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RESEARCH ARTICLE

Synthesis of Novel Heterocyclic Compounds from Coupling Agent of Silane with Natural Fibers

Magda G. El-Meligy[1], *Khadiga M. Abu-Zied[2], and Zenat A. Nagieb[3]

1, 3; Cellulose and Paper Department,National Research Centre, Giza, Egypt

2;Photochemistry Department, National Research Centre, Giza, Egypt.

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Corresponding Author

Magda G. El-Meligy

Abstract

The main goal of our work is to prepare novel heterocyclic compounds using thienopyrimidine moiety as base linked to methylchlorosilane molecule. Thus, on reacting 2-mercapto-5,6,7,8,9,10-hexahydrocycloocta[4,5] thieno-[2,3-*d*]pyrimidin-4(3*H*)-one(**1**)[2] with either dimethyldichlorosilane or methyl Iodide, 2-((chlorodimethylsilyl)thio)-5,6,7,8,9,10-hexahydrocycloocta[4,5] thieno[2,3-*d*]pyrimidin-4(3*H*)-one (**2**) or (**3**) were obtained respectively. Compound **2** or **3** were reacted with phosphorous oxychloride to afford 4-chloro-2-((chlorodimethyl- silyl)thio)-5,6,7,8,9,10-hexahydrocycloocta [4,5] thieno[2,3-*d*]pyrimidine (**2'**) or 2-(methylthio)-5,6,7,8,9,10-hexahydro-cycloocta[4,5]thieno[2,3-*d*]pyrimidin-4(3*H*)-one (**3'**) respectively. Derivative **2'** or derivative **3'** was reacted easily with hydrazine hydrate (99%) to produce **4'** and **5'** respectively. The proposed reaction pathways can be illustrated by Scheme (**I**), Scheme (**II**), Scheme (**III**), and Scheme (**IV**).
The structure of all newly produced compounds are confirmed according to the correct values of microanalyses and different spectral data as ^{1}H-NMR, Mass Spectra, IR, and X-Ray diffraction.

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INTRODUCTION

Natural fibers-based lignocellulosic materials are now considered as potential substitutes for toxic synthetic fibers for the preparation of reinforced composites. The advantages of natural fibers include easy availability, renewability, biodegradability, nontoxicity, low cost, low specific gravity, high toughness, acceptable specific strength and enhanced energy recovery and so forth (1-3). To reduce the content of non-cellulosic compounds that cement the fiber aggregates, thermo-mechanical or pre-hydrolyzed pulping can be used as a pretreatment. By this method, the fibers are liberated from the bundles as individual entities and thus their efficiency as composite reinforcements should increase (4,5).The most important factors in the development of natural reinforced composites are fiber dispersion and fiber matrix interaction (6,7). The lignocellulose hydroxyl group could be used to react with compounds to reduce the hydrophilicity of the fibers and therefore increase their compatibility with thermoplastic matrices (8). Considering different composite systems, one of the most successful and cost effective treatments includes the use of silane based coupling agents for improving the adhesion between fibers and matrix. These chemicals are hydrophilic compounds with different groups appended to silicon, such that one end will interact with hydrophilic compounds and the other end can react with hydrophobic groups. Therefore, hydrophilic and hydrophobic materials can be coupled together with silane coupling agent acting a bridge between them to achieve optimum performance of the end product, sufficient interaction between the matrix resin and the fiber.

Chemical modification by esterification or by using various silanes was found to have a profound effect on the fiber-matrix interaction. The improved fiber-matrix interaction is evident from the enhanced mechanical properties (9,10). Silicones such as polyester, vinyl ester, acrylates and epoxides have high performance adhesives and can be used to manufacture structural lignocellulosic composites (11).

Silanes with different organofunctional groups (vinyl, amines, and fluorine) have been used to pre-coat the fiber in order to examine the influence of silane treatment on the mechanical properties of the composites. The adhesion of the polysiloxane layer depends on the chemical composition of the organofunctional of the silanes (10, 11).

The aim of the work is to produce a new material from agro-fiber (cotton stalk and rice straw) and organofunctional groups of silanes, alternative to wood and has better strength and dielectric properties.

Experimental Part:

All melting points are uncorrected. Microanalyses were carried out at the Micro analytical Unit, Faculty of Science, and Cairo University. The IR spectra (KBr) were recorded on a FT-IR NEXCES Spectrophotometer (Shimadzu, Japan). ^{1}H-NMRwas measured with a Joel ECA 500 MHz (Japan) in DMSO-d_6 or $CDCl_3$ and chemical shifts was recorded in δ ppm relative to TMS. Mass spectra (EI) were run at 70 eV with a Finnegan SSQ 7000 Spectrometer (Thermo-Instrument System Incorporation, USA). All reactions were followed up by TLC.

2-((Chlorodimethylsilyl)thio)-5,6,7,8,9,10-hexahydrocycloocta[4,5]thieno[2,3-*d*]pyrimidin-4(3*H*)-one (2a) and 2-(Methylthio)-5,6,7,8,9,10-hexahydro- cycloocta[4,5]thieno[2,3-*d*]pyrimidin-4(3*H*)-one(2b):

General procedure:

Compound **1** (2.66 g, 0.01 mole) was refluxed with dimethyl dichlorosilane (1.6 g, 0.012 mole)ormethyl iodide (1.72 g, 0.012 mole) in ethanolic potassium hydroxide for at least six hours. The reaction mixture was cooled to room temperature and poured over ice water (100 mL) whereby a precipitate was formed. The precipitate so formed was collected upon filtration, dried and recrystallized from proper solvent to afford the titled compound in good yield.

