Physico-Chemical Properties and Thermal Analysis of *Silybum Marianum* of Dera Ismail Khan and Kohat Regions

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Abstract

Silybum Marianum and Sunflower seeds were collected from Dera Ismail khan (31°49'N 70°55'E) and Kohat (33°35'N 71°26'E) regions. The oils were soxhlet extracted using n-hexane (40-60 °C). The oils samples were placed at ambient temperature (25-30 °C). Fatty acid composition of oils was determined by Gas Chromatography, Fourier Transform Infrared and thermal stability were investigated by Thermogravimetric Analysis. Gas Chromatographic analysis showed that fatty acid composition of Silybum Marianum oil of the two regions differs in their unsaturated fatty acids like oleic acid (20.13, 12.34 %), linoleic acid (59.85, 65.24 %). Similarly, saturated fatty acids such as palmitic acid (2.14, 4.25 %), stearic acid (20.17, 3.76 %) also differed significantly. FT-IR analysis sowed about the same components in both SMO and SFO. The presence of C-H stretching of alkyl group at 2921, 2852 cm^{-1} with 80 % absorbance and at 1743 cm^{-1} the presence of carbonyl group was confirmed with 85 % absorbance in both the oils. TG analysis showed that SMO of D.I. Khan region were thermally less stable and showed 15-18 % ± 1.3SD degradation and Kohat region showed 0 % degradation in 1st phase at 250 °C. These changes in composition of fatty acids were attributed to climatic difference of D.I. Khan and Kohat regions.

Keywords: Silybum Marianum, thermogravimetric analysis, infrared spectroscopy,

Introduction

The most favourite oil used during cooking is vegetable cooking oil. The reason behind it is the chemical constituents they have which ultimately become the part of the food cooked in them (Salunkhe, Chavan, Adsule, (1992)). Vegetable oils are considered to be triglycerides and an

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important constant of every cell. The oils provide energy to the cell and dissolves vitamins as well as drugs (Felsner, Matos, (1998), Khan, Shahidi, (1999)). On the other hands the oils quality its flavour etc deteriorates with the passage of time as well as its processing. The major cause of it can be oxidation of lipids (Gennaro et al (1998)) that may take place through free radical mechanism resulting formation of various unpleasant compounds/ gases (Harwood, Yaqoob (2002), Zunin, et al (1995)).

However, some of the Vegetable oils show great resistance to auto-oxidation as they may contain some anti-oxidants (poly unsaturated acids) (Kanavouras, Hernandez, Coutelieris, et al (2004)). Due to the autocatalysis, oxidation progress quickly as it starts. Various factors like the presence of some metallic compounds, light and temperature enhance the auto oxidation once it is initiated (Kauffman, Feng, Karasek, (2000)). Such circumstances may also arise due to material use for packing, storage environment, transportation process etc (Khan, Shahidi, (1999)). The stability of such material can be enhanced by addressing these constraints, it means adding anti-oxidants, varying degree of saturation, reducing expose to oxygen time particularly at high temperature (Khan, Shama, Khan, Fahim, (2005), Lu, Wong, P (2000)). It is therefore, imperative to know physical characteristics as well as chemical constituents of the oils so that their quality with reference to nutrient values and stability with reference to particularly, thermos oxidative process can be estimated and or controlled (Notte, Romito (1971), Papadopoulos, Boskou (1991), Boskou (1991)).

Though there are several techniques available and in use in industries but thermogravimetric techniques are considered to be more informative and easy to apply (Salunkhe et al (1992), Santos, Santos, Souza (2001), Santos, Santos, Souza (2002), Santos, Santos, Conceição (2004)). Further to it such techniques are also useful in varying the environment ot thermal treatment and studying the thermal behaviour of the oils using very small sample size (Souza, Conceicao. and Macedo. (1998)). On the other hand, FTIR spectroscopy can provide information about the availability of the various constituents of oils and their structure up to some extents Shyam N J, (2016).

Silybum Marianum (L.) is a well-known medicinal plant, native to in addition to other region of world various areas of Pakistan as well (Khan, Shahidi, (1999), Vyazovkin, (2002)). Therefore, we have analysed the oil obtained from various parts of Khyber Pukhtoon Khua, Pakistan using thermogravimetric analysis and FTIR spectroscopic techniques.

