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UV-Visible Determination of Synthetic Compound 1-Phenyl Naphthalene and Extracted Plant Lignans Derivatives

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ABSTRACT

In recent investigation for 1-phenyl naphthalene has been synthesis via friedel craft acylation and Perkin–Oglialoro reaction followed by cyclization reaction. The key precursor use for synthesis of foresaid product by β -benzoyl propionic acid (β -BPA) through friedel craft acetylating reaction by mixture of succinic anhydride, benzene and its derivative with zeolite at streamline time to obtain blended accumulation followed by work-up with cold acid-water (1:1) treatment. The obtaining accumulation on distillation to eliminate benzene liquor and obtained crude mass. It dissolve in aqueous solution of sodium carbonate (1:10) and acidification by hydrochloric acid to form crude β -benzoyl propionic acid (β -BPA) and their derivatives. In perkin acid synthesize by two steps in which butenolides are prepared by β -BPA and aryl aldehyde using weak base catalyst pyridine and followed by cleavage of lactone ring methanolic base hydrolysis to form perkin acid. The perkin acid undergoes cyclization using zeolite gives 1-phenyl naphthalene. The similar contexts the 1-phenyl naphthalene derivatives are extracted from medicinal plant i.e., Cleistanthus collinus and isolated by column chromatography. These entire compounds are determined by UV-Visible spectrophotometry.

Keywords: β -BPA, Distillation of benzene, zeolite, Butenolides, 1-Phenyl naphthalene, *Cleistanthus collinus*, UV-Visible spectrophotometry.

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INTRODUCTION

Studies in the changes in electronic energy levels within the molecule arising due to transfer of electrons from π - or non-bonding orbitals. It commonly provides the knowledge about π -electron systems, conjugated unsaturation, aromatic compounds and conjugated non-bonding electron systems etc. This absorption spectroscopy uses electromagnetic radiations between 190 nm to 800 nm and is divided into the ultraviolet (UV, 190-400 nm) and visible (VIS, 400-800 nm) regions. Since the absorption of ultraviolet or visible radiation by a molecule leads transition among electronic energy levels of the molecule, it is also often called as electronic spectroscopy. The information provided by this spectroscopy when combined with the information provided by NMR and IR spectral data leads to valuable structural proposals [1] (Figures 1 and 2).



Figure 1: UV-visible spectrums.

UV-Visible spectrometry is routinely used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds. A spectrophotometer is employed to measure the amount of light that a sample absorbs. The instrument operates by passing a beam of light through a sample and measuring the intensity of light reaching a detector [2].



Figure 2: Optical system for detection of lignan using UV visible spectrophotometer.

Principles of absorption spectroscopy

Beer's and Lambert's Law, The greater the number of molecules that absorb light of a given wavelength, the greater the extent of light absorption and higher the peak intensity in absorption spectrum. If there are only a few molecules that absorb radiation, the total absorption of energy is less and consequently lower intensity peak is observed. This makes the basis of Beer-Lambert Law which states that the fraction of incident radiation absorbed is proportional to the number of absorbing molecules in its path. When the radiation passes through a solution, the amount of light absorbed or transmitted is an exponential function of the molecular concentration of the solute and also a function of length of the path of radiation through the sample. Therefore,

 $Log Io / I = \varepsilon c l$

Where I_o = Intensity of the incident light (or the light intensity passing through a reference cell), I = Intensity of light transmitted through the sample solution, c = concentration of the solute in mol I^{-1} , l = path length of the sample in cm, ε = molar absorptivity or the molar extinction coefficient of the substance whose light absorption is under investigation. It is a constant and is a characteristic of a given absorbing species (molecule or ion) in a particular solvent at a particular wavelength. ε is numerically equal to the absorbance of a solution of unit molar concentration (c = 1) in a cell of unit length (l = 1) and its units are liters moles⁻¹ cm⁻¹. However, it is customary practice among organic chemists to omit the units. The ratio I/Io is known as transmittance T and the logarithm of the inverse ratio Io/I is known as the absorbance A.

Therefore,

- Log I / Io =- log T =
$$\varepsilon$$
 c l
Log Io / I = A = ε c l
A = ε c l

For presenting the absorption characteristics of a spectrum, the positions of peaks are reported as λ max (in nm) values and the absorptivity is expressed in parenthesis.

