirable odor. Volatile compounds were isolated from commercial stearic acid and separated into acidic and nonacidic compounds. The acidic fraction did not have the characteristic off-odor of the commercial stearic acid and was discarded. The nonacidic fraction was fractionated into pure compounds by repeated gas chromatography, which then were identified by a combination of gas chromatographic retention time and IR and mass spectrometry. A total of 52 compounds was identified positively. They contained a relatively large number of lactones, viz, 7 γ-lactones, 4 δ-lactones, and 2 γ-2-ene lactones. The other identified compounds were 11 saturated hydrocarbons, 7 saturated primary alcohols, 6 saturated methyl ketones, 10 saturated normal aldehydes, 4 saturated esters, and 1 diphenyl ether. In addition, 2 saturated aldehydes and 1 γ-3-ene lactone were identified tentatively. The odors of the saturated and unsaturated lactones were reminiscent of the objec-

[1]Paper of the Journal Series, New Jersey Agricultural Experiment Station, Cook College, Rutgers, The State University of New Jersey, Department of Food Science, New Brunswick, N.J. 08903.

[2]Present address: A.E. Staley Manufacturing Company, Decatur, Ill. 62525.

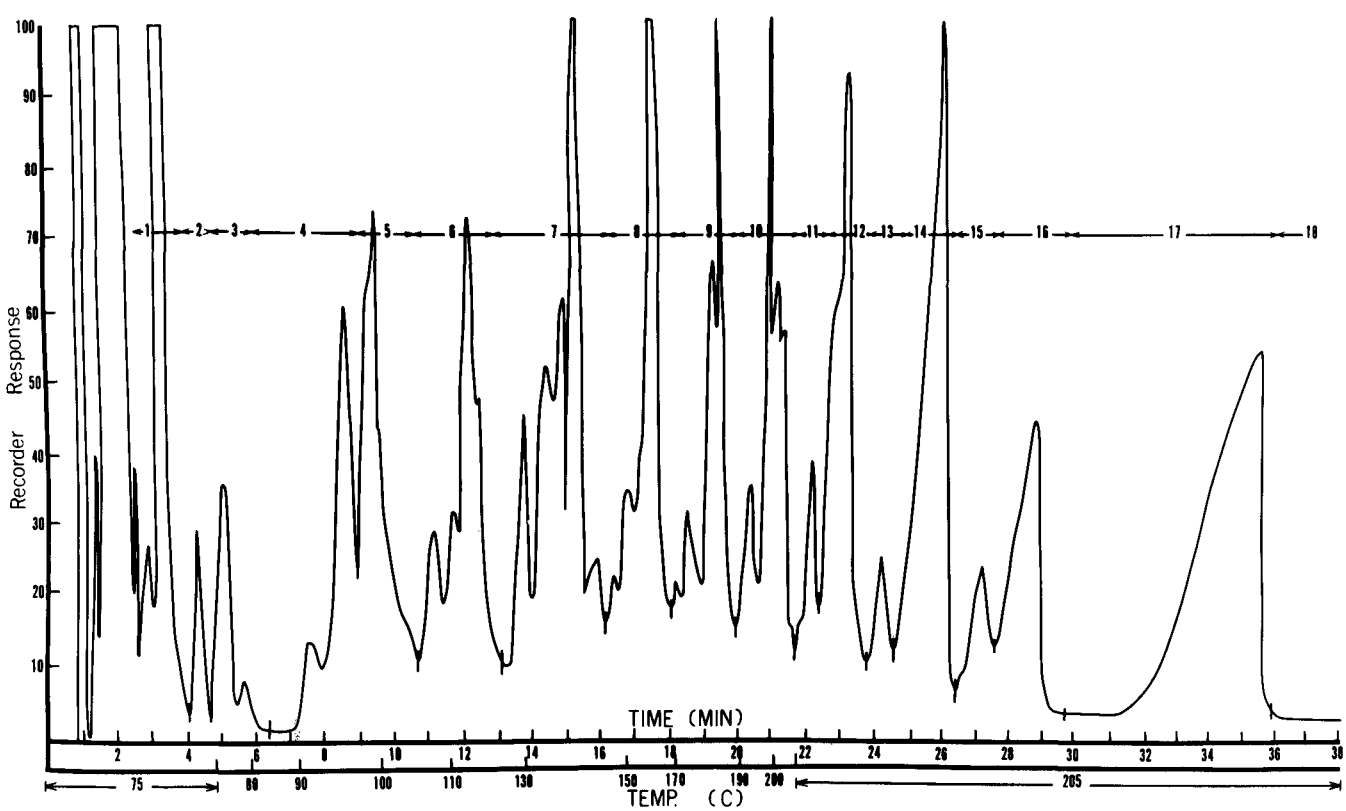

FIG. 1. Gas chromatogram for the collection of the broad fraction of the volatile compounds isolated from aged commercial stearic acid.

