Comparative Study on UV Spectra of Synthetic and Natural 1-Phenylnaphthalene Lignans

[1]Tanishq M Chaudhari, [2]Sujata S. Deo, [3]Farhin Inam

[1,2,3]Priyadarshini J.L. College of Engineering, Nagpur[1], Institute Of Science, Nagpur
Email:tanishqmc@rediffmail.com, sujatadeo24@gmail.com,Inamfarhin@gmail.com

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Abstract-Lignans belong to the largest group of secondary metabolites produced by the plants that have found many applications in the fields of medicine, pharmacy and biology. In the last few years, much interest has been shown on 1-Phenylnaphthalene lignans for medicinal use as antioxidant, anticancer, anti-virus, anti-inflammatory, wound healing, and antibacterial agents. Analytical techniques are one of the promising and efficient methods with high sensitivity and reproducibility for studying 1-Phenylnaphthalene and Pericarbonyl lactone lignans. In our present study a simple, precise UV-Visible Spectroscopic analysis has been carried out for the estimation and comparison of synthetic and natural 1-Phenylnaphthalene lignans. The molar absorptivity (log ε) of the synthetic compounds were found to be in alignment with the molar absorptivity of the plant extracts of Ruta graveolens and Jatropha gossypifolia denoting lignans with similar 1-Phenylnaphthalene systems.

Index Terms— UV Spectra, Lignan, Ruta graveolens, Jatropha gossypifolia, secondary metabolites.

I. INTRODUCTION

Lignans represent a characteristic and important group of biologically active polyphenolic metabolites, derived from two phenylpropanoid units [1].They are major biologically active components of human diet, spices, aromas, wines, beer, essential oils, propolis, and traditional medicine [2].They appear to function primarily in defense against predators and pathogens such as virus, mycoplasma, bacteria, and fungi. They also protect plants against herbivores both insects and mammals; against plant competitors and abiotic stresses like UV light, ozone, and herbicides. They are of big importance for adaptation of plants to continuously changing environmental conditions, they provide reproductive advantages as attractants of pollinators and seed dispersers, they serve as signaling molecules and hormones and they act to create competitive advantage by poisoning of rival species [3].

There is increasing interest from drug companies and institutions devoted to the search for natural and synthetic 1-Phenylnaphthalene lignans for medicinal use as anti-inflammatory [4,5], antibacterial [6,7], antioxidant[8,9], anticancer [10,11], Immuno modulation [12,13] CNS depressants [14,15]etc. Three Phenylnaphthalene lignan derivatives have been synthesized in the laboratory; whereas the study of natural Phenylnaphthalene lignans was carried out by choosing two medicinal plants - Ruta graveolens and Jatropha gossypifolia consisting of lignans showing structural similarity with the synthetic compounds. From the phytochemical studies on Ruta graveolens [16,17] and Jatropha gossypifolia [18,19], it was reported that 1-Phenylnaphthalide lignan - Helioxanthin was present in methanolic extract of Ruta graveolens and lignan Arylnaphthalene in petroleum ether extract of Jatropha gossypifolia.

II. MATERIALS AND METHODS

A. Plant Material

Aerial parts of Ruta graveolens (L) and Jatropha gossypifolia (L) (including branches, leaves, flowers and fruits) were purchased from the local market of herbs and spices in India. Reference specimen has been deposited in the Herbarium of the Department of Botany, RTMNU, Nagpur under the number 9605 & 9606 respectively.

B. Extraction Methodology

Collected plant materials were dried in an oven (35^{o}C) and powdered separately with mechanical blender. The plant material of Ruta graveolens was defatted with petroleum ether (60-80^{o}C) and extracted with methanol for 24 hours in a soxhlet device; whereas Jatropha gossypifolia (about 500g) was exhaustively extracted with petroleum ether for about 30 – 35 complete cycles. The resulting methanolic extract (ME) of Ruta graveolens and petroleum ether extract (PE) of Jatropha gossypifolia were dried in vacuum and refrigerated. The ME and PE were used for the experimental study.

C. Synthetic 1- Phenylnaphthalene derivatives

Aromatic aldehydes were condensed with β-benzoyl propionic acid to give corresponding α-arylidine-γ-phenyl-Δ,β,γ-butenolides via Perkin condensation[20]. The butenolides were cleaved with alcoholic sodium carbonate to afford α-arylidine-β-benzoyl propionic acid and its various derivatives followed by cyclization reactions [21], which ultimately leads to1-Phenylnaphthalene and Pericarbonyl lactone lignans [22,23]. All of the structures were characterized by their UV, ^{1}HNMR and IR.