EXPERIMENTAL PROCEDURE

Materials, methods and measurements

All synthesized compound a Derivatives of β-BPA, substituted butenolides, perkin acid, 1–phenyl naphthalenes and extracted component by pet. ether from *Cleistahnthus collinus*.

Methods: UV-Visible spectrophotometry

Measurements: The UV absorption spectra were determined with quartz cells of 1 cm path length, Band width 0.2 nm using a systronics double beam UV-visible spectrophotometer Type 2202. The probable error in wave length is +/- 0.5 mu for the p-band and +/- 1-2 mu for the α -band. That in the extinction coefficients is about 5% for the p-band and about 20% for the α -band. In order to obtain an accurate value for the stretching frequencies, the wave number scale was extended four times and the

absorption curve was calibrated for each sample by tracing a water vapor spectrum on the same chart paper immediately after running the sample. The probable error in wave number is 1 cm. methanol and pet. Ether were used as the organic solvent throughout the measurements because of the limited solubility of the compounds.

Synthesis of 1-phenyl naphthalene acid derivatives

Synthesis of β - benzoyl propionic acid

β- Benzoyl propionic acid has prepared from succinic anhydride, benzene and activated zeolite H-Beta. In a 2 L three –necked round bottom flask fitted with a mechanical stirrer and two reflux condensers are placed 68 g (0.68 moles) of succinic anhydride and 350 g (4.5 moles) dry, thiophene free benzene. With continuous stirring is started and 200 g (1.5 moles) of powdered, anhydrous alumnium chloride (It acts as highly reactive hydrogen abstracter) is added all at once. Hydrogen chloride fumes are evolved and the mixture becomes hot. the flask is then surrounding by cold water and 300 cc of water is slowly added from a dropping funnel inserted in the top of condensers the excess of benzene is discarded and obtained mass separates as a colorless oil which soon solidifies after cooling to 0°C, it is collected, washed with a cold mixture of 50 cc of concentrated hydrochloric acid and 150 cc of water. The crude β -BPA is dissolved in a solution of 75 g of anhydrous sodium carbonate in 25 cc of water by boiling for fifteen minutes. The clear colourless filtered is transferred to 500 cc of beaker and carefully acidified with 6.5 cc of concentrated hydrochloric acid in freeze condition to maintain temperature 0-5°C by ice-salt bath. The solution is filtered by suction pump, washed with hot water, dry give β –benzoyl propionic acid as shown in Scheme 1 (Figures 3 - 5 and Table 1).

Synthesis of α -Arylidene γ -phenyl δ - β - γ -Butenolide

β-benzoyl propionic acid [2] is treated with the aryl aldehyde, acetic anhydride were refluxed in different catalysts as pyridine or sulphamic acid, refluxed over the heating mantle for three hours, while monitoring the reaction with help of TLC. After completion reaction of the reaction, the intermediate temperature of the reaction mixture as taken out by the thermometer, this is recorded as 40°C. The hot reaction mixture was poured in cold water with stirring and then acidified with conc. HCl. The yellow mass obtained was filtered and crystallized with benzene to give lactone i.e., **α** -Arylidene γ -phenyl **δ** - β - γ -Butenolide product (3a) had shown in Scheme 1 (Figures 6 - 10 and Table 2) [3-5].

Synthesis of perkin acid

The reaction mixture of α -Arylidene γ -phenyl δ - β - γ -: Butenolide (1 g) was refluxed for 5 hours with alcoholic sodium carbonate solution (prepared by dissolving 1gm anhydrous sodium carbonate in 4 ml methanol and 6 ml water). The resulting mixture was filtered, cool and acidified with conc. HCl to get a brown precipitate which was crystallized with aqueous methanol and was identified as α -arylidine β -benzoyl propionic acid as shown in Scheme 1 (Figures 11 - 15 and Table 3) [6-9].

Synthesis of 1-phenyl naphthalene

Take a mixture of 1 mmol of α -arylidine, β -Benzoyl Propionic acid (1 g), 0.5 mmol of activated zeolite H-beta (1 g) and 10 mmol of ethanol [10] as a reaction solvent in 250 ml round bottom flask. Stir the mixture vigorously (using magnetic stirrer) by keeping reflux at 120°C for an appropriate time as reaction mixture was cooled at room temperature and diluted with diethyl

ether $(3 \times 10 \text{ ml})$ to precipitate of zeolite h-beta easy separation. The combined organic layers were dried over anhydrous Na₂SO₄. The solvent was removed and the residue was column chromatograms using petroleum ether: ethyl acetate (2:3) as the eluent, to obtain pure compound (5a to 5 e) shown in Scheme 1 (Figures 16 - 20 and Table 4).





