Isolation and polymerization of allicin which is extracted from dry powder of Allium sativium (garlic)

Haider Abid Al-Kareem Al-Wafi
M.Sc. clinical biochemistry
College pharmacy
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Abstract

The Allicin is isolated with purity from alcoholic extract of dry powder of garlic bulbs. Its was characterized by (IR, UV).

The polymerization is carried out under conditions like stomach conditions in human (pH, temperature). The polymerization is investigated by using DSC tech. several physical and chemical parameters were determinedsuch as, rate of polymerization, energy of activation, in addition to the enthalpy of polymerization.

Introduction

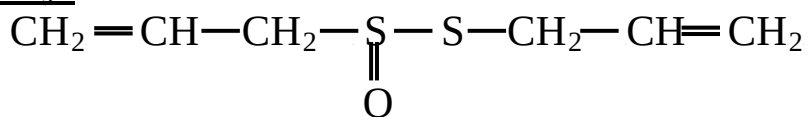
The garlic contains at least 33-sulfur compounds[1] which contain a higher conc. Of sulfur than any other Allium species. The sulfur compounds are responsible bath for garlic pungent odor and many of its medicinal effect[2].there is many studies that indicated the potential clinical benefits of garlic are almost due to Allicin compound as follows:

1-**cardiovascular:** Antilipemic, antihypertensive, anti-atherosclerotic: [3-7].
2-**gastrointestinal/hepatic:** *spasmolytic, hepatoprotectan*[8].
3-**endocrine***: Hypoglycemia*[17].
4-**Hematologic***: Antithrombotic/antiplatelet* [18,19,20].
5-**Reproductive:** *emmenagogue/abortifacient*[21].
6-**Immune modulation:** *immunostimulant*[22].
7-**Antimicrobial**: *Antiviral, antibacterial, antifungal, and antiparasitic*[23,24]
8-**Antineoplastic***: chemoprevention*[25].
9-**Antioxidant***: Antioxidant*[26].

Allicin

Garlic (Allium sativum), like other plants, has an exquisite defense system composed of as many different components as the human immune system. In order to protect itself from insects and fungi, garlic enzymatically produces Allicin when it is injured. Thus, allicin is mother nature s insecticide. Allicin was discovered in 1944 by Cavallito et al.[27]
who first noted its potent antimicrobial activity. Allicin received a patent for its antifungal activity in test tubes. However, no clinical trials have been performed with allicin and were never developed into a drug or commercial product due to its instability, Inability to be absorbed, and offensive odor. Allicin itself is considered to be limited value inside the body and is presently regarded by the scientific community as just a transient compound, which rapidly decomposes to other compounds[28].

Allicin chemistry:

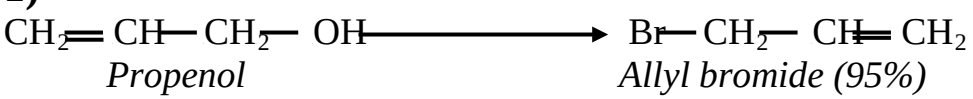


Chemically, Allicin is known as 2-propene-1-sulfinothioc acid S-2-propenyl ester; thio-2-propene-1-sulfinic acid S-allylester[29]. Allicin is produced by an enzymatic reaction when raw garlic is either crushed or somehow injured. The enzyme, alliinase, stored in a separate compartment in garlic, combines with compound called alliin in raw garlic and produces allicin[30]. Because allicin is so unstable, once it is generated it readily changes into other compounds. Thus cooking, aging, crushing and otherwise processing garlic causes allicin to be decomposed into other compounds. According to two studies of garlic preparations, allicin decreased to non-detectable amounts within one[3] to six[4] days[31].