tionable odor characteristic of commercial stearic acid. Quantitative estimation indicated that commercial stearic acid contained: 0.47 ppm of 4-hydroxy-hexanoic acid, lactone; 0.06 ppm of 4-hydroxy-heptanoic acid, lactone; 0.31 ppm of 4-hydroxy-octanoic acid, lactone; 0.06 ppm of 4-hydroxy-nonanoic acid, lactone; and 0.53 ppm of 4-hydroxy-undecanoic acid, lactone.

TABLE I

Nonacidic Volatile Compounds Identified in Commercial Stearic Acid

Fraction[a]	Identified as	Peak size[b]
	Hydrocarbons	
7-1-8	Nonane	XS
6-1-9	Decane	S
7-1-11	Undecane	M
8-1-4	Dodecane	M
10-2-4	Tridecane	L
13-1-1	Tetradecane	S
11-1-1	Pentadecane	L
11-1-2	Hexadecane	L
17-2-3	Heptadecane	XL
18-1-5	Octadecane	XS
18-4-1	Nonadecane	S
	Alcohols	
1-2	Propanol	XS
2-2	Butanol	XS
4-5-1	Pentanol	XS
6-3-1	Hexanol	XS
7-3-1	Heptanol	M
7-3-3	Octanol	S
11-3-1	Decanol	XS
	Ketones	
5-1-3	2-Heptanone	XS
10-3-1	2-Undecanone	XL
11-2-4	2-Dodecanone	L
15-2-2	2-Tridecanone	M
14-5-2	2-Tetradecanone	XS
18-3-3	2-Heptadecanone	XS
	Aldehydes	
3-2	Propanal	S
4-2-1	Butanal[c]	S
4-3-1	Pentanal[c]	XS
5-1-2	Hexanal	XS
6-2-2	Heptanal	M
7-2-4	Octanal	S
9-1-1	Nonanal	XS
8-1-2	Decanal	S
10-4-3	Undecanal	S
13-2-2	Dodecanal	XS
12-2-3	Tridecanal	S
16-2-7	Hexadecanal	S
	Esters	
1-1	Ethyl acetate	XS
14-2-5	Methyl dodecanoate	M
17-3-2	Methyl palmitate	S
18-3-5	Methyl stearate	S
	γ-Lactones	
7-5-1	γ-Hydroxy-hexanoic lactone	M
9-5-1	γ-Hydroxy-heptanoic lactone	XS
9-6-6	γ-Hydroxy-octanoic lactone	M
13-3-1	γ-Hydroxy-nonanoic lactone	XS
13-4-1	γ-Hydroxy-decanoic lactone	M
15-7-2	γ-Hydroxy-undecanoic lactone	M
17-6-1	γ-Hydroxy-dodecanoic lactone	S
	δ-Lactones	
10-7-2	δ-Hydroxy-hexanoic lactone	L
12-4-1	δ-Hydroxy-heptanoic lactone	XS
14-4-3	δ-Hydroxy-octanoic lactone	S
16-6-2	δ-Hydroxy-decanoic lactone	XS
	γ-2-ene-Lactones	
10-7-3	4-Hydroxy-2-nonenoic lactone	XS
15-6-3	4-Hydroxy-2-undecenoic lactone	XS
	δ-3-ene-Lactone	
10-4-4	4-Hydroxy-3-nonenoic lactone[c]	XS
	Aromatic compound	
12-3-2	Diphenyl ether	L

[a]The first, second, and third numerals indicate the number of gas chromatographic peaks during original chromatography and first and second rechromatography, respectively.

[b]XS = extra small (total peak area less than 1250 units); S = small (total peak area 1275-3750 units); M = medium (total peak area 3775-12,500 units); L = large (total peak area 12,525-25,000 units); XL = extra large (total peak area more than 25,000 units).

[c]Tentatively identified.

