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Fatty acid composition of *Sapindus mukorossi* seed oil

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ABSTRACT

Fatty acid methyl ester (FAME) composition of Sapindus mukorossi seed oil was determined by IR, NMR and GC-MS analysis. The FAME of the oil of Sapindus mukorossi consists of 4.78 wt.% of methyl palmitate (C16:0), 58.89 wt.% of methyl oleate (C18:1), 1.78 wt.% of methyl stearate (C18:0), 25.93 wt.% of methyl 11-trans eicosenoate (C 18:2), and 8.61 wt.% of methyl arachidate (C20:0).

Key words: Kekru, *Sapindus mukorossi*, transesterification, non-edible vegetable oil, *Athia*, Biodiesel.

INTRODUCTION

In Manipur (India) there are many non-edible seeds found in both plain and hill areas. Non edible oils can be extracted from such seeds. But such oils find very limited commercial uses and plants producing such oils are slowly disappearing because such plants are considered not important by farmers, governments, any public and private sectors etc. As a result plant diversity is dwindling. Moreover, it is believed that large scale production of biodiesel from edible oils may cause global imbalance to the food supply and demand market. Hence use of non-edible oils as the feedstock for biodiesel industries will spare edible oils for use in other industries of edible products [1]. The use of biodiesel now-a-days has become important for diesel engines and is getting worldwide attention because of its renewability, biodegradability, nontoxicity and carbon neutrality [2-5]. The developed countries like Brazil, Indonesia, Malaysia, USA, UK, Canada, and Germany have already started using biodiesel blended petrodiesel. Our country also desperately needs it as a substitute for petrodiesel of self-reliance [6-7]. It is in this contest that identification of fatty acid constituents in glycerides is essential.

Biodiesel usually consists of methyl esters of long chain fatty acids and is made from nontoxic biological resources such as vegetable oils and animal fats by transesterification with methanol in presence of a catalyst [1, 9-10]. Catalysts may be acid, base and enzyme (lipase). Biodiesel has many advantages and it can contribute to both solving global warming and energy problems [1, 11-13]. Hence, non-edible vegetable oils can be used as alternative feedstocks for the production of biodiesel [14-17].

Sapindus mukorossi, Soapnut in English, kekru in Manipuri is a very large tree belonging to the family *Sapindaceae*. They are native to warm temperate to tropical regions in both the Old World and New World. *Sapindus mukorossi requires* a fertile soil and a frost tree climate and it needs a lot of water. It is both deciduous and evergreen species. Its fruits are commonly known as soapberries or soapnuts [18] because the fruits pulp is used to make soap. Soapnuts contains saponins which are a natural surfactant. Saponin is a 100% natural alternative to chemical laundry detergent and cleansers. When in contact with water, it creates mild suds, which is similar to soap. *Sapindus mukorossi* produces prodigious amounts of a saponifying nut that we can use as a grey water safe laundry detergent, dish and hand soap. It has amazing cleaning power.

Soapnuts are being taken into consideration and applied to commercial use in detergents and cosmetics as well as many other products. [19] [20] They have been used traditionally and historically in folk remedies as a mucolytic agent [21], epilepsy [22], emetic [23], treatchlorosis [21], contraceptive [22] and for treatment of excessive

salivation [21]. In Ayurved, *Sapindus mukorossi* have been used in the manufacture of Ayurvedic shampoos and cleansing agent [22], and also used in Ayurvedic medicine as a treatment for eczema, psoriasis and for removing freckles. Soap nuts are allergy-free and hence are good for our skin especially good for babies, eczema and sensitive skins. They are naturally antifungal and antibacterial and very gentle to the skins. They are both Economical and Ecological as compared to other forms of detergents. We can use soapnuts for washing sinks, floors, windows, glasses, shampooing hair, washing hands, cleaning jewellery, pets, carpet, car etc.