Scheme 1: Graphical representation of synthesis of 1-Phenyl naphthalene.

Extraction of aryl naphthalene from Cleistanthus collinus

Preparation of sample solution

These entire compounds of 1mmol β -Benzoyl Propionic acid, α -Arylidene γ -phenyl δ - β - γ -: Butenolide, α -arylidine, β -Benzoyl Propionic acid and 1-phenyl naphthalene's subsidiaries are prepared by dissolving with 10 mmol of methanol. The plant extract are solubilized in pet. Ether, all these sample solution are examined by UV-Visible spectrophotometry.

RESULTS AND DISCUSSION

Synthetic compounds

Spectroscopic analysis of derivative β-benzoyl propionic acid

In Friedel craft acylation reaction for the synthesis of β -BPA and their derivatives by the reaction mixture of arenes with succinic anhydride in presence of anhydrous AlCl₃ catalyst. The β -BPA has showed that absorbance nm at molar extinction coefficient. β -Toluenyl PA has showed absorbance nm at molar extinction coefficient at . β -Naphthoyl PA has shown absorbance nm at molar extinction coefficient.

S. No	Arenes	Succinic anhydride	Derivative of β-benzoyl propionic acid P (2)	Molecular formula	Absorbance (A)	Molar extinction coefficient (log ê)
1	Benzene	Succinic anhydride	β -benzovl propionic acid (2a)	$C_{10}H_{10}O_3$	276.8	0.404
		, , , , , , , , , , , , , , , , , , ,		- 10 10 - 5	263.6	0.312
2	Toluona	Succinic anhydride	β Toluenyl propionic soid (2b)	СНО	287.9	3.92
2	Toluelle	Succinic annyunue	p-Toluenyi propionic acid (20)	$C_{11} I_{12} O_3$	356.7	1.74
3	Naphthalene	phthalene Succinic anhydride	R Norththeyd propionic said (2a)	CILO	402.52	3.74
			p-Naphthoyi propionic acid (2c)	$C_{14}\Pi_{12}O_3$	430.61	2.33

Table 1: UV-visible spectrophotometric analysis of Derivative β-benzoyl propionic acid.

Spectroscopic analysis of Butenolide

In Perkin reaction for the synthesis of α -Arylidene γ -phenyl δ - β - γ -: Butenolide and their derivatives, the reaction mixture of β -BPA and aryl aldehyde in presence of zeolite H-Beta catalyst. The α -Anisalidene γ -phenyl δ - β - γ -: Butenolide has showd that UV max nm at absortivity. α -Varatralidene γ -phenyl δ - β - γ -: Butenolide has showed ansorbance nm and ebluscopic constant . α -Salicalidene γ -phenyl δ - β - γ -: α -Vanilidene γ -phenyl δ - β - γ -: Butenolide has shown absorbance at and absorbyivity, butenolide has shown absorbance and absorbtivity. α -Benzylidene γ -phenyl δ - β - γ -: Butenolide has showed ansorbance nm and ebluscopic constant of β - γ -: Butenolide has shown absorbance and absorbtivity.

S. No	Aryl aldehyde	β-benzoyl propionic acid(2)	α -Arylidene γ -phenyl δ - β - γ- Butenolide (3)	Molecular formula	Absorban ce (A)	Molar extinction coefficient (log ε)
1	Anisalde hyde	β-benzoyl propionic acid	α-Anisalidene γ -phenyl δ- β - γ-Butenolide (3a)	C ₁₈ H ₁₄ O ₃	294.53 373.24	2.37 3.86 3.67
2	Varatrald ehyde	β-benzoyl propionic acid	α-Varatralidene γ -phenyl δ- β - γ- Butenolide (3b)	C ₁₇ H ₁₂ O ₃	341.62 427.91	1.42
3	Salicalde hyde	β-benzoyl propionic acid	α-Salicalidene γ -phenyl δ- β - γ-Butenolide (3c)	$C_{19}H_{16}O_4$	36.28 472.6 495.4	1.23 1.85 3.27
4	Vanilin	β-benzoyl propionic acid	α-Vanilidene γ -phenyl δ- β -γ- Butenolide (3d)	C ₁₈ H ₁₄ O ₄	342.56 463.17	2.46 3.17
5	Benzalde hyde	β-benzoyl propionic acid	α-Benzylidene γ -phenyl δ- β - γ-Butenolide (3e)	C ₁₇ H ₁₂ O ₂	294.65 552.38	1.47 3.56

