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Catalytic and synthesis of new compound based on geranium oil

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Abstract

Clays, natural resources find applications in various fields: cosmetics, pottery, industry, building materials. Their use in organic chemistry as catalysts has shown their efficiency and contributed to the development of environmentally friendly chemical processes. However, it is necessary to characterize this materials to know its chemical composition and its physicochemical properties. Kaolin is widely used in pharmaceutical and medical applications. The date palm is the main crop of the oases of the Sahara. This culture is threatened by Bayoud, a date palm disease caused by Fusariumoxysporumalbedinis (Foa).

Keywords: Raw Clay, materials, Antifungal, Bayoud, Date Palms.

1. INTRODUCTION

Clays [1] are crystalline porous materials, are used in many separation processes, for example to extract oxygen from the air or to separate the ortho[2],meta and para isomers of xylene from a mixture[3], these methods exploit the adsorption selectivity properties of the molecules in these molecular sievesAs well as clays are among the polides[4], which are used in the industrial field and catalysts[5].

Their fields of application are vast, industrial, sanitary [6], environmental, etc. These polides are used in heterogeneous catalysis, he use of heterogeneous catalysts for organic conversion is growing rapidly on homogeneous catalyst systems due to several advantages of heterogeneous catalysts such as high stability, ease of handling, recovery and reuse, non-corrosive character, long-lasting persistent catalytic activity, and respect for the environment [7] green protocol.

Recently, we reported several clay catalyzed organic transformations[8], for example a solid carrier acid catalyst [9]. It is very cheap, easy to prepare in the laboratory and can be stored for a long time without significant loss of catalytic activity[10], but this time we tested the Raw Clay in a green and efficient synthesis, based on the aza-Michael reaction.

Bayoud

Fusarium wilt, commonly called bayoud, a fungal disease of the date palm caused by the fungus Fusariumoxysporumalbedinis (Foa) [11], the impact of this disease is the most severe in North Africa. As with most vascular diseases caused by soil pathogens, combat strategies are very limited or almost nonexistent. Among these strategies, the deployment of Foa-resistant cultivars seems to be the most appropriate and economical approach[12],but natural resistant genotypes are rare with poor fruit quality and a poor system. Date palm farm is Laborieux. Offered only as a long-term Alternative control measures such as the use of Foa antagonists are, therefore, necessary and should be explored. This strategy is based as shown in other pathosystems involving Fusarium species[13], on the use of microorganisms such as bacteria[14], yeasts or saprophytic fungi that have a significant potential to inhibit pathogens or to enhance the mechanisms of defense[15],in the case of FHB,

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most studies have reported the use of non-pathogenic Fusarium isolates alone or in combination with bacteria such as Pseudomonas fluorescens.

Biocontrol agents [16] provide better control of the disease by microbial antagonism involving direct interaction with the causative agent of the disease and / or an indirect action involving the host The direct effect is usually the result of antagonism between the biological control agent and the pathogen due to antibiosis or competition of nutrients and / or parasitism, while indirect interaction results from the improvement of plant defense mechanisms,association of both effects may be noticeable using some biological control agents.

In the case of the date palm, little is known about the microorganisms that protect plants against Foa and even less about the induction of defense reactions [17], recently, we have shown that pretreatment of date seedlings with a hypoaggressive isolate of Foaprovided protection against further attack by an aggressive Foa isolate,this protection was most likely achieved by early induction of plant defense responses by the hypoaggressive to compensate for the aggressive Foa isolate [18].

In this study, the hypo aggressive isolate exhibited no direct competitive antagonism towards Foa; however, it was able to promote faster accumulation of specific phenolic compounds and to induce earlier peroxidase activity in both susceptible and resistant cultivars tested. The main induced phenolic compounds were previously characterized as hydroxycinnamic acid derivatives and would be biomarkers of date palm resistance [19],among these compounds synthesized de novo, the I2-derived synaptic was the main phytoalexin accumulated in the date palm in response to Foa[20],trials including the hypo aggressive isolate studied are still under way under laboratory conditions to establish different parameters for its use as a biocontrol agent for greenhouse Foa and optimistically in the field[21].