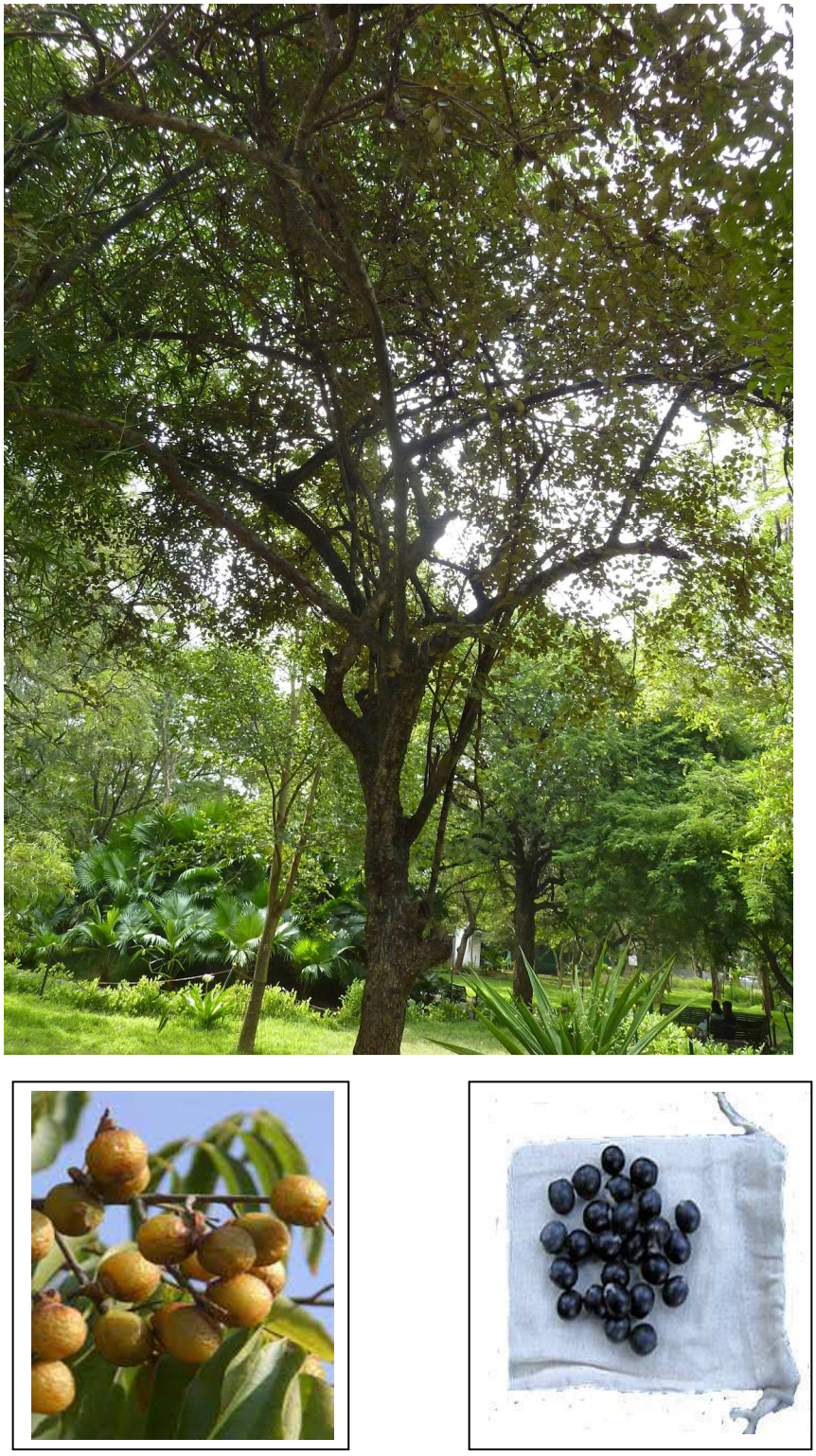

Fig.1. Tree of *Sapindus mukorossi* (Fruit and Seeds)

Sapindus mukorossi (Fig.1) has the leaves which are alternate, 15-40 cm long, pinnate, with 14-30 leaflets and the terminal leaflet is often absent. The flowers form in large panicles, each flower small, creamy white. The fruit is a small leathery shinned drupe 1-2 cm (0.39-0.79 in) in diameter, yellow repining blackish, containing one to three seeds.

Sapindus mukorossi is native to northern India east to the Himalayas including Manipur. Other species of this family are found in different countries like China, southern Asia, India, Florida to Carolina, North America, Hawaii, Mexico, United States, Caribban, island of Hawai, Pakistan, Fiji [18, 23-24], Leenh, American Samoa [18, 20], etc.

MATERIALS AND METHODS

Materials

Sapindus mukorossi seeds were collected from Ukhrul District of Manipur, India during its availability of the season. The seeds were first cleaned and dried in the sunlight for 5-6 days, deshelled and the kernel crushed using a grinder prior to oil extraction. Methanol used was of analytical grade (Mark, Mumbai, India). All other solvents and chemicals used were analytical grade, and they were procured from commercial sources and used as such without further treatment.

