50% saturated acid, and the ratio of stearic/oleic acids varied according to variety from 0.88% to 0.96%. GLC of the sterol fraction showed that β-sitosterol (73%), stigmasterol (16.5%) and campesterol (10.5%) were the main components in mango fat (7). TLC (Fig. 1) revealed that lyso-phosphatidylcholine, phosphatidylcholine, phosphatidylinositol, phosphatidylethanolamine and phosphatidic acid were the major phospholipids of mango fat. Monogalactosyl diglyceride and digalactosyl diglyceride (trace) were also identified by TLC in the glycolipid fraction of mango fat.

ACKNOWLEDGMENT

The work was supported by a research grant from the International Foundation for Science, Sweden. Rezaul Haque determined fat contents.

REFERENCES

1. Mollah, M.R.I., and M.A. Miyan, B.J., Agric. Sci. I 2:90 (1974).
2. Narshima Char, B.L., B.R. Reddy and S.D. Thirunala Rao, JAOCS 54:494 (1977).
3. Bandyopadhya, C., and A.S. Gholap, Curr. Sci. India 48:935 (1979).
4. Dunn, H.C., and Hilditch, T.P., J. Sci. Chem. Ind. London 66:209 (1947).
5. Vanpee, W.M., L.E. Boni, M.N. Foma and A. Hendrikx, J. Sci. Food Agric. 32:485 (1981).
6. Tiscornia, E., V. Paganuzzi and E. Leoni, La Rivis Itali, Delle Sost. Grass. 56:332 (1979).
7. Gafur, M.A., and B. Töregård, unpublished results, 1980.
8. Fore, S.P., N.J. Morris, C.H. Mack, A.F. Freeman and W.G. Bickford, JAOCS 30:298 (1953).
9. Parkhurst, R.M., W.A. Skinner and P.A. Sturm, JAOCS 45, 641 (1968).
10. Brown, D.F., C.M. Carter and K.F. Mattil, JAOCS 51:502 (1974).
11. Sanders, T.H., JAOCS 57:8 (1980).
12. Lakshminarayana, G.J., Oil Technol. Assoc. India 10:75 (1977).
13. Sallans, H.R., JAOCS 41:215 (1964).
14. Fick, G.N., and Zimmerman, JAOCS 50:529 (1973).
15. International Union of Pure and Applied Chemistry, Standard Methods for the Analysis of Oils, Fats and Soap, 5th edn., Pergamon Press, Paris, 1976.
16. Official and Tentative Methods of the American Oil Chemists' Society, 3rd edn., Champaign, IL, 1980.
17. Hirsch, J., and E.H. Ahrens, Jr., J. Biol. Chem. 233:311 (1958).
18. Mangold, H.K., JAOCS 38:707 (1961).
19. Skipski, V.P., R.F. Peterson and M. Barclay, Bio-chem. J. 90:374 (1964).
20. Gardner, H.W., J. Lipid Res. 9:139 (1968).
21. Sims, R.P.A., and J.A.G. Larose, JAOCS 39:232 (1962).
22. Dittmer, J.C., and R.L. Lester, J. Lipid Res. 5:126 (1964).
23. Beiss, U., J. Chromatog. 13:104 (1964).
24. Glass, R.L., J. Dairy Sci. 48:1106 (1965).
25. Osman, S.M., World Congress Abst. Paper ISF, 425 (1980).
26. Gafur, M.A., M.S. Huq, B.K. Mandol and K. Ahmed, Bulletin Published by IFST, Dhaka, 1982.
27. Curchaine, A.J., W.H. Miller and D.B. Stein Jr., Clin. Chem. 5:609 (1959).

[Received December 15, 1983]

✤Oxidative Stability of High Oleic Sunflower and Safflower Oils

RICHARD H. PURDY, Richard H. Purdy Inc., 16 Josefa Ct., Novato, CA 94947

ABSTRACT

High oleic sunflower seed progenies derived from normal seed by chemical mutagenesis were extracted and their oils refined by standard laboratory procedures. Oxidative stability was related directly to linoleic acid content with an AOM value of 100 hr obtained at 1% linoleate. Data is presented comparing linoleate concentration and oxidative stability of oils obtained from normal sunflower seed and high linoleic (normal) and high oleic (naturally induced mutations) varieties of safflower seed.

INTRODUCTION

The ratio of oleic and linoleic acids in sunflower oil triglycerides is to a large extent dependent upon environmental conditions, particularly moisture and temperature during seed development (1,2). Cool northern climates yield high linoleic acid content, whereas warm southern areas result in high oleic acid content. Robertson et al. (3) developed excellent correlations between climate, latitude and fatty acid composition. Although saturates varied little, oleic acid contents ranged from 14% in Idaho to 50% in Texas, and linoleic acid from 41% in Arkansas to 75% in Manitoba. Oxidative stability of crude oils derived from seed grown in southern climates has been shown to be almost twice that of crude oils extracted from northern seed (4).

