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CHEMICAL STUDIES OF SUNFLOWER SEED OIL

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Abstract. Chemical investigations were carried out on the oil extracted from three locally grown imported varieties of H.O.I, Mayak, and Armaviriec 3497. Various constants, oleic and linoleic contents were determined in each case. H.O.I. was then hydrogenated and retested, which showed improvement in some of the values, as expected. Three more varieties, Peredovic, Arrowhead and Mingron were also analysed for fatty acids and the amino acid composition. The results are comparable with the fatty acids of cottonseed and soyabean oil, and with slight adjustment the oil may be employed for most of the fatty acid industries. Better quality oil may even be consumed directly as table oil, cooking oil or for conversion to margarine.

Of the various oil seeds grown in the country, sunflower seed has recently been recognised as a source of cooking oil and margarine. Sunflower is an important oil crop in many countries. In Pakistan sunflower seeds were grown on a relatively small scale and practically none of the seed was milled for oil. This situation has now changed with the introduction of improved varieties of seeds and methods of cultivation, harvesting and milling.

The oil content of the seed compares well with the other economic sources of vegetable oil.[1]

It varies over a wide range. A four-year average[2] of two tall varieties grown in Urbana, Illinois, U.S.A. was 24.2% and 25.0% respectively, while three dwarf varieties yielded 29.2, 30.8 and 27.3%. Dwarf varieties grown in Canada range in oil content from 26.0 to 36.0%. Kernel contained 45–50% oil, which may go up to 50–56%. Varieties with 40–50% oil content have been developed in the U.S.S.R.[3]

Sunflower seed oil in the crude form is light amber and the refined oil is pale yellow. Crude oil contains some phosphatides and mucilaginous matter but less than cottonseed or corn oil. Oil contains distinctive odour which is completely removed by steam deodorization.

The Tropical Products Institute[4] has given the analyses of Russian varieties of high oil content, which were grown at Agricultural Research Station Samaru, Nigeria. These varieties were (i) BH-MK-8883, (ii) BH-1646, (iii) CTE-K. Tropical Product Institute[5] has also studied the Bulgarian commercial and Jupiter varieties of sunflower seed from northern Nigeria.

Earle[6] and others have studied the kernel oil for seeds grown in northern U.S.A. and southern Canada. The oil contains 70% linoleic acid in addition to traces of other acids having C_{17},C_{20},C_{22},C_{24} and linolenic acid.

Putt and Craig[7] studied the variation in composition of sunflower seed oil obtained from different locations in different years. This showed highly significant differences in composition between varieties and between stations in mean values for stearic, oleic and linoleic acids. The greatest variations occurred in lines-inbred for one to three generations. They have shown that great variations occur within the varieties.

Barker and Hilditch[8] have shown that individual ripe head of sunflowers of the same variety grown in the same plot and in the same season vary over a wide range in composition of the oil (may be due to varying cross pollination).

Barker and Hilditch[9] have reported the composition of oil from Tanganika, Kenya and S. Rhodeshia having iodine value 129.8, 132.3 and 136.9 respectively, palmitic acid varying from 4.7 to 7.6% and stearic acid from 1.8 to 3.8% etc.

The African, Australian, American and Asian seed oils investigated by Hilditch and others [9,11] reveals that high linoleic acid results from plants grown in cooler regions and vice versa. The differences in composition were caused by different temperatures of growth. For example oil from N. Australia had only 31–36%, that from Victoria, 36–38% and the one from Queensland had 50–61% linoleic acid. When grown in the same location black seeded varieties produced more unsaturated oils than the cream seeded.

Indian chemists[12] also reported the influence of environment on the composition of the sunflower seed oil, considering the case of a Russian strain of sunflower seed which had been grown for four generation in the U.S.A. where the seed yielded oil of high linoleic acid (60–68%) but when grown in India the component acids of the resulting oil were linoleic 40%, oleic 49% and saturated acids 11% by weight.

The samples of the imported seeds (a) H.O.I. (b) Mayak, and (c) Armaviriec 3497, which form the subject of the earlier part of this paper, were grown at the Agricultural Research Station Tarnab, Peshawar.[13] Superphosphates and ammonium sulphate 16 and 20 lb per acre were applied respectively. Varieties were of black seeded type. The crop had matured during the rains. The results of analyses of the three varieties are given in Tables 1, 2 and 3.