Synthesis of Allicin compound

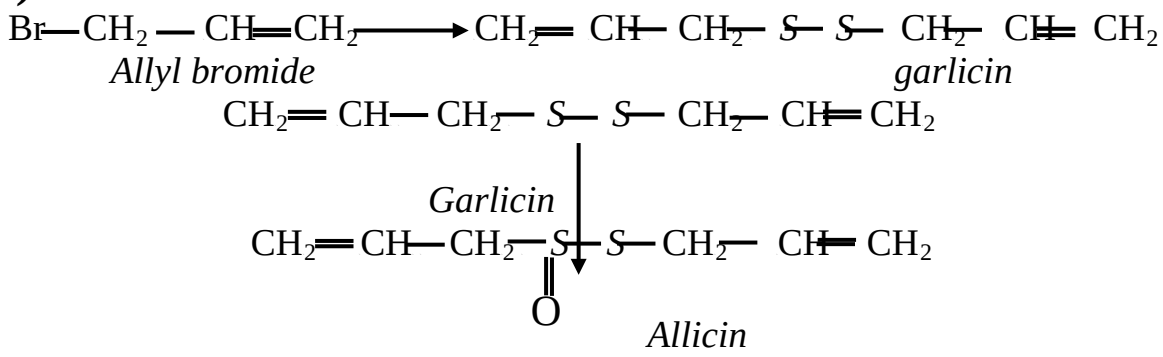
Synthesis of this useful molecule is possible with an easily obtainable starting material in three steps. Starting with propenol (allyl alcohol), allyl bromide is created via substitution and is transformed into garlicin, using sulfur and sodium borohydride in a solvent of methanol, which is then subject to chloroform to give the final product of allicin[30].

1)



Propenol *Allyl bromide (95%)*

2)



Allyl bromide *garlicin*

Allicin

Experiments

Isolation of allicin compound

Depend on the approach clarified by (Cavallito and et al 1944), he puts (400g) from scraped off and milled cloves garlic by electric stirrer to become as paste, he dissolves this paste in round (500ml) ethanol 95%. Then he put the round on magnetic stirrer to 1 hour, filtered by funnel to obtain larger amount of the alcoholic extract. Concentrate the extract by evaporator round to dispose of remaining ethanol, then extract five time with (25ml ether for each 100 ml extract) and sum the products ether from the extractions then remove the ether by evaporator round in room temperature (12^{o}C), he adds to the remain (25ml) distilled water and (10ml) n-hexanol (undissolved allicin) stir the solution for 30 minute, filter the water solution then cool and store in ice bath, to purification the product by extracting the water solution 4 times with (10ml) ether in each time, sum the ether and cool it by ice bath which leads to separate ice crystal (allicin), then dispose of the ether by volatilizing at room temperature.

Spectroscopic measurements:

IR spectra

The IR spectrum for the allicin compound is registered by using (SP.300 infrared. Pye-Unicom spectrophotometer) instrument by using NaCl cell. Table (1) and figure (2) show absorption bands and active groups, which are attributable to them depending on (Silverstein etal 1981).

U.V spectra

The U.V spectrum for the allicin compound is registered by using (SP.8-100 Pye-Unicom spectrophotometer) instrument by using quartz cell. Figure (3) shows one band with absorption (1.43) in wavelength ($264cm^{-1}$) (without acidity) and one band with absorption (0.547) in wavelength ($258cm^{-1}$)(acidity).

DSC of Allicin(polymerization)

The polymerization of acidic Allicin(produce Allicin in aqueous solution at tem. (37C) for 30,60 minute) is studied by using the differential scanning calorimeter (DSC) type Du point thermoanalyser model 1090 with rate of heating $20^{o}C$/min. Under inert nitrogen environment and calibrated the instrument by using standard indium with purity (99-99.9%), figure (4) represents curves DSC Allicin which is exposed to the same conditions in stomach. From the analysis of the curves, degrees of heat are computed to polymerization primary (T_i), top and final temperature (T_f) also I compute the rate of polymerization (R) from slop of the curve in the high temperature (Top) and compute the activation of energy (ΔE) by using arhenous equation and energy of polymerization from area under the curve, table (2) represents the physical functions, which derived from DSC curve to allicin polymerization, the acid condition act as cationic initiator and due to this action allicin consists of as in figure (1)

