Storage studies on mustard oil blends

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Abstract Mustard oil blends were investigated for fatty acid composition and oxidative stability during storage for 3 months at room temperature (15 °C to 35 °C). The blends were prepared using raw mustard oil with selected refined vegetable oils namely; palm, safflower, soybean, rice bran, sunflower and sesame oil (raw). The fatty acid compositions of all these blends were studied using GLC. The developed blends were found to obey the ideal fatty acid ratio as laid down by health agencies i.e. 1:2:1:: SFA:MUFA:PUFA. The oxidative stability of blends was studied by measuring peroxide value (PV), Kries and Thiobarbituric acid (TBA) test. Blends MPSu (mustard oil, palm oil and sunflower oil), MPT (mustard oil, palm oil and sesame oil) and MPGr (mustard oil, palm oil and groundnut oil) were more stable than other blends during storage. The presence of mustard oil in all blends might make them a healthier option for many consumers as it is a rich source of ω -3 fatty acids and has anti-carcinogenic properties.

Keywords Mustard oil · Oil blend · Oxidative stability · Fatty acid composition

Introduction

India is the third largest oilseed producing country in the world and rapeseed-mustard is the second most important

edible oilseed crop of India next to groundnut (Parmer et al. 2005). The growing demand for vegetable oils with increase in population is creating a stage of insufficiency in production of oils, thereby, obviating the alternate sources of cheaper and nutritional oils (Premavalli et al. 1998). Most of the highly unsaturated oils such as rice bran oil, soybean oil, palmolein oil and cottonseed oil are not suitable for frying purposes and also not acceptable by consumers as they are devoid of preferred flavors of oils traditionally consumed in the country. So, in many countries edible oil is often marketed as a blend of two or three oils (Murthi et al. 1987). Blended oils are also gaining popularity worldwide due to improved thermal stability, oxidative stability, nutritional benefits and ability to tailor the desired properties. Yap et al. (1989) investigated the polymorphic stability of hydrogenated canola oil and found that the stability was affected by addition of palm oil. The palm oil was added to hydrogenated canola oil at 5, 10 and 15% levels. Then the samples were subjected to temperature cycling between 5 and 20 °C as well as storage at 5 °C up to 56 days. Addition of palm oil at 10% level proved to be effective in delaying polymorphic instability of hydrogenated canola oil. Ali et al. (2005) also studied the oxidative stability of the blend of rice bran oil with crude mustard oil by measuring peroxide value and accelerated oven stability method at 60 °C. The fatty acid composition of the blend was also determined using gas liquid chromatography. The blend had improved oxidative stability and had a fatty acid profile close to the international standards. Semwal and Arya (2001) prepared edible oil blends namely, refined rice bran oil: unrefined groundnut oil, and refined soybean oil: unrefined groundnut oil in the proportions 80:20 (v/v) and stored in sealed tin containers at room temperature (15–34 °C). Both the oil blends remained stable for 15 months without development of perceptible off-flavor

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or odor. The similar study was conducted by Murthi et al. (1987) who determined the shelf life of different vegetable oil blends containing 25% raw mustard oil and 75% refined rapeseed oil. The physico-chemical properties of the blends like moisture content, free fatty acid, refractive index, iodine value, and saponification value was also reported. The peroxide value of raw edible oil and their blends tended to rise steadily to a maximum and declined gradually thereafter. Consumer acceptance trials indicated no strong dislike for these blended oils in comparison with traditional single oil but a preference for the later in certain instances was evident.

Since mustard oil contains more than 50% erucic acid which is against the desirable and internationally accepted level of <5% (Downey 1983). So quality of the mustard oil can be improved by blending it with other conventional vegetable oils so as to get the desired fatty acid composition of 1:1→2:1:: saturated fatty acids (SFA): monounsaturated fatty acids (MUFA): polyunsaturated fatty acids (PUFA) as suggested by WHO and other health agencies. This can be achieved by mixing or blending of two or more different oils in specific proportions to get desired fatty acid composition (Ali et al. 2005). Therefore, in the present study mustard oil blends were developed by mixing mustard oil with different vegetable oils. The objective of this study was to find the shelf life and the change in fatty acid composition in the developed mustard oil blends during storage of 3 months (15 °C to 35 °C).

Materials and methods

Procurement of oils Raw mustard oil of brand “Fortune”, Olive oil “Figaro”, Palm oil “Shri Hari”, rice bran oil “Ricella” and raw sesame oil “Kesari” were procured from Delhi while Safflower oil “Saffola”, Groundnut oil “Ginni”, Soybean oil “Fortune”, Sunflower oil “Fortune” were procured from the local market of Hisar city.

Determination of fatty acid composition using GLC The fatty acid composition of the nine different oils (as mentioned above) and the developed mustard oil blends were studied using GLC. The table below shows the composition or ratio of mustard oil blends.