Aza-Micheal Reaction

In addition to Michael's reaction a practical process has been developed for the addition of aliphatic or aromatic amines to alkenes by heterogeneous catalysis (Acid or basic) [22], which is called the aza-Michael reaction [23].

Michael's reaction and its modified form such as aza-Michael thio-Michael and carba-Michael reaction is one of the most exploited reactions in organic chemistry[24], amino acids, esters, ketones, nitriles are synthesized for the preparation of many nitrogen products antibiotics and chiral auxiliaries [25], in addition, a large number of biologically active compounds contain parts of β-amino-ketone or ester [26].

This addition is generalized and can be carried out on activated alkenes or not by large group such as esters, ketones, and β-unsaturated nitrile [27].

In general, the aza-Michael reaction requires special conditions, such as the short reaction time, a very good chemo selectivity, a high yield,[28], the ease of purification of the products, the use of a inexpensive and reusable catalyst, are the main features of this protocol. However, in some cases, the use of catalysts in stoichiometric amounts with substrates leads to side reactions [29].

The main objective of our study is the Synthesis of antifungal [30], effective against the fungus Fusariumoxysporumalbedinis (Foa) [31], which causes the vascular Fusarium wilt commonly known as Bayoud Date Palm Diseaseby the use of green catalyst [32],on the one hand, we have based on the reaction aza- Michael [33], the addition of amines on α, β-unsaturated alkenes, catalyzed by the raw Clay, and on the other hand, we have developed a method, of clean and economic synthesis.

Then we move on to biological activity to test the antifungal efficacy [38], of our product on the fungus Fusariumoxysporumalbedinis (Foa), which he gave us very interesting results.

2. Materials and methods:

The IR spectra of the sample (Figure1) are in agreement with the literature .

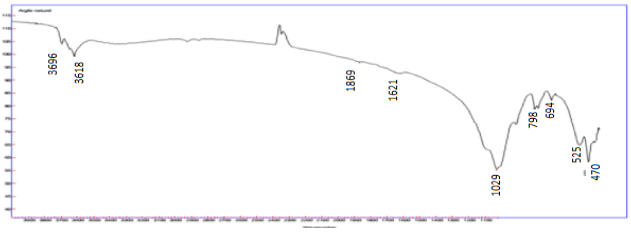


Figure1: The IR spectrum of clay

We observe from the spectra, narrower bands located around 3696 and 3618 cm-1 which are attributed to the elongation of hydroxyl bonds (-OH).

- 1869cm-1 characteristic with carbonate CO_3^{--}

- 1621 cm-1 which is attributed to the H-O-H deformation vibrations of water molecules

- A most intense and widest band located between 900-1200 cm^{-1} and centered around 1029 cm-1 corresponds to the valence vibrations of the Si-O bond the band 798cm-1 couple Al-O and Si-O outside the plans attributed to the impurity of silica and Quartz.

- The band 798 cm-1 is attributed to the vibrations of elongation of the Si-O-Al bonds.

- The bands centered at 694, 525 and 470 cm-1 is respectively allocated to the vibrations of deformations of the Al-OH-Al and Si-O-Al bonds.

Characterization of clay by DRX

The X-ray diffraction diagram (Figure2) of clay, shows the presence of, Kaolinite (K), Illite (I), Quartz (Q), Dolimite (D) and Calcite (C).
The major crystalline phase contained in this clay is composed of Kaolinite (K) (Table1), characterized by an intense peak at (d = 4.21Å, 2θ = 21.093) and illitecharacterized by peaksat 2θ (°)=9,096(d =9,096Å) and at 2θ (°)=30,114(d =30,114Å). Table2, present, Quartz, Dolomite and Calcite.

Crystalline impurities consist mainly of Quartz, Dolomite and Calcite (Table2).

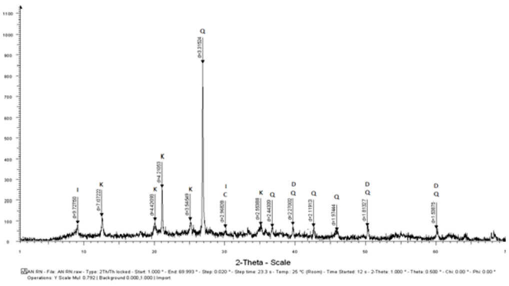


Figure 2: Clay X-ray diffractogram

Table 1: Diffraction angle and inter-reticular distances of Kaolinite and illite.