Table 2: UV-visible Spectrophotometric analysis of α -Arylidene γ -phenyl δ - β - γ - Butenolide.

Spectroscopic analysis of a-Arylidene β- Benzoyl Propionic acid

In Perkin reaction for the synthesis of α -Arylidene β - Benzoyl Propionic acid and their derivatives, the reaction mixture of α -Arylidene γ -phenyl δ - β - γ -: Butenolide and methanolic sodium carbonate. The α -Anisalidene β -benzoyl propionic acid has showd that UV max nm at absortivity. α -Varatralidene β -benzoyl propionic acid has showed ansorbance nm and ebluscopic constant . α -Salicalidene β -benzoyl propionic acid has shown absorbance at and absorbyivity, α -Vanilidene β -benzoyl propionic acid has shown absorbance and absorbtivity. α -Benzylidene β -benzoyl propionic acid has showed ansorbance nm and ebluscopic constant.

S. N o	Butenolide	Alcoholic sodium carbonate	α-Arylidene β- Benzoyl Propionic acid P (4)	Molecula r formula	Absorbanc e (A)	Molar extinction coefficient (log ε)
1	α-Anisalidene γ -phenyl δ- β -γ-Butenolide (3a)	Methanolic sodium carbonate	α-Anisalidene β- benzoyl propionic acid (4a)	$C_{18}H_{16}O_4$	285.91 286.36	3.92 3.28
2	α-Varatralidene γ -phenyl δ- β -γ- Butenolide (3b)	Methanolic sodium carbonate	α-Varatralidene β- benzoyl propionic acid (4b)	C ₁₇ H ₁₄ O ₄	137.63 744.299 428.21	3.82 1.61 2.23
3	α-Salicalidene γ -phenyl δ- β -γ-Butenolide (3c)	Methanolic sodium carbonate	α-Salicalidene β- benzoyl propionic acid (4c)	C ₁₉ H ₁₈ O ₅	314.73 440.28	1.78 3.05
4	α-Vanilidene γ -phenyl δ- β -γ- Butenolide (3d)	Methanolic sodium carbonate	α-Vanilidene β-benzoyl propionic acid (4d)	C ₁₈ H ₁₆ O ₅	226.45 354.82	1.86 3.53
5	α-Benzylidene γ -phenyl δ- β -γ-Butenolide (3e)	Methanolic sodium carbonate	α-Benzylidene β- benzoyl propionic acid (4e)	C ₁₇ H ₁₄ O ₃	230.36 355.18	0.98 2.41

Table 3: UV-visible spectrophotometric of \Box -Arylidene β - benzoyl propionic acid.

Spectroscopic analysis of 1-Phenyl Naphthoic acid

Take a mixture of 1 mmol of α -arylidine, β -Benzoyl Propionic acid (4a), 0.5mmol of activated zeolite H-beta 1] and 10 mmol of ethanol (10 as a reaction solvent in 250 ml round bottom flask . Stir the mixture vigorously (using magnetic stirrer) by keeping reflux at 120°C for an appropriate time as reaction mixture was cooled at room temperature and diluted with diethyl ether (3 × 10 ml) to precipitate of zeolite h-beta easy separation. The combined organic layers were dried over anhydrous Na₂SO₄. The solvent was removed and the residue was column chromatograms using petroleum ether: ethyl acetate (2:3) as the eluent, to obtain pure compound (5a to 5e).