Experimental

Sample Collection

Samples were collected from Himmat, Chashma road and University road in Dera Ismail Khan and Aliabad, Faqir Abad and near Board of Intermediate and Secondary Education, Kohat. The seeds were dried in shadow, cleaned before use, ground with electric grinder and all the samples were stored under dry and dark conditions. *Oil Extraction:* The oils were extracted using n-hexane by Soxhlet method (b.p.40 ^{0}C). The sample was concentrated with the help of rotary evaporator. Oil samples were placed at ambient temperature (25-30 ^{0}C).

Thermo Gravimetric Analysis

Thermo gravimetric analysis of the oil samples was carried out by using Diamond Thermo gravimetric / Differential Thermal analyser (TG/DTA), PerkinElmer, USA. For the purpose a standard method was employed using heating rate of 5, 10, 15 and 20 ºC/min and using nitrogen atmosphere. For the purpose the sample was heated from ambient to 600 ºC and nitrogen flow rate was kept as 100 mL/min.

Fourier Transform-Infrared Analysis

FT-IR spectrophotometer, Tensor 27, Bruker Switzerland was used for the purpose. The results were recorded using 4 cm^{-1} at 64 scans from 4000 to 500 cm^{-1} and processed with the computer software program Spectrum provided by the supplier of the instrument.

Results and Discussion

The oil samples were subjected to thermogravimetric analysis and a typical thermogram is provided in Figure 1. It was noted that all the oil sample showed almost similar trend. The results obtained from such curves are displayed in Table 1. All TG/DTA curves can be divided into four sections for thermal decomposition, between 200 and 600ºC. The first section (200-380 ºC) showed the decomposition of polyunsaturated fatty acids which gave the most important information about the thermal stability of the oils. The second sections (380-480 ºC) displayed decomposition of monounsaturated fatty acids. The third (480-600 ºC) was attributed to decomposition of saturated fatty acids. However, all the oils decomposed up to end and no residues was noted at 600 ºC..

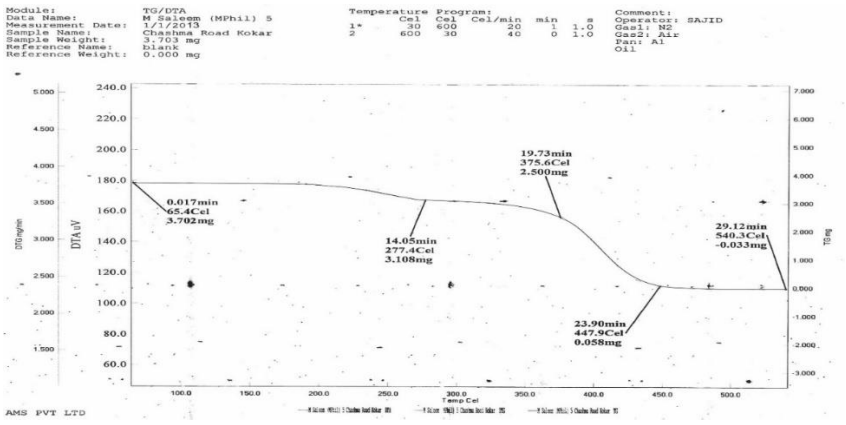

Fig: 1 Thermogram **of Silybum Marianum oil**

Table: 1 Thermal decomposition profile of the different Silybum Marianum oils

S.NO	AREA	1ST PHASE %DSMO (250 °C)	2ND PHASE %DSMO (350 °C)	3RD PHASE %DSMO (450 °C)	4TH PHASE %DSMO (550 °C)
1	Himmat DIK	18	30	97	100
2	Chashma Road DIK	16	32	98	100
3	University Road DIK	15	32	97	100
4	Aliabad Lachi	0	13.9	96	100
5	Faqirabad Lachi	0	7.3	93	100
6	B.I.S.E Kohat	0	8	96	100

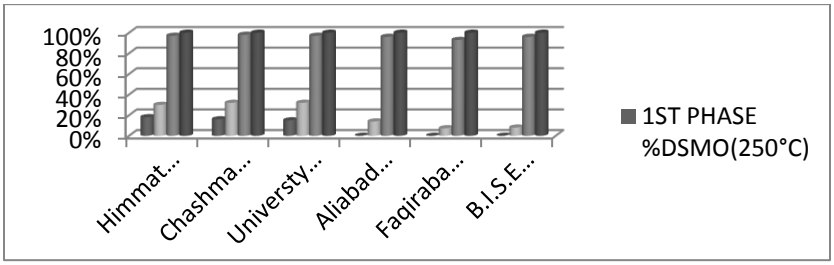

Fig:2 Thermogravimetric results of oils obtained from Kohat and Dera Ismail khan cities

