Journal of Entomology and Zoology Studies

Available online at www.entomoljournal.com

E-ISSN: 2320-7078
P-ISSN: 2349-6800
www.entomoljournal.com
JEZS 2020; 8(2): 1215-1220

Received: 08-01-2020
Accepted: 12-02-2020

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Chemical composition and thermoanalytical analysis of the nest of yellow wasp and mud dauber

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Abstract
A wasp is a name given to groups of insects in the order *Hymenoptera* and suborder *Apocrita* It is different from a bee as well as an ant. Analysis of nests of yellow colored Wasps and Mud Dauber was carried out with the help of thermogravimetric and spectroscopic techniques. TGA analysis results showed the decomposition profile of the yellow paper wasp nest and mud dauber, indicated the percentage of weight loss with respect to temperature, that is similar to that of cellulose, which further demonstrate that cellulose is the fundamental group in the paper wasp structure which is responsible for adhesive nature and strength of the both type nest sample. Three different stages were observed on the TG curve. First stage starting from 25-250 ºC represents the loss of moisture present in the nest which is not chemically bonded. This stage accounts for 15% weight loss which shows there is a significant amount of moisture content in the outer part of the nest. Second stage is between 250-360 ºC which shows the decomposition of hemicellulose and formation of volatile products and char. Weight loss is approximately 40% of the total weight. Third stage accounts for 33% weight loss due to the thermal degradation of cellulose.
The FT-IR spectral analysis showed the presence of different functional groups. The GC-MS analysis of methanol extracts of paper wasp nest and mud dauber nest showed the presence of different types of bioactive compounds. Elemental analysis of samples showed the most prominent minerals are calcium (31.85ppm) followed by phosphorous (12.8 ppm) and magnesium (9.49 ppm) and different elements. Ash content was low as compared to the mud dauber nest; this indicates that it has higher organic content.

Keywords: Chemical composition, thermo-gravimetric analysis, nests of yellow wasps and mud dauber

Introduction
A wasp is a name given to groups of insects of the order *Hymenoptera* and suborder *Apocrita*. It is different from a bee as well as an ant. They usually form habitat around buildings, houses, trees and bridges. The black and yellow mud dauber, *Sceliphron caementarium*, is a common and distributed widely as solitary wasp that hunts spiders and builds characteristic mud nests for their offspring. It was found in muddy places where building materials were easily available [1]. In their nest construction, a mud dauber wasp uses clay as a material. This makes the mixture of nest adhesive and strong [2]. Clay soils are hydrous aluminium phyllosilicates, with different amounts of magnesium, iron, alkali, alkaline earth metals and other electro positive ions [3]. They collect mud, moisten it with their saliva, which may be functioning as binding material. The saliva derived material stick to the building and hence, vertically on the outside of the button-like structure which are normally rich in phosphorous. The nest of paper wasp was found among bunches of leaves in the tree branches. Structurally, it was oval shaped and attached to minute and string stalk [1]. Bioengineering applies engineering principles to the living systems and relates to biotechnology and medical science [5]. Biomathematics or computational biomedical is an interdisciplinary field which aims at modelling natural and biological processes using mathematical tools [6-8]. The aim of our work was to investigate the nature and chemical composition of yellow wasp & mud dauber nests.

Experimental method
Analysis of the nest of paper wasp and mud dauber sample was done by finding the chemical composition of the nest, which includes elemental analysis (ICP-OES), GC-MS and other

spectroscopic techniques such as FT-IR. Thermo gravimetric analysis of the nest of yellow wasp and mud dauber was analyzed using instrumental techniques like TGA and DSC.

FTIR

FTIR (Fourier Transform Infrared Spectroscopy) analysis was performed by using PerkinElmer spectrum version 10.5.3 to find out the functional groups present in a paper wasp nest and the mud dauber sample. The FT-IR instrument guides, radiation of wavelength of about 4000cm^{-1} to 400 cm^{-1} through our sample with some radiation absorbed and few passes from it.

