standard. The NMR estimation of oil content in a seed sample whose "true" oil content is 40%, and whose oil hydrogen content differs from that of the reference oil by 3%, i.e., $D_s = 97$; $D_o = 100$, would yield a value of only 38.8%, an error of 1.2%. The extent of this error will increase with increasing oil content and also with increasing difference between the hydrogen contents.

Thus, before the pulsed NMR technique could be established as an analytical tool for the nondestructive estimation of oil content in seeds, it would be necessary to investigate the hydrogen contents of each oil from a large number of different varieties of seed samples to get an idea of the variation in the hydrogen contents that is likely to arise; this, in turn will decide the uncertainties associated with the NMR estimated values.

## REFERENCES

1. Tiwari, P.N., P.N. Gambhir and T.S. Rajan, *J. Amer. Oil Chem. Soc. 51*:104 (1974).
2. Srinivasan, V.T., *Ibid. 56*:1000 (1979).
3. Srinivasan, V.T., B.B. Singh, P.K. Chidambareswaran and V. Sundaram, *Ibid. 62*:1021 (1985).
4. Tiwari, P.N., and W. Burk, *Ibid. 57*:119 (1980).
5. Gambhir, P.N., and A.K. Agarwala, *Ibid. 62*:103 (1985).
6. Sagare, B.N., and K.T. Naphade, *J. Maharashtra Agri. Univ. 8*:240 (1983).
7. Mansfield, P., *J. Amer. Oil Chem. Soc. 48*:4 (1971).
8. Cobb, W.Y., and B.R. Johnson, in *Physicochemical Properties of Peanuts—Culture and Use, A Symposium*, Stone Printing Co., Virginia, 19, p. 215.
9. Weast, Robert C., in *Chemical Rubber Company Handbook of Chemistry and Physics*, 63rd edition, CRC Press, 1982-83, p. D-225.
10. Pieter, J. van N., and A.E. C. Burger, *J. Amer. Oil Chem. Soc. 62*:531 (1985).
11. Pandey, S.N., and N. Thejappa, *J. Oil Technol. Assoc. India 13*:107 (1981).
12. Anand, I.J., *Ind. J. Gen. 35*:417 (1975),
13. Kirk, J.T.O., and R.N. Oram, *J. Aust. Inst. Agri. Sci. 47*:51 (1981).
14. Jonsson, R., *Hereditas 87*:205 (1977).
15. Robertson, J.A., and W.H. Morrison, *J. Amer. Oil Chem. Soc. 56*:961 (1979).
16. Downey, R.K., and D.I. McGregor, *Curr. Advan. Pl. Sci. 12*:151 (1975).

[Received December 2, 1985]

# High Oleic Sunflower: Physical and Chemical Characteristics

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

**Treatment of normal varieties of sunflowerseed with chemical mutagens and development of their progenies have resulted in hybrids bearing oil with oleic acid contents in excess of 80% and linoleic acid contents less than 10%. Fatty acid compositions are unaffected by climatic conditions. Analyses of the seed, oil and meal produced from the first commercial U.S. production show values not to differ significantly from normal high linoleic sunflower, except where anticipated on the basis of fatty acid composition.**

Sunflowerseed is one of the world's major oilseed crops. Although it originated in the United States, its utilization has been predominantly European. Introduction of high oil-bearing seed in the 1960s increased both production and utilization in the U.S. In recent years, sunflower has become an established crop in Minnesota, North and South Dakota, and Texas.

Numerous technical publications describing the composition and characteristics of sunflowerseed and oil are available in the literature (1-6). One of the more interesting characteristics is the effect of climatic conditions during seed formation on the fatty acid composition of the oil (7,8). Linoleic acid percentages may vary from the low 30s for seed grown in Texas to the mid 70s for Northern seed, with oleic acid values ranging from as high as 60 to less than 20%, respectively.

Soldatov and Kharachenko in Russia treated normal (Peredovik) planting seed with the mutagen dimethyl sulfate (9,10). Selected breeding resulted in progenies (Pervenets) with high oleic acid contents stable to climatic conditions. Fick, in the U.S., developed progenies from the Pervenet variety, demonstrating their environmental stability and incorporating the dominant genes into hybrids suitable for commercial production 9, 11).