Compound 2a:

From compound**1**and dimethyl dichlorosilane.The compound was recrystallized from dioxane (30 ml.) to yield the title product as colorless crystals (66%), m.p. 283-85°C.[$C_{14}H_{19}ClN_2OS_2Si$];(358.04).Required, C, 46.84%; H, 5.33%; N, 7.80%; S, 17.86%. Found: C, 46.64%; H, 5.23%; N, 7.33%; S, 17.71%. IR (KBr) cm^{-1}:3400 (broad NH), 2982 (CHalkyl) and 1680 (CO).^{1}H-NMR (DMSO-d_6)δ ppm: 1.55 (m, 4H, $2CH_2$), 1.80 (m, 4H, $2CH_2$),2.35 (t,*J*= 6.40Hz,4H, $2CH_2$), 2.35 (s,6H, $2CH_3$), 2.55 (t,*J*= 6.51Hz,4H, $2CH_2$), and 8.65 (br.s, 1H,NH, D_2O exchangeable).MS m/z(%): 358 (100.0%).

Compound 2b:

From compound**1**and methyl iodide. The compound was recrystallized from dioxane (30 ml.) to yield the title product as colorless crystals (65%), m.p. 278-880°C. [$C_{13}H_{16}N_2OS_2$](280.07). Required; C, 55.68%; H, 5.75%; N, 9.99%; S, 22.87%. Found: C,55.56; H, 5.60; N, 9.56; S, 22.66.IR (KBr) cm^{-1}:3300 (broad NH), 2980,2968 (CH alkyl) and 1670 (CO).^{1}H-NMR (DMSO-d_6)δ ppm: 1.55 (m, 4H, $2CH_2$), 1.80 (m, 4H, $2CH_2$),2.35 (t,*J*= 6.40Hz,4H, $2CH_2$), 2.35 (s, 6H, $2CH_3$), 2.55 (t,*J*= 6.50Hz,4H, $2CH_2$), and 8.4 (br.s, 1H,NH, D_2O exchangeable).MS m/z(%): 280(100.0%).

4-Chloro-2-((chlorodimethylsilyl)thio)-5,6,7,8,9,10-hexahydrocycloocta[4,5]- thieno[2,3-*d*]pyrimidine(3a) and 4-Chloro-2-(methylthio)-5,6,7,8,9,10-hexa- hydrocycloocta[4,5]thieno[2,3-*d*]pyrimidine(3b):

General procedure:

A solution of compound **2a** (2.66 g, 0.01 mole) or **2b**(2.80 g, 0.01 mole)in dry dioxane (30 ml) was treated with phosphorous oxychloride (7ml) and stirred under reflux for three hours (under TLC control). The reaction mixture was allowed to cool to room temperature and then, poured into crushed ice water (100 ml). The solid precipitate so-formed was filtered-off, dried and recrystallized from proper solvent to give the titled compounds in good yield.

Compound 3a:

From compound **2a.**The compound was recrystallized fromethanol (25 ml) to yield the title compound as colorless powder (60%); m.p. 138-40°C. [$C_{14}H_{18}Cl_2N_2S_2Si$](376.01). Required; C, 44.55%; H, 4.81%; N, 7.42%; S, 16.99%. Found: C, 44.45%; H, 4.56%; N, 7.10%; S, 16.66%.IR (KBr) cm^{-1}: No absorption bands corresponding to NH or (CO) in its region.^{1}H-NMR (DMSO-d_6)δ ppm: 1.55 (m, 4H, $2CH_2$), 1.80 (m, 4H, $2CH_2$),2.35 (t,*J*= 6.40Hz,4H, $2CH_2$), 2.35 (s, 6H, $2CH_3$), 2.55 (t,*J*= 6.50Hz,4H, $2CH_2$).MS m/z(%): 376(100.0%).

Compound 3b:

From compound **2b**.The compound was re-crystallized from ethanol/dioxane (30 ml, 2:1) to yield the title compound as colorless powder (66%); m.p. 147-49°C. [$C_{13}H_{15}ClN_2S_2$](298.85). Required; C, 50.39%; H, 4.22%; N, 11.75%. Found: C, 52.25; H, 5.06; Cl, 11.86; N, 9.37; S, 21.46.IR (KBr) cm^{-1}: No absorption bands corresponding to NH or (CO) in its region.^{1}H-NMR (DMSO-d_6)δ ppm: 1.55 (m, 4H, $2CH_2$), 1.80 (m, 4H, $2CH_2$),2.35 (t,*J*= 6.40Hz,4H, $2CH_2$), 2.35 (s, 6H, $2CH_3$), 2.55 (t,*J*= 6.50Hz,4H, $2CH_2$).MS m/z(%): 298.04 (100.0%), and 299.04 (15%).

2-((Chlorodimethylsilyl)thio)-4-hydrazinyl-5,6,7,8,9,10-hexahydrocycloocta-[4,5]thieno[2,3-*d*]pyrimidine(4a) and 4Hydrazinyl-2-(methylthio)-5,6,7,8,9,10-hexahydrocycloocta [4,5] thieno [2,3-d]pyrimidine(4b):

General procedure:

A solution of compound **3a** (3.72 g, 0.01 mole) or **3b** (2.98 g, 0.01 mole) in dioxane/ethanol (3:1ml), hydrazine hydrate (99%, 1:3) was added. The reaction mixture was refluxed for eight hours(Under TLC control) whereby a precipitate was formed. The reaction mixture was allowed to cool to room temperature and the solid so-formed was filtered-off, washed several time by water, dried and recrystallized from proper solvent to give the titled compounds in moderate yield.

Compound 4a:

From compound **3a**. The compound was recrystallized from dioxane/DMF (40 ml, 3:1) to yield the title compound as colorless powder (66%); m.p. 277-79°C. [$C_{14}H_{21}ClN_4S_2$ Si](372.07). Required; C, 45.08%; H, 5.67%; N, 15.02%; S, 17.19%.Found: C, 44.77%; H, 5.51%; N, 14.71%; S, 16.89%..IR (KBr) cm^{-1}: 3300(NH), 3244(NH_2), and 2986, 2980(aliphatic CHs).^{1}H-NMR (DMSO-d_6)δ ppm: 1.55 (m, 4H, $2CH_2$), 1.80 (m, 4H, $2CH_2$),2.35 (t,*J*= 6.40Hz,4H, $2CH_2$), 2.35 (s, 6H, $2CH_3$), 2.55 (t,*J*= 6.51Hz,4H, $2CH_2$), 6.56 (s, 2H, NH_2, D_2O exchangeable), and 8.4 (br.s, 1H,NH, D_2O exchangeable).MSm/z(%): 372 (100.0%).

