Chemical Composition of Sunflower Seed Hulls[1]

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ABSTRACT

The major components of the sunflower seed hull, lipids, proteins and carbohydrates were studied Lipids represent 5.17% of the total hull weights, 2.96% of which is wax composed of long chain fatty acids (C14-C28, mainly C20) and fatty alcohols (C12-C30, mainly C22, C24, C26). Hydrocarbon, sterol and triterpene alcohol fractions were also examined. The rest of the lipid fraction is an oil with a composition relatively similar to that of the kernel oil. The protein fraction (4% of the total hull weight) is similar to the protein fraction of the oil cake, although it contains hydroxyproline. The carbohydrate fraction is composed mainly of cellulose, but also of reducing sugars (25.7%), mainly pentoses.

INTRODUCTION

The sunflower (*Helianthus annus*) was considered as an ornamental flower until the 19th century after which time it was cultivated as an oilseed plant in Russia (1).

Research done in Russia made possible an increase in the oil percentage of the seed from 25% to 46%. This increase of the oil percentage was possible owing not only to the increase in oil of the kernel, but mainly to a decrease of the ratio of weight between the hull and the kernel. Today the sunflower is one of the oilseed plants which gives the highest oil yield (2).

Because of its high B vitamin and protein content, and also its balance in amino acid composition, the sunflower oil cake can be favorably compared to the best oil cakes (soya, peanut). However, a relatively high percentage of cellulose (7-15%) may limit its usefulness as feed for animal other than ruminants (3).

The only unused part left of the sunflower seed is the hull. As with the other oilseeds, the utilization of the hull is an important industrial problem (4). The production of the oil liberates an enormous quantity of this byproduct, the density of which is very low. It therefore needs a very large volume for storage and the factory must get rid of it.

Because of the low economical value of the hull, it is difficult to find a really profitable way of using it. The following uses have been recommended (5): heating (but the calorific power is less than 3700 calories/g) (6), cattle feeding (7), fertilizer (8), production of agglomerated panels, extractions of xyloses (9), and production of furfural (4).

In the present study, we hope to establish the relative importance of the various constituents of the sunflower hull (lipids, amino acids, carbohydrates). Consequently, this information should be of some help in finding better uses for this byproduct.

EXPERIMENTAL PROCEDURES

Preparation of the Hull

The sunflower seed hulls we used came from an industrial source. We therefore handpicked the hulls to eliminate all fragments, especially the pieces of kernel. Then the compound was ground in an ordinary coffee grinder to have homogeneous particles, or 2 mm long, at most.

Lipids

Extraction of the Total Lipids. Lipids were extracted from the hulls with petroleum ether in a soxhlet for 20 hr. The hull was dried and reextracted for 24 hr. The solvent was eliminated by distillation on a water bath. The last traces of solvent were eliminated under a stream of nitrogen. The percentage of lipids extracted from 10 g of hull was 5.17%. A large scale experiment was also performed; 500 g of hull were extracted with petroleum ether in a metallic percolator for 20 hr and again for 24 hr. This method yielded 3.92% lipids.

The characteristics of these lipids were determined by the following methods: acid number (10); iodine number, Wijs' method (11); and unsaponifiable (12).

Extraction of the Wax. The wax was crystallized from the total lipid extract from petroleum ether (10% solution) at 4 C for 36 hr, and recrystallized under the same conditions for 24 hr. The wax was filtered and washed with cold petroleum ether (13). The characteristics of the wax were determined by the following methods: acid number; same method as for the oil (10), except that the wax was dissolved in benzene; iodine number, Hoffmann-Green method; and hydroxyl value, IUPAC.

Saponification of the Wax. Since the wax was very resistant to saponification, we used the following method. 100 mg of wax is dissolved in the mixture 50:50 (2 N KOH ethanolic-petroleum ether) and refluxed for 10 hr (14). The unsaponifiable material was extracted according to the AOAC official method (12). The solvent was evaporated on a water bath. The traces of water were eliminated by addition of 6 ml of acetone and distillation. The fatty alcohols were in the unsaponfiable layer while the fatty acid soaps were in the aqueous layer.

