Spectrophotometric Studies of Rice Bran Oil and Mustard Oil Mixtures: I

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ABSTRACT

Visible spectra between 520-700 nm of unbleached mustard oil, rice bran oil and their 10 mixtures are reported. Mustard oil shows its characteristic band at 671.5 nm, and rice bran oil shows two characteristic bands at 550 and 564 nm and a contour centered at about 656 nm. The 564 nm band starts emerging in mixtures even by the 5% presence of rice bran oil and takes its well resolved shape at higher ratios. The 671.5 nm mustard oil band shows uniform hypsochromic shift up to 40% of rice bran oil, and at higher concentrations this shifting becomes irregular. An approximate estimation of rice bran oil adulteration in mustard oil can be made by observing the shifted position of 671.5 nm band.

INTRODUCTION

The most common cooking medium of Nepal and North India is mustard oil. Rice bran oil is one of the main adulterants of mustard oil since it is obtained as a cheap by-product of the rice mill industry. It may contain a high free fatty acid (FFA) content, up to 50% or more, which makes it unsuitable for edible purposes (1). Generally the presence of rice bran oil in mustard oil is suspected by a high FFA content of the sample, but no confirmatory opinion can be formed by this test alone. Recently some work on the IR spectroscopic study of mustard oil and rice bran oil mixture has been communicated from this research center (2) and a separate band for C=O stretching was found in mixtures containing more than 30% of high FFA rice bran oil. It is possible to obtain useful information regarding the nature of edible oils and fats by means of visible spectroscopy (3), and some work in this field has been reported in the literature (4-7). In order to find a quick method for detecting the presence of rice bran oil in mustard oil samples, the spectrophotometric study of these two oil mixtures has been done and reported in this paper.

EXPERIMENT

Materials

Mustard (M) oil was extracted from black mustard seeds in a village expeller unit. Pure rice bran (RB) oil was obtained from a manufacturer of this oil where it is extracted by solvent extraction process. Both oils were filtered and stored in polyethene bottles. Some physical constants and values of the oil samples are seen in Table I.

Instrument

A Pye Unicam SP8-100 UV Spectrophotometer, with 10 mm path length silica cuvettes was used. All spectra were recorded by operating the instrument on absorbance limit 1, band width of scanning system on 0.2 nm, wavelength speed 2 nm sec^{-1}, and chart speed 5 sec. cm^{-1}.

TABLE I

Physical Constants and Values of Oil Samples

Constant/values etc.	Mustard oil	Rice bran oil
Saponification value	173	189
Iodine value	101	98
Sp. gr. at 20 C	0.911	0.918
Solidification point	—	0.5-1.5 C
FFA content (calculated as oleic acid)	1.8%	23.5%

Procedure

Standard mixtures of mustard oil with rice bran oil were prepared in different ratios of 95M:5RB to 10M:90RB on volume basis at room temperature (20 C). Spectra were recorded without any cuvette in the reference compartment of the instrument.