S N	α-Arylidene ß- Benzoyl Propionic acid	Derivatives of 1-Phenyl Naphthoic acid (5)	Molecular formula	Absorbance (A)	Molar extinction coefficient (log □)
1	α-Anisalidene β- benzoyl propionic acid (4a)	1-phenyl 7-methoxy naphthalene-3- carboxylic acid (5a)	$C_{18} H_{14} O_3$	270.31 408.82 501.23	1.02 2.33 1.53
2	α-Varatralidene β-benzoyl propionic acid(4b)	1-phenyl 6 Hydroxy naphthalene-3- carboxylic acid (5b)	C ₁₇ H ₁₄ O ₄	286.95 312.52 432.44 500.26	3.97 3.98 2.65 0.93
3	α-Salicalidene β- benzoyl propionic acid (4c)	1-phenyl 6,7-dimethoxy naphthalene-3- carboxylic acid (5c)	C ₁₉ H ₁₈ O ₅	293.1 450.4	1.82 0.68
4	α-Vanilidene β- benzoyl propionic	1-phenyl 6-methoxy 7-Hydroxy naphthalene-3- carboxylic acid (5d)	$C_{18}H_{16}O_5$	215.29 264.72 411.19	1.56 1.23 2.23

	acid (4d)				
5	α-Benzylidene β-benzoyl propionic acid(4e)	1-phenyl naphthalene-3- carboxylic acid (5e)	$C_{17}H_{14}O_3$	238.4 330.8	0.83 0.253





Figure 3: UV- Visible spectrum of β -benzoyl propionic acid (2a).



Figure 4: UV- Visible spectrum of β - toluenyl propionic acid (2b).



Figure 5: UV- Visible spectrum of β -Naphthoyl propionic acid (2c).



Figure 6: UV- Visible spectrum of α -Anisalidene γ -phenyl δ - β - γ -Butenolide (3a).



Figure 7: UV- Visible spectrum of α -Varatralidene γ -phenyl δ - β - γ - Butenolide (3b).



Figure 8: UV- Visible spectrum of \Box -Salicalidene γ -phenyl \Box - β - γ -Butenolide (3c).



Figure 9: UV- Visible spectrum of α -Vanilidene γ -phenyl δ - β - γ - Butenolide (3d).



Figure 10: UV- Visible spectrum of α -Benzylidene γ -phenyl δ - β - γ -Butenolide (3e).



Figure 11: UV- Visible spectrum of α -Anisalidene β -benzoyl propionic acid (4a).



Figure 12: UV- Visible spectrum of α -Varatralidene β -benzoyl propionic acid (4b).



Figure 13: UV- Visible spectrum of α -Salicalidene β -benzoyl propionic acid (4c).



Figure 14: UV- Visible spectrum of α-Vanilidene β-benzoyl propionic acid (4d).



Figure 15: UV- Visible spectrum of α -Benzylidene β -benzoyl propionic acid (4e).



Figure 16: UV- Visible spectrum of 1-phenyl 7-methoxy naphthalene-3- carboxylic acid (5a).



Figure 17: UV- Visible spectrum of 1-phenyl 6 Hydroxy naphthalene-3- carboxylic acid (5b).



Figure 18: UV- Visible spectrum of 1-phenyl 6, 7-dimethoxy naphthalene-3-carboxylic acid (5c).



Figure 19: UV- Visible spectrum of 1-phenyl 6-methoxy 7-Hydroxy naphthalene-3- carboxylic acid (5d).



Figure 20: UV- Visible spectrum of 1-phenyl naphthalene-3- carboxylic acid (5e).

Extracted aryl naphthalene from Cleistanthus collinus

In Figure 21, we are identified that uv-visible results shows that aryl naphthalene has shown six peaks rages between 200- 800 nm. The first peak 243.2 having Molar extinction coefficient (log ε) 1.127 is diphyllin and 267.3 having Molar extinction coefficient (log ε) 1.103 is cleistanone. The another two peak 363.2 nm as Cleistnthus D hving Molar extinction coefficient (log ε) 1.877 and 405.2 nm as Cleistahnthus C, 435 as Cleisthanthus A having molar extinction coefficient (log ε) 2.396 and 660.8 is and having molar extinction coefficient (log ε) 1.411.



Figure 21: UV- Visible spectrum of exracted medicanl plant (Cleistnthus collinus).

CONCLUSION

In above synthesis of 1-phenyl naphthalene from benzene through stable intermediate as β -benzoyl propionic acid, α -Anisalidene γ -phenyl δ - β - γ -Butenolide, α -Arylidene β -benzoyl propionic acid and are identified and 1-Phenyl Naphthoic acid characterized by UV-visible spectrophotometric.

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