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Evaluation of Optical properties of Bisdemethoxycurcumin thin film prepared by spray method

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Abstract

In this work, Bisdemethoxycurcumin was prepared and established by ^{1}H NMR, the spectrum is characterized by a singlet of one proton integral at 6.02 ppm which is assigned to the vinylic proton, In addition the spectrum shows a broad and weak signal at 16.10ppm which agrees with the chemical shifts of the (OH) Proton with the intra hydrogen bonded chelated ring in the enol forms of β– diketons .While IR spectrum characterized by strong band at 3207 cm^{-1} is attributed to the intermolecular hydrogen bonded phenolic(OH) group. The thin film of Bisdemethoxycurcumin has been prepared by spray method. The physical measurements, absorbance (A) and transmittance (T) have been taken by double beam UV-visible spectrophotometer (CE-7200) at room temperature in the range of wavelength (300-900) nm. The optical constant such as absorption coefficients (α), refractive index (n) and extinction coefficient (k) have been investigated. The energy gap (E_g) and Urbach tails (E_u) have been calculated.

Keyword: Bisdemethoxycurcumin, Optical properties, spray method, Energy gap, Urbach tail.

1. Introduction

Curcuma longa L. (turmeric) is a medicinal plant that botanically is related to Zingiberaceae family [1]. Turmeric powder, derived from the rhizome of Curcuma longa, is commonly used as a spice, food preservative, and food-coloring agent [2-4]. It also has a long history of therapeutic uses. Turmeric extract is an oleoresin consisting of a volatile oil (light) fraction and a yellow–brown colour (heavy) fraction. It contains a number of curcuminoids, monoterpenoids and sesquiterpenoids. The compounds showing yellow colour are three curcuminoid compounds; curcumin, demethoxycurcumin and bisdemethoxycurcumin. Curcumin, a yellow bioactive pigment, is the major component of turmeric [4-6]. It has been shown that curcumin have a wide spectrum of biological activities such as

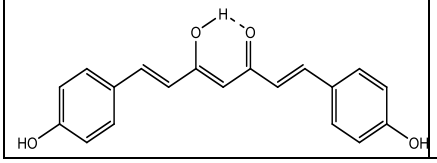
antifungal[1], antidiabetic[2], antioxidant[3,4], anti-inflammatory[7,8], anticancer[9], antiallergic[10], antiprotozoal[11] and antibacterial activities[1,3,12]. The volatile oil of C. longa reported for anti-inflammatory [13], antibacterial [14, 15] and antifungal [15] activities. On the other hand, bisdemethoxycurcumin, is an α,β-unsaturated 1,3- diketone that constitutes one of the three major components of the Indian herb Curcuma longa [16,17]. The aim of this work is prepared of bisdemethoxycurcumin and studies its optical properties by spray method.

2. Experimental details

2.1 Preparation of Bisdemethoxycurcumin [18]

Acetyl acetone (0.05 mol, 5g) and boric oxide (0.035 mol, 2.5g) were stirred for 1 hour. The appropriate p-hydroxyl benzaldehyde (0.1 mol) was dissolved in dry ethyl acetate (50 ml), and tri – (s-butyl) borate (46g, 0.2 mol) were added to the complex, and the reaction mixture was stirred for 5 min. After that the drop wise addition of a solution of n-butyl amine (0.731 g, 0.01 mol) in ethyl acetate over a period of 40 min. The mixture was stirred for a further 4 hours. The solution was set aside over night. 0.4N hydrochloric acid (75 ml) at 60°C was then added, and the mixture stirred for 1 hour. The organic layer was separated and the aqueous layer was extracted three times with ethyl acetate. The combined organic layer was evaporated and the residual paste stirred with dilute hydrochloric acid for 1 hour. The solid product was washed, dried, and recrystallized. The structure and physical properties of bisdemethoxycurcumin was given in table (1).

