Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Pelagia Research Library

Advances in Applied Science Research, 2014, 5(3):404-410

Pelagia Research Library

ISSN: 0976-8610
CODEN (USA): AASRFC

Fatty acid composition of *Paederia foetida* seed oil

Md. Abdul Halim Shah, Kajal Dutta and Dibakar Chandra Deka*

Department of Chemistry, Gauhati University, Guwahati, Assam, India

---

ABSTRACT

Fatty acid methyl ester (FAME) composition of Paederia foetida seed oil was determined by IR, NMR and GC-MS analysis. FAME from Paederia foetida consists of 15.35 wt.% of methyl palmitate (C16:0), 47.70 wt.% of methyl linoleate (C18:2), 30.54 wt.% of methyl oleate (18:1) and 6.40 wt.% of methyl stearate (C18:0).

Key words: Stinkvine, *Paederia foetida*, transesterification, non-edible vegetable Oil, *Athia*, Biodiesel.

INTRODUCTION

Oils of many seeds of Manipur which are non-edible find very limited commercial use and plants producing such oils are slowly disappearing because such plants are not considered important by farmers, governments, any public and private sectors etc. Consequently plant diversity is dwindling. Use of such oil as the feedstock for biodiesel industries will spare edible oils for use in other industries of edible products [1]. It needs no mention that biodiesel is a renewable form of energy and our country desperately needs it as a substitute for petrodiesel of self-reliance [2-4]. It is in this context that identification of fatty acid constituents in glycerides is essential. Developed countries like Germany, Canada, USA, UK have already started using biodiesel blended with petrodiesel.

Biodiesel, an excellent substitute fuel for diesel engines, consists of methyl esters of long chain fatty acids and is made from nontoxic, biological resources such as vegetable oils, animal fats or even used edible oils by transesterification with methanol in presence of a catalyst [1, 5, 6]. Biodiesel is a renewable, biodegradable and nontoxic fuel and can contribute to both solving energy problems and global warming [1, 7-9]. Therefore, alternative feedstocks like non-edible vegetable oils need to be explored for the production of biodiesel cost-effective [10-13].

Proper utilization of the available non-edible oils will open up enormous scope for rural development in terms of employment opportunity for youth and infrastructure development in NE region. The by-product of oil extraction from these seeds and biodiesel production process could also be utilized for organic fertizer, biogas production and soap making.

Paederia foetida, Oinam in Manipuri is a perennial climbing shrub belonging to the family *Rabiaceae* [21]. Introduced as a potential fibre plant in Florida by the U.S. Department of Agriculture prior to 1867 [22], *Paederia foetida* has traditionally been used for medicinal purposes [21]. Methyl mercaptan was reported to be responsible for the fetid odor of the plant [23]. It is used to treat enteromegaly, enteritis, flatulence, gastromegaly, rheumatism, rhinosis, toothache, stomachache and sore in folk medicine [24]. *Paederia foetida* is also a popular shrub used as a remedy for diarrhea and dysentery in Bangladesh [25]. Its stems & leaves, after crushing are applied on the broken part of hands or legs for sucking damaged blood as well as quick healing in Manipur. *Paederia foetida* is evergreen fast growing plant which damages other plants by making blanket over them [22, 26]. It can grow in wet as well as

dry lands. It grows in grassy hillsides, secondary forests, open places in primary forests, river banks, canal banks, waste ground and roadsides.[22]

P. foetida is native to Bangladesh and southern Bhutan; Cambodia; Taiwan and China (in Hong Kong and Macau, and the provinces of Anhui, Fujian, Gansu, Guangdong, Guangxi, Hainan, Henan, Hubei, Hunan, Jiangsu, Jiangxi, Shaanxi, Shandong, Shanxi, Sichuan, Xizang, Yunnan, Zhejiang); India (in Andhra Pradesh, Warangal, Arunachal Pradesh, Assam, Manipur, Meghalaya, Mizoram, Nagaland, Sikkim, in the northern part of West Bengal, and the Andaman and Nicobar islands); Indonesia; Japan (in Honshu, Kyushu, Shikoku prefectures, as well as in the Ryukyu Islands); Laos; Malaysia; Myanmar; Nepal; the Philippines; Singapore; South Korea ; Thailand; and Vietnam [27]

MATERIALS AND METHODS

Materials

Paederia foetida seeds were collected from Imphal, East 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 of 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 45 ^{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 transesterificaion done.