Compound 4b:

From compound **3b**. The compound was recrystallized from dioxane/DMF (40 ml, 3:1) to yield the title compound as colorless powder (66%); m.p. 277-79°C. [$C_{13}H_{18}N_4S_2$](294.10). Required; C, 53.03%; H, 6.16%; N, 19.03%; S, 21.78%.Found: C, 52.66%; H, 5.96%; N, 18.70%; S, 21.66%.IR (KBr) cm^{-1}: 3333(NH), 3245(NH_2), and 2990, 2988(aliphatic CHs).^{1}H-NMR (DMSO-d_6)δ ppm: 1.55 (m, 4H, $2CH_2$), 1.80 (m, 4H, $2CH_2$),2.35 (t,*J*= 6.40Hz,4H, $2CH_2$), 2.48 (s, 3H, CH_3), 2.55 (t,*J*= 6.51Hz,4H, $2CH_2$), 4.25 (br.s, 2H, NH_2, D_2O exchangeable), and 9.11 (br.s, 1H,NH, D_2O exchangeable).MS m/z(%): 372.07 (100.0%).MS m/z(%): 294 (100.0%).

Preparation of compounds 6a', 6b',7a' and 7b':

General procedure:

A solution of either compound **5a'**or compound **5b'** in dry dioxane, compound **3a** or compound **3b'** was added (on the ratio 1:10). The reaction mixture was refluxed for 8-10 hrs. (Under TLC control), cooled to room temperature washed well with cold water, dried and recrystallized from proper solvent to give the titled compounds in good yield.

Preparation of compounds 6a':

From the reaction of compound **5a'** (0.5gm.) and **3a**(5gm). The compound was recrystallized from DMSO (30 ml) to yield the title compound as dark brown fiber type structure (60%); m.p. >300°C.IR (KBr) cm^{-1}: 3430-3400(broad OHs), 2990, 2988(aliphatic CHs), and 1720, 1700-1690 (CO).^{1}H-NMR ($CDCl_3$/CF_3COOH)δ ppm: 1.55 (m, 4H, $2CH_2$), 1.80 (m, 4H, $2CH_2$),2.35 (t,*J*= 6.45Hz,4H, $2CH_2$), 2.35 (s, 6H, $2CH_3$), 2.55 (t,*J*= 6.50Hz,4H, $2CH_2$), 3.45-4.25 (3m, OHs, D_2O exchangeable).

Preparation of compounds 6b':

From the reaction of compound **5b'** (0.5gm.) and **3a**(5gm). The compound was recrystallized from DMSO (30 ml) to yield the title compound as dark brown fiber type structure (55%); m.p. >310°C.IR (KBr) cm^{-1}: 3400-3380(broad OHs), 2960, 2928(aliphatic CHs), and 1720 -1700 (CO).^{1}H-NMR ($CDCl_3$/CF_3COOH)δ ppm: 1.55 (m, 4H, $2CH_2$), 1.80 (m, 4H, $2CH_2$),2.35 (t,*J*= 6.45Hz,4H, $2CH_2$), 2.35 (s, 6H, $2CH_3$), 2.55 (t,*J*= 6.50Hz,4H, $2CH_2$), 3.45-4.25 (3m, OHs, D_2O exchangeable).

Preparation of compounds 7a':

From the reaction of compound **5a'** (0.5gm.) and **3b**(5gm). The compound was recrystallized from DMSO (30 ml) to yield the title compound as dark brown fiber type structure (60%); m.p. > 300°C. IR (KBr) cm^{-1}: 3430-3400(broad OHs), 2990, 2988(aliphatic CHs), and 1720, 1700-1690 (CO).^{1}H-NMR ($CDCl_3/CF_3COOH$)δppm: 1.55 (m, 4H, $2CH_2$), 1.80 (m, 4H, $2CH_2$), 2.35 (t, *J*= 6.45Hz, 4H, $2CH_2$), 2.45 (s, 3H, CH_3), 2.55 (t, *J*= 6.50Hz, 4H, $2CH_2$), 3.45-4.25 (3m, OHs, D_2O exchangeable).

Preparation of compounds 7b':

From the reaction of compound **5b'** (0.5gm.) and **3b**(5gm). The compound was recrystallized from DMSO (30 ml) to yield the title compound as dark brown fiber type structure (55%); m.p. > 300°C. IR (KBr) cm^{-1}: 3400-3380(broad OHs), 2960, 2928(aliphatic CHs), and 1720 -1700 (CO).^{1}H-NMR ($CDCl_3/CF_3COOH$)δ ppm: 1.55 (m, 4H, $2CH_2$), 1.80 (m, 4H, $2CH_2$), 2.35 (t, *J*= 6.45Hz, 4H, $2CH_2$), 2.48 (s, 3H, CH_3), 2.55 (t, *J*= 6.50Hz, 4H, $2CH_2$), 3.45-4.25 (3m, OHs, D_2O exchangeable).

Preparation of compounds 8a', 8b',9a' and 9b':

General procedure:
A solution of either compound **5a'**or compound **5b'** in dry dioxane, compound **4a** or compound **4b'** was added (on the ratio 1:10). The reaction mixture was refluxed for 8-10 hrs. (Under TLC control), cooled to room temperature, washed well with cold water, dried and recrystallized from proper solvent to give the titled compounds in good yield.

Preparation of compounds 8a:

From the reaction of compound **5a'** (0.5gm.) and **4a**(5gm). The compound was recrystallized from DMSO (30 ml) to yield the title compound as dark brown fiber type structure (60%); m.p. >300°C.IR (KBr) cm^{-1}: 3400-3380(broad OHs), 3330-3333(NHs), 2990, 2988(aliphatic CHs), and 1710, 1700-1695 (CO).^{1}H-NMR ($CDCl_3/CF_3COOH$)δ ppm: 1.55 (m, 4H, $2CH_2$), 1.80 (m, 4H, $2CH_2$),2.35 (t,*J*= 6.45Hz,4H, $2CH_2$), 2.35 (s, 6H, $2CH_3$), 2.55 (t, *J*= 6.50Hz,4H, $2CH_2$), 3.45-4.25 (3m, OHs, D_2O exchangeable).