INTRODUCTION

Commercial stearic acid may have an iodine value of less than 0.5. However, it develops a characteristic objectionable odor quite rapidly. Presumably, the development of this off-odor is due to the autoxidation of the fatty acid. Brodnitz and Nawar (1) reported that the initiation of the autoxidation of pure saturated fatty esters is extremely slow at temperatures of 60 C or below. However, the presence of even extremely small amounts of peroxides or unsaturation may supply the necessary free radicals to initiate the autoxidation. Commercial stearic acid, indeed, does contain some unsaturation.

The volatile decomposition products produced by saturated fatty acids or their esters through oxidation at high temperatures under catalytic conditions have been studied extensively (2-7). Acids, aldehydes, ketones, lactones, and hydroxyl compounds have been identified. However, the volatile decomposition products produced by saturated fatty acids or their esters under autoxidative conditions have not been investigated. This article reports the identification of the volatile odoriferous compounds in commercial stearic acid which has been stored at room temperature.

EXPERIMENTAL PROCEDURES

Material Used

Triple-pressed commercial stearic acid (140 lb) produced from fancy beef tallow was used for this investigation. The material was stored in glass bottles in the dark at 31±1 C during the 8 months required to complete the isolation procedure.

Isolation of Volatile Odoriferous Compounds

Commercial stearic acid (8 lb) mixed with 2.5 liter of porcelain 1/2 in. Rashing rings was packed in a 12 liter, 3-necked round bottom flask which was placed in a water bath, maintained at 50-55 C. The flask was connected to a series of three traps cooled with dry ice. A vacuum pump was connected to the end of the traps through a 2 way stopcock of 6 mm bore. The apparatus was evacuated to 0.005-0.01 mm Hg and maintained for 1 week. The condensates collected in the cold traps were washed out with ethyl ether and stored at -10 C until the isolation of volatiles from the 140 lb sample was completed. All the condensates then were combined.

The sample of stearic acid, after being used once for the isolation of volatile compounds, was stored at 31±1 C for another 1 week period and then subjected to the isolation procedure again before being discarded.

All the samples had a mild characteristic off-odor when they were submitted to the odor isolation process.

Fractionation of the Isolated Volatiles

The isolated volatile compounds were separated into acidic and nonacidic fractions by dissolving them in ethyl ether and then extracting with 10% aqueous sodium carbonate solution.

The nonacidic compounds were separated into 18 broad fractions with the use of an Aerograph A-90P gas chromatograph (Varian Aerograph, Walnut Creek, Calif), as shown in Figure 1. A 10 ft x 1/4 in. aluminum column, packed with 15% SE-30 methyl silicone on 70-80 mesh Anakrom ABS (Analabs, Hamden, Conn.), was used at a helium flow rate of 70 ml/min.

The temperature of the column was programed nonlinearly from 75-205 C in 22 min, after which it was

maintained isothermally for an additional 33 min. Each of the 18 fractions, thus, obtained was collected in a trap, according to the method of Deck, et al. (8). They were individually chromatographed again, using an F&M 810 gas chromatograph (Hewlett-Packard, Palo Alto, Calif.) with a hydrogen flame ionization detector. The splitter for the effluent gas was adjusted to a ratio of 1:12. A 1/8 in. x 20 ft stainless steel column, packed with 10% Carbowax 20 M on 60-70 mesh Anakrom ABS, was used. The temperature was programed at an optimum rate for each fraction to obtain the highest resolution. A total of 88 fractions was collected with r-shaped capillary glass traps, according to the method of Thompson (9), Each of the subfractions was chromatographed for the third time with a 1/8 in. x 20 ft. stainless steel column packed with 15% SE-30 methyl silicone on 70-80 Anakrom ABS. A total of 256 final fractions was collected and spectrometrically analyzed.

Peak Size

The volume of ether solution for each fraction from the first and second chromatographic separation was recorded. The area of each peak from the second and third separation was calculated by injection of a measured amount of ether solution. If this fraction was identified as a pure compound, the total peak area was calculated according to the ratio of the ether solution injected to the total solution of this fraction. If more than one fraction was identified as the same compound, the areas of the fractions were combined. The peak size was considered extra large if the total peak area was more than 25,000 units; large if 12,525-25,000; medium if 3775-12,500 units; small if 1275-3750 units; and extra small if less than 1250 units.

Identification of Gas Chromatographic Fractions

The nonacidic gas chromatographic fractions were identified by their IR spectra with the use of the Sadtler standard spectra, according to the technique of Kawada, et al. (10). The identifications then were confirmed by comparison with retention times of authentic compounds.