GC-MS

GC-MS analysis of methanol extract of Paper Wasp and Mud Dauber Nest was done. The methanol extract of paper wasp nest and mud dauber nest were analysed by GC-MS (Agilent 5975B MSD) was used in the scan mode of (m/z 35-1050) to find out the amount of bio active compound. Gas chromatograph induced with mass spectroscopy is one of the widely used instruments used to identify as well quantify the blend of the complex mixtures with variable molecular weight can be measured with the highest accuracy and precision.

Elemental analysis (ICP-OES)

ICP-OES (PerkinElmer) was used to analyse the elemental composition of the sample. The procedure is based on the warm plasma driven by argon gas causing ionization of the sample.

TGA & DSC

TGA determines the quantity and the frequency of the weight variation of the samples against temperature and time in a controlled atmosphere (the purging of nitrogen gas) [4]. TGA of the sample is carried out by using TGA 4000 (PerkinElmer) in the atmosphere of nitrogen. It can be used to primarily investigate thermal strength and viscoelastic property of different nest sample. DSC is a thermo-analytical technique measuring the difference between heat taken from the sample and the reference.

The parameters used for mud dauber

Temperature: 30-250 °C
Heating Rate: 20 ˚ per minute

The parameters used for a paper wasp nest

Temperature: 30-350 ˚C
Heating rate: 20 ˚ per minute
Different nests, building material samples were ground into fine powder, kept in sterilized vials and labelled accordingly.

Ash Content

Determination of ash content in a polymer helps to measure the total amount of inorganic content that is minerals present in the polymer. The sample was heated at 550 ˚C for 4 hours in a Muffle furnace during which all the organic content decomposes and vaporize as carbon dioxide, water vapour and other gases. This process is used to estimate the number of residual solids (ash) in the polymer.

First, the sample was weighed then it is kept in the muffle furnace at 550 ˚C for 4 hours. Sample from the furnace was again weighed till it becomes a constant and final weight gave us the ash content.

Results and Discussion

Paper wasp nest sample results

TGA (Thermogravimetric analysis)

The thermogravimetric analysis of the yellow paper wasp nest was carried out and results were compared with the TGA curve of cellulose fibre obtained from the library. We also noticed different stages in which there was a weight loss with respect to temperature. Figure 1 & 2 shows the curve of thermal decomposition of the outer portion of a paper wasp nest. The experiment was performed in the range of 30-600 ˚C at a rate of 20 °C / minutes.