Preparation of compounds 8b:

From the reaction of compound **5b'** (0.5gm.) and **4a**(5gm). The compound was recrystallized from DMSO (30 ml) to yield the title compound as dark brown fiber type structure (55%); m.p. >310°C.IR (KBr) cm^{-1}: 3360-3380(broad OHs), 3330-3340(NHs), 2960, 2928(aliphatic CHs), and 1720 -1700 (CO).^{1}H-NMR ($CDCl_3/CF_3COOH$)δ ppm: 1.55 (m, 4H, $2CH_2$), 1.80 (m, 4H, $2CH_2$),2.35 (t,*J*= 6.45Hz,4H, $2CH_2$), 2.48 (s, 3H, CH_3), 2.55 (t, *J*= 6.50Hz,4H, $2CH_2$), 3.45-4.25 (3m, OHs, D_2O exchangeable).

Preparation of compounds 9a':

From the reaction of compound **5a'** (0.5gm.) and **4b**(5gm). The compound was recrystallized from DMSO (30 ml) to yield the title compound as dark brown fiber type structure (60%); m.p. > 300°C. IR (KBr) cm^{-1}: 3400-3380(broad OHs), 3430-3400 NHs), 2980, 2988(aliphatic CHs), and 1700, 1698-1690 (CO).^{1}H-NMR ($CDCl_3/CF_3COOH$)δppm: 1.55 (m, 4H, $2CH_2$), 1.80 (m, 4H, $2CH_2$), 2.35 (t, *J*= 6.45Hz, 4H, $2CH_2$), 2.47 (s, 6H, $2CH_3$), 2.52 (t, *J*= 6.50Hz, 4H, $2CH_2$), 3.45-4.25 (3m, OHs, D_2O exchangeable).

Preparation of compounds 9b':

From the reaction of compound **5b'** (0.5gm.) and **4b**(5gm). The compound was recrystallized from DMSO (30 ml) to yield the title compound as dark brown fiber type structure (55%); m.p. > 300°C. IR (KBr) cm^{-1}: 3400-3380(broad OHs), 3300-3330(NHs), 2960, 2928(aliphatic CHs), and 1720 -1700 (CO).^{1}H-NMR ($CDCl_3/CF_3COOH$)δ ppm: 1.55 (m, 4H, $2CH_2$), 1.80 (m, 4H, $2CH_2$), 2.35 (t, *J*= 6.45Hz, 4H, $2CH_2$), 2.49 (s, 3H, CH_3), 2.55 (t, *J*= 6.50Hz, 4H, $2CH_2$), 3.45-4.25 (3m, OHs, D_2O exchangeable).

Martial and Method:

Raw Material:(Compounds 5a',5b')
Rice straw and cotton stalk were the raw materials used; maleic anhydride was used as a reagent.
Treatment of the raw material

Rice straw and cotton stalk, after cutting into smaller pieces, were cooked in a heated autoclave (two revolutions per minute) for 1.5 h at 120 ^{o}C; the liquor ratio of water to pulp 4:1. The samples were washed properly and dried in an oven at 60^{o}C for 24 h, then the dried rice straw and cotton stalk were ground and passed through a mesh 25. Cotton stalk and rice straw were esterified maleic anhydride according to method described in (8).

Preparation of the composite:

The composite samples were prepared from the ground cotton stalk and rice straw by **(Scheme II)**.

The homogenous mixture was then processed as follows:

1.4 gm dry sample were placed in a disc form, diameter 2.5cm, heated to 150 ^{o}C and then pressed under 140 kg/cm^3 for 3 min.

Measurements

The composites samples were subjected to the following measurements

a) Density:

The density was measured using the following equation

$$\text{Density} = \frac{\text{Weight of the composite sample}}{\text{Volume of the composite sample}}$$, Where the volume of the sample cane be calculated by multiplying thickness of composite sample by area.

Table (**1**) Density, hardness and water absorption of different types of composites prepared cotton stalk and rice straw

	Types of composite	**Density gm/cm^3**	**Hardness kp/mm^2**	**Water absorption percent after immersion**		
				Boiling water for 2h	**water for 24h**	**water for 7days**
5a	Untreated cotton stalk	0.87	1.3			
5a'	treated Cotton stalk by maleic anhydride	0.92	1.7			
8a'	Treated cotton stalk by maleic anhydride and silaneorgano functional group	1.2	4.2	13.6	13.6	21.4
5b	Untreated rice straw	0.75	1.2			
5b'	Treated rice straw with maleic anhydride	0.8	1.5			
8b'	Treated rice straw with maleic anhydride and silaneorgano functional group	1.1	3.5	17.8	17.5	28.9

b) Water Absorption:

A specific weight of composite was immersed in boiling water for 2 h and for 24 h and 7 days at room temperature. After that, weight of the composites was measured again. Water absorption percent can be calculated as follows: $Waterabsorptiom\% = \frac{Ww - Wi}{Wi} * 100$, where Wi and Ww are the initial and wet weights of the composites, respectively. This test was measured according to the method of D5701ASTM (12)

c) Hardness:

It is the property of a material that enables it to resist plastic deformation usually by penetration. Hardness of material has been assessed by resistance to scratching or cutting. The test was carried out under load 5 kg and by using apparatus and calculated as Kpp/mm^2

d) Electrical Measurement :

The capacitance of sample in farad was recorded from apparatus and the conductivity (δ) of the samples was calculated by using this equation $\delta = Gx(\frac{d}{A})$ where (G) is the conductance of the sample, (d) is the sample thickness and (A) is the area of the used electrode. (d and A) were measured in cm. The Capacitance (C) and conductance (G) were measured using computerized HOKI3532-50 LCRHITESTER, Japan.