Oil Extraction

Oil was extracted from crushed and powdered kernel in petroleum ether (bp 40 - 60 ^{o}C) (10 ml/g) by stirring magnetically at room temperature (22-23 ^{o}C) for 4 hours. The solvent was removed at 15 ^{o}C using a rotary vacuum evaporator (BUCHI Rotavapour R-200) to yield the crude oil. This process was repeated 2-3 times with the seed cake using fresh solvent each time in order to extract most of the oil which was further dried using vacuum pump. The oil was purified by column chromatography over silica gel (60-120 mesh) using a mixture of petroleum ether and ethyl acetate (20:1) as the eluent prior to transesterification done.

Transesterification of seed oil

The purified oil was transesterified to fatty acid methyl esters (FAME) using a catalyst derived from the peels of *Athia* [16]. A mixture of oil in methanol (10 ml/g of oil) and the catalyst (20 wt.% of oil) was stirred vigorously magnetically at room temperature (33 ^{o}C) and the conversion/completion of the reaction was monitored by TLC. After completion of the reaction, the product mixture was extracted with petroleum ether (bp 40-60 ^{o}C). The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum to yield the crude product which was further purified by column chromatography over silica gel using petroleum ether and ethyl acetate (20:1) as the eluent. The product was concentrated and evaporated to dryness on a rotary evaporator which was further dried using vacuum pump to remove the last traces of solvents to yield pure biodiesel (FAME).

Analysis of FAME

The composition of FAME mixtures was estimated using Perkin Elmer Clarus 600 GC-MS. The column used was Elite 5 MS with dimension 30.0 m x 250 mm. The oven temperature was initially held at 140 ^{o}C for 5 min, increased to 240 ^{o}C at 4 ^{o}C/min, and then held for 5 min. The injector, transfer and source temperatures were 250 ^{o}C and 150 ^{o}C respectively. Carrier gas was helium and total scan time 35 min. EI mode of ionization was applied and mass scan was from 20 to 400 Da. For identification of FAME library search was carried out using NIST, NBS and Wiley GC-MS library. Fatty acid profile of biodiesel from *Sapindus mukorossi* seed oil is reported in Table 1. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCI_3$ at 300 and 75 MHz respectively using Bruker Advance III 300 MHz/54 mm NMR spectrometer. IR spectrum was recorded with a Perkin Elmer RX 1 FT-IR spectrometer as a thin film on KBr plate. ^{1}H NMR (300 MHz, $CDCl_3$) : δ 0.86-0.90 (m), 1.25 (s), 1.59-1.64 (m), 2.00-2.02 (m), 2.28-2.35 (m), 3.67 (s), 5.32-5.36 (m). ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.06, 22.63, 24.89, 27.10, 27.15, 29.03, 29.06, 29.09, 29.20, 29.26, 29.31, 29.40, 29.47, 29.54, 29.64, 29.71, 30.87, 31.85, 34.05, 51041, 129.69, 129.93, 174.38. FT-IR (thin film): 737, 880, 1018, 1116, 1171, 1198, 1246, 1362, 1437, 1459, 1508, 1540, 1651, 1742, 2854, 2925, 3006 cm^{-1}.
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RESULTS AND DISCUSSION

Sapindus mukorossi, Kekru in Manipuri, soapnut in English, is a very large soap nut tree growing abundantly in both plain and hill areas in Manipur. The nut has medium hard outer shell and can be easily dehusked before carrying out the estimation of the oil content. Kernel content is moderate (about 20 g kernel in 30 g seed, 40.47 wt.%). Free Fatty acids in oil sample were removed by column chromatography before transesterification. Transesterification of seed oil to FAME was carried out using methanol as the solvent in the presence of a catalyst derived from the peels of *Athia* [25]. The yield of FAME was 91.49 wt.% at room temperature (29 ^{o}C) within 3.5 hours. The transesterified products were purified by column chromatography and analysed.

Fatty acid composition of the FAME prepared from *Sapindus mukorossi* seed oil was determined by GC-MS analysis. The each peak of the gas chromatogram (Fig. 2) was analysed and the fatty acid identified using MS database. Relative percentages of fatty acid esters were calculated from the total peak areas in chromatogram by computerized integrator and results are presented in the Table 1. FAME from *Sapindus mukorossi* consists of 4.78 wt.% of methyl palmitate [C16:0], 58.89 wt.% of methyl oleate [C18:1], 1.78 wt.% of methyl stearate [C18:0], 25.93 wt.% of methyl 11-trans eicosenoate [C18:2], and 8.61 wt.% % of methyl arachidate [C20:0].