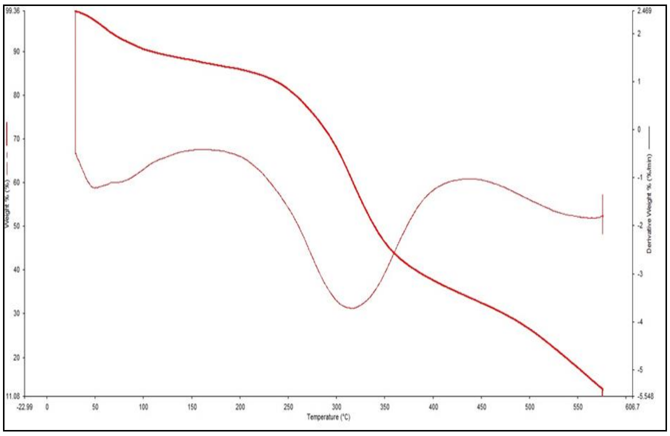

Fig 1: The weight loss with respect to temperature in the paper wasp nest sample

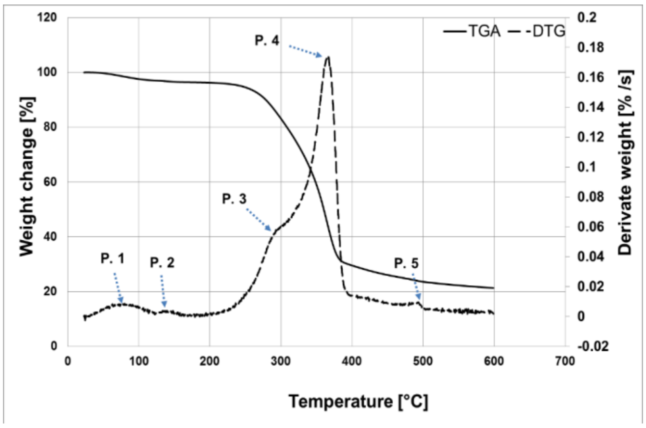

Fig 2: The weight change with respect to temperature in cellulose fibre

Table 1: Comparison between two curves

Stages	Yellow paper nest sample (degree Celsius)	Cellulose fiber (degree Celsius)
First stage	25-250	25-255
Second stage	250-360	255-380
Third stage	360-550	380-600

Three different stages were observed on the TG curve. First stage starting from 25-250 represents the loss of moisture present in the nest, which is not chemically bonded. This stage accounts for 15% weight loss which shows there is a significant amount of moisture content in the outer part of the nest. Second stage is between 250-360 which shows the decomposition of hemicellulose and formation of volatile products and char. Weight loss is approximately 40% of the total weight. Third stage accounts for 33% weight loss due to the thermal degradation of cellulose (Table 1, Table 2).

DSC (Differential Scanning Calorimetry)

DSC is the most widely accepted method to investigate the thermal properties of polymers (both natural and synthetic) such as melting point (Tm), glass transition temperature (Tg), crystallization, oxidation, decomposition stages (Figure 3).

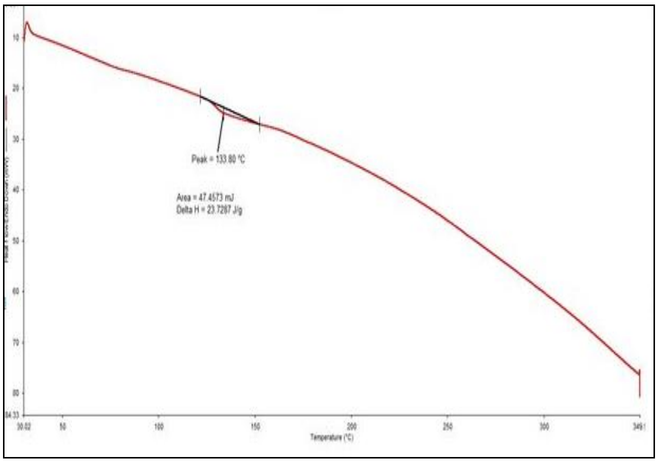

Fig 3: DSC Curve of Paper Wasps Nest Sample

Mud dauber wasp nest results

TGA (Thermogravimetric analysis)

We have carried out the thermo gravimetric analysis of this nest and compared its result with the TGA curve of soil obtained from the library. We have mentioned different stages in which weight loss is occurring with respect to temperature (Figure 4, 5).