Table 1: Chemical structure and physical properties of Bisdemethoxycurcumin[18]

Chemical structure	Physical state	Melting Point (°C)	Color	Molecular Weight
	**powder**	**223-224**	**Orange**	**308**

2.2 Preparation of thin film

(0.01 mol. 3 gm.) of Bisdemethoxycurcumin dissolved in 25 ml of ethanol, then the solution filtered by using of filter papers. The bisdemethoxycurcumin thin film has been deposited on the clean glass substrate of dimensions of (2.7x 2.5 cm), by repeat-spray technical method were the distance between glass substrate and the device 30 cm, the temperature was 70 C° and time of spray 3 second. The nitrogen gas has been used for produce thin film with 60 torr, used because its inert gas, the thickness of the thin film has been calculated by using of equation below [19].

$$\mathbf{d= m_2 – m_1/ \rho\ d} \qquad \mathbf{(1)}$$

Where d is the thickness of thin film, m_1: the mass of glass substrate, m_2: the mass of glass substrate and the bisdemethoxycurcumin, ρ: the density of bisdemethoxycurcumin and d: the area of thin film. The thin film thickness was determined to be 60 nm.

3. Results and Discussion

3.1. IR Spectrum

FTIR spectrum of compound is listed in Table (2). The spectrum was characterized by strong band at 3207 cm^{-1} as shown in Figure (1). The attributed to the intermolecular hydrogen bonded phenolic OH group. As well a strong absorption bands within the range 1450-1600 cm^{-1} which was attributed to the stretching vibration of C=C groups aromatic and olefinic. The most important band in Bisdemethoxycurcumin is the C=O stretching vibration which appears at 1620 cm^{-1}.

Table 2: Major IR absorption bands (cm^{-1}) of Compound 1.

Functional group	OH	C=O	C=C Aromatic& Olefinic	C=C-H Olefinic O.O.P deformation	C=C-H aromatic O.O.P deformation
ν(cm^{-1})	3207	1620	1600-1450	957	831

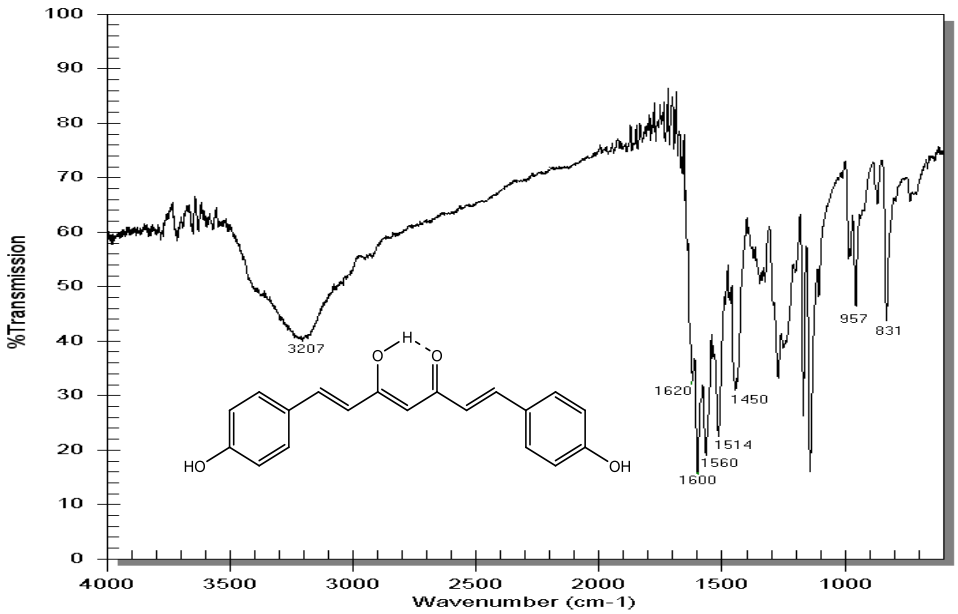


Fig.(1) IR spectrum of Bisdemethoxycurcumin

3.2. ^{1}HNMR Spectrum

The spectrum experimental data is gathered in Table (3). It is well known that the ^{1}H NMR spectrum of bisdemethoxycurcumin contains one singlet at 16.40 ppm due to the protons of two hydroxyl groups which reflects its symmetric structure, see Figure(2). The spectrum is also characterized by a singlet of one proton integral at 6.02 ppm which is assigned to the vinylic proton. The olefinic protons have doublet peaks at ranges 6.41- 7.46 ppm, while the chemical shifts of aromatic protons appear at the range 6.78-7.46 ppm.

Table 3: Chemical shifts (δ, ppm) ^{1}H NMR of the studied compound 1.

