Technical

Spectrophotometric Studies of Cheuri (*Madhuca butyracea*) Fat and Ghee Mixtures: I

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ABSTRACT

Visible spectra of cheuri (*Madhuca butyracea*) fat, ghee (clarified butter fat) and 10 of their mixtures are reported. Pure ghee showed no absorption band in the visible range whereas the cheuri fat samples showed an absorption band with maxima between 640 and 680 nm. Even 5% cheuri fat content in ghee had a small absorption in this range. An index R (maximal absorbance of band between 640 and 680 nm$-A_{700}$) was found suitable for estimating the amount of cheuri fat in ghee samples.

INTRODUCTION

The problem of adulteration in food items is universal and efforts are continuously made to detect such adulteration. Ghee is a common cooking medium of the Indian subcontinent. It is reported (1,2) that in Nepal, ghee is often adulterated with *M. butyracea* seed fat, commonly known as Cheuri in Nepal and as Phulwara butter elsewhere. Cheuri often contains a high free fatty acid (FFA) content and saponin, both of which make it unsuitable for human consumption.

Many methods for detecting adulteration in ghee are reported in the literature (3-9). Chakrabarty et al. (10,11) have reported that 5-10% of Mahua (*M. latifolia*) oil in ghee can be detected by thin layer chromatography (TLC) of trisaturated glycerides of rearranged pure and adulterated ghee. Tamrakar (12) seems to have studied this problem—adulteration of ghee with cheuri—first and has reported Reichert Meissl (RM) value, Polenske value, saponification value, hydroxamic acid index and unsaponifiable matter of pure ghee, cheuri and 6 mixtures containing 10-70% of cheuri in ghee samples.The RM value determines the amount of steam-volatile, water-soluble fatty acids (13,14) such as butyric and caproic acids, whereas Polenske value determines the steam-volatile, water-insoluble fatty acids (13,14) such as caprylic and capric acids. The RM value is particularly valuable in detecting adulteration in butter (15), and Tamrakar (12) has also concluded that the RM value is suitable for detecting the adulteration of ghee (RM value of his sample, 33.9) at as low a level as 10% of cheuri fat in it (RM value of mixture, 30.8). But at the same time, the author has accepted that the RM value for pure ghee varies between the range 26.5 and 38.5 (minimal RM value accepted by Nepal Standard Committee being 26). It means that by using this RM index, a pure ghee sample having a RM value 26 may wrongly be reported as adulterated with 25% cheuri fat. Moreover, Singh and Singh (16) have reported that the range of RM value for buffaloes' ghee is 19.31 to 38.5 and for cow's ghee is 20.9 to 29.7, which further creates doubt about the reliability of RM value as an index for detecting adulteration of ghee with cheuri fat. The case is similar with other indices. It therefore seems desirable that a more precise method of detecting cheuri fat in ghee samples be developed.

Recently, work on the "Spectrophotometric Studies of Rice Bran Oil and Mustard Oil Mixtures" was reported from this Centre (17,18), and it was suggested that that method could be used to detect as little as 5% rice bran oil adulteration in mustard oil. This method has now been extended to the detection of ghee and is reported herein.

EXPERIMENTAL

Materials

Pure ghee (G) was prepared from Buffaloes' milk by the traditional method (1). Cheuri fat (CF) was obtained from Natural Resources Development Unit of this Centre. These two samples were treated as reference samples. Other ghee and cheuri fat samples were collected from other sources for comparative study. Some physical constants and values for these reference materials are reported in Table I.

TABLE I

Physical Constants and Values of Ghee and Cheuri Fat Reference Samples

Constants/values	Ghee	Cheuri fat
Saponification value	226	196.5
Iodine value	30.9	42.5
RM value	25.0	0.9
Solidification point	34.0 C	36.0 C
BR index at 40 C	43	48.6

Instruments

A Pye Unicam SP8-100 UV spectrophotometer, with 10 mm path length silica cuvettes, was used. 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}.

Procedure

Standard mixtures of ghee (G) with cheuri fat (CF) were prepared in different ratios of 95 G:5 CF to 10 G:90 CF on a volume basis in molten state at 40 C. Spectra of all the samples in the visible region were taken by putting neat molten fat in the sample compartment and an empty cuvette in the reference compartment of the instrument.