In 1984, high oleic seed was grown commercially in the United States for the first time in North Dakota, California and Texas. This paper will report the composition and analytical characteristics of seed samples from the three growing areas; the crude oils and meals obtained from the commercial processing, and refined oil produced in the laboratory.

## EXPERIMENTAL

Seed samples were drawn directly from trucks arriving at seed warehouses in Breckenridge, North Dakota; Fresno, California, and Plainview Texas, using state-approved procedures. The samples were split mechanically to a suitable size and hand-cleaned to remove foreign material.

Crude oil and meal samples were drawn from production storage tanks, but are not necessarily representative of the entire crushing operation at each location.

California production samples were identified as "CSE" (California Solvent Extracted) and "CPP" (California Pre-Pressed). Texas production included a limited quantity of North Dakota seed, and was

identified as "TSE" (Texas Solvent Extracted) and "TPP" (Texas Pre-Pressed).

All analyses were conducted according to the Official Methods of the American Oil Chemists' Society (12), except where noted. Data for "normal" sunflowerseed, oil and meal was drawn from the literature, using recognized sources, or from typical commerical production.

Laboratory refining was conducted in all glass apparatus using conventional techniques including phosphoric acid pretreatment followed by alkali refining with 16° Baumé caustic. Vacuum bleaching utilized 2% Filtrol grade 105. Deodorization was conducted at 240 C and 3-4 mm vacuum. Texas prepressed and solvent extracted crude oils were combined in a 2 to 1 ratio prior to refining.

## RESULTS AND DISCUSSION

Table 1 compares the fatty acid composition of oil extracted from high oleic seed grown in the three areas shown with data for normal seed reported by Robertson (2). Very little difference in either oleic or linoleic acid levels was obtained from the three high oleic areas. The climatic effect in the normal seed values is readily apparent. The crude oil fatty acid compositions are based on the commercial productions compared with data provided in the literature by Robinson (3,13) and Earle (6). It is important to note the similarity in the longer chain fatty acids, especially C:22 (behenic). The trace amounts reported as linolenic are probably artifacts.

The composition of high oleic seed is compared with

**TABLE 1**

**Fatty Acid Composition of Sunflower Oils**

| | % of Total Fatty Acids | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 16:0 | 18:0 | 18:1 | 18:2 | 18:3 | 20:0 | 20:1 | 22:0 | 24:0 |
| Normal seed[a] | | | | | | | | | |
| Minnesota | 5.6 | 6.5 | 19.1 | 67.0 | | | | | |
| California | 7.0 | 4.5 | 25.0 | 61.9 | | | | | |
| Texas | 9-10 | | 37 -59 | 32 -53 | | | | | |
| High oleic seed | | | | | | | | | |
| North Dakota | 2.7-3.0 | 4.2-5.0 | 80.5-86.7 | 4.0-8.5 | | | | | |
| California | 3.5-4.0 | 3.4-4.2 | 81.6-83.5 | 6.0-7.6 | | | | | |
| Texas | 3.1-4.2 | 3.9-5.0 | 80.8-86.0 | 4.0-8.3 | | | | | |
| Crude Oil | | | | | | | | | |
| CSE | 3.8 | 4.0 | 82.8 | 7.4 | tr | .4 | .3 | 1.0 | tr |
| PP | 4.0 | 3.6 | 82.4 | 8.1 | tr | .4 | .2 | .8 | tr |
| TSE | 3.6 | 4.5 | 81.5 | 8.3 | tr | .4 | .3 | 1.3 | tr |
| TPP | 3.6 | 4.4 | 81.1 | 8.4 | tr | .4 | .3 | 1.3 | tr |
| Normal[b] | 4.1-7.2 | 1.4-6.9 | 13.7-59.3 | 31.8-75 | tr-.2 | tr-.5 | tr-.1 | .7-1.0 | tr-.2 |

[a]See Ref. (2).
[b]See Ref. (3, 6, 13).