Functional group	Hydroxyl proton	Hydroxyl Proton(Hydrogen bonding)	Vinylic proton	Olefinic & Aromatic protons
(δ, ppm)	10.02	16.40	6.02	6.65-7.56

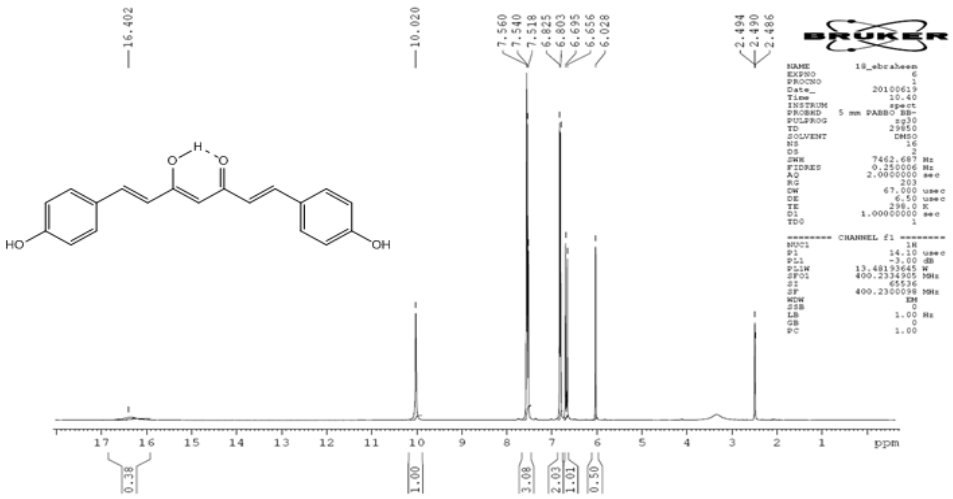


Fig.(2) ^{1}HNMR of Bisdemethoxycurcumin.

3.3. The optical properties

The absorption (A) and transmittance (T) have been investigated in the range of wavelength (300 – 900) nm. The measurements have been taken by double beam UV-visible spectrophotometer (CE-7200) at room temperature. The curves of the absorption and transmittance of the thin film are shown in figure (3), the high values of absorption of thin film appeared in the UV- visible region and the maximum of it was (500) nm, which represents the transition (π-π^*) founds in (-c=c-) bond, corresponding to the lowest value of transmittance [20]. The low absorbance which lays in visible – NIR region (600-900) nm is favorable for electronic devices such as solar cells.

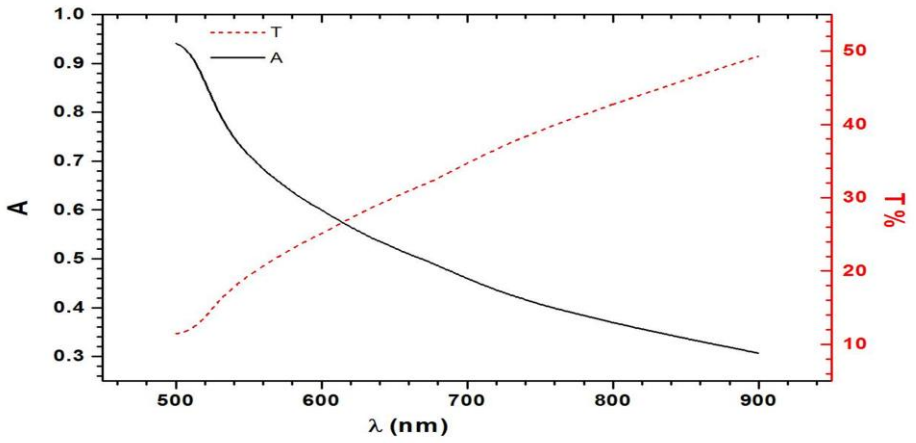


Figure (3): The absorption and transmittance curves of thin film

For optical constants, the reflectance R of the sample surface was calculated by using the exponential relation between the transmittance and absorption R= 1-(A+T) [21]. Figure (4) shows the increasing of reflection with the increasing of wave length.

