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GREEN SYNTHESIS AND CHARACTERIZATION OF CINNAMYLIDENEACETOPHENONE COMPOUND USING Fe_3O_4 MAGNETIC AS CATALYST

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Abstract: Cinnamaldehyde is a compound found in the skin of cinnamon plants which has various bioactivity. In this study, the compound cinnamaldehyde was modified with the help of Fe_3O_4 which was synthesized with the help of seaweed extract as a heterogeneous catalyst. Fe_3O_4-MNPs are synthesized using $FeCl_3$ and *Sargassum filipendula* extracts as their natural reducing agents. The catalytic ability of Fe_3O_4 was evaluated in the reaction between cinnamaldehyde and aromatic ketone compounds synthesized by the reflux method. Structure Analysis and elucidation of the synthesized compounds were carried out by measuring the vibrations of the functional groups by FTIR, and the determination of H and C atoms by HNMR and CNMR analysis. The FTIR, proton and carbon NMR analysis have identified that the synthesized product was cinnamylideneacetophenone by the name 1,5-diphenylpyenta-2,4-dien-1-one. The optimum conditions were obtained at a catalyst concentration of 10% w/w for five hours with a yield of 36%. The yield of this reaction was better than the reaction without a catalyst.

Keywords: green synthesis, Fe_3O_4-MNPs, cinnamaldehyde, *Sargassum filipendula*

Abstak: Sinamaldehid merupakan senyawa yang terdapat pada kulit tanaman kayu manis yang memiliki berbagai bioaktivitas. Pada penelitian ini senyawa sinamaldehid dimodifikasi dengan bantuan Fe_3O_4 yang disintesis dengan bantuan ekstrak rumput laut sebagai katalis heterogen. Fe_3O_4-MNPs disintesis menggunakan $FeCl_3$ dan ekstrak *Sargassum filipendula* sebagai reduktor alaminya. Kemampuan katalitik Fe_3O_4 dievaluasi dalam reaksi antara senyawa sinamaldehid dan keton aromatik yang disintesis dengan metode refluks. Analisis dan elusidasi struktur senyawa hasil sintesis dilakukan dengan pengukuran vibrasi gugus fungsi dengan FTIR, serta penentuan atom H dan C dengan analisis HNMR dan CNMR. Analisis FTIR, proton dan karbon NMR telah mengidentifikasi bahwa produk yang disintesis adalah cinnamylideneacetophenone dengan nama 1,5-diphenylpyenta-2,4-dien-1-one. Kondisi optimum diperoleh pada konsentrasi katalis 10% b/b selama lima jam dengan rendemen 36%. Rendemen reaksi ini lebih baik dibandingkan dengan reaksi tanpa katalis.

Kata kunci: green synthesis, Fe_3O_4-MNPs, cinnamaldehyde, *Sargassum filipendula*

INTRODUCTION

The reduction in the use of chemicals in green chemistry is of concern to recent researchers. Various instrument modifications and the use of natural materials are often used as alternatives. Such as synthesis without the use of chemical solvents, the use of microwave-assisted methods or ultrasonic irradiation instruments, and often also utilize natural polymers and plant extracts (Benelli, 2019; Fierascu et al., 2019; Khalaj et al., 2020; Mahmoud et al., 2015; Rajendaran et al., 2019; Sadjadi et al., 2017). In addition, modification of particle size in the nano-scale provides advantages in surface area that affects the intermolecular interaction and the rate of a reaction (Chng et al., 2013; Liandi et al., 2020; Nasir Baig et al., 2015). In this study, the use of Fe_3O_4 magnetic nanoparticles was chosen as a catalyst in an organic reaction synthesized with the help of seaweed extract.