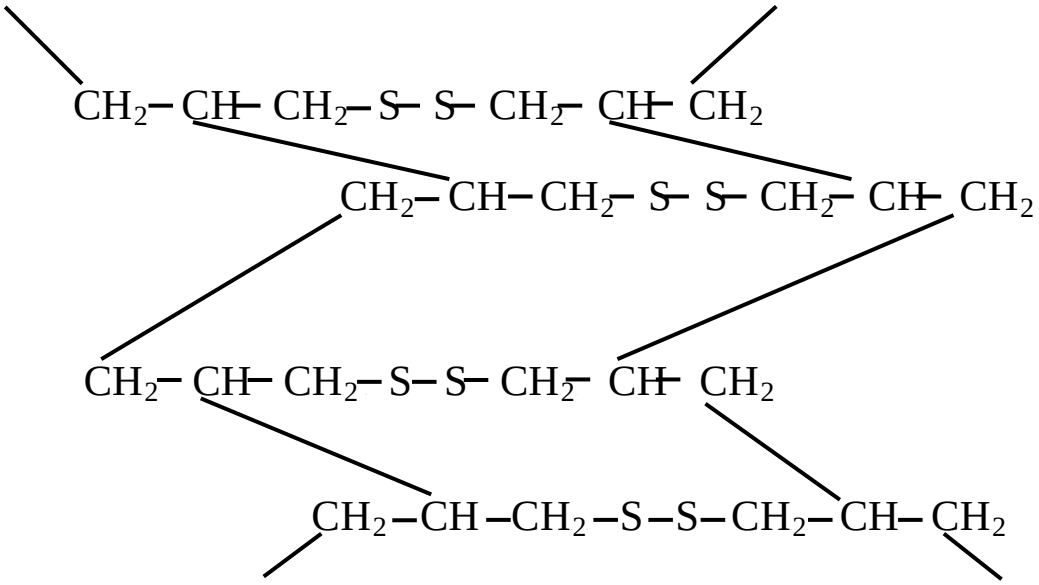


Figure (1) cross linking polymer of allicin in condition like to stomach

Chemical groups	Bands(cm^{-1})
Asym. , Sym. CH_2 Stretching	2890. 2820
Asym., Sym. – CH = Stretching	3000. 2940
Asym. , Sym. CH_2= Stretching	3055. 3020
C=C	1550
C=S	1050
C–S	695

Table (1)

Absorption bands for Allicin compound

Therm. Functions Time (minute)	Temp. C^O			R V/min	Ecur J/G	ΔE KJ/mole
	T_i	T_{op}	Jf			
15 30	120 108	155 145	212 207	2.1 1.4	18.3 18.1	37.9 32.6

Table(2)
DSC data for allicin polymerization

Discussion

Among many studies, both (Adoga GI. 1987) and (Newall CI. And et al 1996) seem to study the use of Garlic in the medicine field on both animals and humans, they showed the biological activity in this plant produced (depending on and supported by studies) existence sulfur compound named Allicin produced from Alliin by activated Alliinase enzyme by scraping the clove of Garlic, therefore, Allicin compound is considered one of the important compounds in Garlic plant.

What guided me to this study are the conclusions I drew from some studies exclusively two studies via (Cavallito C.J. and et al 1944) and (Lagnodo J. 2004) which isolated and identified Allicin compound by different means, they found this compound contains two groups every one contains double bond named allyl. In addition to that it is shown by study of (Lawson L.D. et al 1992) the Allicin compound or any of sulfur derivatives and after intaking the powder Garlic (25g) equal to (10 cloves) approximately (90mg) of Allicin, its concentration in the blood or in Urine after (1-24) hour is nonsignificant and hasn't any biological activity. I conclude that after the allicin compound reaches the gastric or intestinal does not obtain any absorption in it, therefore, there two possible ways to fate the allicin compound

First: the decomposition of the allicin and transportation to sulfur derivatives of compound, therefore, the biological activity will be missed and this is certain by all the researchers.

Second: I prove it in this study and there is no indication for this previously. The polymerization of Allicin compound in gastric conditions (pH, temp).