Transesterification of seed oil

The purified oil was transesterifed 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/the completion of the reaction was monitored by TLC. After completion of the reaction, the product mixture was extracted with petroleum ether. (by 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 were 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 °C for 5 min, increased to 240 °C at 4 °C/min, and then held for 5 min. The injector, transfer and source temperatures were 250 °C, 200 °C and 150 °C respectively. Carrier gas was helium and total scan time 35 min. Gas Chromatogram of the biodiesel is shown in Fig.1. 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 *Paederia Foetida* seed oil is reported in Table :1. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz respectively using Bruker Advance III 300 MHz/54 mm NMR spectrometer. IR spectrum was recorded .with a Perkin Elmer RX1 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), 1.30 (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}.

RESULTS AND DISCUSSION

Paederia foetida, Oinam in Manipuri, is a fast growing plant having wide-ranging adaptability to different light, soil and salt conditions. It is popular for its stems and leaves which are used in traditional medicine. Its seeds have soft outer shells and hence pose no problem to dehusk before carrying out oil extraction. Seeds with soft shell contain little kernel (about 10 g kernel from 45 g seed, 22.2 wt.%) but the kernel is rich in oil (22.26 wt.%). Free fatty acid from oil sample was removed by column chromatography before transesterification. Transterification of seed oil to FAME was carried out using methanol as the solvent in presence of a catalyst derived from the peels of Athia [11]. The yield of FAME from *Paederia foetida* seed oil was 91.71 wt % at room temperature (32 ^{o}C) within 4 hours.

The transesterified products were purified by column chromatography and analysed. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz respectively using Bruker Advance III 300 MHz/ 54 mm NMR spectrometer. IR spectra were recorded with a Perkin Elmer RXIFT- IR spectrometer as a thin film on KBr plate. Composition of a FAME mixture was estimated using Perkin Elmer Clarus 600 GC-MS.

Falty acid profile of the FAME prepared from *Paederia foetida*, seed oil was determined by GC-MS analysis. The individual peaks of the gas chromatogram (Fig. 1) were analysed and the fatty acids were identified using MS database. Relative percentage of fatty acid esters was calculated from the total ion chromatography by computerized integrator and results are presented in the Table 1. FAME from *Paederia foetida* consists of 15.35 wt.% of methyl palmitate [C16:0], 47.70 wt.% of methyl linoleate [C18:2] , 30.54 wt.% of methyl oleate [C18:1] and 6.40 wt.% of methyl stearate [C18:0].

Table 1. Fatty acid profile of FAME from *Paederia foetida* seed oil

Retention time (min)	FAME	wt. %
18.55	Methyl Palmitate	15.35
22.78	Methyl Linoleate	47.70
22.94	Methyl Oleate	30.54
23.30	Methyl Stearate	6.40