The use of Fe_3O_4-MNPs as heterogeneous catalysts in a reaction is of concern because of its superiority. The magnetic properties of Fe_3O_4-MNPs make it easy to be separated from the mixture of solutions with the help of external magnets, so there is no need for special filtering devices to separate them (Kharisov et al., 2019; Mahdavian & Mirrahimi, 2010). Previous studies that have successfully synthesized Fe_3O_4 using natural ingredients reduction included research conducted by Salem et al. by utilizing brown (*Colpomenia sinuosa*) and red (*Pterocladia capillacea*) seaweed extracts, EL-KASSAS Hala et al. using seaweeds extracts of *Padina pavonica* and *Sargassum acinarium,* Yew et al. using seaweeds extracts of *Kappaphycus alvarezii,* and Mahdavi et al. using seaweeds extracts *Sargassum muticum* (El-Kassas et al., 2016; Mahdavi et al., 2013; Salem et al., 2019; Yew et al., 2016). They explained that the use of seaweed extracts could reduce $FeCl_3$ to Fe_3O_4. In this study, the seaweed used to reduce and form Fe_3O_4 was *Sargassum filipendula*.

Modification of cinnamaldehyde which is one of the main components of cinnamon bark is often done to obtain new bioactivity or increase bioactivity (Wang et al., 2016; Yen & Chang, 2008). Sinamaldehyde is able to act as an antimicrobial used in medicine, food and preservatives. However, there are limitations in applying it because the smell is very pungent and volatile (Jo et al., 2015). In this reseach, cinnamaldehyde was modified by recombining it with a ketone compound by using Fe_3O_4-MNPs as a catalyst.

METHOD

Materials

All chemicals and solvents were used for the analytical grade that purchased from commercial suppliers (Merck, Fluka, and Sigma-Aldrich) without any further purification. Some chemicals used in the synthesis of catalysts Fe_3O_4 and cinnamylideneacetophenone compound were $FeCl_3.6H_2O$, NaOH, aquademin, ethanol, n-hexane, ethyl acetate acetophenone, and cinnamaldehyde. TLC analysis used the Kiesel-Gel F_{254} silica plate with a ratio of n-hexane: ethyl acetate (4: 1) solvent. Melting point analysis was performed on an open capillary tube on the Electrothermal-9100 device. FTIR (Fourier Transform Infrared) was performed using a Shimadzu Prestige-21 FTIR spectrophotometer, UV-Vis analysis was performed by a UV-Vis spectrophotometer Shimadzu 2450 instrument. Morphological analysis was measured by SEM (Scanning Electron Microscopy) and elemental analysis was measured by EDX (Energy Dispersive X-Ray Spectroscopy) ASTM E1508-2012. NMR analysis was measured by Agilent 500 MHz NMR spectrometer with DD2 console system

Extraction of active compounds from Sargassum filipendula

The brown seaweed extraction process was carried out by the reflux method with aquademin. 5 g of Sargassum filipendula was cut into small pieces to increase the surface area and refluxed with 100 mL aquademin for 1 hour at the boiling point temperature of the water. After that, the separation of seaweed extracts and pulp was conducted by filtering. The extract of seaweed obtained is brown.

Synthesis of Fe_3O_4 magnetic nanomaterials

The Fe_3O_4 magnetic synthesis with support of seaweed extracts that have been obtained was carried out by the co-precipitation method. In this synthesis, 1 mmol of $FeCl_3$ and 5 mL of seaweed extract were dissolved in aquademin and stirred until homogeneous. Then, 6 M NaOH was added dropwise until it reached pH 11. The mixture was stirred for 2 hours. Then the mixture was decanted with a magnet from the outside and rinsed with ion free water and ethanol. Hereinafter, the synthesized product was dried at 40°C using an oven.