RESULTS AND DISCUSSION

Visible spectra, in the 600-700 nm region, of ghee and

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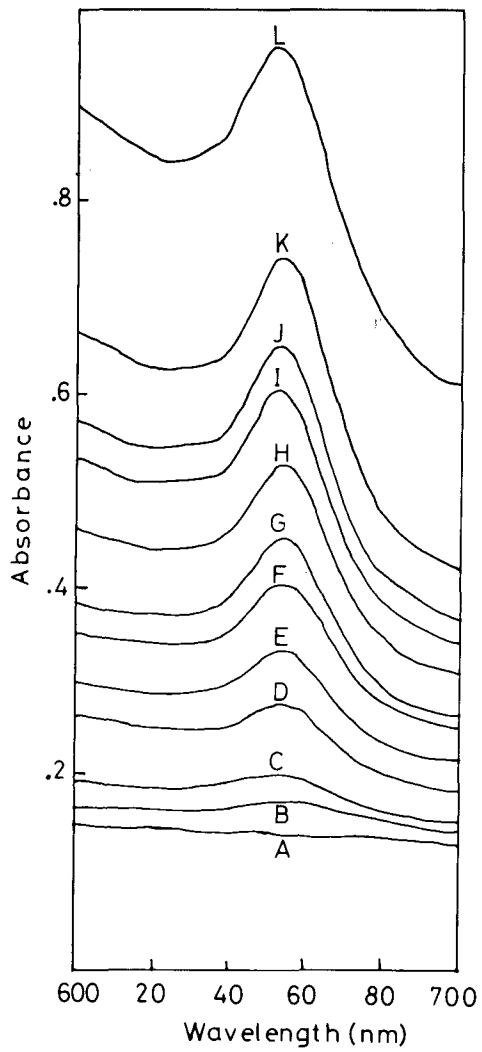

FIG. 1. Visible spectra of ghee, cheuri fat and their mixtures. (A) Ghee, (B) 95G:5CF, (C) 90G:10CF, (D) 80G:20CF, (E) 70G:30CF, (F) 60G:40CF, (G) 50G:50CF, (H) 40G:60CF, (I) 30G:70CF, (J) 20G:80CF, (K) 10G:90CF, and (L) Cheuri Fat.

cheuri fat reference samples and of their 10 mixtures are shown in Figure 1. Spectra of reference ghee sample as well as of other samples obtained from different sources were found to be identical and showed no band between the 500 to 760 nm range. The spectral plot was almost a straight line showing slight increase in absorbance as the wavelength decreased (curve A, Fig. 1). Below 500 nm, the spectra showed a rapid increase in absorbance exceeding 1.0 below 400 nm. Spectra of cheuri fat reference sample and of other samples collected from different sources (some samples were 2-3 years old) were found to be almost similar. All the samples showed either a sharp band or a contour-like band, having an absorbance of 0.8 to 0.95, between 640 and 680 nm (curve L, Fig. 1). Below 620 nm, the spectra of cheuri fat exhibits a continous increase in absorbance value exceeding 1.0 below 560 nm.

The reason for this difference in the visible spectra of molten ghee and cheuri fat is obvious. Though in solidified form both the fats are of slightly yellow color, their colors in molten state are different. Molten ghee sample looks almost colorless or very slightly yellowish and hence shows no absorption band in the visible region, whereas the color of molten cheuri fat is slightly brownish and therefore shows a distinct band in this region. This color of cheuri fat, which is of vegetable origin, may be due to the presence of some unsaponifiable constituent.

Curves B to K show the spectra of various mixtures of ghee and cheuri fat reference sample in order of increasing amount of cheuri fat from 5 to 90%, respectively. It is clear from Figure 1 that even 5% presence of cheuri fat in ghee sample shows a small band (curve B) between the 640 to 680 nm region in an otherwise straight spectrum of ghee (curve A). The intensity of this band increases as the amount of cheuri fat increases in the mixtures. Table II shows the intensity of cheuri band and an index R (maximum abs. between 640 to 680 nm−abs. at 700 nm) for the various amounts of cheuri fat in ghee.

It is clear from the data (Table II) that R varies directly with the cheuri fat content in ghee. It was observed that the value of R for other samples of cheuri fat were in the range 0.30-0.38. Hence, it is expected that the experimental value of cheuri fat percentage in the mixture should not have an error of more than ± 15%. A few cheuri fat and ghee mixture samples were prepared from other samples of these fats and the amount of cheuri in ghee was determined

TABLE II

Percentage of Cheuri Fat in Ghee, Intensity of Its Band Peak and Value of Index R