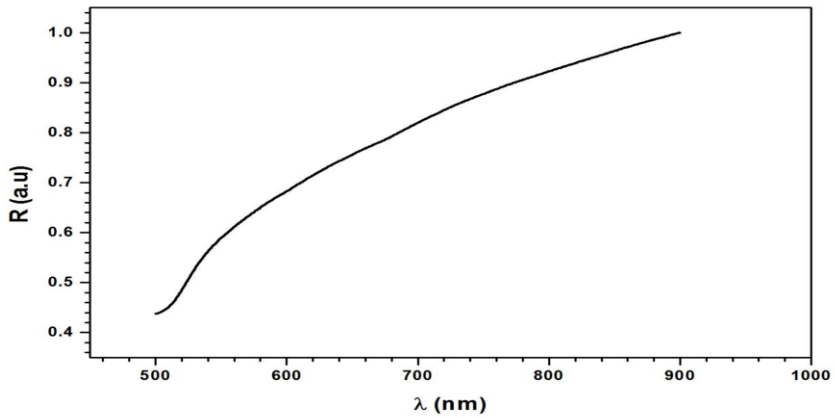


Figure (4): The reflection curve of thin film

The refractive index $n = (1+ R^{1/2})/(1-R^{1/2})$ and extinction coefficient ($K=\alpha\lambda/4\pi$) of bisdemethoxycurcumin thin film are shown in figure (5).[22,23]

The reflective index (n) and the extinction coefficient (k) are very interested optical properties [24].

From the figure (5), it can be observed that, the refractive index value 3at wavelength 900 nm and the extinction coefficient 0.14 at wavelength500 nm. The deviation in optical constants for thin films might be attributed to the formation of organic aggregation.

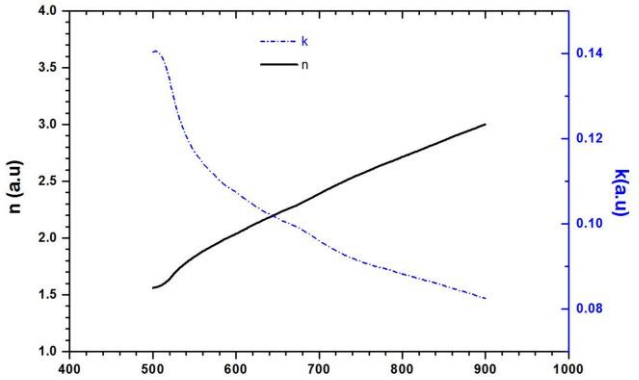


Figure (5): The refractive index and extinction coefficient of thin film

The absorption coefficient (α) determined by using of Beer-Lamberts law [25].
$\alpha = 2.303\ A / d$ …….. (2)
Where (A) and (d) are the absorption and the thickness of the thin film respectively. The behavior of the absorption coefficient (α) with incident photon energy (hν) is shown in the Figure (6)

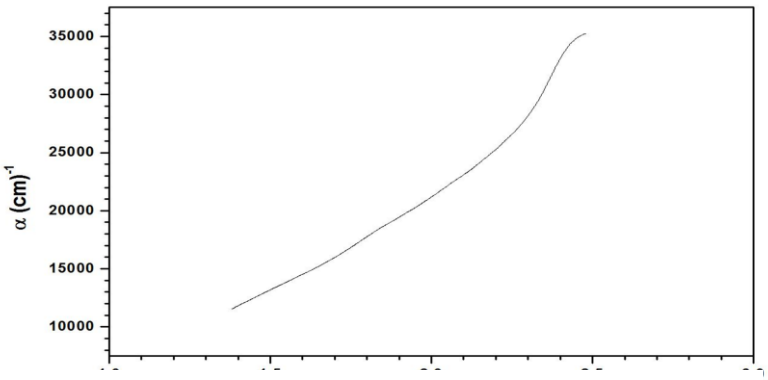


Figure (6): The absorption coefficient of thin film.

The absorption coefficient (α) identifies the type of the transitions between the electronic levels. The transition is direct if α greater than 10^4 cm^{-1} or it's indirect if α less than10^4 cm^{-1}, in this study the transitions were direct, and subsequently the optical energy gap E_g was direct, by using Tauc's approach $\alpha h\upsilon = A(h\upsilon - E_g)^{1/2}$ of direct band-gap energy[26] , Figure (7) shows the extrapolating the linear curve to the photon energy axis, we found that the band-gap energy was 2.12 eV. The bisdemethoxycurcumin thin film appears semiconductor behavior.