Table 1: Fatty acid profile of FAME from *Sapindus mukorossi* seed oil

Retention time (min)	FAME	wt.%
18.16	Methyl palmitate	4.78
22.54	Methyl oleate	58.89
22.89	Methyl stearate	1.78
26.80	Methyl 11-*trans* eicosenoate	25.93
27.28	Methyl arachidate	8.61

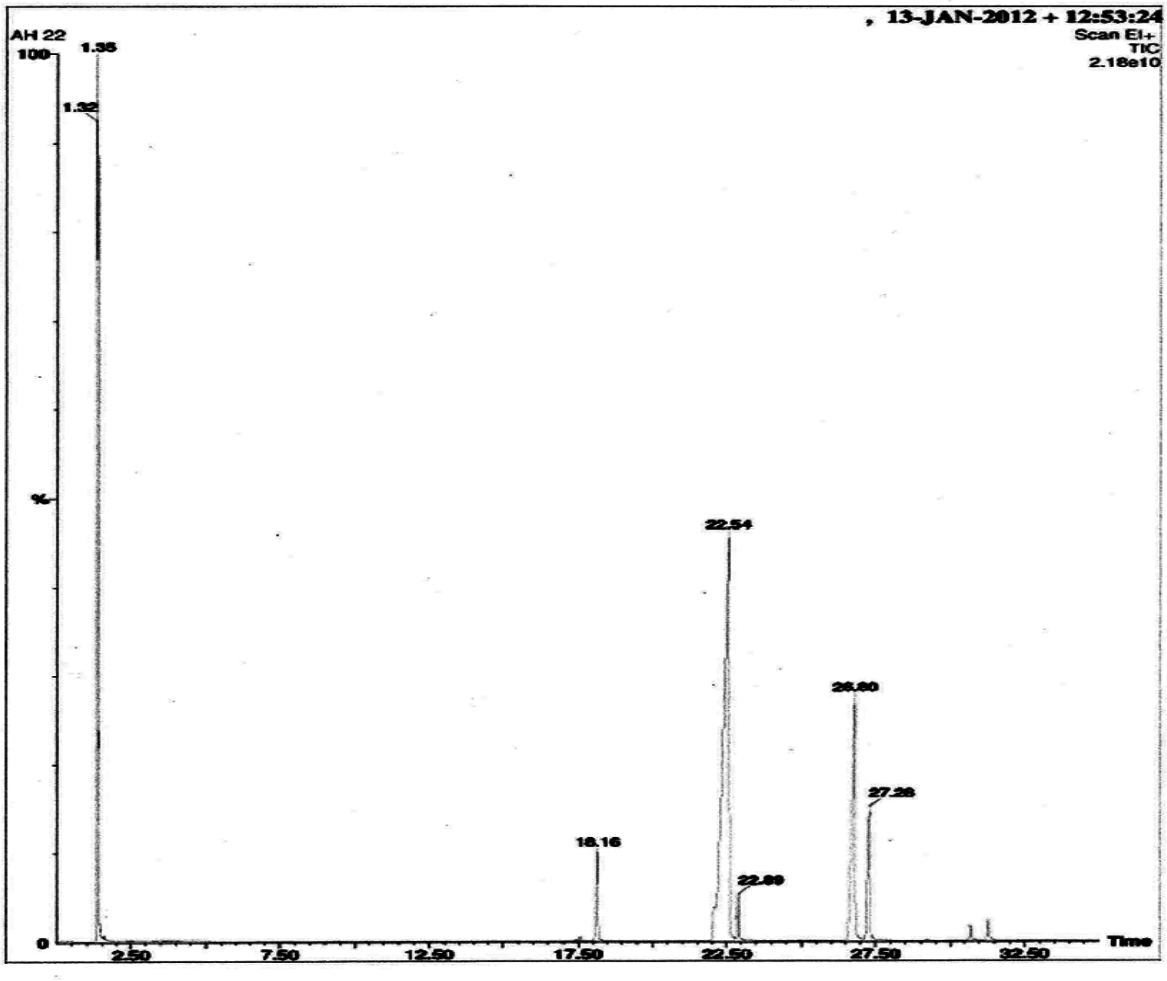

Fig.2. Gas Chromatogram of FAME from *Sapindus mukorossi* seed oil

Table 2 : Molecular ion and base peaks of FAME from seed oil from *Sapindus mukorossi* seed oil

FAME	Molecular ion peaks (m/z)	Bass peak (m/z)
Methyl palmitate	270	74
Methyl oleate	296	55
Methyl stearate	298	55
Methyl 11-*trans* eicosenoate	324	74
Methyl arachidate	326	74