	Kaolinite					Illite	
2θ (°)	12,537	20,075	21,093	25,153	35,143	9,096	30,114
d (Å)	7,072	4,420	4,210	3,545	2,553	9,727	2,968

Table 2: Diffraction angle and inter-reticular distances of Quartz, Dolomite and Calcite.

	Quartz						
2θ (°)	26,865	36,772	40,029	42,675	46,013	50,321	60,133
d (Å)	3,315	2,44	2,270	2,119	1,974	1,813	1,538

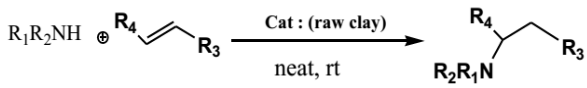
	Dolomite			Calcite
2θ (°)	40,029	50,321	60,133	30,114
d (Å)	2,27	1,813	1,538	2,968

From these results it can be shown that this clay is comparable to that of type 7(Å), which is a Kaolinite.

On the other hand, Clay cleanses the skin and promotes healing. The clay absorbs toxins, which helps the lesions to heal. On a wound or an abscess, it captures the germs without altering the healthy cells around, carrying with it the impurities. Zinc and alumina accelerate healing, as well as rematerializing and regenerating silica of the skin. As part of the effective anti-fungal synthesis against Bayoud, a disease of date palms through the use of Crude Clay as a green catalyst, we have chosen the following approaches:

We adopted a strategy for our realization of organic synthesis; based on the aza Michael reaction will be respectful of the environment, so-called green synthesis, Schema1.

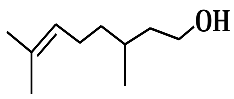
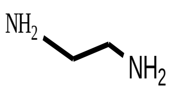
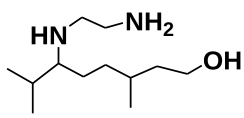
Schema1: General reaction

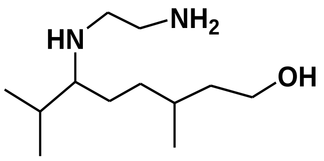


R3=ROH, R4 = H, CH2 -CH3, CH3

The conditions of the reaction are presented in Table 3. Product of the reaction (Figure3), R19, is 6-(2-aminoethylamino)-3,7-dimethyloctan-1-ol.

Table3: Antifungal products synthesized by the catalyst (Raw Clay)

Entry	Alkenes	Amines	Product	Time (mn)	Yield (%)	Catalyst
01				**10**	**96**	Raw Clay



6-(2-aminoethylamino)-3,7-dimethyloctan-1-ol

Figure 3: Product R19 antifungal against the fungus Fusariumoxysporumalbedinis (Foa)

An excellent yield, and better product R19 as antifungal, has been observed, obtained by the reaction of aza-Michael, by reacting a mixture (1.2 equivalents) of amine with (1.0 equivalents) of alkenes in the presence (100 mg) of crude clay as a catalyst, at room temperature, and the reaction without solvent.
The product giving an excellent yield (96%) after a short time (10) minutes.
The pure product can be obtained by removing the catalyst by filtration and then removing the excess amines by a rotary evaporator.

3. Results and discussion

After 72 hours, we find that the growth activity of the fungus is continued in the box of testifies and, but showed no growth or activity of the fungus in the box R19 which contained our product.