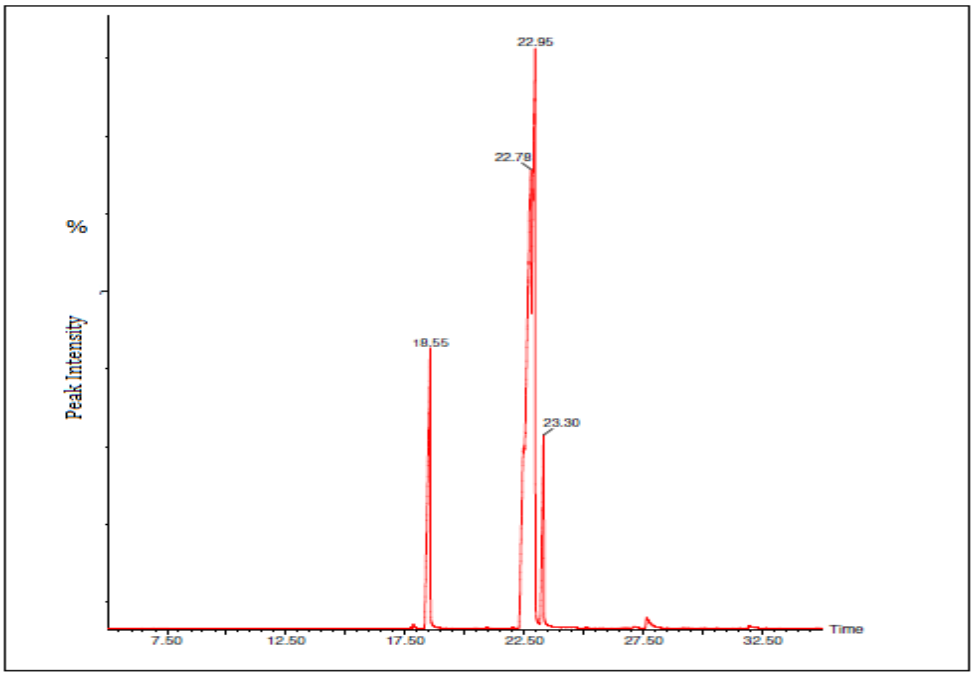

Fig. 1. Gas Chromatogram of FAME from *Paederia foetida* seed oil

Table 2. Molecular ion and base peeks of FAME from *Paederia foetida* seed oil

FAME	Molecular ion peak (m/z	Base peak (m/z)
Methyl Palmitate	270	74
Methyl Linoleate	294	55
Methyl Oleate	296	55
Methyl Stearate	298	74