Three varieties of seed from Haripur Hazara (i) Peredovic,(ii) Arrowhead, and (iii) Mingron were also

analysed by the junior author for fatty acids and the amino acid composition. Results of these analyses are rereported in Tables 4 and 5.

Oil from sample H.O.I. was hydrogenated at 110–130°C for 2 hr using hydrogen free from CO_2 and H_2S in the presence of Ni-catalyst (.02–.06%) obtained by the reduction of nickel formate. The various values determined as before are given in Tables 6 and 7.

The results obtained in this investigation have shown that the oil is of good quality, similar to that of other vegetable oils. The composition of oil is similar to that of cottonseed oil.[1] In case of all the samples of seed, the oil content is low as compared with the results of the Tropical Products Institute, London.[5,6] It seems that the dry climatic conditions have affected the oil content.

Tarnab Research Institute[13] has reported 42% of oil in these samples which is high as compared to the results of this investigation. However, our results are in agreement with the results, 33% reported by Ayub Institute, Lyallpur.[14] All the three samples of oil of present investigation differ in chemical composition because of varietal differences etc. The effect of different forms of fertilizers on the oil content and composition[15] is understandable because of the direct effect, they have on the growth of the plant. The comparison of our results with those obtained by Tropical Products Institute for Russian variety shows that all the samples analysed have higher free fatty acid content. However, the percentage of free fatty acids is nearly the same as reported by Tropical Products Institute for Bulgarian variety. The darker colour of the oil is probably due to the deterioration which had taken place, owing to the fact that the seeds (A,B and C) were harvested during the rainy season. Acid value is influenced by the moisture content.[16] Hence harvesting during the rainy season is to be avoided.

Comparison of the acid values and iodine values of the three samples of oil with moisture contents of the seeds shows that they are related to each other very closely. With increase of the percentage of free fatty

TABLE 1. COMPOSITION AND CHEMICAL CHARACTERISTICS OF SUNFLOWER SEED OIL FROM LOCALLY GROWN IMPORTED SEEDS.

Values	H.O.I (A)	Mayak (B)	Armaviriec 3497 (C)
Moisture(%)	4.7	5.3	4.9
Oil (%)	32.0	26.6	30.0
Cake(%)	63.1	68.1	65.1
Acid value	1.12	3.93	2.24
Saponification value	199.2	189.3	193.5
Iodine value	118.4	108.0	112.8
Thiocyanogen value	75.9	75.2	77.0
R.M. value	0.79	0.41	0.33
Saturated and unsaponifiable matter (%)	14.7	15.3	13.6
Total fatty acid (%)	90.6	89.1	90.0
Olein (%)	42.9	44.4	42.4
Linolein (%)	42.4	40.3	44.1

TABLE 2. ANALYSIS OF FATTY ACIDS SEPARATED FROM THE OIL.

Sample	Saponification value	Iodine value	Thiocyanogen value	Solid acids	Liquid fatty acids
H.O.I.	227.2	136.8	80.09	18.5	81.5
Mayak	210.3	125.4	78.90	17.6	82.4
Armaviriec 3497	217.3	132 5	87.40	19.1	80.9

TABLE 3. ANALYSIS OF SEED CAKE.

Sample	volatile matter (%)	Moisture and ash (%)	Carbohydrates (cellulose) (%)	Protein (%)	Minerals (mg/g)				
					Na	K	Ca	Fe	P
H.O.I	2.75	3.50	69.85	26.0	0.700	0.833	0.407	0.005	4.166
Mayak	2.25	2.80	78.88	18.5	0.633	0.767	0.350	0.003	1.688
Armaviriec 3497	3.50	3.125	72.74	23.5	0 667	0.800	0.417	0.007	3.366

TABLE 4. FATTY ACID COMPOSITION OF THE OIL (%).