The product which is reached by (Lawson L.D et al 1992), proves the products which I Obtained, whereas after the allicin enters gastric and because of the temperature (37^oC) and the Acidity (pH=1), the allicin converts to polymer with high molecular weight because it contains two active groups each one contains double bond, therefore, after consisting bulk group from allicin polymer, the intestinal cannot absorb the polymer that's lead to nonsignificant concentration of allicin in blood or Urine.

It's possible that the polymer will eliminate with stools and his biological activity by Constituted and remain it in gastric for some time.

In this study, allicin compound is isolated by (Cavallito and et al 1944) then characterized the compound by IR technology as in figure (2) table (1) and UV technology figure (3) considering room temperature during this time is (12^oC) this aids to stabilize the compound without volatile compound. Then I arise the polymerization under conditions like Stomach conditions (pH=1, temperature = 37^oC), after studying the polymerization by DSC Technology and computing the physical functions, I am certain that the compound is polymerized Table (2), result to this linear compound, its potential possible the polymer will be liner reticulm figure (1).

In addition to that by UV technology and after acidic the compound I noted the decrease in concentrations of double bond (significantly) figure (3-A). This indicates the opening the double bond and combining it from two sides and transporting the allicin to polymer.

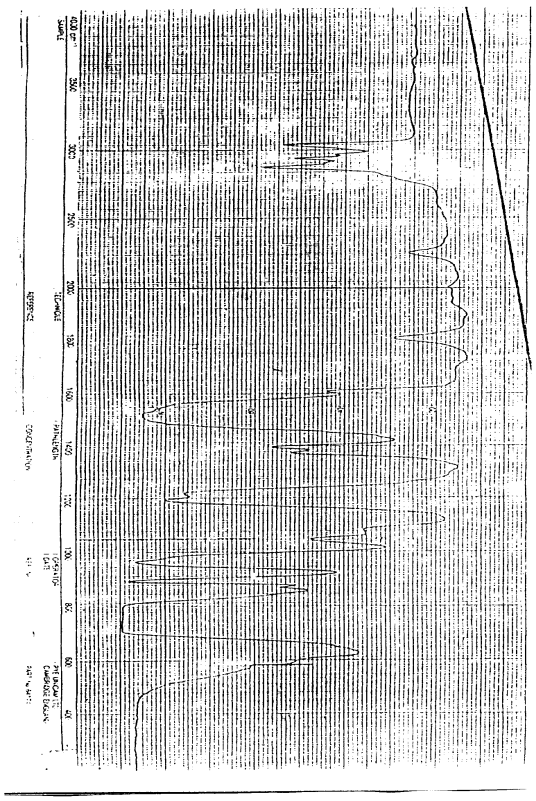


Figure (2)
IR spectrum for Allicin compound which isolated from alcoholic extract