Acid Composition of the Wax. The fatty acids were liberated from the soap by boiling in 10 ml of 0.2 N HCl. The methyl esters were prepared as described by Metcalfe and Schmitz (15).

Alcohol Composition of the Wax. The alcohols were acetylated by refluxing with an excess of acetic anhydride for 45 min, the acetates being analyzed by GLC. Since the lengths of the alcohols were very different, we used a polar phase for the short alcohols (C_{12} to C_{23}) and a nonpolar phase for the long alcohols (C_{23} to C_{32}).

Hull Oil Fatty Acid Composition. The fatty acids were analyzed by GLC under the same conditions as for the wax fatty acids.

Hydrocarbon Composition. The hydrocarbons were isolated from the unsaponifiable fraction by column chromatography (Merck, acid-washed 100-200 mesh alumina) according to the Kuksis procedure (16). The purified hydrocarbons represented 1.55% of the total lipid extract and were analyzed by GLC under the same conditions as for the wax long alcohols.

Separation and Quantitative Study of the Other Constituents of the Unsaponifiable Extract. The other constituents (sterols and triterpenic alcohols) were separated by TLC (20 x 20 cm) on alumina G (0.25 mm thick).

A 0.5 ml strip of unsaponifiable solution (40 mg/ml) was streaked on to the plates which were developed with hexane-ether (80:20). Each plate was sprayed with dichlo-

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TABLE I

Analytical Characterization of the Lipid Fractions

Methods	Total lipid extract	Wax	Hull oil
Acid number	64.5	13.5	91.2
Iodine number	18.2	0.92	
Hydroxyl number		43	
Unsaponifiable	9.3%	98%	6.4%
Melting point		81-82 C	

rofluorescein 0.2%. and examined under short wave UV light (17). After development, the areas corresponding to the sterols and to the triterpenic alcohols were removed from the plate. The compounds were extracted with ether, dried, and the residue weighed (18). The sterols were also titrated by digitonin precipitation (19).

Sterol and Triterpenic Alcohol Composition. The triterpenic alcohols and sterols isolated by TLC were analyzed by GLC under the same conditions as for the wax alcohols. The peaks were identified according to Capella (20).

GLC Methods. The GLC analyses were conducted on a Carlo Erba Fractovap, Model C chromatograph, equipped with a flame ionization detector and using nitrogen as carrier gas (gas flow 42 ml/min).

The fatty acid esters and short alcohol acetates (0.2 µl per injection) were determined on a 2 m x 3 mm stainless steel column packed with 11.5% polyethylene-glycol succinate on 60-80 mesh Gaschrom P. Injection and column temperatures were respectively 240 and 180 C.

The long alcohol acetates, hydrocarbons, sterols and triterpenic alcohols (0.2 µl per inhection) were determined on a 1.5 x 3 mm stainless steel column packed with 4% silicone grease SE_{30} on 60-80 mesh Chromosorb W. Injection and column temperatures were respectively 300 and 250 C.

The Amino Acids

The percentage of protein nitrogen was determined by the Kjeldahl method (21).

Hydrolysis of the Proteins and Purification of the Amino Acids. The proteins (0.1 mg N2/ml) were submitted to acid or alkaline hydrolysis by boiling in 6N NCl for 20 hr or in 5 N Na OH for 15 hr (22). The hydrolyzate was dried by distillation in vacuo.

The amino acids were purified by column ion exchange chromatography on 200-400 mesh Dowex 50 x 4 as described by Thompson et al. (23).

One-Dimensional Chromatography. The amino acids were chromatographed on Whatmann No. 1 (50 x 55 cm) paper in each of the following solvents: butanol-acetic acid-water (40:10:50) (24) and phenol-water (80:20) in ammoniacal atmosphere (25).