All samples measured at 30, 70 and 110^{o}C and at different frequencies ranging from 20.000 to 100.000 Hz.

Cotton stalk as a woody lignocelluloses and rice straw as a non0woody lignocelluloses were cooked mechanically, to remove low cellulose fraction and cementing materials. This led to better orientation and better packing cellulose chains.

In order to obtain a better composite from polar hydrophilic lignocelluloses (cotton stalk and rice straw) and polar hydrophobic organo-functional silane compound, chemical modification by maleic anhydride was done to improve interfacial interaction between the fiber and material matrix.

Different types of composites were prepared from cotton stalk and rice straw before and after treated by maleic anhydride, and also before and after reacted with silaneorgano-functional group.

Table (**1**) Density, Hardness and Water absorption of different types of composites prepared cotton stalk and rice straw

Table (**1**) shown that the density and hardness increased after treatment cotton stalk by maleic anhydride from 0.87 to 0.92, 1.3 to 1.7 respectively for cotton stalk and from 0.75 to 0.8, 1.2 to 1.5 respectively for rice straw. According to Lewis acid interaction two groups or more of maleic anhydride can be interact and formed the hydroxyl group on the surface of cellulose fiber and formed strong acid/base interaction. i.e formation hydrogen bonding between cellulose fiber and this lead to internal strength between fibers and hence enhanced density and hardness strength of produced composite. Treated or untreated composites by maleic anhydride were deformed by water.

Also, table (**1**) shown that the density of the composites prepared from treated fiber by maleic anhydride and organo-function silane compound raised from 0.87 to 1.2 for cotton stalk and from 0.75 to 1.1, while hardness raised from 1.3 to 4.2 for cotton stalk and from 1.2 to 3.5 for rice straw. In this case, maleic anhydride creating covalent bond to the fiber surface and extensive molecular entanglement to improve properties to interface which lead to enhancement of adhesion between fiber and matrix. Silane with different organo-functional groups compounds **5a,b**, **5a',b'**,and **8a',b'**. (Scheme **(IV)**) have been used to pre-coat the fiber in order to examine the influence of silanes treatment on the mechanical properties of composites. The adhesion of silane depends on the chemical composition of the organo-functional group of it. The bonding of the organo-functional of silane can take place in several forms. It can form an interpenetrating polymer network or diffuse into fiber matrix and crosslink at the fabrication temperature (13). This lead to stronger fiber matrix adhesion i.e increased the mechanical properties of composite such hardness resistance.

Composite containing untreated or treated fiber by maleic anhydride as in exp. 1, 2, 4 and 5 the composite has been deformed but the composite fiber treated by maleic anhydride and silane-organo functional compound were resisted to water penetration. The water absorption percent were 13.5, 13.6 and 21.4 after immersion in boiling water, 24 hours and seven days respectively for cotton stalk (exp. 3) and the water absorption percent were 17.8, 17.5 and 28.9 after immersion in boiling water for 2 hours to 24 hours and for 7 days respectively for rice straw (exp. 6). This may explain the voids between composite fibers are decrease to a large extent due to react with hydrophobic materials as in case of silane stronger organo-function group. This led to stronger adhesion between fiber-matrix and also reduces the water absorption (8, 10).

Cotton stalk as a woody lignocellulose (hard wood) has fiber length and hollow cellulose best than rice straw (non-woody lignocellulose), so cotton stalk give better results for density, hardness and water absorption compared to rice straw. (14)

Electrical properties of the prepared composite:

Electrical capacity and alternating current conductivity were measured for the prepared composite at three frequencies 20.000, 60.000 and 100.000 Hz and at three temperature 30, 70, and 110 ^{o}C. The electrical capacity of all decreased by increasing frequency due to increment of charge carries (electrons, ions, holes….etc).

Table 2, 3 and 4 shown that the electrical capacity of composite prepared from cotton stalk and rice straw increased after treated the fiber by maleic anhydride, and increased more after reacted with silaneorgano-functional group. At the same time the conductivity decreased. For example, at 20.000 frequency and temperature 70^{o}C the electrical capacity were 2.5, 4.1 and 8.4 for untreated cotton stalk, treated cotton stalk by maleic anhydride, treated cotton stalk by maleic anhydride and silaneorgano-functional group respectively and the conductivity were 13.5, 11.8 and 9

respectively. For rice straw, at 20.000 frequency and temperature 70°C, the electrical capacity was 4.8, 6.7 and 10.4 for untreated rice straw; treated rice straw by maleic anhydride and silaneorgano-functional group respectively and the conductivity were 11.1, 9.2 and 8.1 respectively.

At all frequencies and all temperatures, there is an increase in electrical capacity by treating composite by maleic anhydride only or with silaneorgano-functional

Table (**2**) Electrical Properties of the Different Types of Composites from Cotton Stalk and Rice Straw at Frequency 20.000

No	**Types of composite**	**Temp.**	**Electrical Capacity (Farad)**	**Conductivity**
5a	Untreated cotton Stalk (Blank)	30°C	2.7 E-12	13.2 E-8
5a'	treated Cotton stalk by maleic anhydride		4.5E-12	10.9 E-8
8a'	Treated cotton stalk by maleic anhydride and silaneorgano functional group		8.5 E-12	8.9 E-8
5b	Untreated rice straw		5.09 E-12	10.8 E-8
5b'	Treated rice straw with maleic anhydride		7.1 E-12	9 E-8
8a'	Treated rice straw with maleic anhydride and silaneorgano functional group		10.6 E-12	8 E-8
5a	Untreated cotton Stalk (Blank)	70°C	2.5 E-12	13.5 E-8
5a'	treated Cotton stalk by maleic anhydride		4.1 E-12	11.1 E-8
8a'	Treated cotton stalk by maleic anhydride and silaneorgano functional group		8.4 E-12	9 E-8
5b	Untreated rice straw		4.8 E-12	11.1 E-8
5b'	Treated rice straw with maleic anhydride		6.7 E-12	9.2 E-8
8b'	Treated rice straw with maleic anhydride and silaneorgano functional group		10.4 E-12	8.1 E-8
5a	Untreated cotton Stalk (Blank)	110°C	2.4 E-12	13.8 E-8
5a'	treated Cotton stalk by maleic anhydride		3 E-12	11.2 E-8
8a'	Treated cotton stalk by maleic anhydride and silaneorgano functional group		8.3 E-12	9 E-8
5b	Untreated rice straw		4.5 E-12	11.3 E-8
5b'	Treated rice straw with maleic anhydride		6.5 E-12	9.4 E-8

8b'	Treated rice straw with maleic anhydride and silaneorgano functional group		10.2 E-12	8.2 E-8

group and the conductivity decrease in the same cases. This due to the maleic acid anhydride can be interact with the hydroxyl group (OH^-) of the cellulose and this caused a decreasing for the motion of hydroxyl groups led to decrease the mobility of dipoles or charge carries and hence enhancement in electric insulation (15).