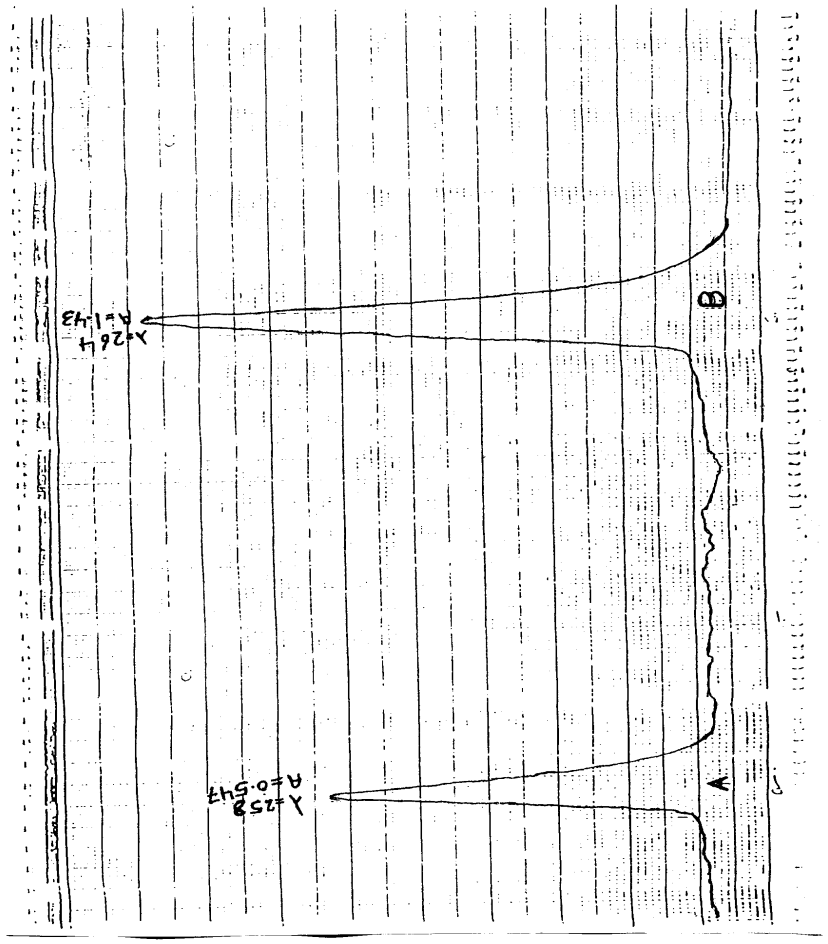


Figure (3)
UV spectrum for Allicin compound A-acidity B-without acidity

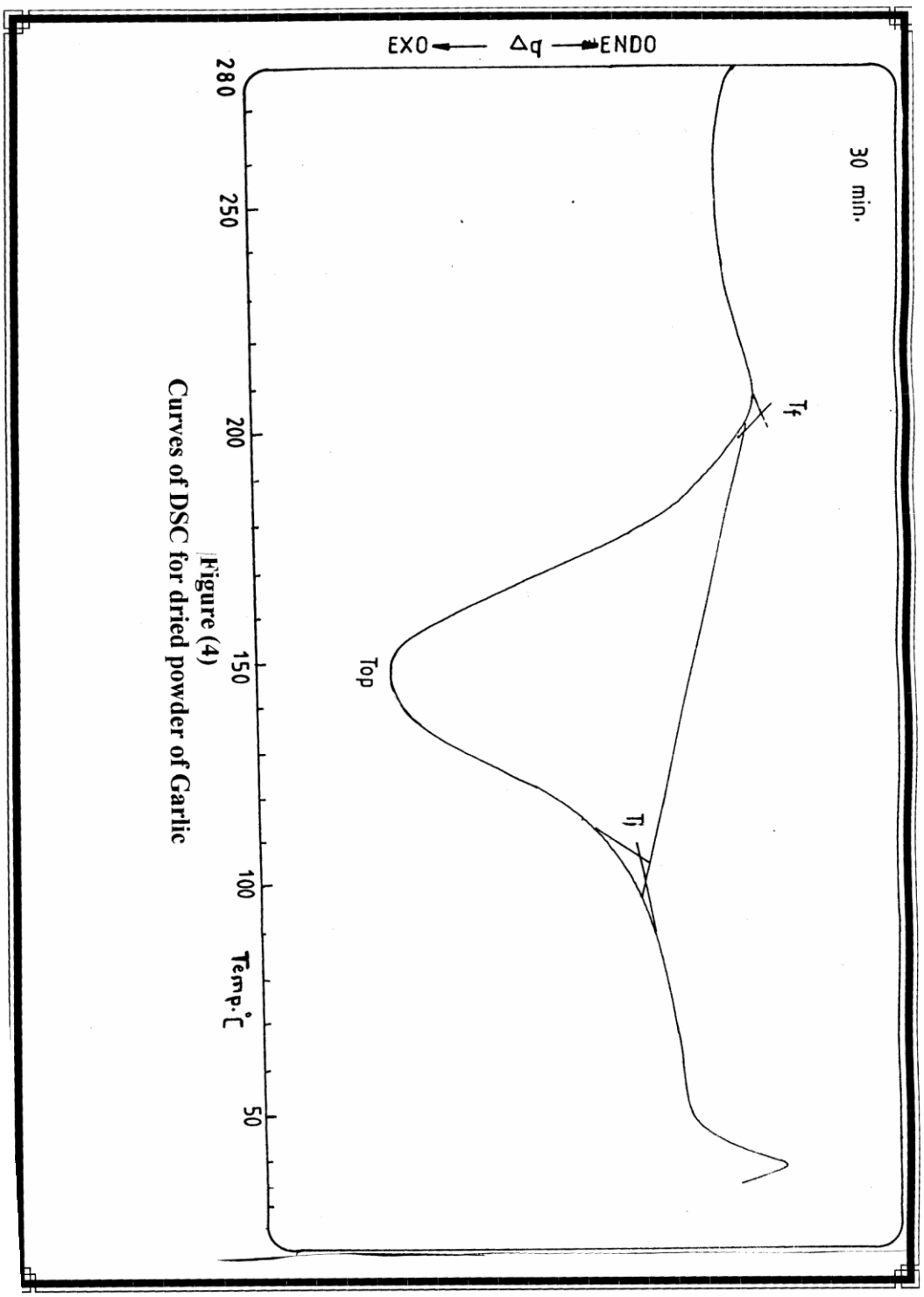


Figure (4)
Curves of DSC for dried powder of Garlic

Conclusion

The conclusion which is obtained in addition to the ability isolate the allicin compound we can polymerize it in condition like Gastric conditions, hence, the production of the natural polymer from garlic plant.

To complete this study enable to make study proves the products apparently which I reached it, by study the existence polymer of allicin in stool of volunteers.

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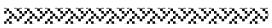
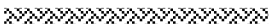
ملخص

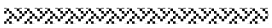
تم عزل مركب الاليسين بنقاوة من المستخلص الكحولي لمسحوق بصيلات نبات الثوم الجاف وشخص المركب بتقنية ((IR, UV. أجريت عملية البلمرة لمركب الاليسين المعزول تحت ظروف مشابهة لظروف المعدة في الإنسان من حيث درجة الحرارة والحموضة (temperature, pH) باستخدام طريقة المسح الحراري التفاضلي (differential scanning colorimeter)ثم حساب بعض الدوال الفيزيائية المهمة لعملية البلمرة مثل سرعة البلمرة, طاقة التنشيط, بالإضافة ألي الطاقة الحرارية الناتجة أثناء عملية البلمرة.

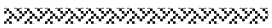
الاستنتاج

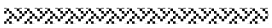