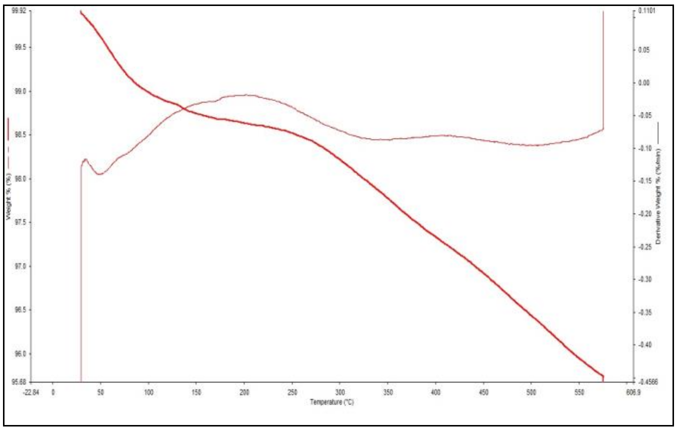

Fig 4: TGA curve of Mud Dauber Nest sample

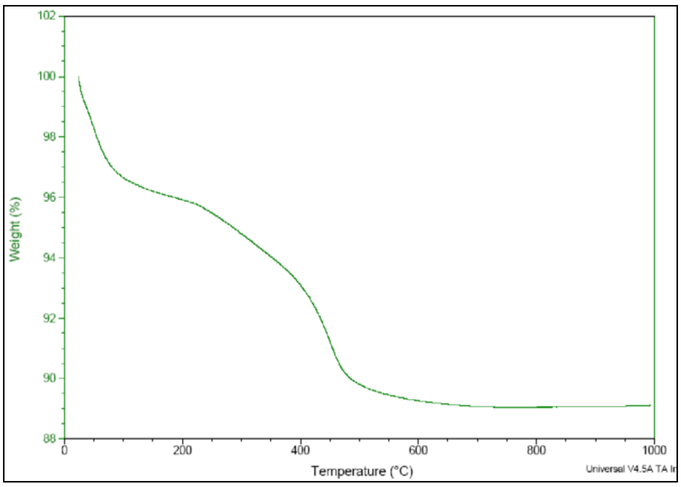

Fig 5: TGA curve of Soil Sample

Comparison between two Curves

Table 2: Comparison between Mud Dauber Nest and soil

Stages	Mud Dauber Nest	Soil
First Stage	25-80	25-90
Second Stage	80-290	90-250
Third Stage	290-550	250-450
Fourth Stage	-	>450

DSC (Differential Scanning Calorimetry)

DSC analysis was carried out to find out the thermal properties of the sample (Figure 6).

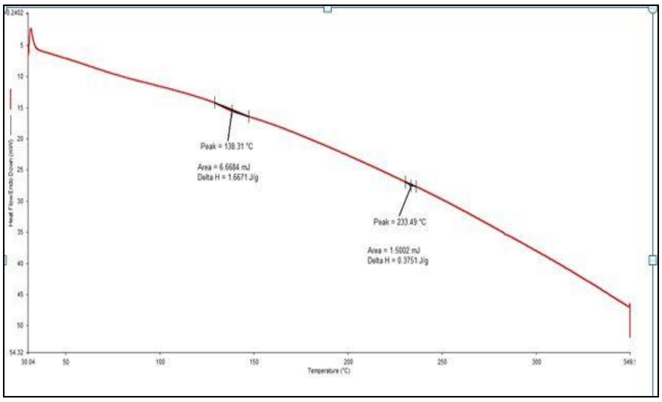

Fig 6: DSC curve of Mud Dauber Nest Sample

Fourier Transform Infrared (FTIR) analysis of Paper Wasp Nest

Transmission FTIR (Fourier Transform Infrared Spectroscopy) analysis was performed to find out the functional groups present in a paper wasp nest sample. Some of the prominent functional groups are listed in the table given below (Figure 7) (Table 3).

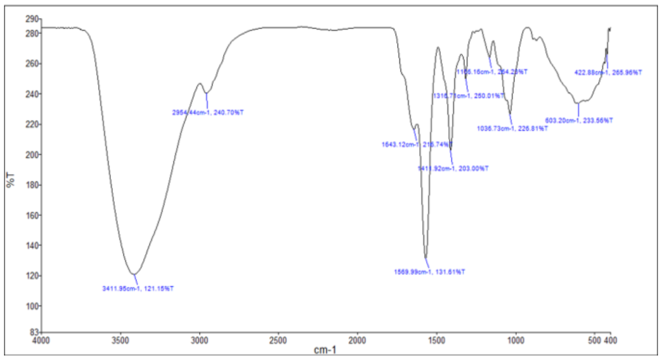

Fig 7: FT-IR spectrum of paper wasp nest sample

Table 3: The functional groups of different wave numbers

Peaks (Wave Number)	Functional Groups
3411.95	Hydroxyl
1643.12	Carbonyl groups
1559.99	Aromatic rings
1411.92	CH_2 and CH_3 bending vibration
1035.73	C-O stretching
603.20	CH_2-, CH_3- rocking