Synthesis of cinnamylideneacetophenone compound

The ability of Fe_3O_4 magnetic as a catalyst was evaluated by synthesizing the cinnamylideneacetophenone compound reacted from 1 mmol acetophenone and 1 mmol cinnamaldehyde. The reaction conditions were carried out using 10 mL ethanol as a solvent by the reflux method at the boiling point temperature of the solvent. A number of Fe_3O_4 magnetic catalysts were added and the reaction was carried out with time variations. The process of product formation was monitored by thin-layer chromatography (TLC). After the reaction was complete, the catalyst was separated by decantation using a magnet from the outside. Then, the product was purified by evaporating the solvent and recrystallized with hot ethanol. The purified product was characterized and analyzed by FTIR spectroscopy, UV–vis spectrophotometer, HNMR, and CNMR Spectroscopy.

RESULTS AND DISCUSSION

Synthesis and characterization of Fe_3O_4 from Sargassum filipendula

The use of heterogeneous catalysts is of concern nowadays because of its environmental friendliness and reusability. Fe_3O_4 which has magnetic properties is an advantage in green chemistry. This catalyst can be separated from the reaction mixture without any special filtration equipment because it can be decanted and separated by magnets. In addition, Fe_3O_4 can be synthesized with nano-scale size which has a larger surface area, thereby increasing molecular interactions. The use of the natural product in the synthesis of Fe_3O_4 in this study was carried out using brown seaweed (*Sypassum filipendula). S. filipendula* is known to contain sulfate polysaccharides which will act as reducing and stabilizing agents that reduce iron chloride to Fe_3O_4. The content of *S. filipendula* extract was analyzed by EDX and FTIR. EDX data of Sargassum filipendula extract (Table. 1) confirmed that *S. filipendula* extract is composed of elements C (33.03%) and O (40.03%) which dominates (polysaccharide compilers) and S (2.26%) with minor amounts. In addition, some minerals in minor quantities are commonly found in brown seaweed.

The analysis of functional groups of seaweed extracts and Fe_3O_4 synthesized were characterized by FTIR. The seaweed extraction FTIR spectrum (Figure 1a) showed several functional group absorption peaks. Among these peaks at 3315 cm^{-1} (O-H stretching vibration), 2931 cm^{-1} (C-H stretching vibration), 1603 cm^{-1} (C=O stretching vibration), 1412 cm^{-1} (C-C), 1241 cm^{-1} (sulfate group stretching vibration), 1039 cm^{-1} (C-O-SO_3), and 818 cm^{-1} (C-H bending vibration). Fe_3O_4 FTIR spectrum (Figure 1b) showed the absorption peak which was not much different from the absorption peak of seaweed extracts. The spectrum in Figure 1.b showed some shifts in the absorption of the synthesized Fe_3O_4 functional group, namely 3203 cm^{-1} (O-H stretching vibration), 3002 (C-H stretching vibration), 1612 (C=O stretching vibration), 1491 (C-C), and 1325 (sulfate group stretching vibration). Then, the main peak that indicated the formation of Fe_3O_4 is the peak at the absorption of 499. This peak is the vibration of the Fe-O functional group.

Table 1. Element composition of *Sargassum filipendula* extract

Element	Composition (%massa)
C	33.03 ± 1.70
O	47.03 ± 0.83
Na	2.20 ± 0.14
Mg	2.14 ± 0.28
Al	0.97 ± 0.23
Si	1.75 ± 0.42
S	2.26 ± 0.20
Cl	0.73 ± 0.20
K	5.59 ± 0.74
Ca	3.76 ± 0.22
Zn	0.54 ± 0.54

The surface morphology of the Fe_3O_4 synthesized by seaweed extract and particle size was studied by scanning electron microscope (SEM). The surface of Fe_3O_4 is shown in Figure 2a, 2b, and 2c with variations of magnification. The results of this SEM analysis, it appears that Fe_3O_4 was formed in the form of agglomeration. This is due to the magnetic properties which causes the fusion between particles so that no visible particle shape. The size distribution of the synthesized Fe_3O_4 particle was below 100 nm.