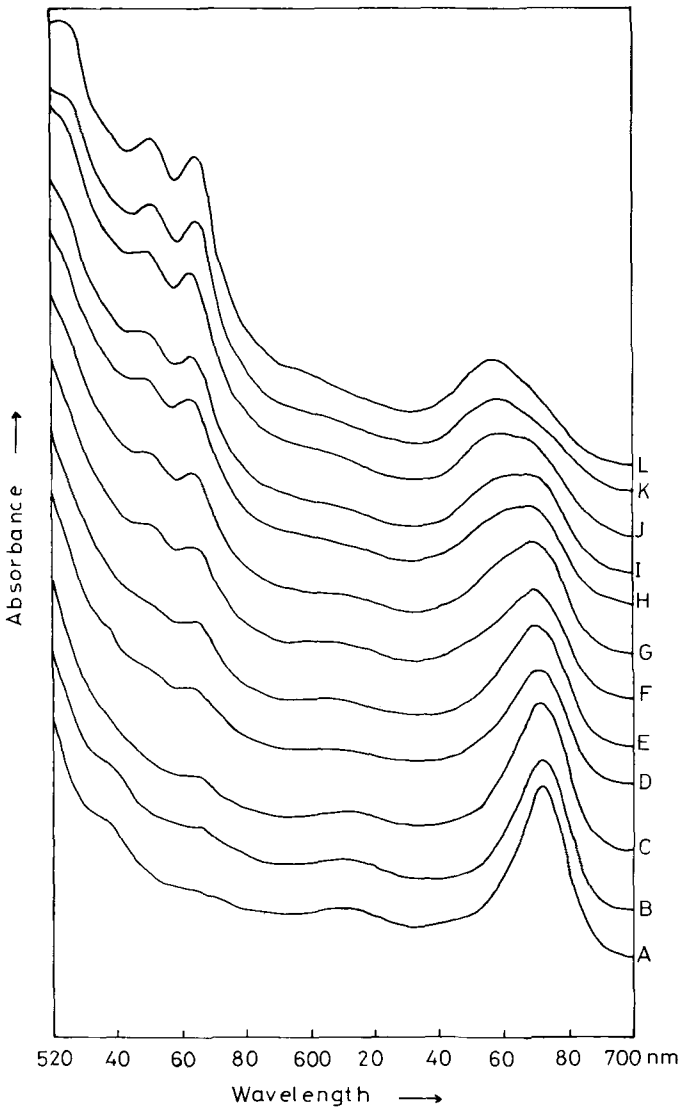

FIG. 1. Visible spectra of mustard oil, rice bran oil and their mixtures. (A) M oil, (B) 95M:5RB oil mixture, (C) 90M:10RB oil mixture, (D) 80M:20RB oil mixture, (E) 70M:30RB oil mixture, (F) 60M:40RB oil mixture, (G) 50M:50RB oil mixture, (H) 40M:60RB oil mixture, (I) 30M:70RB oil mixture, (J) 20M:80RB oil mixture, (K) 10M:90RB oil mixture, and (L) RB oil.

TABLE II

Shifting of 671.5 nm Mustard Oil Band in Presence of Rice Bran Oil

Sample	Percent of rice bran oil in rice bran-mustard oil mixtures	Position of 671.5 nm mustard oil band
B	5	671.25 nm
C	10	671.00 nm
D	20	670.50 nm
E	30	670.00 nm
F	40	669.50 nm
G	50	668.50 nm
H	60	667.00 nm
I	70	664.00 nm
J	80	658.50 nm
K	90	657.00 nm

RESULTS AND DISCUSSION

Visible spectra, in the region 520 to 700 nm, of pure mustard oil, rice bran oil and their 10 mixtures are shown in Figure 1. Below 520 nm wavelength the absorbance of all these samples exceeded an absorbance of 1 and hence are not shown. Curves A and L represent the spectra of pure mustard oil and rice bran oil, respectively. Curves B to K are the spectra of various mixtures of these two oils in order of increasing percentage of rice bran oil in the mixture. It is observed that mustard oil shows a characteristic absorbance peak at 671.5 nm and a shoulder between 532 and 538 nm. The 671.5 nm band of mustard oil is very close to the 670 nm peak shown by rapeseed oil (3,4), and this closeness can be attributed to the fact that general properties of these two Brassica oils are similar (8). Rice bran oil spectra (L) shows one shoulder having its center at 523 nm, two characteristic bands at 550 and 564 nm, and a broad contour having its center at ca. 656 nm. Since the apparent color of a substance is always the complement of the color absorbed, the 523, 550 and 564 nm bands seem to be in accordance with the reddish-purple appearing rice bran oil (9). Intensity of all these 523, 550 and 564 nm bands of rice oil is higher than the 671.5 nm mustard oil band. The 656 nm broad band is of low intensity in comparison to all above mentioned bands.