The oils were thermally degraded using TGA and DTA techniques (Fig.1). The results are illustrated in Figure 2. Figure 2 showed degradation of Silybum Marianum oil by increasing the temperatures *Silybum Marianum* oil of Himmat, Chashma road and University road of Dera Ismail khan showed 15 % degradation in 1st phase while oil of Kohat region showed 0 % degradation. In the 2nd phase Dera Ismail khan oil showed 33 % degradation while Kohat oils showed 15 % only. In 3rd and 4th phase both the oils degraded up to 98 % and 100 % respectively. TGA study showed that the oils of Kohat region were thermally more stable than the oils of Dera Ismail khan.

Results of FT-IR spectra of various oil samples were recorded and one of such spectra is displayed in Figure 3. The results extracted from the spectra are listed in Table 2. The table conclude there is no difference in the bands around 3000-2800 cm^{-1} assigned to the C- H stretching vibration of the aldehydes group. 1743cm^{-1} frequency showed that carbonyl group is present. In carbonyl compounds esters are in the frequency range of 1750-1730 cm^{-1}. The absorbance of 80-85 % showed their composition. Two consecutive bands of 1742 cm^{-1} and 1710 cm^{-1} showed anhydride compound having two carbonyl groups.

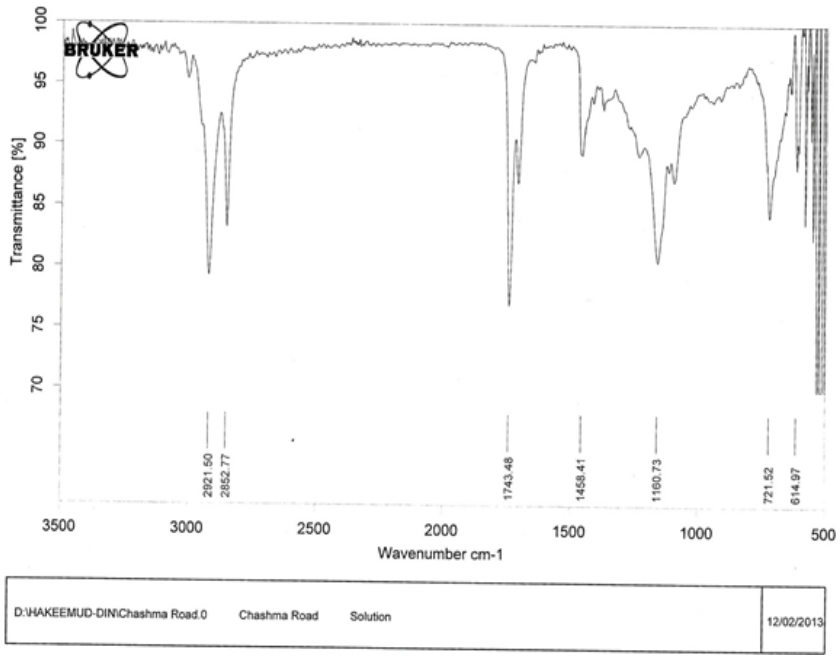

Fig: 3 FTIR spectrum of Silybum Marianum oil

Table 2: Evaluation of the FT-IR spectrum

S. No	Wave numbers (cm^{-1})	% age absorption	Functional Group
1	2921, 2852	80	C-H stretching vibration in aldehydic group
2	1743	76	Carbonylic group mostly esters
3	1742,1710	85	Two carbonyl groups of anhydrides
5	1160	80	C-C stretching vibration

Conclusion

The seeds of *Silybum Marianum* and Sunflower contain fixed oil of 28 % and 24 % respectively. FT-IR analysis sowed about same components in both SMO and SFO. The oils of Kohat region have high degree of polyunsaturated fatty acid content due to lower temperature of the region than D.I. Khan. TG analysis showed that SMO of D.I. Khan region were thermally less stable than that of Kohat region. These changes in composition of fatty acids were due to changed climatic conditions of D.I. Khan and Kohat regions.

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