FTIR-ATR

The FTIR-ATR of the yellow paper wasp nest was performed and tissue paper and then compared their curves. This shows that our sample is cellulose based and could have some properties similar to that of tissue paper (Figure 8, 9)

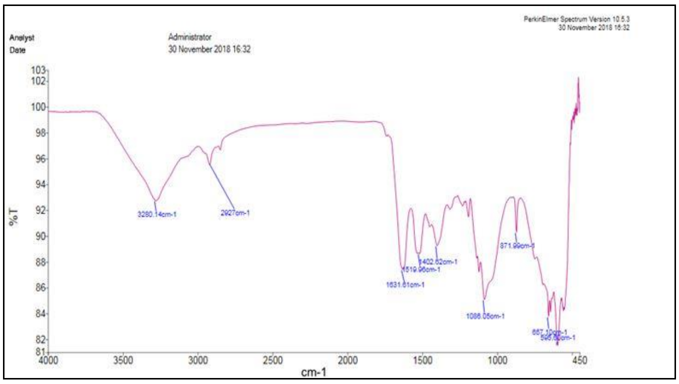

Fig 8: FT-IR ATR Curve Paper Wasp Nest

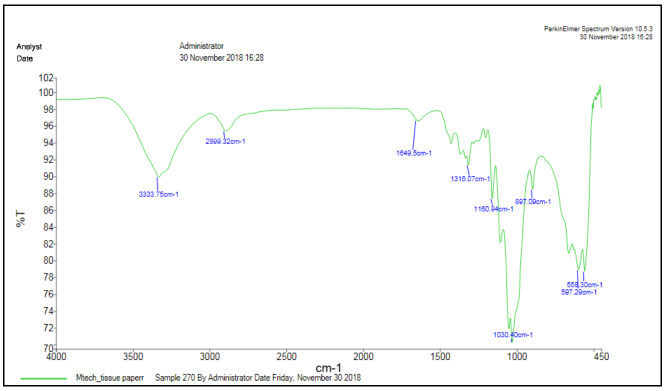

Fig 9: FT-IR ATR curve of Tissue Paper

FTIR Results of mud dauber nest sample

Transmission FTIR (Fourier Transform Infrared Spectroscopy) was performed to find out the functional groups present in the sample (Figure 10). Some of the prominent functional groups are listed in the Table 4.

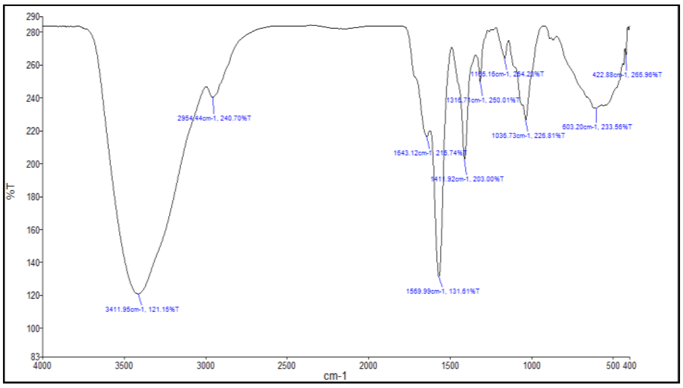

Fig 10: FT-IR curve of Mud Dauber Nest sample

Table 4: Peaks at Different Wave Number corresponding to Different Groups

Peaks (Wave Number)	Functional Groups
3405.93	A hydroxyl group (O-H stretching)
2925.72	Aliphatic SP$_3$ C-H stretching
2854.96	CH_2 stretching of the alkyl group
1622.55	Aromatic Carbonyl group
1432	CH_2 bending vibration of methylene
1319.30	CH_3 bending vibration of methyl
1028.37	C-O stretching of alcohol

GC-MS Analysis of methanol extract of paper wasp nest and mud dauber nest

The methanol extract of paper wasp nest and mud dauber nest were analysed by GC-MS; to give the gas chromatogram. The details of all the identified bioactive compounds present in nest samples are shown in Table 5 and Table 6.