Mustard oil blends	Ratio
Mustard oil: palm oil: safflower oil (MPSa)	30: 58: 12
Mustard oil: palm oil: soybean oil (MPSo)	29: 56: 15
Mustard oil: palm oil: rice bran oil (MPRb)	20: 44: 36
Mustard oil: palm oil: sunflower oil (MPSu)	24: 58: 18
Mustard oil: palm oil: sesame oil (MPT)	18: 54: 28
Mustard oil: palm oil: groundnut oil (MPGr)	14: 45: 41

Preparation of methyl esters

The fatty acid compositions of the different oils as well as of mustard oil blends were determined as methyl esters. Methyl esters were prepared according to the method described by Luddy et al. (1968). In a test tube 10–15 mg of lipid sample was taken and 0.4 ml of sodium methylate (0.4 N) was added. Sodium methylate was prepared by adding 1 g of metallic sodium pieces cut under petroleum ether to 100 ml of redistilled absolute methanol in amounts slightly in excess of that required for desired normality (0.4 N). After addition of sodium methylate, we cover the test tube with aluminum foil and heated in water bath at 65 °C for 2–3 min. The test tube was removed from water bath and cooled to room temperature. Add 1 ml of carbon disulphide to it and shake test tube for 1–2 min. The lower layer in the test tube contained all the methyl esters of fatty acids. The oil samples were taken in three replicates for preparation of methyl esters.

Fractionation of methyl esters by GLC

About 0.2–0.4 µl of the prepared methyl esters of oils and blends were taken for each injection and separated in MICHRO-9100, NETEL chromatography equipped with flame ionization detector. Stainless steel column (10'×1/8") was packed with 20% DEGS (diethylene glycol succinate) on 60 to 80 mesh chromosorb W. The oven temperature and the injection port temperature were kept at 200 °C whereas the temperature of detector port was 190 °C. The flow of nitrogen carrier gas was maintained at 35 ml/min.

On the basis of fatty acid composition, seven oils were selected viz. palm oil, safflower oil, soybean oil, rice bran oil, sunflower oil, sesame oil and groundnut oil for blending with mustard oil in different proportions so as to achieve nearby ideal fatty acid ratio i.e. 1:2:1 :: Saturated fatty acids: monounsaturated fatty acids: polyunsaturated fatty acids. Mustard oil blends thus prepared were stored at room temperature (15 °C to 35 °C) for 3 months and analyzed every month in three replicates for peroxide value as explained by Paquot (1979) and for kries and thiobarbituric acid tests as described by Ranganna (2003).

Peroxide value

Five gram of oil was taken in a 100 ml glass stoppered conical flask and 10 ml of chloroform was added to dissolve the sample by stirring it. Fifteen millilitre of acetic acid and 1 ml of saturated KI solution were added. The flask was shaken for 1 min and left for exactly 5 min. away from the light. Seventy-five millilitre of distilled water was added to the above solution. It was titrated with 0.01 N sodium thiosulphate solution using starch solution as

Fig. 1 GLC profile of Mustard oil

indicator. A blank test was carried out simultaneously. The analysis was done in three replicates. The peroxide value was calculated as:

$$\text{Peroxide value (meq O}_2\text{/kg oil)} = \frac{(B - S) \times N \times 1000}{W}$$

Where, B and S indicates volume of sodium thiosulphate used for blank and sample, respectively; W indicates weight of sample and N indicates normality of sodium thiosulphate.

Kries test

One millilitre of oil was taken in a test tube and 1 ml of concentrated HCl was added along with 1 ml of 1 per cent phloroglucinol in diethyl ether and mixed thoroughly. A pink color indicated that oil was slightly oxidized while red color indicated that oil was oxidized or test was positive. The test was replicated three times.

Table 1 Fatty acid composition (%) of different vegetable oils*

Oils	Palmitic (C _{16:0})	Oleic (C _{18:1})	Linoleic (C _{18:2})	Linolenic (C _{18:3})	Eicosenoic (C _{20:1})	Behenic (C _{22:0})	Erucic (C _{22:1})	MUFA	PUFA
Mustard	2.7	10.5	14.3	11.4	7.0	0	54.0	26.48	9.51
Sesame	9.6	43.9	44.3	2.1	0	0	0	4.57	4.83
Sunflower	5.5	34.8	58.6	0	0	0	0	6.32	10.65
Safflower	6.1	17.4	76.4	0	0	0	0	2.85	12.52
Groundnut	13.4	45.4	36.8	0	1.4	2.8	0	2.88	2.27
Soybean	11.9	24.8	55.3	7.9	0	0	0	2.08	5.31
Olive	14.8	70.0	12.7	1.0	0	0	0	4.73	0.92
Rice Bran	19.0	43.2	37.2	0	0	0	0	2.27	1.95
Palm	39.8	45.9	13.4	0	0	0	0	1.15	0.33
SEM	0.25	0.27	0.28	0.084	0.12	0.096	0.58	—	—
CD at 5%	0.741	0.793	0.832	0.251	0.357	0.286	1.71	—	—