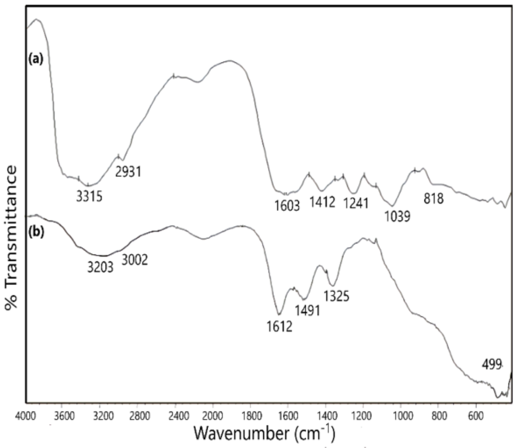
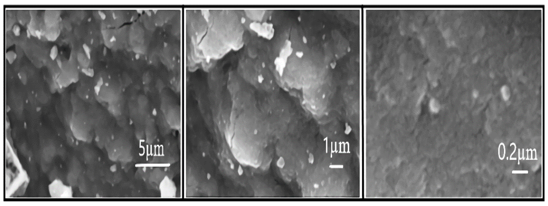


Figure 1. FTIR spectra of (a) *Sargassum filipendula* extract and (b) synthesized Fe_3O_4



(a) (b) (c)

Figure 2. SEM images of Fe_3O_4 (a) 5000 times, (b)10000 times, and (c) 60000 times of magnification

Synthesis and characterization of cinnamylideneacetophenone compound

The synthesis of cinnamylideneacetophenone compound was carried by the reflux method. The reaction occurred between acetophenone and cinnamaldehyde with the assistance of the Fe_3O_4 catalyst. The reaction was carried out with variations in time and catalyst concentration. The optimum conditions were obtained at a catalyst concentration of 10% w/w for 5 hours with a yield of 36%. The addition of catalyst concentration and higher reaction time did not result in an increase in product yield. Characterization of compound cinnamylideneacetophenone was performed by functional group vibration analysis with FTIR and identification of H and C with ^{1}H-NMR and ^{13}C-NMR. FTIR spectrum of compound cinnamylideneacetophenone (Figure 3) showed the presence of some functional group absorption (Cahyana et al., 2017). Among them, the vibration stretching of the functional group C-H sp^2 at 3065 cm^{-1} while the C-H sp^3 at 3023 cm^{-1}. Besides, there was also a functional group at the absorption of 1653 cm^{-1}. The aromatic constituent C=C was found in the absorption of 1590 cm^{-1}.

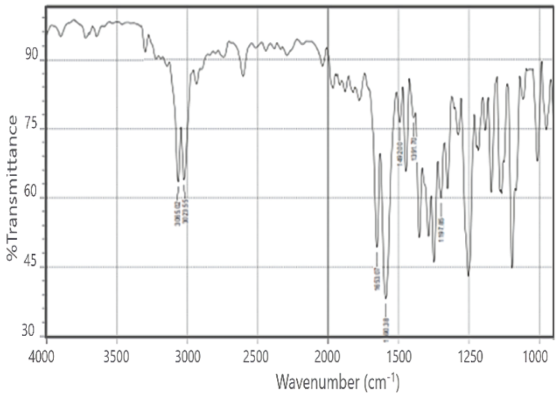


Figure 3. FTIR spectrum of cinnamylideneacetophenone compound

The synthesized cinnamylideneacetophenone compound was confirmed using ^{1}H-NMR and ^{13}C-NMR to determine the molecular structure by analyzing the proton and carbon shift values. ^{1}H-NMR analysis (Figure 4) was carried out using chloroform solvents. The number of H atoms in the target compound is 14 atoms according to the molecular formula. Also, this study carried out structure elucidation with ^{13}C-NMR for carbon shift value analysis (Figure 5). ^{13}C-NMR analysis using chloroform solvents. Cinnamylideneacetophenone compound consists of 17 C atoms, while the ^{13}C-NMR analysis results obtained there are 13 atomic peaks. This shows the existence of equivalent C atoms.