On each sheet, 0.4 µl of an aqueous solution (50 mg/ml) of each of 15 known amino acids was spotted. Also, 0.6 µl of the mixture of the 15 known amino acids and 0.1-0.4-0.6 µl of the unknown solution were spotted.

Even though the solvent front reached the bottom of the sheet (24 hr), this was insufficient to allow separation of all the amino acids. Therefore, they were allowed to develop for 48 hr. Then the sheets were dried and the spots detected by spraying with a solution of 0.2% of ninhydrin in methanol. The area of each spot was measured by planimetry.

Two-Dimensional Chromatography. The amino acids were chromatographed in the solvent (butanol-acetic acid-water) for 24 hr and in the perpendicular direction with the solvent (phenol-water) in an ammoniacal atmosphere for 24 hr. The spots were identified by their relative positions (26).

TABLE II

Wax Fatty Acids Composition

Fatty acids	Per cent[a]
Myristic	1.94
Pentadecanoic	0.4
Palmitic	6.8
Heptadecanoic	0.2
Iso-stearic	0.35
Stearic	5.6
Oleic	4.72
Nonadecylic	3.07
Linoleic	0.78
Iso-arachidic	1.3
Arachidic	46.5
Iso-medullic	0.9
Medullic	0.7
Behenic	16.3
Tricosanoic	0.53
Lignoceric	4.5
Pentacosanoic	0.23
Montanic	2.2

[a]Unknown peaks account for the difference between the total and 100%.

Quantitative Results. We assumed that the area of the spots was proportional to the quantity of amino acids. By interpolation between different reference samples, we can evaluate the quantity of each amino acid present in the solutions being analyzed.

Carbohydrates

Titration of the Cellulose and the Lignin. Cellulose and lignin were titrated by the AOAC official method (27).

Extraction of the Carbohydrates. The carbohydrates were hydrolyzed by boiling in N HCl for 80 min. Then the proteins were precipitated by addition of alcohol (80%). The sugars were purified by ion exchange column chromatography on Dowex 50 x 4. The water was eliminated by distillation in vacuo.

Titration of the Reducing Sugars. The reducing sugars were titrated by the Shaffer Hartmann method (28).

Qualitative Analysis of the Carbohydrates. The carbohydrates were analyzed by paper chromatography (29) and the spots were detected by spraying with a solution of aniline phosphate (1 g aniline, 2 g H_3PO_4, in 100 ml of ethyl alcohol) (30).

One-Dimensional Chromatography. The carbohydrates were chromatographed on Whatmann No. 1 (50 x 55 cm) paper in butanol-acetic acid-H_2O (40:10:50) for 48 hr. On each sheet 4 µl of an aqueous solution (50 µg/µl) of each of eight known carbohydrates and 4 and 6 µl of the unknown solution were spotted. The area of each spot was measured by planimetry.

Two-Dimensional Chromatography. This was done by using the following solvents: butanol-acetic acid-H_2O (40:10:50) and in the perpendicular direction: phenol/H_2O (80:20), and quantitated by planimetry.

Ash, Moisture

The ash percentage was determined by ignition of the hull and weighing the residue (31). The moisture was determined by the air-oven method (32).

RESULTS AND DISCUSSION

Lipids

Total Lipid Extract. The total lipid extract represents 5.17% of the total hull weight. The extract is a greenish yellow compound having the consistency of honey, without a real melting point (Table I).

The Wax. The wax is a white crystallized material and

TABLE III

Wax Fatty Alcohols Composition

Alcohol	Per cent[a]
Dodecanol	0.16
Tridecanol	0.24
Tetradecanol	traces
Pentadecanol	traces
Hexadecanol	0.2
Heptadecanol	0.17
Octadecanol	3.0
Oleilol	0.15
Nonadecanol	0.17
Eicosanol	2
Heneicosanol	0.5
Docosanol	12
Tricosanol	0.4
Tetracosanol	34.6
Pentacosanol	3.45
Hexacosanol	14.35
Octacosanol	6.65
Nonacosanol	5.75
Triacontanol	2.17

[a]Unknown peaks account for the difference between the total and 100%.

represents 2.96% of the total lipid extract (Table I).