استنتجت بالإضافة إلى إمكانية عزل مركب الاليسين يمكن بلمرة هذا المركب تحت ظروف مشابه إلى ظروف المعدة من حيث درجة الحرارة والحموضة وهذا يؤدي إلى إنتاج بوليمر طبيعي من المسحوق الجاف لبصيلات نبات الثوم الجاف.

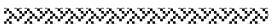
Haider Abid Al-Kareem Al-Wafi 

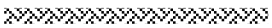
Haider Abid Al-Kareem Al-Wafi 

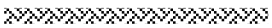
Haider Abid Al-Kareem Al-Wafi 

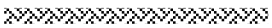
Haider Abid Al-Kareem Al-Wafi 

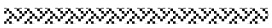
Haider Abid Al-Kareem Al-Wafi 

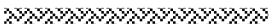
Haider Abid Al-Kareem Al-Wafi 

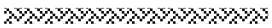
Haider Abid Al-Kareem Al-Wafi 

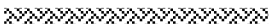
Haider Abid Al-Kareem Al-Wafi 

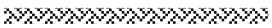
Haider Abid Al-Kareem Al-Wafi 

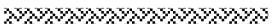
Haider Abid Al-Kareem Al-Wafi 

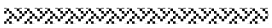
Haider Abid Al-Kareem Al-Wafi 

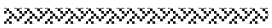
Haider Abid Al-Kareem Al-Wafi 

Haider Abid Al-Kareem Al-Wafi 

Haider Abid Al-Kareem Al-Wafi 

Haider Abid Al-Kareem Al-Wafi 

Haider Abid Al-Kareem Al-Wafi 

Haider Abid Al-Kareem Al-Wafi 

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