* The values are average of three replications

MUFA and PUFA were calculated taking SFA as 1.0

SFA Saturated fatty acids, MUFA Monounsaturated fatty acids, PUFA Polyunsaturated fatty acids

Table 2 Fatty acid composition (%) of mustard oil blends*

Oil Blends	Storage period (months)											
	0			1			2			3		
	SFA	MUFA	PUFA	SFA	MUFA	PUFA	SFA	MUFA	PUFA	SFA	MUFA	PUFA
MPSa (30:58:12)	24.2	48.7	26.6	24.9	47.2	27.8	24.9	50.9	24.2	24.3	50.5	25.1
MPSo (29:56:15)	25.6	48.3	26.4	24.9	49.1	25.9	25.3	48.6	25.3	25.7	46.9	27.3
MPRb (20:44:36)	25.3	48.3	26.4	25.4	47.6	26.9	24.6	49.6	25.4	24.8	49.6	25.5
MPSu (24:58:18)	25.4	49.2	25.1	25.2	48.3	26.4	25.5	48.6	25.9	25.6	49.1	25.8
MPT (18:54:28)	23.7	48.3	26.6	25.3	47.1	27.5	25.3	49.3	25.3	25.9	49.5	24.5
MPGr (14:45:41)	24.8	47.6	27.4	23.7	49.5	26.7	24.7	48.8	26.5	24.7	48.9	26.3
SEM	0.14	0.27	0.27	0.3	0.6	0.51	0.24	0.28	0.28	0.36	0.19	1.12
CD at 5%	0.424	0.823	0.828	0.896	1.84	1.56	0.744	0.868	0.850	1.09	0.579	3.46

* The values are average of three replications

Thiobarbituric acid test

Two milliliter of oil was taken in a test tube and 10 ml of carbon tetrachloride was added to it. Then add 10 ml of TBA reagent and shake thoroughly for 4 min. The contents were transferred to separating funnel and aqueous layer was drawn in another test tube. The test tubes containing aqueous layers were immersed in boiling water bath for 30 min, cooled and color was noted. The formation of pink color indicated positive test. The test was replicated three times.

Statistical analysis

The data were analyzed statistically according to the methods described by Snedecor and Cochran (1967). The overall differences were tested by 'F' test of significance at 5 per cent level of probability. In case of significant F test, critical differences were calculated for comparing means of different blends.

Result and discussion

The GLC profile for mustard oil is presented in Fig. 1 and Table 1. The retention time (minutes) of different fatty acids of mustard oil were 4.28 (palmitic acid), 8.53 (oleic acid), 10.79 (linoleic acid), 14.44 (linolenic acid), 22.49 (eicosenoic acid) and 25.43 (erucic acid). Results of the fatty acid composition of mustard, sesame, sunflower, safflower, groundnut, soybean, olive, rice bran and palm oils are shown in Table 1. Palmitic acid ranged from 2.7% to 39.8% and was found maximum in palm oil and minimum in mustard oil. The oils differed significantly ($P \leq 0.05$) in palmitic acid. Oleic, linoleic and linolenic acids were found to be in the range of 10.5% to 70.0%, 12.7% to 76.4% and 1.0% to 11.4%, respectively; and all the nine oils were significantly different in these fatty acids ($P \leq 0.05$). However, erucic acid (54.0%) was found only in mustard oil and behenic acid (2.8%) was reported only in groundnut oil. Eicosenoic acid in oils differed significantly ($P \leq 0.05$) and was found maximum (7.0%) in mustard oil followed by groundnut oil

Table 3 Peroxide value, Kries and Thiobarbituric acid (T.B.A.) test of blends during storage*

Oil Blends	Storage period (months)											
	Peroxide value (meq of O ₂ /kg oil)				Kries test				T.B.A. test			
	0	1	2	3	0	1	2	3	0	1	2	3
MPSa (30:58:12)	11.8	14.9	25.1	27.3	–	–	–	++	–	–	+	++
MPSo (29:56:15)	9.3	12.9	21.7	22.3	–	–	–	++	–	–	+	+
MPRb (20:44:36)	9.2	13.1	20.2	25.0	–	–	–	+	–	–	–	+
MPSu (24:58:18)	16.7	19.6	29.7	31.9	–	–	–	+	–	–	+	+
MPT (18:54:28)	13.5	16.2	17.5	19.9	–	–	–	–	–	–	+	+
MPGr (14:45:41)	8.5	8.9	9.2	18.7	–	–	–	+	–	–	+	+
SEM	0.03	0.017	0.057	0.041	–	–	–	–	–	–	–	–
CD at 5%	0.090	0.053	0.174	0.127	–	–	–	–	–	–	–	–