When the IR spectrum alone was insufficient for the chemical characterization of a gas chromatographic fraction, its mass spectrum was determined with a Hitachi model RMU-7 mass spectrometer. After the instrument was evacuated to 1 x 10^{-7} torr pressure, the sample was injected directly into the instrument through the liquid introducer by syringe. When necessary, the sample was diluted with methanol. In such cases, the parent ion of m/e 32 for methanol simply was ignored during interpretation of the spectra.

A compound was considered identified if the structure postulated by the interpretation of IR or mass spectra was confirmed by retention times. Otherwise, the compound was considered tentatively identified.

RESULTS AND DISCUSSION

The nonacidic volatile compounds isolated from a sample of aged commercial stearic acid had an odor which was quite characteristic of such samples. A total of 52 compounds was identified positively and three more tentatively identified as components of the nonacidic volatiles (Table I).

Most of the compounds identified were the ordinary autoxidative decomposition products of fatty esters. Recently, Brodnitz and Nawar (1,11) reported that the initiation of the autoxidation of pure saturated fatty acids is extremely slow at temperatures of 60 C or below. However, the presence of even extremely small amounts of peroxides or unsaturation may supply the necessary free radicals to initiate the autoxidation. Commercial stearic acids, such as those used in this investigation, do, indeed, contain some unsaturation. Furthermore, it has been reported (12) that commercial stearic acid contains highly oxidized polar materials which were considered as minor constituents. Such minor constituents were shown to have measurable peroxide numbers and can accelerate the darkening of the fatty acid during heating at 200 C. These constituents evidently also could initiate the autoxidation of commercial stearic acids.

It was extremely interesting to note that a large number of saturated γ and δ lactones were found in relatively large amounts compared with other identified compounds (Table I). In addition, a few unsaturated γ lactones also were found in relatively small quantities. Their IR and mass spectra have been published by Krishnamurthy and Chang (13). These lactones have a strong, coconut-like odor at relatively high concentrations. However, at extremely low concentrations, they had an odor reminiscent of that of the characteristic off-odor of commercial stearic acids. Quantitative estimation by calculation from the peak area of the identified compounds, using the peak areas of known compounds at known concentrations as references, indicated that the aged stearic acid contained: 0.47 ppm of 4-hydroxy-hexanoic acid, lactone; 0.06 ppm of 4-hydroxy-heptanoic acid, lactone; 0.31 ppm of 4-hydroxy-octanoic acid, lactone, 0.06 ppm of 4-hydroxy-nonanoic acid, lactone; and 0.53 ppm of 4-hydroxy-undecanoic acid, lactone.

ACKNOWLEDGMENT

This work was supported by a research fellowship from the Fatty Acid Producers' Council and the Agricultural Research Service, U.S. Department of Agriculture, Grant 12-14-100-9893 (73), administered by the Eastern Regional Research Center, Philadelphia, Pa.

REFERENCES

1. Brodnitz, M.H., and W.W. Nawar, Lipids 3:59 (1968).
2. Hrdlicka, J., and J. Pokorny, Vysoke Skoly Chem. Tech., Praze, oddil Fak Potravinareske Technol. 6:161 (1962).
3. Paquot, C., and F. de Goursac, Bull. Soc. Chim. France 172 (1950).
4. Crossley, A., T.D. Heyes, and B.J.F. Hudson, JAOCS 39:9 (1962).
5. Thaler, H., and W. Saumweber, Fette Seifen Anstrichm. 63:945 (1961).
6. Thaler, H., and W. Saumweber, Ibid. 63:1045 (1961).
7. Nobori, H., J. Soc. Chem. Ind. (Japan) 45:453 (1942).
8. Deck, R.E., J.A. Thompson, and S.S. Chang, J. Gas Chrom. 392 (1965).
9. Thompson, J.A., Ph.D. Thesis, Department of Food Science, Rutgers University, New Brunswick, N.J. (1968).
10. Kawada, T., B.D. Mookherjee, and S.S. Chang, JAOCS 43:237 (1966).
11. Brodnitz, M.H., and W.W. Nawar, Lipids 3:65 (1968).
12. Cheng, H., Ph.D. Thesis, Department of Food Science, Rutgers University, New Brunswick, N.J. (1972).
13. Krishnamurthy, R.G., and S.S. Chang, JAOCS 44:136 (1967).

[Received November 14, 1973]