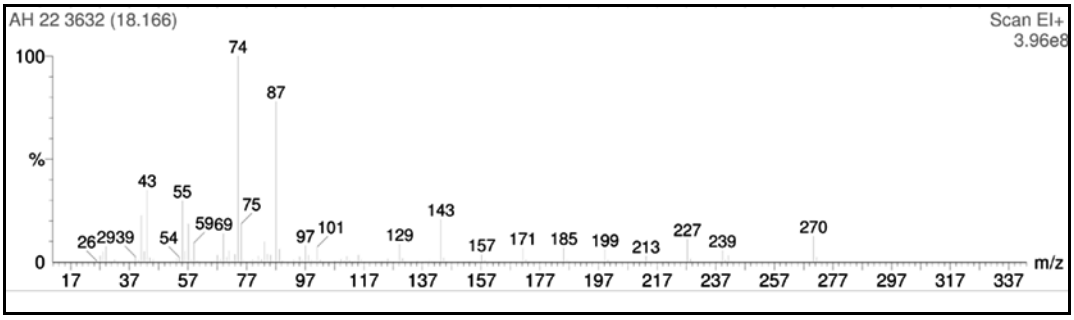

Fig. 3a. Mass spectrum of methyl palmitate

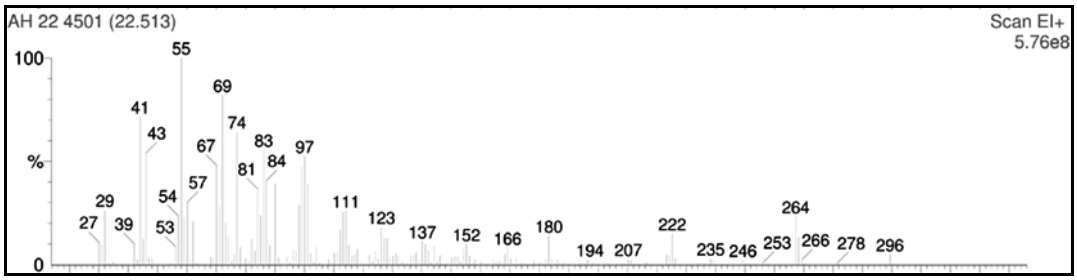

Fig. 3b. Mass spectrum of methyl oleate

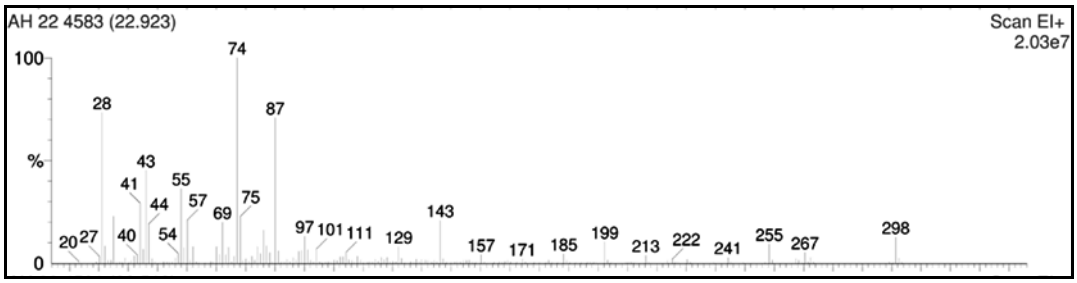

Fig. 3c. Mass spectrum of methyl stearate

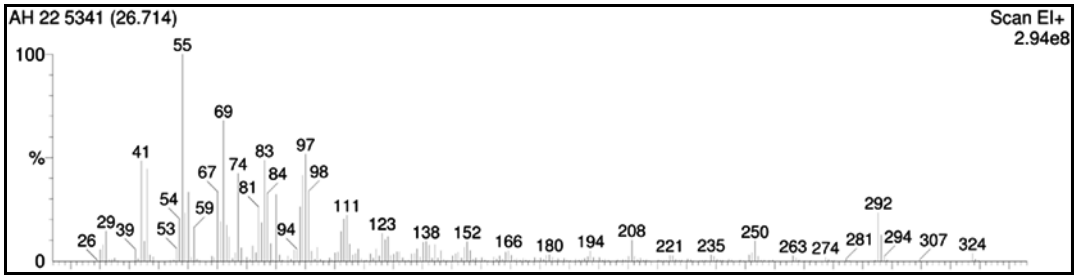

Fig. 3d. Mass spectrum of methyl 11-trans eicosenoate

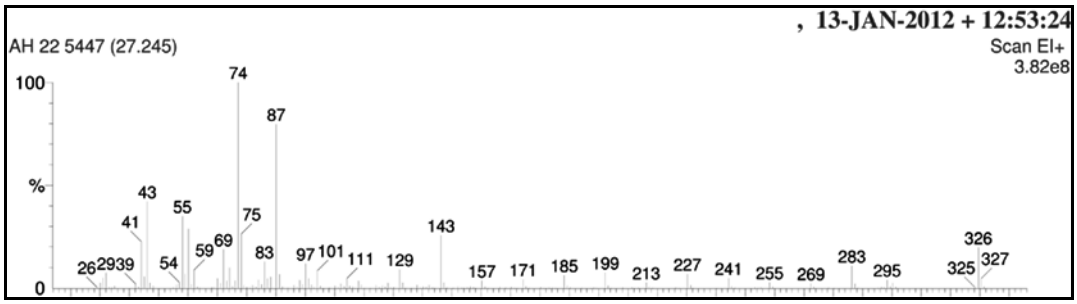

Fig. 3e. Mass spectrum of methyl arachidate

The mass spectra of biodiesel from *Sapindus mukorossi* seed oil are shown in Figs. 3a to 3e. Molecular ion peaks and base peaks of the FAME are given in Table 2 and they are in the expected values. The molecular ion peaks of methyl palmitate, methyl oleate, methyl stearate, methyl 11-*trans*-eicosenoate and methyl arachidate were observed at 270, 296, 298, 324 and 326 respectively as was expected.

The ^{1}H NMR spectrum of FAME from *Sapindus mukorossi* seed oil is shown in Fig. 4. The multiplet at δ 5.32-5.36 ppm represents the olefinic protons (-CH=CH-). A singlet signal at δ 3.67 ppm is representing methoxy protons of the ester functionality of the biodiesel. The signal at about δ 2.8 ppm indicates the presence of bis-allylic protons (C=C- CH_2C=C-) of the unsaturated fatty acid chain. The bis-allylic proton signal of polyunsaturated fatty acid (Linoleic acid) generally appears at around δ 2.8 ppm. The multiplet at δ 2.28-2.33 ppm may be due to the methylene protons close to the ester group (-CH_2-CO_2 Me). The α-methylene protons to double fond (-CH_2-C=C-) is seen as a multiplet at δ 2.00-2.02 ppm. The β- methylene protons to ester (-CH_2C-CO_2Me) also appear as a mulltiplet at δ 1.59-1.64 ppm. The singlet signals at 1.25 and 1.30 ppm are due to the protons of backbone methylenes of the long fatty acid chain. The terminal methyl protons (C-CH_3) at δ 0.86-0.90 ppm appears as a multiplet.