Silaneorgano-functional group can diffuse into the fiber matrix and crosslink with free hydroxyl group at the fabrication temperature and perhaps silane-organofunctional group blocked the charge carries (hydroxyl groups) at the internal composite boundary layers (8,10,11). This led to increase the electrical insulation for the prepared composite.

Composites were prepared from rice straw, has higher electric insulation compared by cotton stalk. Since the rice straw contain 7-9 % silica (11) which is a bad material for electric conductivity.

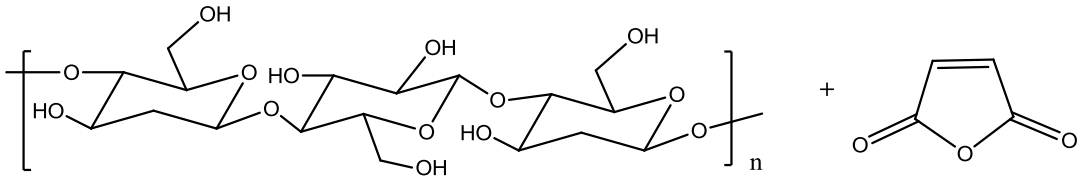
Table (**3**) Electrical Properties of the Different Types of Composites from Cotton Stalk and Rice Straw at Frequency 60.000

Types of composite	**Temperature**	**Electrical Capacity (Farad)**	**Conductivity**
5a	30^oC	1.25 E-12	39.7 E-8
5a'		3.65 E-12	30.9 E-8
8a'		5.1 E-12	24.2 E-8
5b		3.8 E-12	28.4 E-8
5b'		5.33 E-12	24.6 E-8
8b'		6.3 E-12	21.3 E-8
5a	70^oC	1.2 E-12	40.1 E-8
5a'		3.5 E-12	30.2 E-8
8a'		5 E-12	24.3 E-8
5b		3.6 E-12	28.9 E-8
5b'		4.9 E-12	24.8 E-8
8b'		6.1 E-12	21.5 E-8
5a	110^oC	1.1 E-12	40.5 E-8
5a'		3.2 E-12	30.4 E-8
8a'		4.9 E-12	24.3 E-8
5b		3.3 E-12	29.1 E-8
5b'		4.8 E-12	25 E-8
8b'		5.9 E-12	21.6 E-8

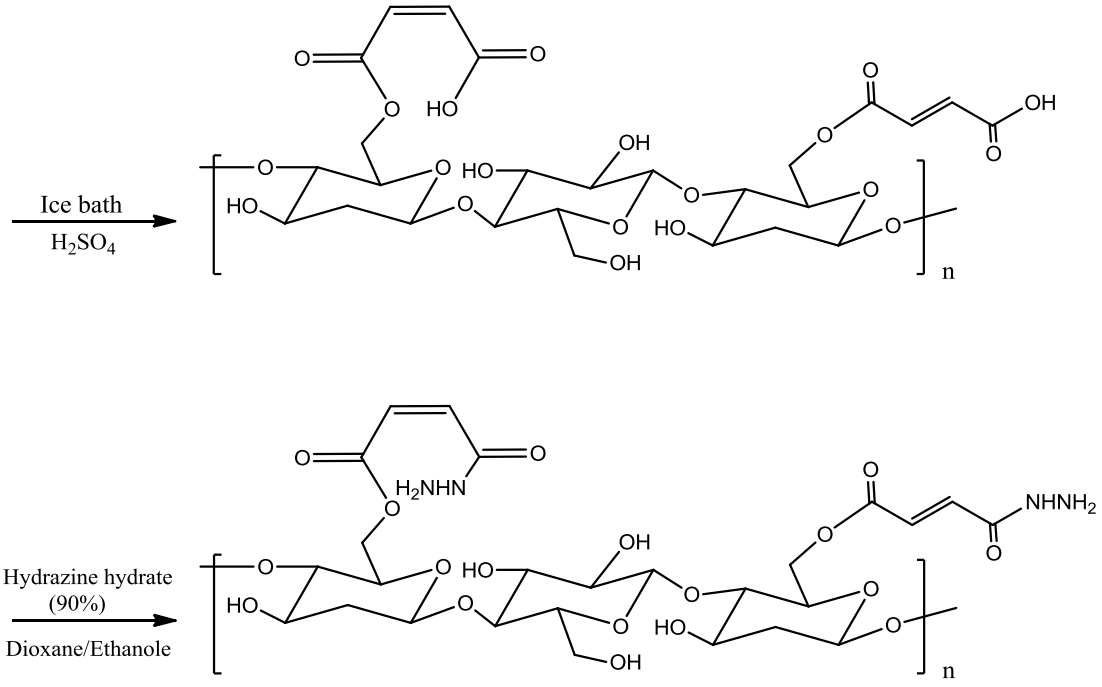
Table (**4**) Electrical Properties of the Different Types of Composites from Cotton Stalk and Rice Straw at Frequency 100.000