**TABLE 2**

**Composition of Sunflowerseed and Meal**

| | North Dakota | California | Texas | Normal[a] |
|---|---|---|---|---|
| Seed[b] | | | | |
| Oil content | 45.9 | 47.9 | 43.3 | 43 |
| Protein | 18.7 | 20.7 | 20.4 | 20 |
| Fibre | 15.4 | 14.5 | 16.7 | 16 |
| Ash | 3.1 | 4.2 | 3.6 | 4 |
| Hull | 33 | 24 | 32 | 36 |
| Chlorogenic acid[c] | | 1.8 | 1.8 | 1.5-2.0 |
| Meal[d] | | | | |
| Oil | | 1.5 | 2.0 | 28.4 |
| Protein | | 24.7 | 28.2 | 8.4 |
| Fibre | | 23.1 | 17.2 | 23.2 |
| Ash | | 5.9 | 5.3 | 6.4 |
| Calcium | | .25 | .64 | .42 |
| Phosphorus | | .86 | .84 | .83 |

[a]Typical commercial production, PVO International Inc., Northern seed (1978-1981).
[b]g/100 g seed, dry basis.
[c]Dehulled.
[d]g/100 g, 10% moisture basis.

typical normal (Northern) seed used for crushing by PVO International, 1978 to 1981 (Private communication, R.J. Schneider) in Table 2. All of the high oleic seed values, including those for chlorogenic acid, would be considered typical of normal sunflower oilseed varieties currently produced in the U.S. Sunflower meal produced from Texas and California high oleic seed is similar to that produced from normal (Northern) seed.

Table 3 shows the analytical characteristics of the hybrid oils in comparison to normal (Northern) sunflower oil. The data appear typical of normal sunflower oil except for those analytical characteristics associated with fatty acid composition. The higher oleic acid content leads to a significantly higher viscosity (similar to olive oil), as expected. A slight reduction in density is noted. The lower saponification values probably are due to lower palmitic acid contents.

The phospholipid data shown in Table 4 was developed by Chapman and compared with his previously published data (14) and that of Borodulina (15) for normal sunflower. Phosphatidic acid appears to be substantially higher in both Texas and California solvent extracted crudes. The phospholipid fatty acid compositions reflect the triglyceride composition, as expected.

Sterol and tocopherol data are shown in Table 5. The composition of sterols in high oleic sunflowerseed oils is similar to the normal sunflower oil data reported by Itoh (4). Although some of the values appear slightly lower, the general distribution is reasonably comparable to that for normal sunflower oil. Most important is the presence of Δ-7-stigmasterol, which is rather specific to sunflower. HPLC methodology shows a predominance of α-tocopherol comparable to normal sunflower oil, but with somewhat lower values for γ and a definite presence of β. McLaughlin (16) did not show β-tocopherol for normal sunflower using GLC techniques, but its presence was found in both high oleic and normal sunflower oil solvent extracted and prepressed oil (4-6%) by GLC in another laboratory (Private communication, R.L. Winter,

TABLE 3

**Analytical Characteristics of Crude Sunflower Oil**

| Test | CSE | CPP | TSE | TPP | Normal[a] |
|---|---|---|---|---|---|
| Free fatty acid (% as oleic) | .7 | .3 | 1.1 | 1.0 | 1.0 |
| Moisture & volatile, % | .07 | .08 | .06 | .11 | .06 |
| Insol. imp., % | .06 | .08 | .08 | .04 | .05 |
| Color, Gardner | 7 | 7 | 10 | 9.5 | 10 |
| Unsap., % | .94 | .78 | .86 | .91 | .8 |
| Wax, % | .03 | .06 | .10 | .06 | .02-.35[b] |
| Phosphatide, % | .22 | tr | .52 | tr | .65-1.2[c] |
| Tocopherols, mcg/100 g | 87.0 | 78.4 | 86.8 | 82.7 | 55-77[d] |
| Sterols, % | .53 | .42 | .56 | .48 | .25-.4[c,e] |
| Visc., cp @ 25 C | 69 | 67 | 70 | 67 | 50 |
| Density @ 25 C | .913 | .913 | .912 | .912 | .917 |
| Iodine Value, Wijs | 84.4 | 86.5 | 84.4 | 84.4 | 130 |
| Sap. value | 188.2 | 188.7 | 188.1 | 188.1 | 190 |
| Ref. index, $n_D$ @ 25 C | 1.4677 | 1.4677 | 1.4677 | 1.4677 | 1.4742 |