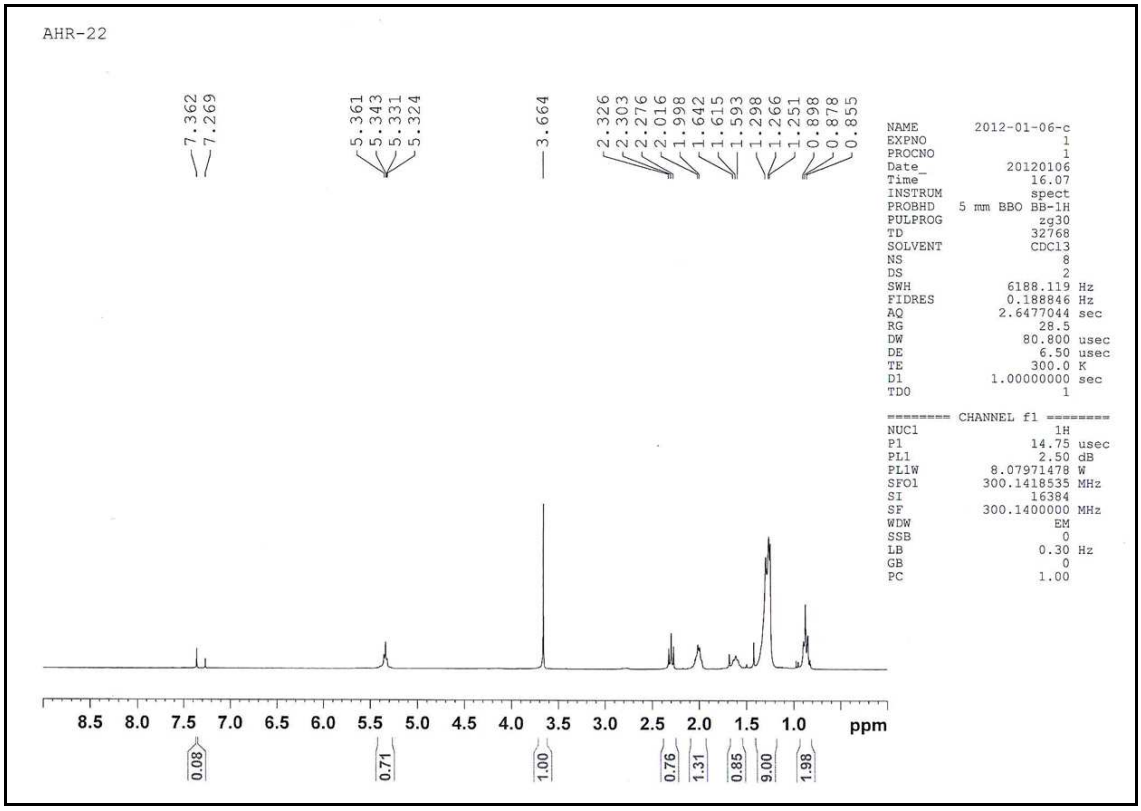

Fig.4. ^{1}H NMR spectrum of FAME from *Sapindus mukorossi* seed oil

The ^{13}C NMR spectrum of biodiesel from *Sapindus mukorossi* seed oil is shown in Fig. 5. The signal at δ 174.29 ppm represents the carbonyl carbon of the ester moiety and the olefinic carbons appear at δ 128.32, 129.74, 129.40, 129.92 and 129.99 ppm. The methylene and methyl carbons of fatty acid moiety appear in the range from δ 14.3 to 34.65 ppm.

The IR Spectrum of FAME from *Sapindus mukorossi* seed oil (Fig. 6) shows a sharp signal at 1743 cm^{-1} which is indicative of strong adsorption by ester carbonyl stretching frequency. The weak signal at 1655 cm^{-1} may be due to C=C stretching frequency. Sharp and strong signals at 2855 and 2926 cm^{-1} are due to C-H stretching frequencies. The absorbance at 3009 cm^{-1} indicates the =C-H stretching vibrations. The bands at 1018, 1170, 1198 and 1248 cm^{-1} are expected for C-O-C stretching vibrations. The observation of an adsorption peak at 722 cm^{-1} suggestes the CH_2 rocking.