Types of composite	**Temperature**	**Electrical Capacity (Farad)**	**Conductivity**
5a	30^oC	1.05 E-12	50.6 E-8
5a'		1.69 E-12	45.3 E-8
8a'		2.7 E-12	38.9 E-8
5b		2.9 E-12	41.5 E-8
5b'		4.32 E-12	36.3 E-8
8b'		5.2 E-12	31.2 E-8
5a	70^oC	1.02 E-12	50.9 E-8
5a'		1.5 E-12	45.5 E-8
8a'		2.7 E-12	39.1 E-8
5b		2.6 E-12	42 E-8

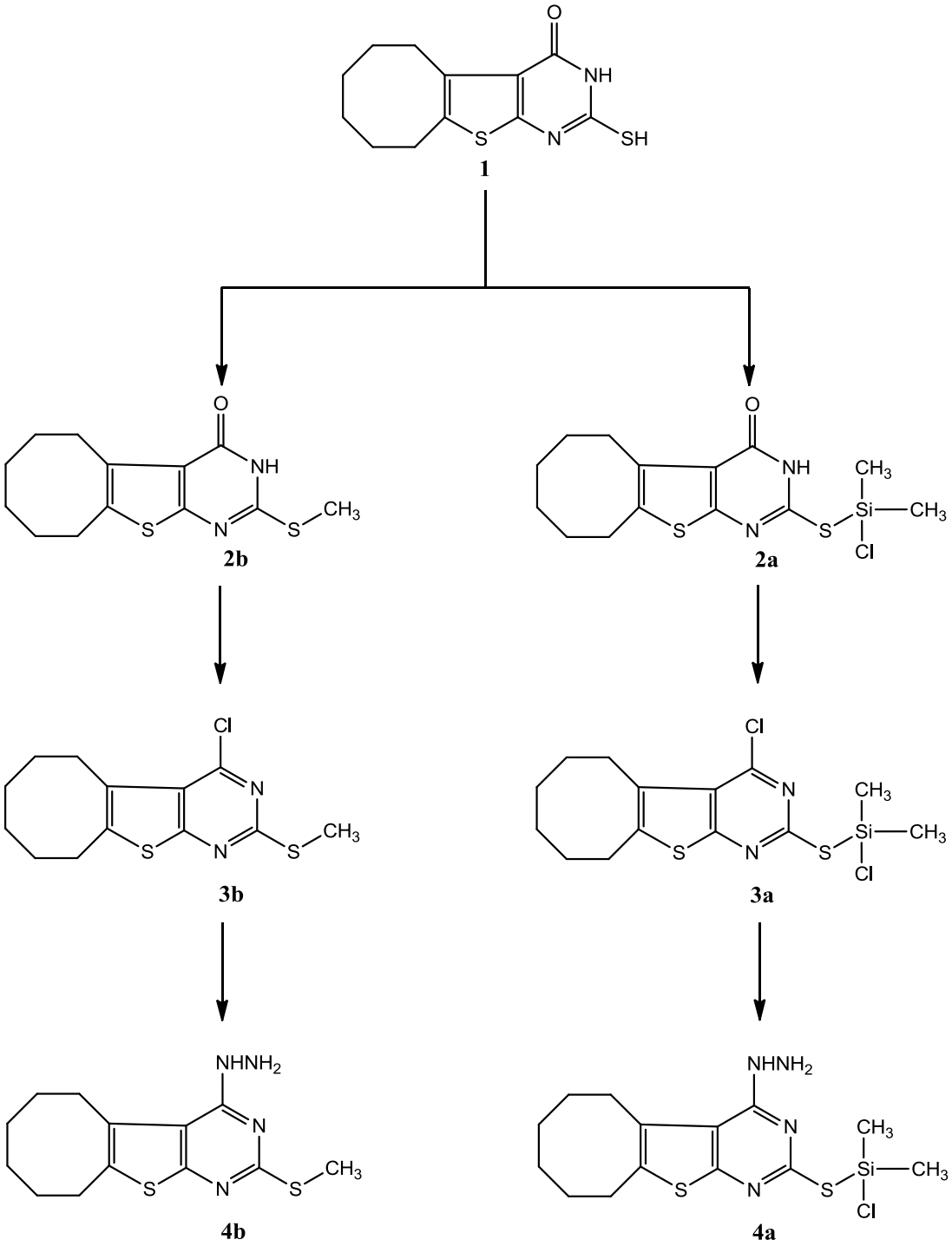
5b'		4.1 E-12	36.9 E-8
8b'		4.9 E-12	31.5 E-8
5a		1 E-12	51.2 E-8
5a'		1.4 E-12	45.6 E-8
8a'		2.7 E-12	39.1 E-8
5b	110°C	2.4 E-12	42.3 E-8
5b'		4 E-12	37.1 E-8
8b'		4.9 E-12	31.6 E-8



Cotton stalk or Rice straw



Scheme (**1**)