D. UV-Visible Spectroscopy

UV-visible spectra was recorded on UV-Visible spectrophotometer1700S, Shimatzu in a scanning range of 200-400 nm UV and 200-800 nm UV-visible. Light in the near-ultraviolet (UV) and visible (VIS) range of the electromagnetic spectrum has an energy of about 150–400 kJ mol^{-1}. The energy of the light is used to promote electrons from the ground state to an excited state. A spectrum is obtained when the absorption of light is measured as a function of its frequency or wavelength [24].

The Beer-Lambert Law is the principle behind absorbance spectroscopy:

A = €bc

A is absorbance (unitless, usually seen as arbitrary units), ε is the molar absorptivity of the compound or molecule in solution (M-1cm-1), b is the path length of the cuvette or sample holder (usually 1 cm), and c is the concentration of the solution (M).

D. Preparation of sample solutions of synthetic and natural 1-Phenylnaphthalene compounds:

For UV-visible spectral analysis, the sample solutions of synthetic 1-Phenylnaphthalene compounds and Jatropha gossypifolia (ME) were prepared in methanol while that of Ruta graveolens (PE) were prepared in petroleum ether at a concentration of 20µg/ml.

III.RESULTS AND DISCUSSION

Spectrophotometric study on both the plants and synthetic compounds (1-Phenylnaphthalene systems) predict that the molar absorptivity or extinction coefficient (log ε) of the synthetic compounds were in alignment with the molar absorptivity of the lignan containing plant extracts of Ruta graveolens and Jatropha gossypifolia.

Table 1. Uv-Visible spectrophotometry of synthetic compounds-1-phenylnaphthoic acids

Sr. No.	**1-Phenylnaphthoic acid**	**Formula**	**UV λ max nm (log ε)**
1	a- $R_1 = R_2 = OCH_3$, $R_3 = H$	$C_{19}H_{16}O_4$	235 (4.21) ,282 (4.08)
2	b- $R_1 = R_2 = O\text{-}CH_2\text{-}O$, R_3=H	$C_{19}H_{12}O_4$	210 (4.66), 250 (4.74) ,406 (4.77)
3	c- $R_1 = OCH_3$, $R_2 = OH$, $R_3 = H$	$C_{18}H_{14}O_4$	252 (4.80) , 282 (3.98)

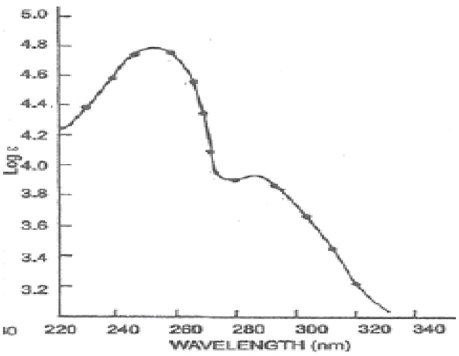


Fig 1.1-Phenyl-6, 7-dimethoxy naphthalene-3-carboxylic acid

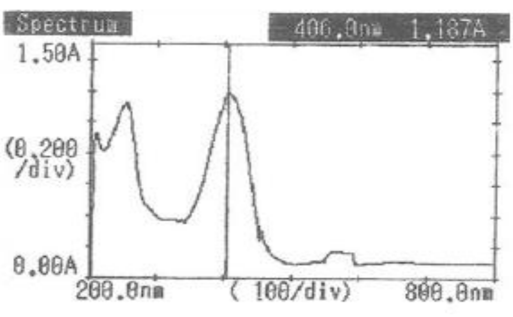


Fig 2.1-Phenyl-6, 7- methylenedioxy naphthalene-3-carboxylic acid

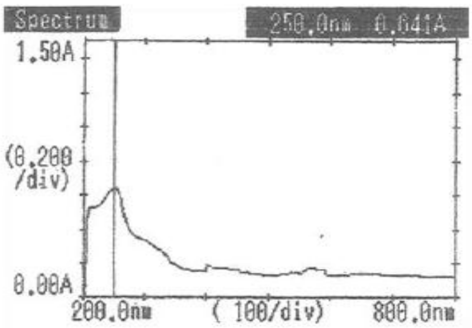


Fig 3.1-Phenyl-6-methoxy-7-hydroxy-naphthalene-3 carboxylic acid

Table 2 Uv-Visible spectrophotometry of synthetic compounds-1-Phenylnaphthalene lactones