Sample no.	Curve	Cheuri fat in ghee sample (%)	Maximum abs. of 640-680 nm band peak	Abs. at 700 nm	R
1	A	0	0.14	0.13	0.01
2	B	5	0.16	0.14	0.02
3	C	10	0.20	0.155	0.045
4	D	20	0.28	0.20	0.08
5	E	30	0.33	0.215	0.115
6	F	40	0.40	0.25	0.15
7	G	50	0.45	0.26	0.19
8	H	60	0.53	0.31	0.22
9	I	70	0.60	0.34	0.26
10	J	80	0.65	0.36	0.29
11	K	90	0.74	0.42	0.32
12	L	100	0.96	0.61	0.35

TABLE III

Comparison of Actual and Experimental Cheuri Fat Percentages

Sample no.	Actual % of cheuri fat in ghee sample	Index R	Cheuri fat % according to curve plotted from Table II data	Percent error in result
1	10	0.045	9	-10
2	15	0.070	17	+13.3
3	20	0.09	22	+10
4	25	0.095	23	- 8
5	35	0.12	31	-11.4
6	80	0.26	71	-11.2

by the straight line curve drawn from the plot of percentage of cheuri fat vs R. Table III shows the actual and experimental values of cheuri fat.

Although the color present in a vegetable fat or oil is unstable, the presence of this band in a three-year-old sample is quite interesting. As such, it can be suggested that presence of band in visible spectra of ghee may be due to adulteration and if the band is between the 640 to 680 nm region, it may be due to cheuri fat. This information, along with other physical constants and values, would be helpful in confirming the presence of cheuri fat in ghee.

ACKNOWLEDGMENT

K.L. Shrestha provided facilities and granted permission to publish this paper. P.P. Manandhar determined some values of the fat samples.

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[Received June 19, 1980]

Functionalization at the Double Bond Region of Jojoba Oil: I. Bromine Derivatives

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ABSTRACT

Addition of bromine to jojoba oil and its *trans*-isomer yielded tetrabromojojoba, which upon elimination afforded the acetylenic and allenic components, respectively, when reacted with excess of base. The bromoolefinic products were obtained when limited amount of base was used. Allylic bromination of the liquid wax and its *trans*-isomer, and subsequent HBr elimination, yielded the two conjugated diene systems on both parts of the ester (jojoba tetraene).

INTRODUCTION

Jojoba oil (I) is a promising agricultural product, as are its derivatives (1,2). Its chemical structure dictates the chemical reactions and the possible products and derivatives which can be derived from it. In our previous studies, we have concentrated on the ester function of the wax and prepared the quaternary ammonium salts (3), the amide (4) and muscalure (5). Introduction of new groups at the double bond region enables one to transform the hydrophobic wax into much more polar compounds with different chemical, physical and technological properties. In this paper, we present the results of bromination reactions at the double bond region on the natural oil with Z-double bonds, as well as the isomerized oil, with E-double bonds. Elimination of HBr from these products increases unsaturation of the hydrophobic ester.

$$(\underline{Z},\underline{Z})\text{-}CH_3(CH_2)_7CH{=}CH(CH_2)_m\overset{\displaystyle O}{\overset{\|}{C}}O(CH_2)_nCH{=}CH(CH_2)_7CH_3$$

I: m = 7,9,11,13; n = 8,10,12,14.

EXPERIMENTAL PROCEDURES

General

The general procedure of solvent purification, work-up of reactions and nuclear magnetic resonance (NMR) technique for monitoring the reactions have been described earlier (3-5). LiCl and Li_2CO_3 (CP) were dried prior to the reaction, at 120-130 C for 2 hr. Melting points were taken on a Thomas Hoover Capillary melting point apparatus, and are not corrected. The NMR spectra were determined on a Varian XL-100 in CCl_4 or $CDCl_3$ solution, with chemical shifts expressed in δ. The infrared (IR) spectra were determined with a Perkin Elmer 377, the sample usually being neat or in $CHCl_3$ solution. The ultraviolet (UV) spectra were taken on a Bausch and Lomb Spectronic 210 in C_6H_{12} solution. Iodine value (Wijs) of 81.5 indicates ca. 95-96% double bond equivalence. Microanalyses were performed in the Microanalytical Laboratory of the Applied Research Institute, Ben-Gurion University of the Negev, Israel.

Double Bond Isomerization and Separation of *trans*-Jojoba (Ia)

A solution of 500 g of jojoba oil in 500 mL petroleum ether (60-80 C) and 50 mL of 2 M $NaNO_2$ was heated until reflux and then 16 mL of 6 M HNO_3 was added by drops within 5 min, after which heating was continued for 15-20 min. The hot solution was immediately transferred to a separatory funnel and was washed with hot water (50 C) (5 × 50 mL), until pH 7 was reached. The solvent was evaporated and the residue was left in a beaker to solidify