[a]Typical commercial production, PVO International Inc., Northern seed (1978-1981).
[b]See Ref. (18).
[c]See Ref. (2).
[d]See Ref. (15).
[e]See Ref. (4).

TABLE 4

**Sunflower Oil Phospholipid Composition**

| | CSE | CPP | TSE | TPP | Normal[a] |
|---|---|---|---|---|---|
| % of total phospholipid | | | | | |
| Choline | — | | 40.0 | | 48.7/55.4 |
| Inositol | <<PA | | 23.0 | | 27.9/24.0 |
| Phosphatidic acid | =PE | | 23.0 | | 2.2/2.2 |
| Ethanolamine | <PC | | 13.2 | | 21.2/18.2 |
| % of total fatty acids | | | | | |
| 16:0 | 3.0 | 3.8 | 3.7 | 3.6 | 27.1 |
| 18:0 | 3.4 | 4.1 | 5.0 | 5.0 | 6.4 |
| 18:1 | 83.1 | 78.4 | 76.6 | 77.0 | 18.1 |
| 18:2 | 8.4 | 11.3 | 11.7 | 11.6 | 48.0 |
| 18:3 | — | — | — | — | — |

[a]See Ref. (14) and (15).

**TABLE 5**

**Sterol and Tocopherol Composition of Crude Sunflower Oils**

| | % of Total | | | | |
|---|---|---|---|---|---|
| | CSE | CPP | TSE | TPP | Normal |
| Sterols[a] | | | | | |
| Campesterol | 8.5 | 8.9 | 9.8 | 10.1 | 11-12 |
| Stigmasterol | 9.3 | 8.4 | 10.0 | 10.1 | 8-11 |
| β-Sitosterol | 54.8 | 57.4 | 58.2 | 57.3 | 62-75 |
| Δ-7-Stigmasterol | 21.8 | 20.7 | 13.5 | 14.5 | 20 |
| Δ-7-Avenasterol | 5.5 | 4.6 | 5.1 | 4.9 | 4 |
| Δ-5-Avenasterol | tr | tr | 3.3 | 3.2 | 4 |
| Tocopherols[b] | | | | | |
| Alpha | 95.6 | 96.2 | 94.9 | 93.8 | 91.3 |
| Beta | 3.9 | 3.3 | 3.9 | 4.4 | — |
| Gamma | 0.5 | 0.5 | 1.2 | 1.8 | 8.7 |
| Delta | tr | tr | tr | tr | tr |

[a]See Ref. (4) for normal sunflower oil values.
[b]See Ref. (16) for normal sunflower oil values.

**TABLE 6**

**Amino Acids in Sunflowerseed Protein**

| | g/16 g Nitrogen | | |
|---|---|---|---|
| | California | Texas | Normal[a] |
| Cysteine (half) | 1.5 | 1.2 | 1.5 |
| Tyrosine | 2.9 | 2.9 | 2.0 |
| Glycine | 5.9 | 5.3 | 5.2 |
| Serine | 4.7 | 4.2 | 3.8 |
| Alanine | 4.7 | 4.3 | 3.9 |
| Aspartic acis | 11.8 | 10.6 | 8.6 |
| Glutamic acid | 22.9 | 18.4 | 21.5 |
| Proline | 4.3 | 4.0 | 3.8 |
| Ammonia | 1.0 | 1.4 | 2.2 |
| Lysine | 3.5 | 3.4 | 3.1 |
| Tryptophan | 1.3 | *b* | 1.3 |
| Arginine | 6.7 | 8.6 | 8.2 |
| Methionine | 2.1 | 0.9 | 2.1 |
| Histidine | 2.5 | 2.6 | 2.2 |
| Threonine | 2.0 | 3.3 | 3.2 |
| Leucine | 6.6 | 6.2 | 6.0 |
| Isoleusine | 4.6 | 4.0 | 3.9 |
| Valine | 5.4 | 4.8 | 4.2 |
| Phenylalanine | 4.6 | 4.9 | 4.3 |

[a]See Ref. (5).
[b]Not determined.