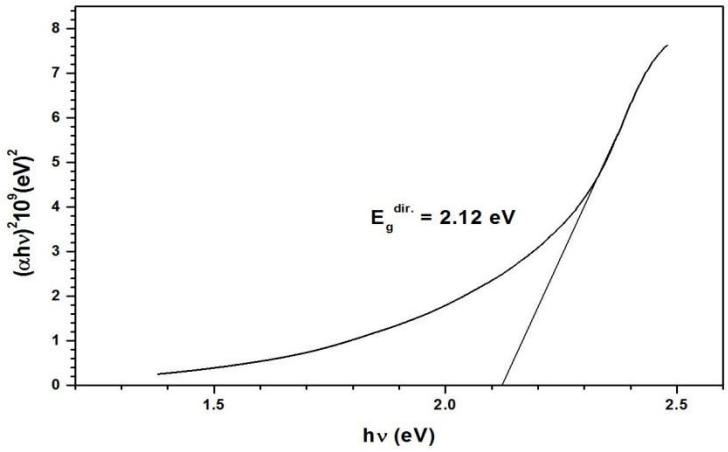


Figure (7): The direct energy gap of thin film.

The chemical disorder in material is called Urbach energy or tails, appears in polymers and pigments, for example, have high molecular weight [27]. It was calculated by using Equation (3)[28].

$Ln(\alpha) = Ln(\alpha_\circ) + h\nu / E_u$

Were $\alpha_\circ$ is primary extinction coefficient and E_u Urbach energy, calculating by taking inverse of the slope of the linear portion of the curve in figure (8). It was 1.02 eV.

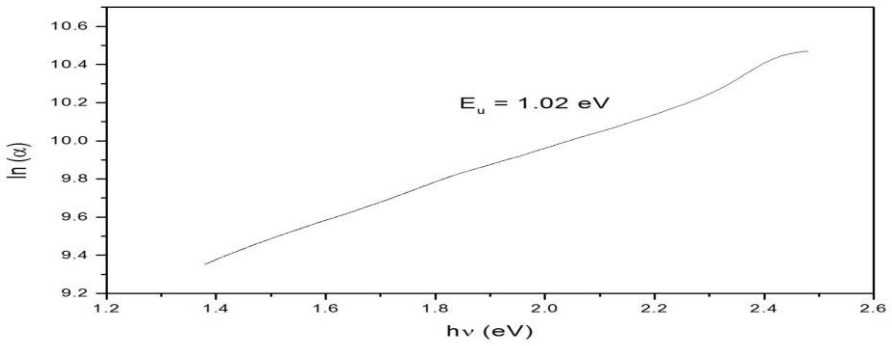


Figure (8): The Urbach tail of thin film.

Conclusions

This work includes preparation of bisdemethoxycurcumin and the structure of product were established by ^{1}HNMR and IR. The absorption in thin film of Bisdemethoxycurcumin has been prepared by spray method is broad and extending from the UV to the near-IR. Energy gap and absorption coefficient of the film are obtained from UV-Vis spectral analysis. The energy gap value was 2.12 eV, corresponding to semiconductor behavior. The Urbach tail depending on the absorption coefficient was 1.02 eV means high disorder in the structure of bisdemethoxycurcumin.

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تقييم الخواص البصرية لغشاء ثنائي دي ميثوكسي كركمين المحضر بطريقة الرش

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الخلاصة

في هذا البحث تم تحضير مركب ثنائي دي ميثوكسي كركمين وتشخيصه بواسطة طيف الرنين النووي المغناطيسي للبروتون اذ تميز طيفه بظهور اشارة مفردة عائدة لبروتون مجموعة الفينايل تقع عند6.02 جزء من مليون، بالاضافة الى ظهور اشارة مفردة عريضة وضعيفه عند 16.10جزء من مليون تعزى الى بروتون مجموعة الهيدروكسيل التي تشترك في تاصر هيدروجيني ضمني في الحلقة المخلبية للشكل الاينولي للبيتا داي كيتونات. بينما تميز طيف الاشعه تحت الحمراء بظهور حزمة عريضة وقويه تقع عند 3207 سم$^{-1}$ تعزى الى الاهتزاز الاتساعي لمجموعة O–H المتاصرة تاصرا هيدروجينيا بينيا. كما حضر غشاء رقيق من مركب ثنائي دي ميثوكسي كركمين بطريقة الرش واخذت القياسات الفيزيائية كالامتصاصية (A) والنفاذيه (T) باستخدام جهاز المطياف الضوئي نوع (CE–7200) في المنطقتين المرئية وفوق البنفسجية عند درجة حرارة الغرفة ضمن المدى (300–900) نانومتر، حيث تم حساب الثوابت البصرية (معامل الامتصاص (α) ومعامل الانكسار (n) ومعامل الخمود (k) وفجوة الطاقة (E_g) المباشرة وذيل ارباخ (E_u)).