Sr No.	1-Phenylnaphthalene lactone	Formula	UV λ max nm (log ε)
1	d - $R_1 = OCH_3$, $R_2 = OH$, $R_3 = H$	$C_{20}H_{16}O_4$	256 (4.60), 312 (4.06)
2	e - $R_1 = R_2 = R_3 = OCH_3$	$C_{21}H_{19}O_5$	248 (4.21)

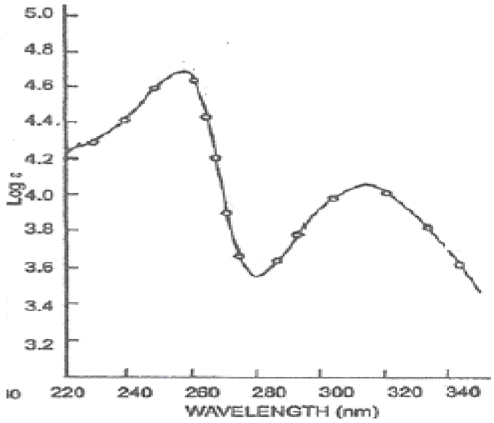


Fig 4.1-Phenyl- 6-methoxy -7-hydroxy naphthalene lactone

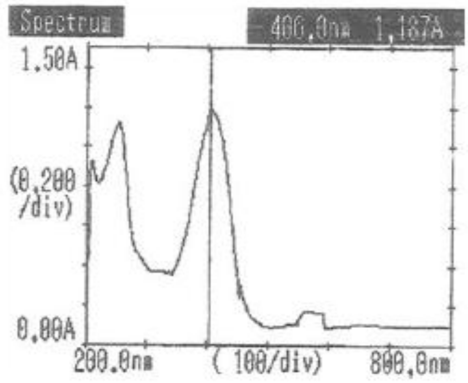


Fig 5. 1-Phenyl-6, 7, 8-trimethoxy naphthalene lactone

Table 3 Uv-Visible spectrophotometry of synthetic compounds-1-Phenylnaphthoates

Sr No.	1-Phenylnaphthoates	Formula	UV λmax nm (log ε)
1	f - $R_1 = R_2 = OCH_3$, $R_3 = H$	$C_{20}H_{18}O_4$	257 (4.71) , 306 (4.05)
2	g - $R_1 = R_2 = O\text{-}CH_2\text{-}O$, $R_3=H$	$C_{21}H_{14}O_4$	258 (4.67) , 304 (4.09) ,342 (3.51)

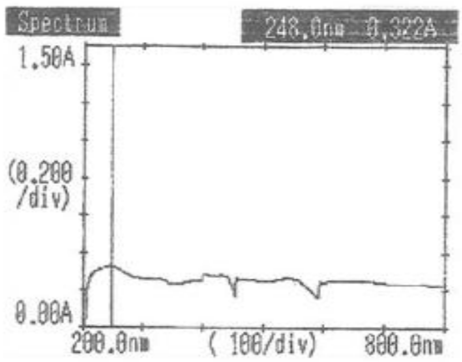


Fig 6. 1-Phenyl-3-carbomethoxy-6, 7-dimethoxy naphthoate

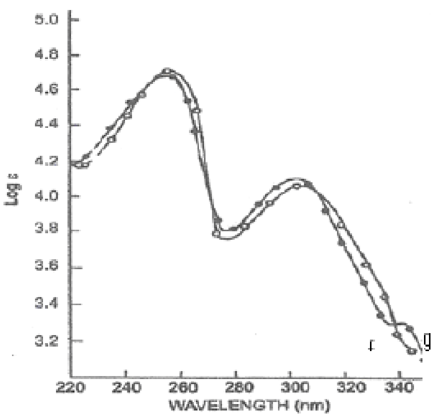


Fig 7. 1-Phenyl-3-carbomethoxy-6, 7 methylenedioxy naphthoate

UV-Visible Spectra of Plant Lignans

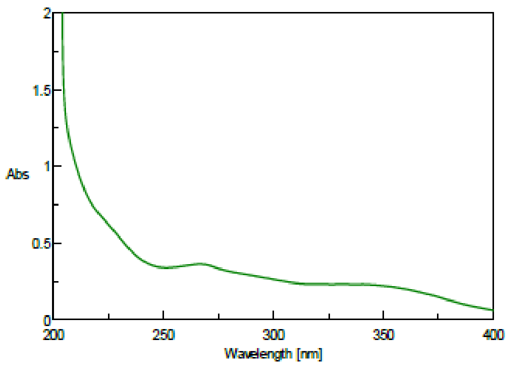


Fig 8.UV Spectra of Ruta graveolens (methanol)