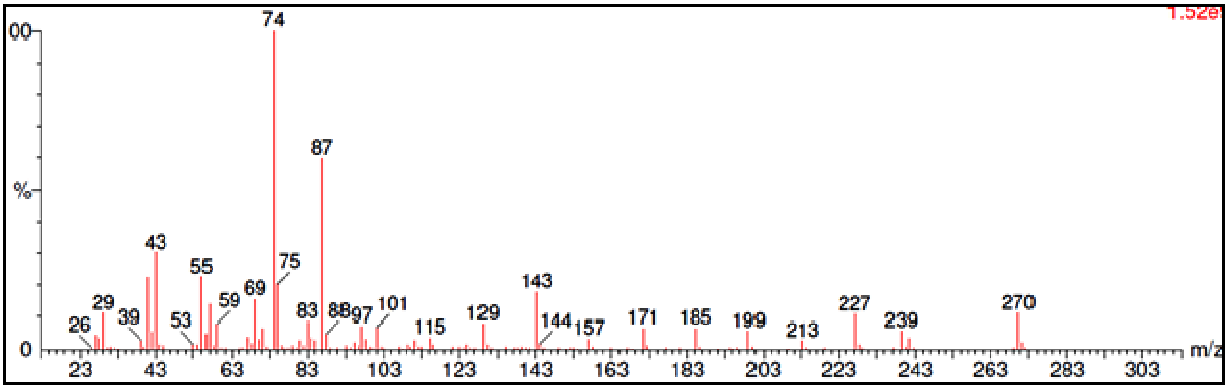

Fig. 2a. Mass spectrum of methyl palmitate

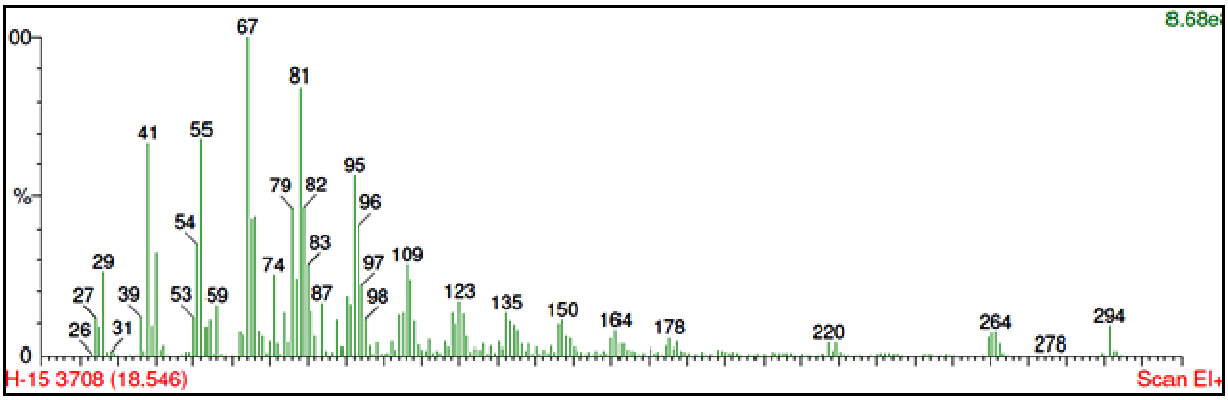

Fig. 2b. Mass spectrum of methyl linoleate

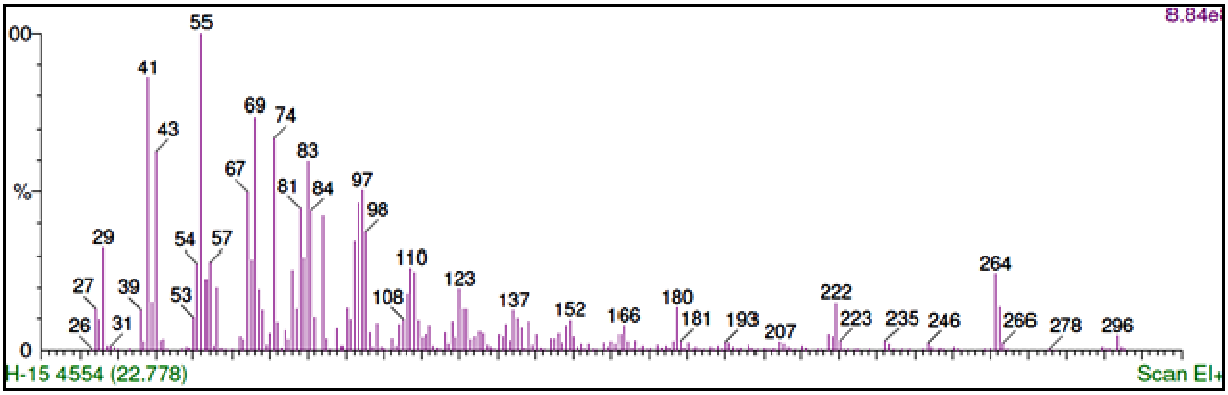

Fig. 2c. Mass spectrum of methyl oleate

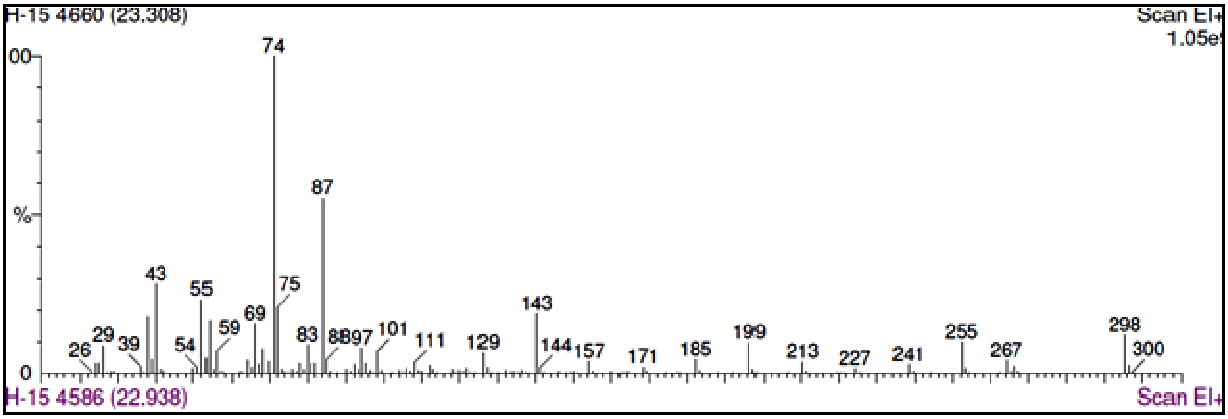

Fig. 2d. Mass spectrum of methyl stearate

The mass spectra of biodiesel from *Paederia foetida* seed oil are shown in Figs. 2a to 2d. Molecular ion peaks and base peaks of the FAMEs are shown in Table 2 and they are in the expected values. The molecular ion peaks of methyl palmitate, methyl oleate, methyl stearate, and methyl linoleate were observed at 270, 296, 298 and the 294 respectively as was expected.

The ^{1}H NMR spectrum of FAME from *Paederia foetida* seed oil is shown in Fig. 3. The multiplet at δ 5.28 -5.38 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 in the ^{1}H NMR spectrum of biodiesel from *Paederia foetida* seed oil 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 around δ 2.8 ppm . The multiplet at δ 2.28-2.35 ppm is due to the methylene protons next to ester (-CH_2-CO_2Me). The α-methylene protons to double bond (-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 multiplet at δ 1.59-1.64 ppm. The singlet signals at δ 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 appear as a multiplet.