Table 5: Chemical compounds identified in the methanol extract of a paper wasp nest

Peak No.	Name of compound	R. Time	Area %	Molecular formula	Molecular Weight
1	1H-imidazole, 2-ethyl-	12.709	0.32	$C_5H_8N_2$	96
2	2-Propyldecan-1-ol	12.966	0.62	$C_{13}H_{28}O$	200
3	Octadecane	14.251	1.42	$C_{18}H_{38}$	254
4	Delta. -terpineol. Beta. epoxide (. Alpha., alpha. -dimethyl-3-cyclohexyl	14.978	0.39	$C_{10}H_{18}O_2$	170
5	Cyclohexane ethanol, 4-ethenyl-4-methyl-. Beta. -methylene-3-(1-methyl	15.925	0.39	$C_{15}H_{24}O$	220
6	5-Azulenemethanol, 1,2,3,4,5,6,7,8-octahydro-. Alpha.,. Alpha., 3,8-tetramethyl-	16.271	2.41	$C_{15}H_{26}O$	222
7	Patchouli alcohol	16.542	4.76	$C_{15}H_{26}O$	222
8	Acetamide, n-(1-adamantan-1-ylpropyl)-2-(benzooxazol-2-ylsulfan	16.890	0.83	$C_{22}H_{28}N_2O_2S$	384
9	Acetyl cedrene	17.521	4.85	$C_{17}H_{26}O$	246
10	trans-. alpha. -Bergamotene	17.694	0.94		
11	1,6-Methanonaphthalen-1(2h)-ol, octahydro-4,8a,9,9-tetramethyl-	17.774	1.90	$C_{15}H_{26}O$	222
12	2 (3H) -Naphthalenone, 4,4a,5,6,7,8-hexahydro-4,4a-dimethyl-6-(1-methylethylidene)-	18.364	1.57	$C_{15}H_{22}O$	218
13	Zizanyl acetate	18.454	1.13	$C_{17}H_{26}O_2$	262
14	Hexadecanoic acid, methyl ester	19.016	5.22	$C_{17}H_{34}O_2$	270
15	1,2-Benzenedicarboxylic acid, dibutyl ester	19.369	18.08	$C_{14}H_{18}O_6$	282
16	1,9-Cyclohexadecadiene	20.659	1.33	$C_{16}H_{28}$	220
17	8,11,14-Docosatrienoic acid, methyl ester	20.715	4.50	$C_{23}H_{40}O_2$	348
18	Phytol	20.818	1.01	$C_{20}H_{40}O$	296
19	Heneicosanoic acid, methyl ester	20.948	1.71	$C_{22}H_{44}O_2$	340
20	Hexane, 2,3,4-trimethyl-	22.508	0.35	C_9H_{20}	128
21	Undecane, 2,4-dimethyl-	24.787	0.59	$C_{13}H_{28}$	184
22	1,2-Benzenedicarboxylic acid	25.291	17.08	$C_{24}H_{38}O_4$	390
23	Oxalic acid, 6-ethyloct-3-yl heptyl ester	28.467	2.41	$C_{19}H_{36}O_4$	328
24	Squalene	29.372	0.79	$C_{30}H_{50}$	410
25	Octadecane, 1-chloro-	30.423	1.09	$C_{18}H_{37}Cl$	288
26	Nonadecane	30.825	1.10	$C_{19}H_{40}$	268