The fatty acid composition of the oil from safflower seed grown commercially in the United States is relatively consistent, varying little with climate or location (5). Linoleic acid contents range primarily from 76% to 79% with occasional values of 75% to 76% in Arizona and 80% in Montana. Oleic acid may vary from 12% to 15% in most locations. In 1957, Horowitz et al. (6) reported a natural mutant which revealed a reversal of the linoleate-oleate ratio. Breeding research resulted in stable varieties with oleic acid values of 77% to 80% and linoleic acid values as low as 12% to 13%. The oil derived from the high oleic seed exhibited excellent resistance to oxidative deterioration (7).

Soldatov (8) developed high oleic sunflower seed by treating "normal" planting seed with a solution of 0.5% of the mutagen dimethyl sulfate. Selected breeding resulted in some plants containing seeds with as high as 80% to 90% oleic acid. Whereas the "normal" seed increased in linoleic acid from 21% to 54% during the process of seed formation and ripening, with a subsequent reduction in oleic acid from 62% to 36%, the new cultivars showed a decrease in linoleic acid from 26% to 15% and an oleic acid increase from 64% to 79%.

Kharachenko (9) studied both "normal" (Peredovik) and a progeny derived from mutagen treated seed (Pervenets) under controlled environmental conditions. High temperature conditions promoted rapid oleic acid development during the initial stages of triglyceride synthesis in both varieties. However, biosynthesis of linoleic subsequently intensified at the expense of oleic in the Peredovik variety, whereas the Pervenets' oleic content continued to rise. Seeds of the high oleic Pervenets variety apparently contain a change of the seed genotype responsible for an irreversible blockage of the desaturating enzyme system.

Fick (10) developed progenies from the Pervenets cultivar that varied only 4% to 5% in their oleic content when

TABLE I.

Fatty Acid Composition and AOM Values of Sunflower and Safflower Oil

	Fatty Acid Composition (% of total)				AOM
	16:0	18:0	18:1	18:2	(hours)
Safflower, normal[a]	7	2	12	70	10
Safflower, high-oleic[a]	5	tr	80	15	35
Sunflower, Northern I[c]	7	5	18	69	11
Sunflower, Northern II[b]	6	5	26	62	11
Sunflower, Southern	5	4	51	38	18
Sunflower, high-oleic A	3	5	79	12	38
Sunflower, high-oleic B	3	5	83	7	60
Sunflower, high-oleic C	4	4	89	1	100

[a]See Ref. (7).
[b]See Ref. (4).
[c]1983 typical commercial production (National Sunflower Assn.).

grown in Minnesota, Texas, Argentina and Chile. Although his initial studies indicate that high oleic acid is controlled by a single partially dominant gene, additional oleic directing genes may be present in the Pervenets cultivar. The gene(s) may be easily incorporated into inbred lines suitable for hybrids.

Sunflower oils with such high oleic contents and, more importantly, their accompanying low linoleic acid levels, should prove even more resistant to oxidation than high oleic safflower oil. The purpose of this study is to determine the effect of the mutagen directed fatty acid composition changes in sunflower oil on its oxidative stability.

EXPERIMENTAL

Three samples of sunflower seed identified as A, B and C, all progenies of the cultivar Pervenets developed by G.N. Fick (Sigco Research, Inc.), were extracted, refined and deodorized using procedures similar to those used with the safflower seed (7).

Extraction

One kilogram portions of seed were ground in a Waring Blender, adjusted to a 10% moisture level, and cooked in a sealed vessel for one hr at 130 C. Extraction was performed in a Butt type extractor using commercial grade hexane for 4 hr. The seed was reground for an additional 4 hr of extraction. The solvent was removed from the miscella, first by distillation to a pot temperature of 75 C and finally under reduced pressure.

Refining

The crude extracted oil was treated with sufficient 16° Be' sodium hydroxide solution to neutralize the free fatty acid plus 1.8% excess (basis total oil) for 5 min at 65 C. under moderate agitation. The heavy soap phase was separated by centrifugation. Residual soap and impurity removal was accomplished by washing with approximately 15% by volume of water for 5 min at 90 C, followed by bleaching the clear oil obtained by centrifugation with 1% acid activated earth at 10 to 20 mm mercury pressure and 95 C. for 10 min, separating the earth by suction filtration.

Deodorization

Approximately 300 g of bleached oil were treated in an all glass deodorizer with 5% steam at 250 C under 4 mm mercury pressure for 1½ hr. (All three deodorized oils exhibited colors lighter than 10 yellow/1 red Lovibond, free fatty acids less than 0.05%, zero peroxide values and bland flavors with no trace of odor. Anisidine values were less than 0.5, indicating a minimum of oxidation occurred during the processing.)