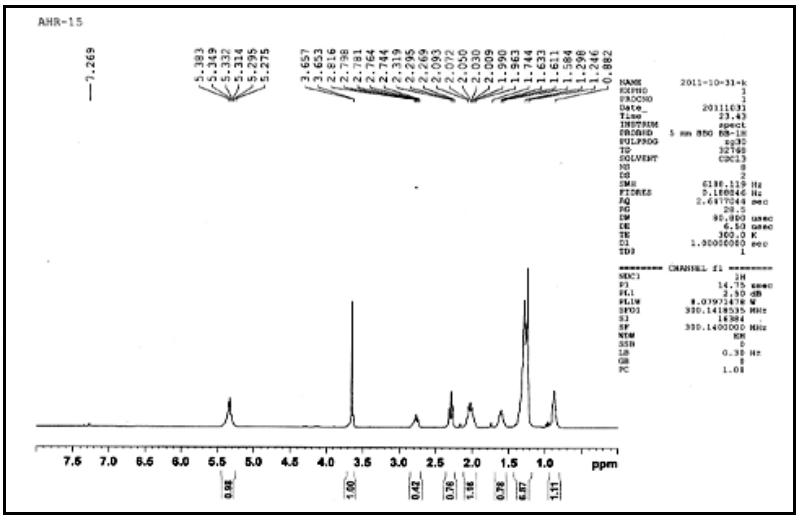

Fig. 3. ^{1}H NMR spectrum of FAME from *Paederia foetida* seed oil

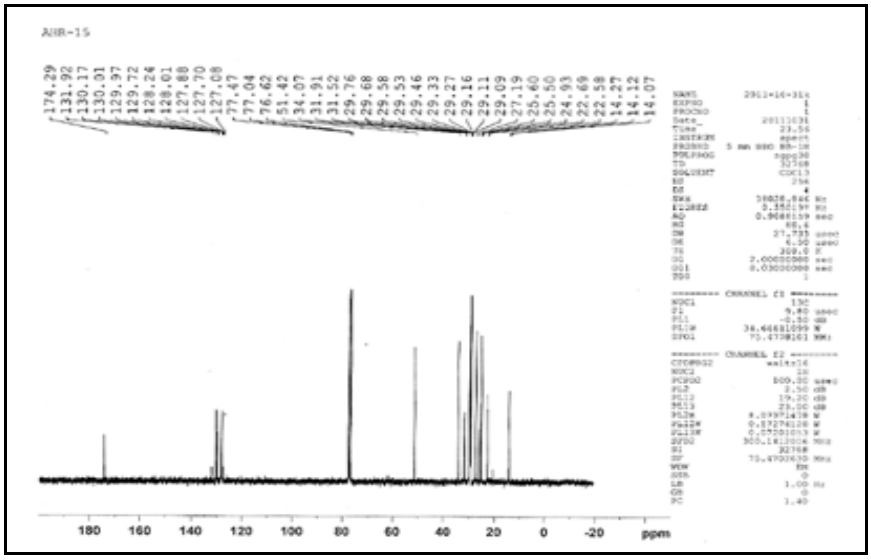

Fig. 4. ^{13}C NMR spectrum of FAME from *Paederia foetida* seed oil

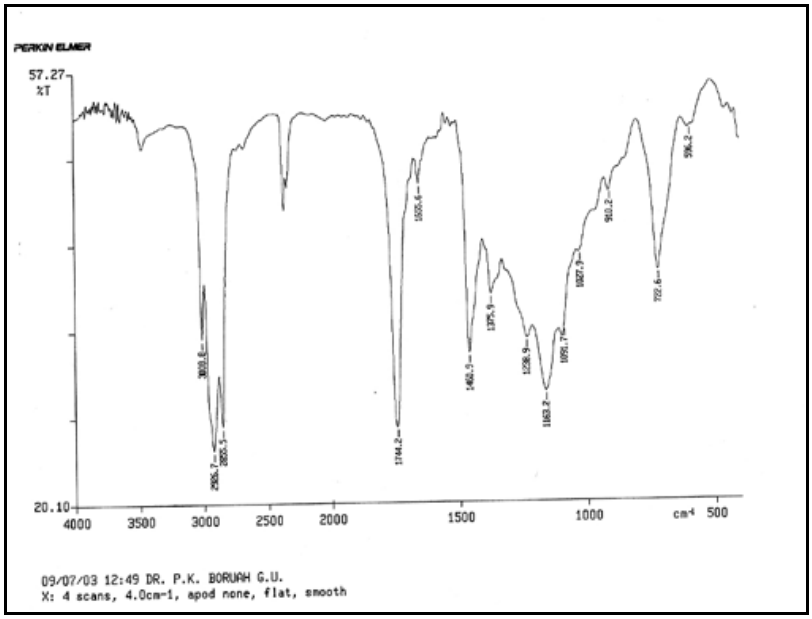

Fig. 5. IR spectrum of FAME from *Paederia foetida* seed oil

The ^{13}C NMR spectrum of biodiesel from *Paederia foetida* seed oil is shown in Fig. 4. The signal at δ 174.29 ppm represents the carbonyl carbon of the ester molecules and the olefinic carbons appear at δ 127.08, 127.70, 127.88, 128.01, 128.24, 129.72, 129.97, 130.01, 130.17, 131.92 ppm. The signal at δ 51.42 ppm in the ^{13}C NMR spectrum of biodiesel is due to methoxy carbons of esters. The methylene and methyl carbons of fatty acid moiety appear in the range from δ 14.07 to 34.05 ppm.

In IR spectrum of FAME from *Paederia foetida* seed oil (Fig. 5), a sharp signal at 1743 cm^{-1} is indicative of strong absorption by ester carbonyl stretching frequency. The weak signal at 1652 cm^{-1} may due to C=C stretching frequency. Strong and sharp signals at 2853 and 2924 cm^{-1} are due to C-H stretching frequencies. The absorbance at 3005 cm^{-1} indicates the =C-H stretching frequency. The bands at 1115, 1172, 1197 and 1246 cm^{-1} are expected for C-O-C stretching vibrations. The observation of an absorption peak at 736 cm^{-1} suggests the CH_2 rocking.