The main constituents of the methanol extract of paper wasp nest were Phytol (1.01%), Nonadecane (1.1%), Zizanyl acetate (1.13%), 1,9-Cyclohexadecadiene (1.33%), Octadecane (1.42%), 2(3H)-Naphthalenone, 4,4a,5,6,7,8-hexahydro-4,4a-dimethyl-6-(1-methylethylidene (1.57%), 1,6-Methanonaphthalen-1(2h)-ol, octahydro-4,8a,9,9-tetramethyl-, (1.9%), 5-Azulenemethanol, 1,2,3,4,5,6,7,8-octahydro- alpha, alpha,3,8-tetramethyl-(2.41%), Oxalic acid, 6-ethyloct-3-yl heptyl ester (2.41%), Heneicosanoic acid, methyl ester (1.71%), 1,2-Benzenedicarboxylic acid (17.08%), 8,11,14-Docosatrienoic acid, methyl ester (4.5%), Patchouli alcohol (4.76%), Acetyl cedrene (4.85%), Hexadecanoic acid, methyl ester (5.22%), 1, 2-Benzenedicarboxylic acid, dibutyl ester (18.08%) (Table 6). Hexadecanoic acid methyl ester, are reported to have anti-inflammatory, cancer preventive, hepatoprotective, antiarthritic, and anticoronary properties [9].

Table 6: The major bioactive components identified in methanol extract of mud dauber nest

Peak No.	Name of compound	R. Time	Area %	Molecular formula	Molecular Weight
1	Undecane, 4,7-dimethyl-	14.250	1.34	$C_{13}H_{28}$	184
2	3-Methoxy-5-propylphenol	14.475	3.55	$C_{10}H_{14}O_2$	166
3	Flopropione	14.899	1.60	$C_9H_{10}O_4$	182
4	1,6-Methanonaphthalen-1(2h)-ol, octahydro-4,8a,9,9-tetramethyl-	16.546	1.51	$C_{15}H_{26}O$	222
5	Benzoic acid, 2-hydroxy-4-methoxy-3,5,6-trimethyl-, methyl ester	16.872	1.10	$C_{12}H_{16}O_4$	224
6	1,6-Methanonaphthalen-1(2h)-ol, octahydro-4,8a,9,9-tetramethyl-	17.775	0.69	$C_{15}H_{26}O$	222
7	Neophytadiene	18.092	1.11	$C_{20}H_{38}$	278
8	Pentadecanoic acid, 14-methyl-, methyl ester	19.008	3.91	$C_{17}H_{34}O_2$	270
9	Dibutyl phthalate	19.362	17.99	$C_{16}H_{22}O_4$	278
10	9,12-Octadecadienoic acid, methyl ester	20.649	1.68	$C_{19}H_{34}O_2$	294
11	7-Hexadecenoic acid, methyl ester, (Z)-	20.707	4.26	$C_{17}H_{32}O_2$	268
12	Phytol	20.810	1.17	$C_{20}H_{40}O$	296
13	Octadecanoic acid, methyl ester	20.940	1.68	$C_{19}H_{38}O_2$	298
14	1H-imidazole, 4,5-dihydro-2-(phenylmethyl)-	22.780	4.58	$C_{10}H_{12}N_2$	160
15	Hexane, 3, 3-dimethyl-	24.781	0.43	C_8H_{18}	114
16	1, 2-Benzenedicarboxylic acid	25.283	24.61	$C_{24}H_{38}O_4$	390
17	Hexane, 3, 3, 4-trimethyl-	28.017	0.38	C_9H_{20}	128
18	1-Dodecanol, ethoxy-	28.433	3.43	$C_{14}H_{30}O_2$	230
19	Squalene	29.364	0.90	$C_{30}H_{50}$	410
20	2-Bromotetradecane	30.418	1.79	$C_{14}H_{29}Br$	276
21	Dotriacontane, 1-iodo-	30.810	1.28	$C32H_{65}I$	576
22	Vitamin E	33.983	0.92	$C_{29}H50O_2$	430