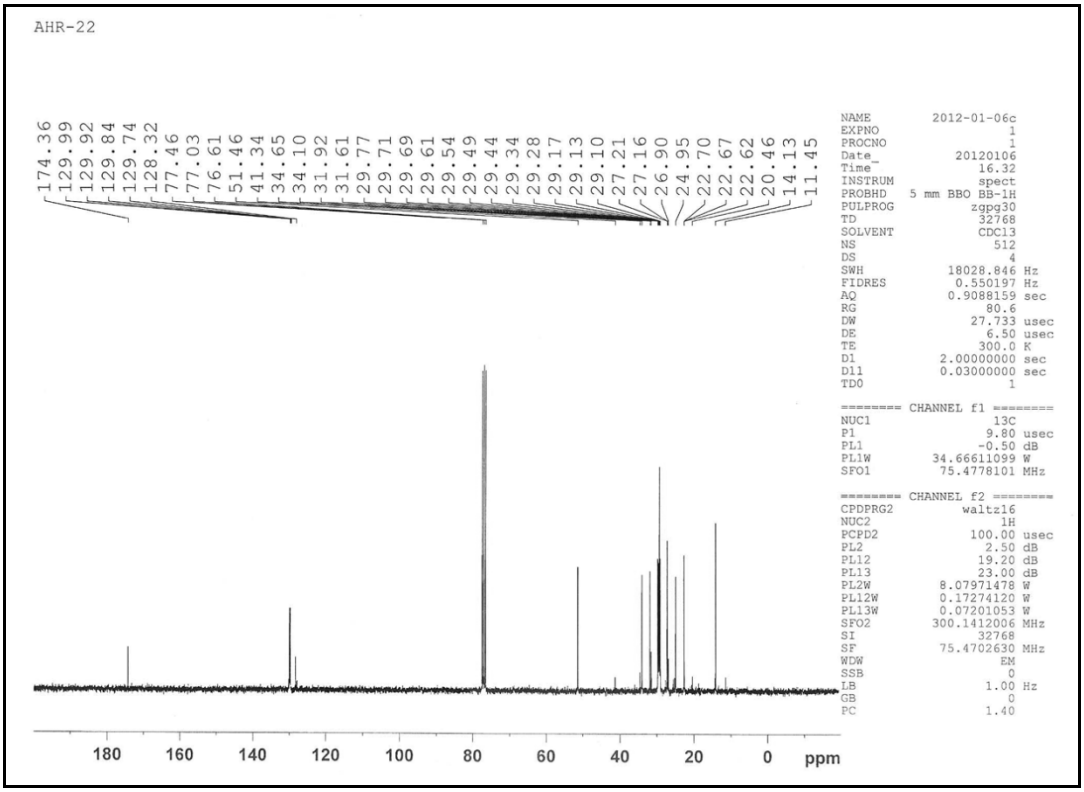

Fig.5. ^{13}C NMR spectrum of FAME from *Sapindus mukorossi* seed oil

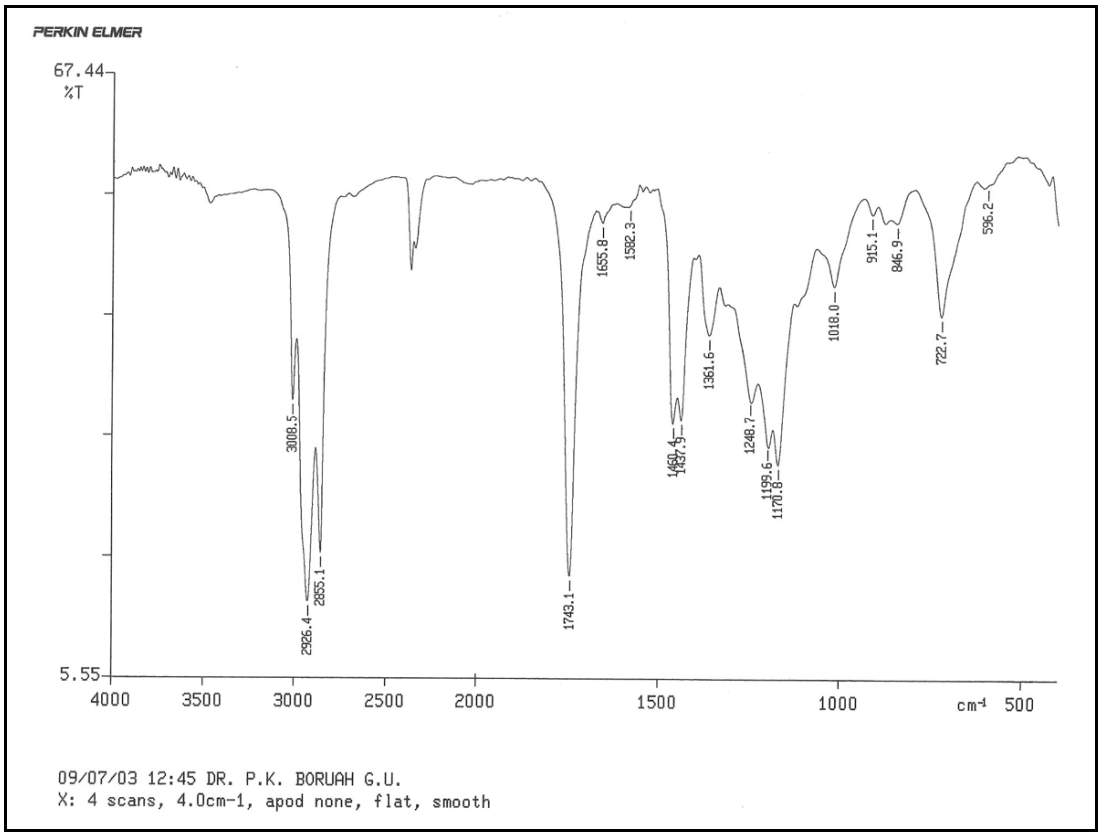

Fig.6. IR spectrum of FAME from *Sapindus mukorossi* seed oil

CONCLUSION

The biodiesel from *Sapindus mukorossi* seed oil, after extraction and purification by column chromatography, was prepared by heterogeneous transesterification process and analyzed for its fatty acid methyl esters composition using IR, NMR and GC-MS. This study found that FAME from *Sapindus mukorossi* seed oil consists of 4.78 wt.% of methyl palmitate (C16:0), 58.89 wt.% of methyl oleate (C18:1), 1.78 wt.% of methyl stearate (C18:0), 25.93 wt.% of methyl 11-*trans*-eicosenoate (C18:2) and 8.61 wt% of methyl arachidate (C20:0).

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