The sunflower hull wax is essentially composed of esters of long fatty acids and fatty alcohols. Acids and alcohols are almost exclusively saturated. The majority of the acids are in C_{20}-C_{22}, the alcohols being longer (C_{22}-C_{29}) (Tables II,III).

Hull Oil. This oil consists of the total lipid extract without wax. Its color and consistency are very similar to those of the total lipid extract (Table I).

The fatty acid composition is very similar to the composition of the sunflower kernel oil.

Hydrocarbons. They represent 1.55% of the total lipid extract. The composition is somewhat different from that found by Kuksis (16) for the sunflower oil. However, heptacosane, nonacosane and hentriacontane also represent about 70% of the total hydrocarbons (Table IV).

Sterols. The precipitation by digitonin gives a greater percentage of sterols than by TLC because with digitonin compounds which are not sterols are also extracted. Thus, total lipid extract is by TLC 0.78%, by digitonin, 1.16%.

TABLE IV

Hydrocarbon Composition

Hydrocarbon	Per cent
Tetradecane	0.19
Pentadecane	0.1
Hexadecane	5.6
Heptadecane	0.55
Octadecane	1.43
Nonadecane	0.73
Eicosane	1.40
Iso-heneicosane	0.23
Neneicosane	1.21
Docosane	1.03
Tricosane	1.95
Tetracosane	1.59
Iso-pentacosane	0.32
Pentacosane	1.91
Iso-hexacosane	0.35
Hexacosane	1.26
Iso-heptacosane	0.23
Heptacosane	6.65
Iso-octacosane	0.32
Octacosane	3.1
Nonacosane	27.2
Triacontane	1.83
Hentriacontane	35.5
Dotriacontane	0.18
Tritriacontane	1.88
Tetratriacontane	2.75

TABLE V

Sterol Composition

Sterol	Per cent
Campesterol	11.38
Stigmasterol	9.17
β-Sitosterol	68.81
Unidentified sterol	10.64

TABLE VI

Triterpenic Alcohol Composition

Triterpenic alcohols	Per cent
Euphol	9.1
β-Amyrine	7.9
Cycloartenol	79
24 Methylene cycloartenol	4.3

The sterols represent only 57% of the compounds precipitated by the digitonin. From the color of the Liebermann-Burchard reaction, and from the position of the peaks from GLC chromatogram, we assumed that the unidentified compounds were diterpenes (18). β-Sitosterol represents almost 70% of the total sterol content of the hull (Table V).

Triterpenic Alcohols. They are present in a very small quantity; 0.36% of the total lipid extract. The cycloartenol represents 79% of the total triterpenic alcohols (Table VI).

Amino Acids

The hull contains 4.0% protein. Its amino acid composition was determined by paper chromatography. This very small percentage of protein in the hull explains why this material has a very poor food value. The percentage of each amino acid is not very different from that found in the oil cake protein (3). However, we found some differences, especially in that the hull protein contains hydroxyproline. Since the planimetry method is not very precise, the quantitative results have only relative value (Table VII).

TABLE VII

Composition of the Protein Fraction of the Sunflower Seed Hull

Amino acid	Per cent
Aspartic acid	13.4
Glutamic acid	10.1
Serine	7.3
Glycine	7.3
Threonine	5.8
Asparagine	5.8
Hydroxyproline	9.1
Alanine	8
Histidine	2.5
Tryptophane	4.4
Valine	1.64
Methionine	3.1
Proline	7.3
Lysine	5.1
Arginine	3.6
Leucine	2.2
Phenylalanine	3.25

TABLE VIII

Reducing Sugars of the Hull

Sugar	Per cent
Xylose	52
Arabinose	27
Galactose	8.6
Galacturonic acid	12.4

Carbohydrates

Cellulose and lignin (almost 50% of the entire hull weight) are the principal constituents of the hull. The reducing sugars (25.7% of the entire hull weight) are the second major constituent of the hull, which explains why the hull can be used for the extraction of xylose and production of furfural (Table VIII). Carbohydrates are therefore the only compounds present in the hull in a large enough quantity to permit an industrial extration.