O
NH
S
N
SH
1
O
NH
S
N
S
CH3
2b
O
NH
S
N
S
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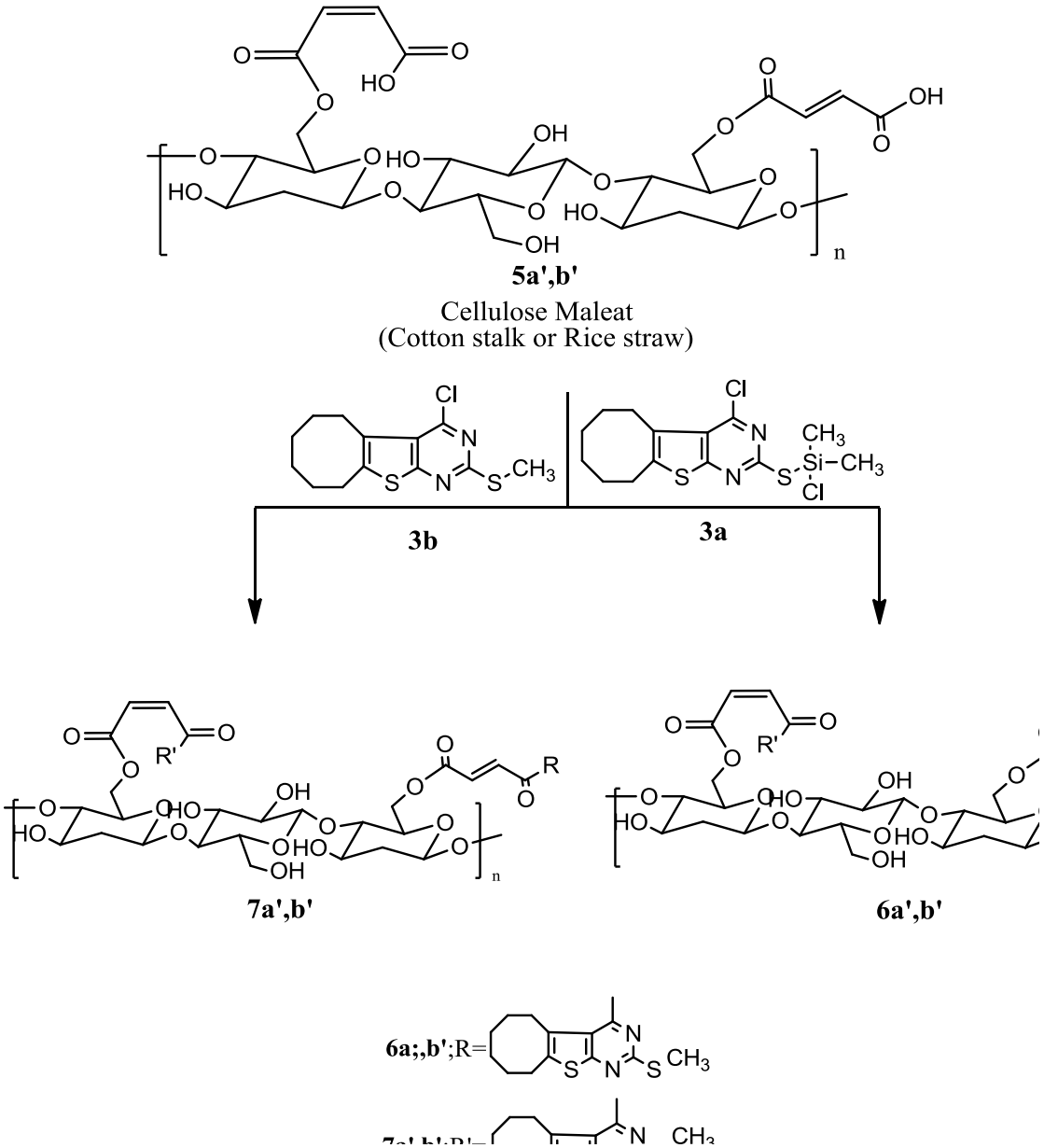
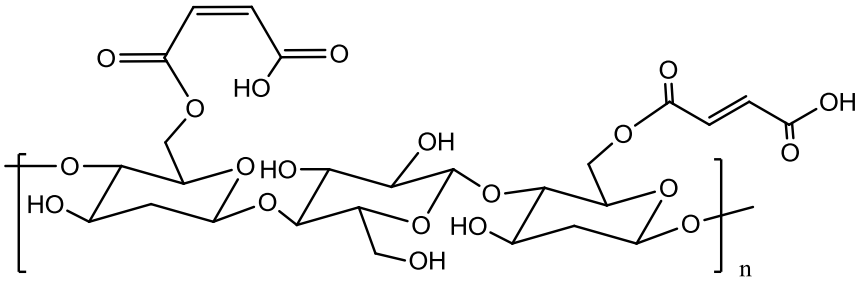
CH3
Cl
2a
Cl
N
S
N
S
CH3
3b
Cl
N
S
N
S
Si
CH3
CH3
Cl
3a
NHNH2
N
S
N
S
CH3
4b
NHNH2
N
S
N
S
Si
CH3
CH3
Cl
4a

Scheme (**1I**)

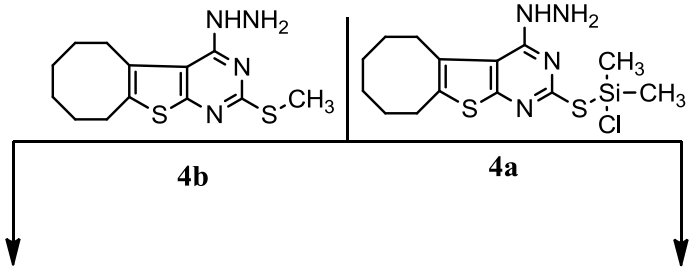

5a',b'
Cellulose Maleat
(Cotton stalk or Rice straw)
3b
3a
7a',b'
6a',b'
6a;,b';R=

Scheme **(III)**

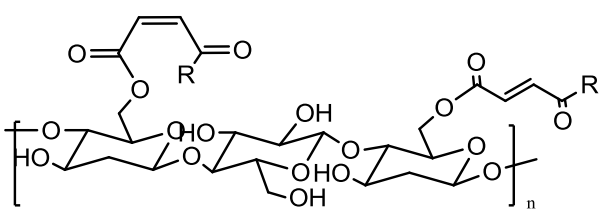


5a',b'

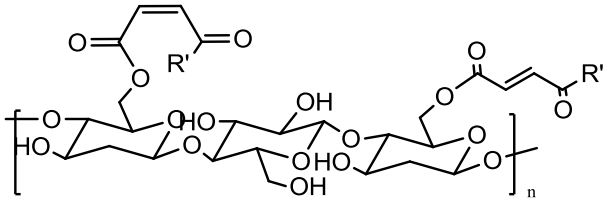
Cellulose Maleat
(Cotton stalk or Rice straw)



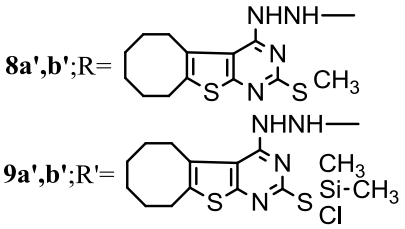
4b **4a**



9a',b'



8a',b'



Scheme **(IV)**

Notes:

Some of the resultant compounds in schemes (**I**), (**III**), and (**IV**) are key compounds to open a new research points.

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