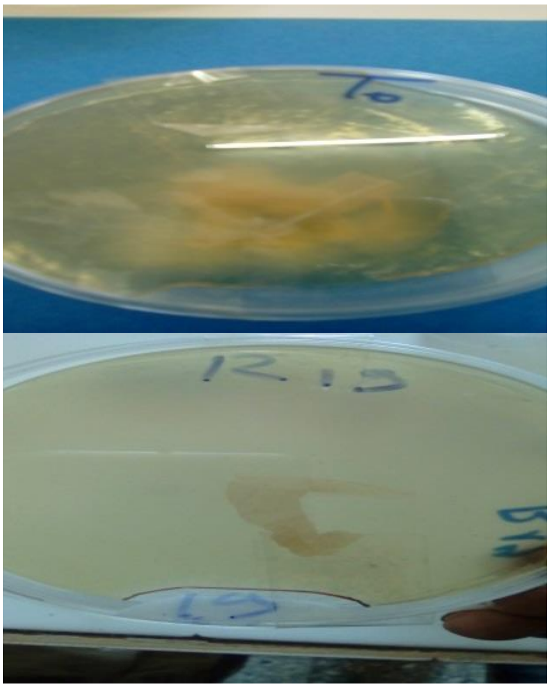


Figure 4: Test results of R19 product on the fungus Fusariumoxysporumalbedinis (Foa) after 72H.

Fusariumoxysporumalbedinis (Foa) spread spread throughout the box testifies and the box R19 show no growth or activity of the fungusFusariumoxysporumalbedinis (Foa), a case of date palm disease (Bayoud), according to these excellent results.

We find that our product R19 has been completely destroyed the fungus (FOA) and effective antifungal against Bayoud, date palm disease.

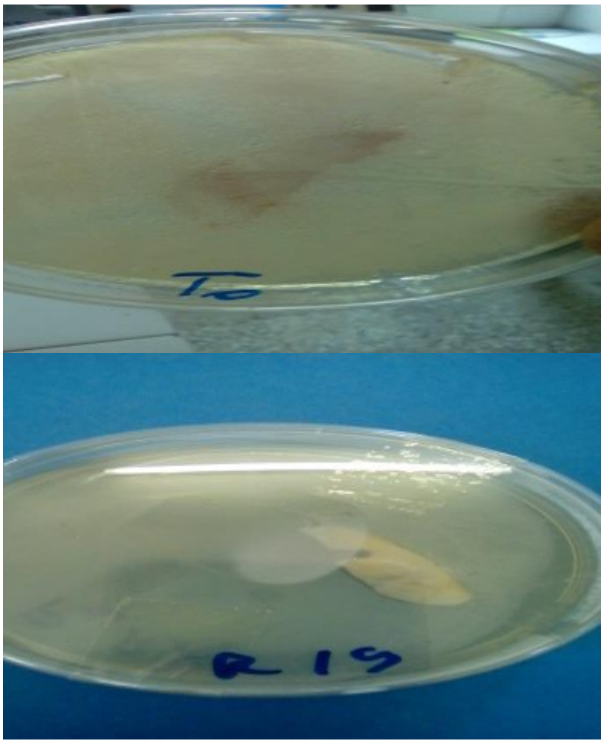


Figure 5: Results of the tests of our product R19 on the fungus Fusariumoxysporumalbedinis (Foa) after 18 days
In the same context and after the completion of the biological tests; It has been observed that, an excellent yield, and better product as antifungal, obtained by the reaction of Aza-Michael.
The product gives an excellent yield (96%) after a short time 10 minutes. The product was characterized by 1H NMR spectroscopy.

Uses of clay kaolin in medicine and application pharmacology

Kaolin is a type of clay obtained from granite rocks.

Clinical data

Anti diarrheal preparations containing kaolin have been used in the treatment of enteritis, cholera,

Kaolin has been recognized as a coagulation activator and has been incorporated into various laboratory testing to measure activated clotting time (ACT), used to guide heparin anticoagulation to prevent thrombosis, and reduce inflammation.

The use of kaolin-soaked gauze or in other dressings in surgical procedures (including ear, nose, and throat, and cardiovascular surgery) as a haemostatic agent has been reported.

Other uses

Antacid

Venezuelan kaolin was tested in the presence of hydrochloric acid and pepsin in order to determine its neutralization capacity. Achievement of normal gastric pH occurred with 250 mg of the modified kaolin clay compared with 400 mg of original clay, leading to the conclusion that modified kaolin clay might be useful as a cheap and effective antacid.

Insecticide

Kaolin has been used as an insecticide against various arthropods that affect crops.