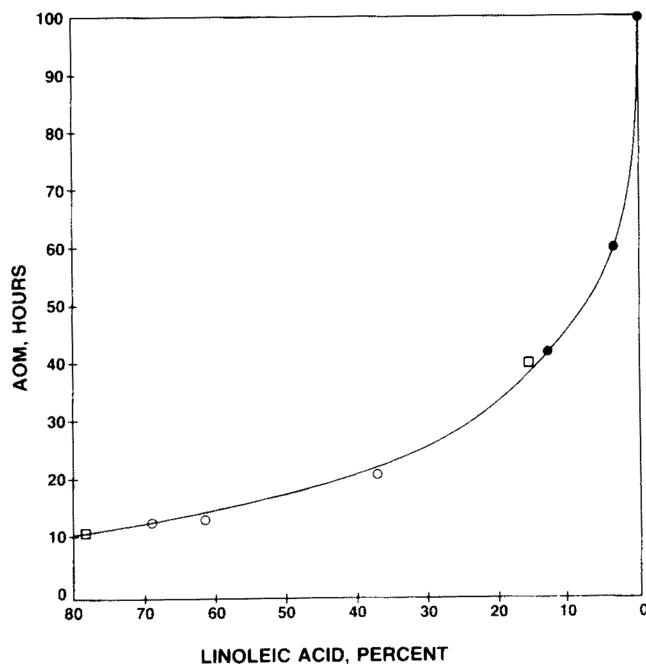

FIG. 1. The effect of linoleic acid concentration on AOM stability of sunflower and safflower oils. □ = safflower oils; ○ = sunflower oils (referenced); ● = sunflower oils (experimental).

Fatty acid compositions were determined by a modified version of the AOCS procedure Ce 1-62 (11) using a 3.2 m x 3.2 mm stainless steel column packed with 11.4% 3-cyano propyl silicone on chromosorb W-AW 100/120 mesh. AOM (Active Oxygen Method) determinations were conducted according to AOCS method Cd 12-57 (11).

RESULTS AND DISCUSSION

The relationship between the degree of unsaturation of lipids and their susceptibility to oxidative deterioration is well known (12). Comparison of non-hydrogenated commercially available fats and oils, however, is hampered by the effects of the anti- and pro-oxidant components of their non-triglyceride fractions. As with the high oleic safflower mutations, the chemically directed mutagenesis of sunflower seeds offers the opportunity to compare the oxidative stability of oils of differing fatty acid composition derived from essentially the same plant source.

The fatty acid composition of safflower and sunflower oils and their AOM values are presented in Table I. A fivefold reduction of safflower oil's linoleic acid content improved AOM hours 3½ times. Almost identical results were found in comparing high oleic sunflower oil sample A with the oils from "northern" sunflower seed. Further reductions in linoleic acid contents to 7% and 1% in high oleic sunflower samples B and C resulted in substantially increased AOM values. (In all cases there appears to be a direct exchange between linoleic and oleic acids with only minor changes in saturated fatty acid contents.)

Linoleic acid contents and AOM values from Table I are depicted graphically in Figure 1. A regression analysis of the data yields the equation $y = a + bc^x$, where y is the AOM value and x the per cent linoleic acid. Values for a, b and c are 11.7 ± 1.4, 97.2 ± 3.2 and 0.904 ± 0.006. The data suggest that mutations of both safflower and sun-

flower oils with 1% or less of linoleic acid have the potential of achieving 100 hr AOM values.

ACKNOWLEDGMENTS

G.N. Fick, Sigco Research, Inc., and J.R. Smith, Oilseeds International, Ltd. supplied the samples of sunflower seed used for extraction.

REFERENCES

1. Kinman, M.L., and F.R. Earle, Crop Sci. 4:417 (1964).
2. Fick, G.N., JAOCS 60:1252 (1983).
3. Robertson, J.A., W.H. Morrison and R.L. Wilson, USDA Publication ARR-S-3/October 1979.
4. Morrison, W.H., JAOCS 52:522 (1975).
5. Knowles, P.F., Econ. Botany 19:53 (1965).
6. Horowitz, B., and G. Winter, Nature 179:582 (1957).
7. Purdy, R.H., and B.J. Campbell, Food Technology 21:31A (1967).
8. Soldatov, K.I., Proc. 7th Int'l. Sunflower Conf. (Krasnodar, USSR) 352 (1976).
9. Kharachenko, L.N., Fiziologiya Rastenii 26:1226 (1979).
10. Fick, G.N., Research Workshop (Bismarck, N.D., February 1, 1984).
11. Official and Tentative Methods of the American Oil Chemists' Society, 3rd edn., 1958 (revised 1973) AOCS, Champaign, IL.
12. Lundberg, W.O., Progress in the Chemistry of Fats and Other Lipids, Volume IV, 377-406 (1968).