Variety	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Arachidic and behenic
Peredovic	4.80	5.6	24.0	63.4	—	2.8
Arrowhead	8.00	2.0	18.0	66.4	0.1	4.0
Mingron	7.99	1.9	18.2	66.5	0.4	3.8

acids, iodine value decreases and the acid value increases. These findings have been confirmed by the determination of linoleic, oleic and saturated fatty acid composition of the oil. When the composition of the oil obtained in this investigation was compared with[7,8,11–13] that of the oil obtained from other parts of the world, it was noticed that the differences were almost wholly in accordance with the difference in the temperatures of growth, rather than the varietal differences. Environment is the main cause of difference in the seed oil composition, therefore, it can be said that the predominant factor is the rate of development of the seed. The quick ripening will tend to give oil of lower linoleic acid and higher oleic acid content and vice versa. The environment has important implications regarding the use of such seed oils for a number of technical purposes. It is apparent that in cooler conditions of growth and slower attainment of maturity in these seeds, the seed contain more of the linoleic acid and less oleic acid. There is very little alteration in the proportion of saturated acids throughout.

From these investigations it appears that these samples are quite inferior for use in paints or alkyl resin. These samples may, however, be grouped as semidrying oils which are susceptible to atmospheric oxidation but do not produce hard film, while H.O.I. sample, reported to have 67% linoleic acid, may be a good drying oil It means that on theoretical bases, it contains about 90% of glycerides containing either two or three linoleic groups in the molecule. Hence, it may be pointed out that of different varieties of sunflower obtained under different conditions of growth should be classified by their fatty acid composition rather than by the species from which they are originated. Sunflower seed oil is most sensitive to variation in composition owing to different conditions of growth. As such H.O.I. which is more black-seeded variety produced more unsaturated oil than other samples.

Analysis of the hydrogenated oil (H.O.I) showed that there was an increase of 3.3% in saturated glycerides and of 10.72% in olein accompanied by a decrease of linolein, iodine and thiocyanogen values. There was no hope that the oil would be hydrogenated under the conditions of the experiment but low concentration of the catalyst and low iodine value of the oil gave encouraging results.

Analysis of the extracted seed showed that carbohydrate content decreased with the increase of lipids. Decrease in the protein content was associated with an increase of carbohydrate content of the seed cake. The cake had a high mineral and protein content and may be useful as poultry and cattle food and also as fertilizer.

The oil is well suited for use as a salad and cooking oil and when hydrogenated for use in magarine fats.

TABLE 5. RELATIVE AMINO ACID COMPOSITION OF THE PROTEIN FROM THE SEED.

	Peredovic	Arrowhead	Mingron
Lysine	3.66	3.56	3.80
Methionine	1.92	2.00	1.80
Cystine	1.91	2.00	2.20
Phenylalanine	4.80	5.00	4.90
Tyrosine	2.65	2.31	2.50
Tryptophan	1.20	1.10	0.90
Isolucine	4.00	3.80	4.20
Lucine	6.21	6.00	6.30
Threonine	3.20	3.20	3.40
Valine	4.80	4.90	5.00
Histidine	2.39	2.30	2.40
Arginine	9.00	8.90	8.70
Glycine	5.10	5.00	4.90
Serine	3.60	3.40	3.50
Alanine	4.00	4.00	4.10
Aspartic acid	8.30	9.00	9.20
Glutamic acid	21.0	20.40	19.81
Proline	5.10	5.00	4.80
Ammonia	2.00	2.20	2.50

TABLE 6. ANALYSIS OF PARTIALLY HYDROGENATED OIL.

	Saponification value	Iodine value	Thiocyno-gen value	Linolein (%)	Olein (%)	Saturated and un-saponifi-able matter
Before hydrogenation	199.5	118.4	75.94	42.38	42.95	14.66
After hydrogenation	199.5	96.0	69.71	28.28	53.67	18.04

TABLE 7. ANALYSIS OF SEED HULLS (%).

Variety	Cellulose	Alcohol–benzene soluble	Benzene soluble wax	Ash	Silica	Pentosans
Peredovic	61.00	2.22	1.38	3.25	0.10	26.78
Arrowhead	61.41	2.40	1.80	2.30	0.15	28.20
Mingron	66.00	1.80	0.70	1.80	0.25	31.10

The oil may be refined with a low loss. Total unsaturated matter of the oil is comparable with soyabean oil, but linolenic acid found in soyabean oil is lacking in sunflower oil, which is an additional advantage of sunflower oil when used as food. It is not a good paint oil, but is good material for manufacture of soaps, ghee, candles and greasing etc.

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