* The values are average of three replications
(–) = Negative, (+) = Low, (++) = High

(1.4%). The fatty acid composition of mustard oil comprised of 2.7% SFA, 71.5% MUFA and 25.7% PUFA. The fatty acid ratios of different oils are presented in Table 1 and it is noticed that no single conventional oil obeyed the ideal fatty acids ratio standards as laid down by health agencies i.e. 1:2:1:: SFA:MUFA:PUFA. Such type of observations was also reported by Chandra (2005) who found no conventional oil to be perfect from nutritional point of view. Therefore, mustard oil was blended with different vegetable oils and six blends were prepared to acquire ideal fatty acids ratio close to 1:2:1:: SFA:MUFA:PUFA as shown in Table 2. These blends were analyzed for the fatty acid composition and the oxidative stability tests during storage of 3 months at room temperature (15 °C to 35 °C). The six blends contained 23.5–25.6 per cent SFA and 25.1–27.4 per cent PUFA which were found to be significantly different ($P \leq 0.05$) during 0 month of storage. The percentage level of MUFA in oil blends during 0 month of storage was not significant different ($P \leq 0.05$) and it ranged from 47.6 to 49.2. During first month of storage, the difference in SFA, MUFA and PUFA of blends were found to be non-significant ($P \leq 0.05$). During second month of storage, SFA was noticed maximum in blend MPSu (25.5%) and minimum in blend MPGr (24.7). There was no significant difference in SFA among different blends ($P \leq 0.05$) during second month of storage while the difference in MUFA and PUFA was found to be significant ($P \leq 0.05$) during this period. During third month of storage, significant difference ($P \leq 0.05$) was found in SFA and MUFA while non-significant difference ($P \leq 0.05$) was found in PUFA of different blends. No remarkable change in the percentage of saturated (SFA), monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids was noticed in all the blends during storage. However, slight increase in MUFA and decrease in PUFA was observed. The maximum increase in MUFA was found in the blend MPSa and it was from 48.7% to 50.5% (Table 2). The maximum decrease in PUFA was found in blend MPT and it was from 26.6% to 24.5% (Table 2). This might be due to the oxidation of mono- and polyunsaturated fatty acids. But the change in fatty acid profile of blends overall did not affect the fatty acid ratio of these blends. All the mustard oil blends had fatty acid ratio close to ideal ratio of 1:2:1:: SFA:MUFA:PUFA during 3 months of storage and are considered nutritionally superior over individual oils. The fatty acid ratio in the oil blends MPSa, MPSo, MPRb, MPSu, MPT and MPGr was 1:2.07:1.03, 1:1.82:1.06, 1:1.99:1.02, 1:1.91:0.98, 1:1.91:0.94 and 1:1.97:1.06, respectively during 3 months of storage.

During storage, the maximum increase in peroxide value was found in blend MPRb and it ranged from 9.15 to 24.99 meq O_2 /kg oil and the minimum increase was in blend MPT and it varied from 13.45 to 19.91 meq O_2 /kg oil as shown in Table 3. The mustard oil blends were found to be significant different ($P \leq 0.05$) in peroxide value during

3 months of storage. The increase in peroxide value might be due to auto-oxidation, thermal polymerization and hydrolysis of fatty acids which occurred in blends during prolonged storage. Kries test and Thiobarbituric acid (TBA) test of all the blends during storage is shown in Table 3. Kries and TBA tests indicated the extent of oxidation of fatty acids in oil and were used for evaluating the onset of rancidity at early stages. Higher degree of oxidation (++) was observed only in blend MPSa while lower degree of oxidation (+) were seen in blends MPSo, MPRb, MPSu, MPT and MPGr.

From the following study it was concluded that no single conventional oil had the desired ideal fatty acid ratio. Hence, the mustard oil blends so developed had the desired fatty acid ratio of SFA: MUFA: PUFA (1:2:1), therefore, these designed blends found to be nutritionally superior over the individual oils. These blends were nutritionally better because palm oil exhibits better polymorphic stability and is a rich source of antioxidants and vitamin A. The results of the study also concluded that blends MPSu, MPT and MPGr had better oxidative stability than other blends due to less increase in their peroxide values and also less extent of oxidation as indicated by Kries and Thiobarbituric acid test. The major oil present in these blends was mustard oil which has anticarcinogenic properties and has appreciable amount of ω -3 fatty acids. Therefore, these blends might be useful for the patients suffering from cancer and coronary heart disease.

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