The 550 and 564 band centers of rice bran oil are found to be shifted slightly as the mustard oil ratio increases in the mixtures (see curves K to B). The 564 and 550 nm bands appear as shoulders in the mixtures when the rice bran oil is 5% (curve B) and 30% (curve E), respectively. As the rice bran oil ratio increases, they gradually change into well resolved bands. The convex shapes of 564 and 550 nm bands appear at 40% and 80% rice bran oil content, respectively. The 523 nm shoulder emerges in the spectra of mixtures at 90% rice bran oil composition. Absorption intensity of 564 and 550 nm bands increases regularly with the rise in rice bran oil percentage in mixtures. The shoulder at ca. 535 nm in mustard oil spectra disappears when the rice bran oil content in the mixture is more than 10%. These effects seem logical when the nature of spectra of pure mustard and rice bran oils are considered.

Shifting of 671.5 nm Mustard Oil Band

The 671.5 nm band of mustard oil gradually shifts towards lower wavelength and becomes wider as the rice bran oil ratio in the mixture increases. This hypsochromic shift of band center may be due to the solvent effect of rice bran oil and particularly to 656 nm band of it. Table II shows the shifting at different rice bran oil percentages of the mixture.

It is clear from Table II that the shifting of characteristic 671.5 nm mustard oil band is regular up to 40% of the rice bran oil content, and beyond this it shifts haphazardly for every 10% increase of rice bran oil content. It may be inferred from the above discussion that the adulteration of rice bran oil in mustard oil can be detected up to a minimum limit of 5% by observing a slight shoulder at ca. 560-564 nm. A rough quantitative estimation can be made by observing the shifted position of 671.5 nm band. To test the validity of this method, some samples of mustard oil adulterated with rice bran oil (other than the reference samples) were prepared. The percentage of RB oil in these samples was determined by observing the shifted position of 671.5 nm peak and reading the corresponding value of RB oil % on the curve obtained from the plot of values given in Table II. Comparison of actual and experimental values have been shown in Table III.

The reason of about ± 15% variation at higher RB oil content seems due to the broad contour-shaped nature of the 656 nm band, whose central position varies slightly from sample to sample.

This paper is based entirely on the determination of color differences between the two oils in their unbleached forms since mostly they are used as such after being extracted by small expellers in villages and also by small oil mills. The color of such oils is likely to be variable, both at source and after storage. However, samples stored for more than one year and collected from different places showed similar spectra.

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TABLE III

Comparison of Actual and Experimental RB Oil Percentages

S.No.	Actual % of RB oil in the M oil sample	Position of the shifted 671.5 nm band	RB oil % according to the curve plotted from Table II data	Percent error in the result
1.	10	671.0 (slightly less)	10.5	+5
2.	15	670.8	14.5	-3.3
3.	25	670.4	24.0	-4
4.	35	669.7	36.5	+4.3
5.	45	668.6	48.5	+7.7
6.	55	668.8	48.0	-12.7
7.	65	660.7	75.0	+15.5

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Spectrophotometric Studies of Rice Bran Oil and Mustard Oil Mixtures: II

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ABSTRACT

Visible spectra, between 400 to 500 nm range, of rice bran oil, mustard oil and their 7 mixtures, diluted 10 times in carbon tetrachloride, are reported. Mustard oil spectra shows three characteristic bands centered at wavelength 428, 453 and 482 nm, while no such band has been observed in rice bran oil spectra in this range. Intensity of 428 nm band increases as the rice bran oil percentage increases in the mixture of two oils. Five indices, R_1 to R_5, have been suggested for the approximate determination of rice bran oil adulteration in mustard oil. Plots of R_2 and R_3 against percentage of rice bran oil in the mixture have been found to be straight lines. The index R_3, equal to $1000(A_{428}-A_{482})$, has been found to be the most useful for this approximate estimation of rice bran oil in mustard oil.