The main chemical constituents of the methanol extract of mud dauber nest were:- Vitamin E (0.92%), Neophytadiene (1.11%), Phytol (1.17%), Dotriacontane, 1-iodo-(1.28%), Undecane, 4,7-dimethyl (1.34%), 1, 6-Methanonaphthalen-1(2H)-ol, octahydro-4,8A,9,9-tetramethyl-, (1.51%), Flopropione(1.60%), Octadecanoic acid, methyl ester (1.68%),9,12-Octadecadienoic acid, methyl ester (1.68%), 2-Bromotetradecane (1.79%), 1-Dodecanol, ethoxy-(3.43%), 3-Methoxy-5-propylphenol (3.55%), Pentadecanoic acid, 14-methyl-, methyl ester (3.91%), 1H-imidazole, 4,5-dihydro-2-(phenylmethyl)- (4.58%), 7-Hexadecenoic acid, methyl ester, (Z)- (4.26%), Dibutyl phthalate (17.99%), 1,2-Benzenedicarboxylic acid (24.61%).

Vitamin E is a fat-soluble chiral compound which has high antioxidant potential. It has eight stereoisomers: α, β, γ, δ tocopherol and α, β, γ, δ tocotrienol (with double bonds in side chain) in which α-Tocopherol is the most bioactive form, found in humans [10]. Since, it is fat-soluble, α-tocopherol protects cell membranes from damage by free radicals. Its antioxidant capacity mainly resides in the protection against lipid peroxidation.

Phytol is an acyclic diterpene alcohol that can be used as a precursor for the manufacture of synthetic forms of vitamin E [11] and vitamin K1 [12]. In ruminants, the gut fermentation of ingested plant materials liberates phytol, a constituent of chlorophyll, which is then converted to phytanic acid and stored in fats [13] in shark liver it yields pristane.

Inductively Coupled Plasma (ICP)

Various mineral were find out from the nest sample described in Table 7.

Table 7: Various Metal Ions Present in Mud Dauber Nest Sample

Metal Found	Amount (PPM)
Magnesium	9.49
Calcium	31.85
Titanium	0.70
Copper	0.12
Nickel	0.02
Boron	0.08
Aluminium	8.81
Silicon	0.73
Barium	0.13
Fluoride	8.94
Phosphorous	12.8
Zinc	0.35
Lead	0.06
Vanadium	0.02
Manganese	0.3
Cobalt	0.02
Chromium	0.07

Ash Content

Determination of ash content in a polymer helps to measure total amount of inorganic content that is minerals present in the polymer. The sample was heated at 550 °C for 4 hours in a Muffle furnace during which all the organic content decomposes and vaporizes as carbon dioxide, water vapour and other gases.

Final weight (ash content) = 0.9061
Initial weight of the sample = 1.0064 g
The difference in initial and final weights = 0.1003g

The difference in initial and final weight is low as compared to the yellow paper wasp nest, this implies that it has more inorganic content.

In case of mud dauber
Initial weight of the sample = 1.0040g Final weight (ash content) = 0.3135g
Difference in initial and final weights = 0.6905g
Difference in initial and final weights is more as compared to mud dauber; this implies it has more organic content.

Conclusion
TGA and DSC analysis of nest samples revealed that there was weight loss with respect to temperature, heat transfer and showed thermal stability. The GC-MS, FT-IR and ICP-OES showed the presence of different types of the chemical compound, functional groups and elements such as hydroxyl, phenolic, carbonyl, calcium, magnesium, titanium, copper, manganese, silicon, phosphorus, zinc, cobalt and aluminium in varying quantities that are responsible for the adhesive nature and strength of the Mud Dauber wasp and yellow wasp nest.

Acknowledgement
Author would like to express gratitude towards Delhi Technological University for the financial support.

Conflict of interest statement: None

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