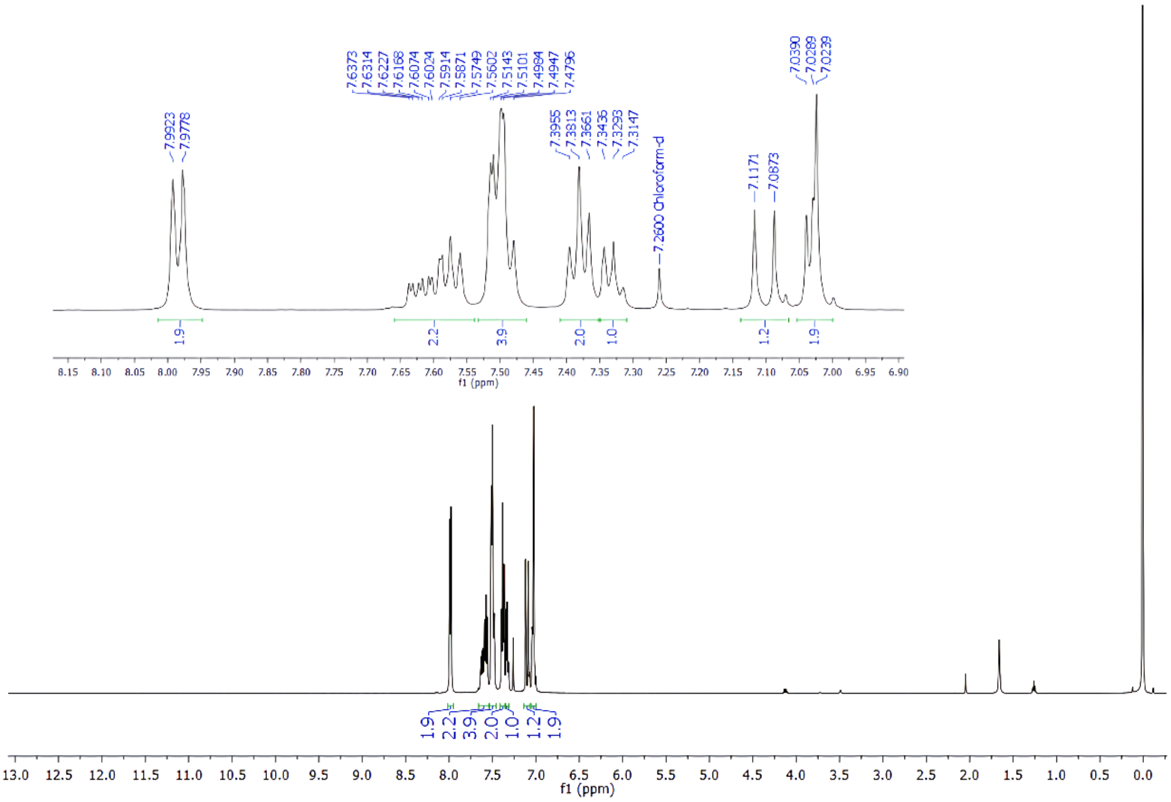


Figure 4. ^{1}H-NMR analysis of cinnamylideneacetophenone compound

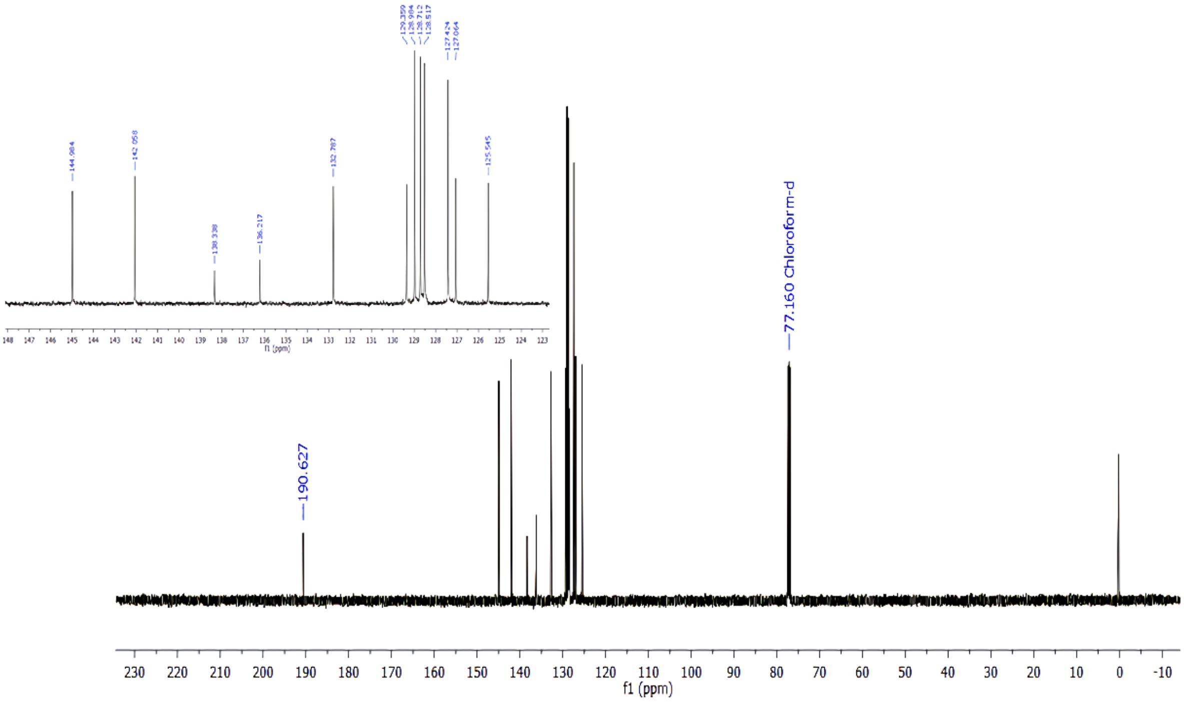


Figure 5. ^{13}C-NMR analysis of cinnamylideneacetophenone compound

The ^{1}H-NMR spectrum of the synthesized compound showed a chemical shift at δ 7,10 (d, 1H); 7.62 ppm (m, 1H); 7.02 ppm (d, 1H); and 7.03 ppm (d, 1H), each compound showing a proton at position C-2, C-3, C-4 and C-5 (Table. 2). In α, β-unsaturated ketones, protons next to carbonyl (Hα) will have small δ (shielded) and Hβ will have higher (deshielded). At the C-2, C-3, C-4, and C-5 positions, the most significant chemical shift is at the C-3 (Hβ) position. This can be explained because there is a resonance in α, β-ketones unsaturated so that the carbon in Hβ (proton at C-3) is relatively more positive than the carbon on Hα (proton at C-2). As a result, the electron density at Hβ is smaller than the electron density at Hα. In addition, there are geometric or spatial effects of carbonyl on C-1, so that C-3 is more deshielded than C-2, C-4, and C-5. The chemical shift at δ 7.99 ppm shows the proton at the position of the C-2' and C-6' atoms with the peak of the doublet, which is the highest peak. This is because in addition to the anisotropic effect, there is also an aromatic effect so that H in the C-2' and C-6' positions is deshielded. In the first aromatic ring, the aromatic compound is bound to the C carbonyl group (ketone), because the C carbonyl group which is bound to the aromatic compound attracts electrons, there are three types of protons obtained, which are ortho, H meta and H para with chemical shift (δ) Ho> Hp> Hm. This can be explained because there is a resonance in aromatic compounds, carbonyl groups attract electrons so that ortho carbon is relatively more positive compared to para carbon and para carbon is more positive than meta carbon. Chemical shifts at δ 7.51 and δ 7.58 ppm indicate protons at positions C-3', C-5' and C-4'. In the second aromatic ring, the chemical shift at δ 7.49 ppm indicates the proton at the position of the C-2'' and C-6'' atoms. The chemical shift at δ 7.33 ppm shows the proton at the position of the C-4'' atom with the top of the triplet. The chemical shift at δ 7.38 ppm shows the proton at the position of the C-3'' and dan C-5'' atoms with the top of the triplet.