Laboratory Testing

Kaolin has been used in the diagnosis of tuberculosis using the kaolin agglutination test (KAT). Kaolin has also been used experimentally to induce hydrocephalus in animal models in order to assess the effects of the condition on sensor motor development. Additionally, kaolin has been studied for its effects when testing horse serum for conversion against equine influenza virus, which causes a major respiratory disease among horses.

Wastewater Purification

One small study suggested that the addition of kaolin to oil field wastewater can result in removal of chemical oxygen demand, removal of scaling ions, such as iron, calcium, and magnesium, improvement in membrane filter index, bactericidal effects, and inhibition of corrosion.

1H R.M.N
Product 01
RF= 0.80 (Hexane-EtoAc): 2/1

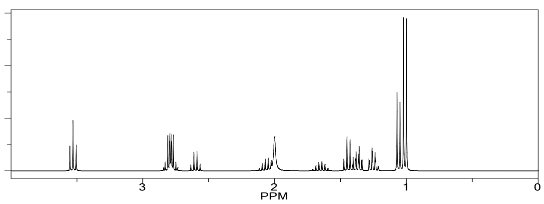
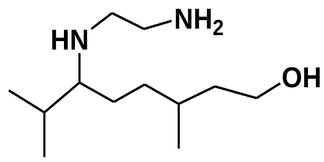


Figure 6: Spectral 1H R.M.N.

Product of the reaction (Figure3), R19, is 6-(2-aminoethylamino)-3,7-dimethyloctan-1-ol.
RMN**H^1 ($CDCl_3$, 300 MHz) □□□ 1.04 (**d, 6 H, (C**H**$_3$)$_2$CH [d ,3H, CH-C**H**$_3$); (q, 6H, C**H**$_2$- C**H**$_2$-CH(CH_3)-, (CH- C**H**$_2$- CH_2)-CH-] ; 1.65 (m , 1H, CH_2-C**H**(CH_3)-(CH_2)$_2$-N) ; 2.0 (s, 3H, NH_2, NH) , 2.06 (m, 1H,(CH_3)$_2$ C**H**- CH-N) ; 2.65 (q , 1H, CH_2-C**H**-N H) ; 2.77-2.81 (t , 4H, N-C**H**$_2$-C**H**$_2$-N) ; 3.53 (t , 2H, CH_2-C**H**$_2$-OH) .
The proton of hydroxyl group does not appear in the spectrum, there is an isotopic exchange



6-(2-aminoethylamino)-3,7-dimethyloctan-1-ol

Figure7: Product of the reaction is 6-(2-aminoethylamino)-3,7-dimethyloctan-1-ol.

4. Conclusion

The use of the material (Crude Clay) as a catalyst for synthesizing antifungals is satisfying the objective by the aza Michael addition reaction of amines to alkenes, and this antifungal to a significant efficiency. It destroys the fungus Fusarium oxysporum albedinis (Foa).

The use of an inexpensive and reusable raw clay catalyst, and a solvent-free reaction, a short duration of time, excellent chemical selectivity, high yield and easy purification of the products are the main features of this elegant protocol.

Most drug interaction studies of kaolin have involved administration of kaolin pectin. Kaolin pectin can form insoluble complexes with a number of drugs and should be avoided in patients receiving drugs that may chelate with aluminum salts (eg, digoxin28, 29, 30 clindamycin31 lincomycin32 and penicillamine33. Until more information is available, interactions that occur with kaolin pectin should be considered to occur with kaolin alone. Additionally, concomitant administration of kaolin pectin and trimethoprim resulted in a reduced area under the curve for trimethoprim and decreased the average blood concentration of trimethoprim by 42%. An in vitro study suggests that quinidine absorption may be reduced with concomitant administration of kaolin-pectin preparations.To avoid potential drug interactions, kaolin should be used at least 3 hours before or after any other medications.36 When used topically for anorectal itching, petrolaturm or greasy ointments should be removed before applying kaolin-containing products in order to allow for proper adherence to the skin. Additionally, cocoa butter, cod liver oil, hard fat, lanolin, mineral oil, shark liver oil, petrolaturm, or white petrolaturm cannot be combined with kaolin because of limited skin adherence.

5. Acknowledgements

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