Henkel Corp.).

Table 6 shows the amino acid distribution of defatted seed in g/16 g nitrogen. All values appear normal with the exception of methionine for the Texas high oleic seed samples. Replicate values of 0.7 and 1.0 were reported, compared to 2.00 and 2.10 for the California seed. The determinations were conducted in the same laboratory used for the data reported for normal sunflowerseed (5).

Accomplishment of a major objective in developing a high oleic sunflower oil, i.e., improved resistance to oxidative deterioration, is indicated by the high Active Oxygen Method (AOM) values achieved as shown in Table 7. Previous laboratory work (17) reported AOM's of 60 hr with a linoleic acid content of 7%, and 100 hr with oil extracted from experimental high oleic seed with 1% linoleic acid. These values represent substantial improvement in oxidative stability over typical Northern sunflower oil.

**TABLE 7**

**Laboratory Refined High Oleic Sunflower Oil**

| | CSE | CPP | TPP/SE | Normal[a] |
|---|---|---|---|---|
| FFA, % | .03 | .02 | .04 | .03 |
| Color, Lovibond red | .3 | .3 | .4 | 1.0 |
| Anisidine value | .6 | .6 | 1.2 | 6 |
| Odor/flavor | bland | bland | bland | bland |
| AOM, hr. | 56 | 51 | 51 | 13 |

[a]Typical commercial production, PVO International Inc., Northern seed (1978-1981).

## ACKNOWLEDGMENTS

Amino acid and chlorogenic acid analyses were performed by F.W. Sosulski, University of Saskatchewan; tocopherol and sterols by E.G. Perkins, University of Illinois; phospholipids by G.W. Chapman Jr., USDA (Athens, Georgia), and waxes by W.H. Morrison III, USDA (Athens, Georgia). Samples were supplied by M.J. Hein, SVO Enterprises Corp., and J.R. Smith, Oilseeds International Ltd.

## REFERENCES

1. Carter, J.F., *Sunflower Science and Technology*, ASA, CSSA and SSSA, Inc., Publishers, 1978.
2. Robertson, J.A., *Crit. Rev. in Food Sci.*, July, 1975, pp. 201-239.
3. Robertson, J.A., *J. Food Sci. 36*:873 (1971).
4. Itoh, T., T. Tamura and T. Matsumoto, *J. Amer. Oil Chem. Soc. 50*:125 (1973).
5. Sosulski, F.W., and S.E. Fleming, *Ibid. 54*:100A (1977).
6. Earle, F.R., C.H. Vanetten, T.F. Clark and I.A. Wolff, *Ibid. 45*:876 (1968).

7. Kinman, M.L., and F.R. Earle, *Crop Sci. 4*:417 (1964).
8. Fick, G.N., *J. Amer. Oil Chem. Soc. 60*:1252 (1983).
9. Soldatov, K.I., *Proc. 7th Int'l. Sunflower Conf.* (Krasnodar, USSR) 352 (1976).
10. Karachenko, L.N., *Fiziologiya Rastenii 26*:1226 (1979).
11. Fick, G.N., *Proceedings, Sunflower Research Workshop*, p.9 (Bismarck, N.D., February 1, 1984).
12. *Official and Tentative Methods of the American Oil Chemists' Society*, 3rd edn., 1958 (revised 1973) AOCS, Champaign, IL.
13. Robertson, J.A., W.F. Morrison III and R.L. Wilson, ARS-S-3, October 1979.
14. Chapman, G.W. Jr., *J. Amer. Oil Chem. Soc. 58*:299 (1980).
15. Borodulina, A.A., P.S. Popov and I.N. Harchenko, *Proc. 6th Int'l. Sunflower Conf.*, Res. Inst. for Cereal and Industrial Crops, Fundulea, Ilfov, Romania, 1974.
McLaughlin, P.J., and J.L. Reichrauch, *J. Am. Diet. Assoc. 75*:662 (1979).
17. Purdy, R.H., *J. Amer. Oil Chem. Soc. 62*:523 (1985).
18. Morrison, W.H. Jr., and J.A. Robertson, *Ibid. 53*:485 (1976).