INTRODUCTION

Rice bran oil is suspected to be one of the main adulterants of mustard oil. We have been engaged in the spectrophotometric study of the mixtures of rice bran and mustard oil with a view to have a quick method of its detection. It was reported earlier (1) that rice bran oil of high free fatty acid content (FFA) gives a C=O stretching band at 1710 cm^{-1}, not observed in mustard oil sample. This band emerges as a shoulder in the rice bran-mustard oil mixture, when rice bran oil content is 30% in the admixture. Experiments with neat oil samples as such in the cuvettes show that the presence of rice bran oil even at low concentration (5%) was sufficient to show a shoulder due to characteristic 564 nm rice bran oil band and their absorbance was found to be quite high between 400-500 nm region (2).

To understand the nature of spectra in this region it was thought desirable to extend these investigations using a suitable solvent. This paper reports the results of spectrophotometric study of mustard oil, rice bran oil and their mixtures using carbon tetrachloride as solvent.

EXPERIMENTAL

The samples of mustard (M) oil and rice bran (RB) oil were the same, used in earlier work, and their details have been already mentioned (2). Mixtures of mustard oil and rice bran oil were prepared in different ratios on volume basis at room temperature (20 C). All the samples were dissolved and diluted 10-fold with carbon tetrachloride. Pye Unicam SP8 – 100 UV Spectrophotometer was used to run the spectra of samples employing usual technique.

RESULTS AND DISCUSSION

Figure 1 shows visible spectra, between 400 to 500 nm, of mustard oil, rice bran oil and their mixtures. Since the oil samples are diluted in carbon tetrachloride, the intensity of various bands shown by neat oil samples (2), (500 to 760 nm) decreases to such an extent that the same almost merge in the main curve and so have not been shown in Figure 1.

Curves A and I show the spectra of mustard oil and rice

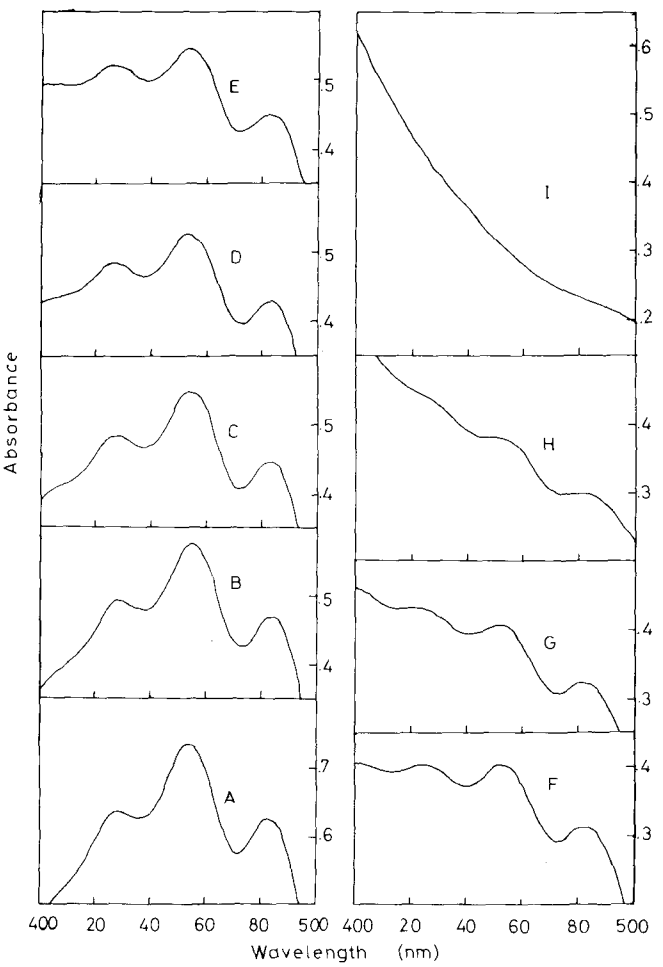

FIG. 1. Spectra of mustard oil, rice bran oil and their mixtures at 1/10th dilution in carbon tetrachloride. (A) 100M:0RB; (B) 90M:10RB; (C) 80M:20RB; (D) 70M:30RB; (E) 60M:40RB; (F) 50M:50RB; (G) 40M:60RB; (H) 20M:80RB; (I) OM:100RB; oil mixtures.