[Received June 5, 1984]

Derivatization of Keto Fatty Acids: VI. Synthesis, Oxidation and Mass Spectrometry of Dithiolanes

MUSHFIQUDDIN KHAN, MAZZAZ HASHMI, F. AHMAD and S.M. OSMAN*
Department of Chemistry, Aligarh Muslim University, Aligarh-202 001, India

ABSTRACT

The synthesis of alkyl chain-substituted dithiolanes, bisdithiolane and disulfolanes from oxo acids and their decomposition to original oxo acids are described. Reactions of ethanedithiol with 2 oxo esters, methyl 10-oxoundecanoate and methyl 12-oxooctadecanoate, give excellent yield of the corresponding dithiolanes, which are oxidized to the respective disulfolanes by m-chloroperbenzoic acid (m-CPBA). A similar reaction of ethanedithiol with methyl 9,10-dioxooctadecanoate affords bisdithiolane. Retroreactions of the dithiolanes and bisdithiolanes under acidic conditions and of disulfolanes under alkaline conditions yield the parent oxo acids. The structures of the individual reaction products have been established from analytical and spectral data and confirmed by a study of their mass spectra.

INTRODUCTION

Ketalization of ethanedithiol with various ketones using different reaction conditions (1,2) has been described both as a preparative method and masking methodology of oxo function. Compounds containing dithiolane grouping have become of interest in recent years due to their pharmacological (3) and industrial potential (4). Some dithiolanes have been identified as components of the anal gland secretion of the ferret (5) and also tested as radioprotectants (6). Interest for sulfones has been renewed recently for their antitubercular activity (7) and applications as primary plasticizers (8) and stabilizers (9). Thus, in recent years there has been increasing interest in the synthesis (10) and reactions (11,12) of dithiolanes. Peracid oxidation of dithiolanes to the corresponding disulfolanes (12,13) and its reactions (13-15) have been reported. For this reason, it was considered of interest to undertake the present work on the sulphur heterocyclic fatty derivatives.

Chain-substituted mono- and bisdithiolanes were prepared from oxo acids. Dithiolanes were oxidized to disulfolanes by m-CPBA. Retroreaction of these spiro compounds also was done, to regenerate the original oxo acids. Mass spectra (MS) of dithiolanes and one of the disulfolanes as a model compound were studied to obtain basic fragmentation patterns and to establish the nature and position of the heterocyclic ring in fatty acid chain.

*To whom correspondence should be addressed.

EXPERIMENTAL PROCEDURES

Infrared (IR) spectra were obtained with a Perkin-Elmer 621 spectrophotomer (liquid film or in 1% solution in CCl_4). Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ with a Varian A60 spectrometer. Chemical shifts were measured in ppm downfield from the internal standard, tetramethylsilane (∂ = 0). MS were measured with an AEI MS 902 mass spectrometer.

Thin layer chromatographic (TLC) plates (20 × 5 cm) were coated with a layer of silica gel G (0.25 mm thickness), and a mixture of petroleum ether-ether-acetic acid (80:20:1, v/v/v) was normally used as the developing solvent. Components on the TLC plates were visualized by charring the sprayed plates with a 20% aqueous solution of perchloric acid.

Methyl esters were prepared by refluxing the acids with absolute methanol containing catalytic amounts of H_2SO_4.

Materials and Methods

10-Oxoundecanoic acid (mp 58-59C), 12-oxooctadecanoic acid (mp 82-82.5C) and 9,10-dioxooctadecanoic acid (mp 86C) were prepared as discussed in our earlier publication (16).

Preparation of (Ia)

A solution of methyl 10-oxoundecanoate (I, 2.14 g, 10 mmol) in acetic acid (1 ml) and freshly distilled BF_3-etherate (10 ml) was treated with 1,2-ethanedithiol (2 ml) and allowed to stand at room temperature for 15 min. The TLC of the reaction mixture showed complete conversion to a product having higher R_f than the starting material. The reaction mixture was poured into water after addition of a few drops of methanol and extracted with ether. The ethereal layer was washed several times with water and sodium bicarbonate (5%) and then dried over anhydrous sodium sulfate. Removal of the solvent gave a product which on column chromatographic purification afforded a viscous liquid in 98% yield. (Found: C, 57.79; H, 8.98. Calcd. for $C_{14}H_{26}S_2O_2$: C, 57.89; H, 9.02%). IR(CCl_4): 1735 ($COOCH_3$), 1445 (CH_2-S deformation), 1250 (CH_2-S wag.) and 680 cm^{-1} (C-S stretch.). NMR: ∂ 1.75 (3H, C_{11}