[Received December 23, 1985]

# The Effects of Surfactant Concentration and Crystal Size on the Olein Yield from the Detergent Fractionation of Tallow

**David A. Glassner** and **Eric A. Grulke**
Department of Chemical Engineering and Food Science and Human Nutrition, Michigan State University, East Lansing, MI 48824-1226

**The surfactant concentration, the electrolyte concentration, the detergent solution to tallow weight ratio and the crystal surface area affect the olein yield from the detergent fractionation of tallow. Three crystal sizes were produced by using various rates of cooling for the partial crystallization step. The amount of sodium dodecyl sulfate (SDS) needed to maximize olein yield was proportional to the surface area of the crystals. The olein yield of the separation increased with increasing detergent solution to tallow weight ratio and increased with increasing electrolyte concentration up to their optimum levels.**

Several authors have studied the detergent fractionation of tallow (1-6). The process consists of a partial crystallization step followed by the addition of a detergent solution to form an aqueous dispersion. The dispersion is centrifuged to yield an olein fraction and a fraction with solid fat entrained in the water phase. The olein fraction recoverable from a specific tallow sample depends primarily on the crystallization temperature. The actual olein yield from the dispersion process depends on the crystal size and the amount of surfactant used (7).

For a given partially crystallized tallow, the olein yield from the centrifugation will increase as the surfactant concentration is increased from zero. The maximum in olein yield with surfactant concentration marks the point at which emulsion formation occurs. The emulsion phase has a density between those of the water and olein phases, and reduces the olein yield. At greater surfactant concentrations, olein yield is sporadic and may be only half of its maximum value. Surfactant preferentially wets the crystal surfaces until most of the solids have been enclosed by a water droplet. At this point, extra surfactant appears to be available for forming an oil-in-water emulsion. The emulsion phase entrains olein and makes the centrifugation more difficult, thereby lowering the olein yield.

The wetting of the fat crystals by the surfactant solution can be considered similar to the wetting of fibers by detergent solutions (7). The rolling up of oil from the crystal is caused by the detergent solution preferentially wetting the solid surface. The surfactant concentration must be above the critical micelle concentration (CMC) for the detergency phenomenon to occur. Showing that surfactant levels for good dispersing solutions were above the CMC would constitute a partial confirmation of the proposed detergent mechanism. A number of solution properties change when the surfactant concentration changes through the critical micelle point (8). The surface tension of a surfactant solution exhibits a distinct dip or discontinuity near the CMC as surfactant concentration is changed and can be used to determine the CMC. Surfactant in excess of the CMC value would be available for adsorption on the crystal surface. Presumably, the amount of excess surfactant needed to completely wet all crystals should be a function of their total surface area. Surfactant molecules which do not contact and wet solids into the aqueous phase, and are not part of the micelle structures, would be available for forming an emulsion.

The two primary objectives of this study were: to obtain more evidence confirming the detergency mechanism and to develop qualitative relationships between crystal size (surface area), surfactant concentration and olein yield. This information should lead to an improved understanding of emulsion formation and might help determine operating conditions for an industrial process.

Different crystal sizes of partially crystallized tallow were produced using different time-temperature histories. The recovery of olein from products of these different procedures was studied while varying the surfactant concentration and the ratios of detergent solution to tallow weight. Separations also were made using various concentrations of electrolyte. The separation mechanism concept was reviewed using the new data.

## EXPERIMENTAL METHODS

*Sample preparation.* Tallow was obtained in a 55-gallon