CONCLUSION

In this study, *Paederia foetida* seed oil was analyzed for its fatty acid methyl ester composition using IR, NMR and GC-MS. The study found that FAME from *Paederia foetida* consists of 15.35 wt.% of methyl palmitate (C16:0), 47.70 wt.% of methyl linoleate (C18:2), 30.54 wt.% of methyl oleate (18:1) and 6.40 wt.% of methyl stearate (C18:0).

REFERENCES

[1] Leung DYC, Wu X, Leung MKI, *Appl. Energy*, **2010**, 87, 1083.
[2] Diwani GIE, Rafei SAE, Hawash SI, Enin SAE, *Der Chemica Sinica*, **2011**, 2, 12.
[3] Aliyu A, Godwin O, Hamza A, *Der Chemica Sinica*, **2011**, 2, 286.
[4] Rejila S, Vijayakumar N, Jayakumar M, *Asian J. Plant Sci. Res*., **2012**, 2, 123.
[5] Moser BR, Knothe G, Vaughn SF, Isbell TA, *Energy Fuels*, **2009**, 23, 4149.
[6] Zabeti M, Ashri WM, Daud W, Aroua MK, *Fuel Process. Technol*., **2009**, 90, 770.
[7] Satyarthi JK, Srinivas D, Ratnasamy P, *Energy Fuels*, **2009**, 23, 2273.
[8] Knothe G, *Energy Fuels*, **2010**, 24, 2098.
[9] Li E, Rudolph V, *Energy Fuels*, **2008**, 22, 145.
[10] Srivastava A, Prasad R, *Renew. Sustain. Energ. Rev*., **2000**, 4, 111.
[11] Zhang Y, Dube MA, McLean DD, M Kates, *Bioresour. Technol*., **2003**, 89, 1.
[12] Aliyu A, Lomsahaka E, Hamza A, *Adv. Appl. Sci. Res*., **2012**, 3, 615.
[13] Aliyu A, Adoyi O, Hamza A, *Adv. Appl. Sci. Res*., **2012**, 3, 611.
[14] Okoroigwe E, Li Z, Stuecken T, Saffron C, Onyegegbu S, *J. Appl. Sci*., **2012**, 12, 369.
[15] Choudhury PP, *Agric. Sci. Res. J*., **2012**, 2, 131.
[16] Deka DC, Basumatary S, *Biomass Bioenergy*, **2011**, 35, 1797.
[17] Chien YC, Lu M, Chai M, Boreo FJ, *Energy Fuels*, **2009**, 23, 202.
[18] Tariq M, Ali S, Ahmad F, Ahmad M, Zafar M, Khalid N, Khan MA, *Fuel Process. Technol*., **2011**, 92, 336.
[19] Moser BR, Vaughn SF, *Biomass Bioenergy*, **2010**, 34, 550.
[20] Knothe G, *Energy Fuels*, **2010**, 24, 2098.
[21] Uddin B, Nahar T, Basunia MA, Hossain S, *Advances in Biologial Research*, **2011**, 5(5) : 267
[22] Pemberton RW, Pratt PD, *U.S. Department of Agriculture, Agricultural Research Service, Invasive Plant Research Laboratory, Fort Landerdale, Florida, U.S.A.*
[23] Bose PK, Banerjee AK, Ghosh C, *Chemical investigation of P.F.L. Trans Bose' Reseach Institute*, **1953**, 1977.
[24] Johnson T, *CRC Ethnobotany Desk Reference CRC Press*, **1999**, PP : 580
[25]Ghani A, *Asiatic Society Bangladesh*, **1998**, PP : 253-254
[26]Starr F, Starr K, Loope L, *United States Geological Survey –Biological Resources Division Haleakala Field Station, Mani, Hawai'i*, March-**2003**.
[27]"*Peaderia foetida information from NPGS/GRIN*". *Taxonomy for Plants*. National Germplasm Resources Laboratory, Beltsville, Maryland: *USDA, ARS, National Genetic Resources Program*. Retrieved August 9, **2010**.