Table 2. ^{1}H-NMR and ^{13}C-NMR data of synthesized compound

Atom Number	δ_H (ppm)	δ_C (ppm)
1	-	190,6
2	7,10 (d, 1H, J = 14,9 Hz)	129,4
3	7,62 (m, 1H)	145,0
4	7,02 (d, 1H)	125,5
5	7,03 (d, 1H)	142,1
1'	-	138,3
2'	7,99 (d, 1H)	129,0

3’	7,51 (m, 1H)	128,7
4’	7,58 (dd, 1H)	132,8
5’	7,51 (m, 1H)	128,7
6’	7,99 (d, 1H)	129,0
1’’	-	136,2
2’’	7,49 (m, 1H)	128,5
3’’	7,38 (t, 1H)	127,4
4’’	7,33 (t, 1H)	127,1
5’’	7,38 (t, 1H)	127,4
6’’	7,49 (m, 1H)	128,5

The ^{13}C-NMR spectrum has a much wider chemical shift of 0-230 ppm, compared to 1H-NMR which ranges between 0-14 ppm. The ^{13}C-NMR spectrum of the synthesized compound showed a chemical shift at δ 138.3 ppm and 136.2 ppm, respectively as carbon C-1’and C-1’’. The low peak intensity at the chemical shift δ 138.3 ppm and 136.2 ppm indicates that the C atom is C quaternary because there are no H atoms directly bound to the C atom. The chemical shift at δ 190.6 ppm is C carbonyl from ketones (C = O). Chemical shifts at δ 145.0 and 142.1 ppm indicate the presence of carbon at C-3 and C-5. Chemical shifts at δ 129.4 and 125.5 ppm indicate the presence of carbon at C-2 and C-4. The chemical shift at 127.4 - 132.8 ppm indicates the presence of carbon in the aromatic ring. The equivalent C atom is found in C-2' with C-6'; C-3' with C-5'; C-2" with C-6" and C-3" with C-5". Characterization data showed that the compound obtained was in accordance with the expected target compound, namely 1,5-diphenylpyenta-2,4-dien-1-one (Figure 6).

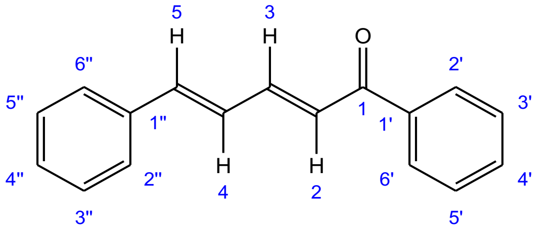


Figure 6. molecular structure of cinnamylideneacetophenone compound

CONCLUSION

In summary, green synthesis of compound cinnamylideneacetophenone with a magnetic catalyst Fe_3O_4 has been successfully carried out. The use of natural materials (seaweed) can reduce $FeCl_3$ to magnetic Fe_3O_4 which is the catalyst in this study. The optimum conditions were obtained at a catalyst concentration of 10% w/w for 5 hours with a yield of 36%. The yield of this reaction was better than the reaction without a catalyst. The proton and carbon NMR analysis have identified that the synthesized product is cinnamylideneacetophenone by the name 1,5-diphenylpyenta-2,4-dien-1-one.

Therefore, this method provides an effective and environmentally friendly way to synthesize Fe_3O_4 nanoparticles and showed the good catalytic ability in synthesis of cinnamylideneacetophenone.

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