Ashes, Moisture

The hull contains 8.2% of water of the total hull weight. The ashes represent 2.1% of the total weight.

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REFERENCES

1. Andre, D., ITERG Journees d'information sur le tournesol 1965:71.
2. Guilhaumaud, M.Y., ITERG Ibid. 1965:15.
3. Jacquot, R., and P. Ferrando, "Les Tourteaux" Vigot Frere, Paris, 1957.
4. Francois, R., ITERG Journees d'information sur les produits derives de l'huilerie 1964:60.
5. Fetrow, G., and S. Dimakon, Maslob, Zhir, Delo. 36:40 (1932).
6. Nefedov, S.A., Maslob. Zhir, Prom. 25:4,38 (1959).
7. Kitchiguine, Y.P., Maslob. Zhir. Prom. 24:12,30 (1958).
8. Kutovog, M.M., Maslob. Zhir. Prom. 30:2,41 (1964).
9. Plyuskin, E.Z., and N.M. Cetverikov, Zh. Prikl. Khim. 7:1008,1028 (1934).
10. Horwitz, W., Editor, "Official Methods of Analysis," Association of Official Agricultural Chemists, Washington, D.C., 1955, 26-30.
11. Horwitz, W., Ibid., 26-18.
12. Horwitz, W., Ibid., 26-35.
13. Guillaumin, R., and N. Drouhin, Rev. Fr. Corps Gras 1965:10.
14. Guillaumin, R., and N. Drouhin, Ibid. 1966:3.
15. Metcalfe, L.D., and A.A. Schmitz, Anal. Chem. 33:363 (1961).
16. Kuksis, A., Biochemistry 3:1086 (1964).
17. Walbecq, M., Rev. Fr. Corps Gras 1965:12.
18. Wolff, J.P., and M. Walbecq, ITERG Journees d'etude sur les constituants des corps gras 1965:27.
19. Boughton, B., and V.R. Wheatley, Biochem. J. 73:144 (1959).
20. Capella, P., E. Fedeli and M. Cirimele, Chem. Ind. 39:1590 (1963).
21. Horwitz, W., Editor, "Official Methods of Analysis," Association of Official Agricultural chemists, Washington, D.C., 1955, 2-23.
22. Block, R.J., E.L. Dunun and G. Zweig, "A Manual of Paper Chromatography and Paper Electrophorisis," Academic Press, New York, 1958.
23. Thompson, J.F., J. Morris and R.K. Gering, Anal. Chem. 31:1028 (1959).
24. Partridge, S.N., Biochem. J. 42:241 (1948).
25. Condsen, R., A.H. Gordon and A.P. Martin, Ibid. 38:224 (1944).
26. Biserte, G., Th. Plaquet, P. Boulanger and P. Paysant, J. Chrom 3:25 (1961).
27. Horwitz, W., Editor, "Official Methods of Analysis," Association of Official Agricultural Chemists, Washington, D.C., 1955, 22-33.
28. Shaffer, P.A., and A.F. Hartmann, J. Biol. Chem. 45:365 (1920).
29. Dedonder, R., Bull. Soc. Chem. Biol. 34:157 (1952).
30. Bryson, J.L., and T.J. Mitchell, Nature 167:864 (1951).
31. Horwitz, W., Editor "Official Methods of Analysis," Association of Official Agricultural Chemists, Washington, D.C., 1955, 13.6.
32. Horwitz, W., Ibid. 13-4.

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