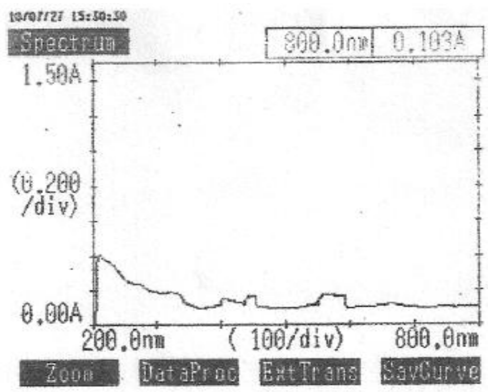
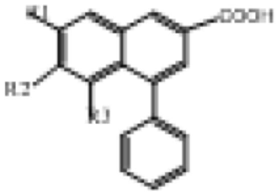
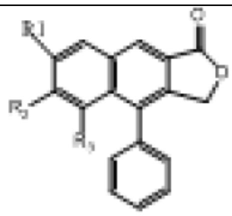
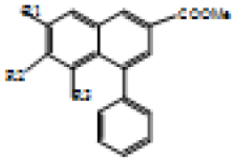
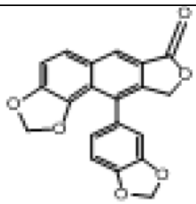
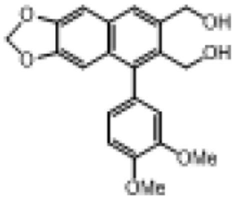


Fig 9.UV Spectra of Jatropha gossypifolia (pet ether)

Table 4. UV-Visible spectrophotometric comparison of synthetic and natural lignans

Sample	**Lignans**	**Structure**	UV analysis λmax nm (log ε)
Synthetic Compounds	1] 1-Phenyl naphthoic acid	 **1]**	a) - 235 (4.21), 282 (4.08) b)- 210 (4.66), 250 (4.74), 406 (4.77) c) - 252 (4.80) , 282 (3.98)
	2] 1-Phenyl naphthalene lactone	 **2]**	d)- 256 (4.60), 312 (4.06) e)- 248 (4.21)
	3] 1-Phenylnaphthoate	 **3]**	f)- 257 (4.71) , 306 (4.05) g)- 258 (4.67), 304 (4.09), 342 (3.51)
Ruta graveolens	4] Helioxanthin	 **4]**	h)- 267 (4.66), 290 (3.70), 354 (3.88)
Jatropha Gossypifolia	5] Arylnaphthalene lignan	 **5]**	i) - 247 (4.74), 290 (3.92), 332 (3.43).

Substitutions:

(i) $R_1 = R_2 = R_3$=OCH_3 (ii) R_1=R_2=O-CH_2-O, R_3=H (iii) R_1=R_2=OCH_3, R_3=H

a) 1-Phenyl-6, 7-dimethoxy naphthalene-3- carboxylic acid

b) 1-Phenyl-6, 7- methylenedioxy naphthalene-3- carboxylic acid

c) 1-Phenyl-6-methoxy-7-hydroxy-naphthalene-3 carboxylic acid

d)1-Phenyl 6-methoxy -7-hydroxy naphthalene lactone

e) 1-Phenyl-6, 7, 8-trimethoxy naphthalene lactone

f) 1-Phenyl-3-carbomethoxy-6, 7-dimethoxy naphthoate

g) 1-Phenyl-3-carbomethoxy-6, 7-methylenedioxy naphthoate

h) Ruta graveolens (ME)

i) Jatropha gossypifolia (PE)

IV. CONCLUSION

UV-Visible spectrophotometry paved a good path for studying the lignans having Phenylnaphthalene systems of natural and synthetic origin. These compounds and their derivatives show extraordinary biological properties, some of them being found among the most widely prescribed chemotherapeutic agents.

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