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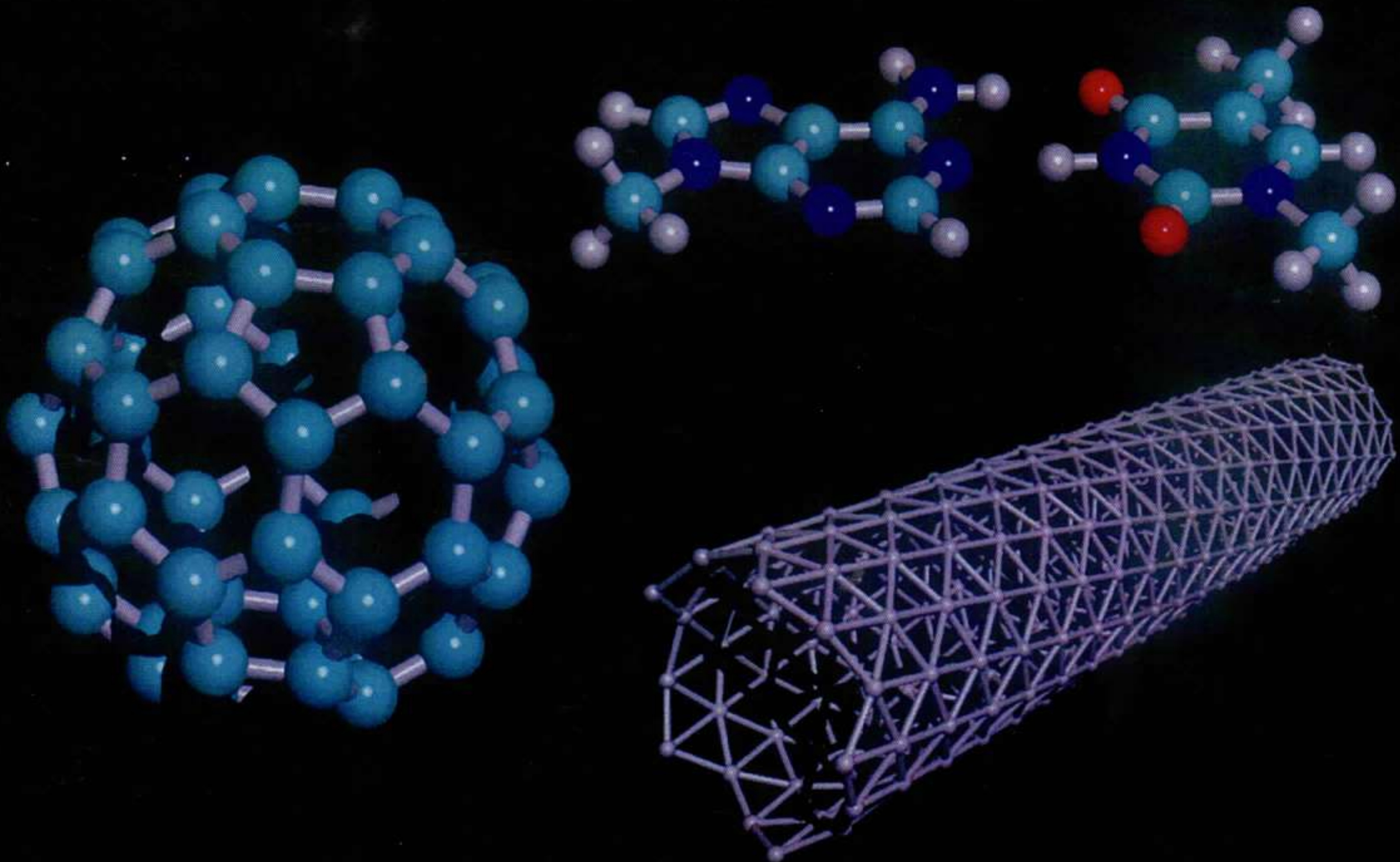

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Characterization of Liquid Smoke from Coconut Shell as a Natural Pesticide for *Hexamitodera Semivelutinia* Beetle on Clove Trees

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Abstract

A study has been done on characterization of liquid smoke from coconut shell as pesticide on *Heramitodera Semivelutinia* beetle. Liquid smoke was made by way of pyrolysis in high temperature in which prior to being analyzed, a purification was conducted to the liquid smoke by filtration and distillation methods. Characterization for acidity was by pH meter, testing acidity total level was using AOAC (1990) method, gas cromatography analysis and mass spectometry gas chromatography.

The result of GC-MS analysis showed that liquid smoke from coconut shell produced 7 peaks in which based on GC-MS library data, 2 chromatogram peaks of gas cromatography cromatogram indicate compound from groups of organic acids, phenol and carbonyl compounds, which are methyl acetate, and 1-hydroxy-2-butanones suspected as pesticides.

The application of liquid smoke on borer caterpillar (*Hexamitodera Semivelutinia)* on clove trees with concentrations of 20%, 15%, 10% showed that the level of death of clove caterpillar at concentration of 20% was quite positive compared to concentrations of 15% and 10% at the clove tree age of 8-10 years.

Keywords: liquid smoke, borer caterpillar, Hexamitodera Semivelutinia

INTRODUCTION

Coconut shell is found on the inner side of the fiber, and the thickness of shell is between 3-5 mm. Weight of the shell is 15%-19% from the weight of coconut. From 1000 coconuts, 19,05% of shell is obtained, in North Sulawesi province, the weight of coconut shell is 17-18% from the weight of the coconut.

According to Child in Suhardiyono L (2002), the chemical composition of coconut shell is as follows:

Table 1. Chemical composition of coconut shell

No	Component	%
1	Cellulose	26,60
2	Pentosan	27,70
3	Lignin	29,40
4	Ash	0,60
5	Extractive'Solvent	4,20
6	Uronate anhidrate	3,50
7	Nitrogen	0,11
8	Water	8,00

Source: Suhardiyono L, 2002

The production of coconut shell liquid smoke through the process of pyrolysis. After the shell is cleaned, it is put into drum that covered firmly and equipped with spiral smoke distribution pipe which functions as condenser and passed through drum containing water as cooler (Tahir I. 1992).

Heating is conducted at temperature range of 400ºC-600ºC in enclosed chamber with a relatively low oxygen level. The shell smoke is trapped inside the drum and exits through the distribution pipe, some of the smoke changes from gas form into solid colloid called tar, some other through the spiral pipe thus the smoke changes into liquid (liquid smoke). The liquid smoke which is obtained directly from pyrolysis of coconut shell still contains tar which is dangerous for health so that separation of tar from liquid smoke is needed with the process of distillation. The main compounds that make up liquid smoke in which 3 of them work synergically are phenol compound, carbonyl compound and acid compounds which function as preservatives (Setiaji, B. 2007). The content of phenol compound in smoke is really depends on material temperature that being pyrolized. Phenol quantity is depends on raw material that being pyrolized. Phenol compound that usually contained in liquid smoke and smoked products are guaiacol and siringon (Girard 1992).

Phenol compounds that contained in liquid smoke are generally aromatic hydrocarbon which arranged from benzene ring with a number of hydroxy groups bound in which these phenol compounds may also bind other groups such as aldehydes, ketones, acid, and ester (Maya 1987). Acid compounds together with phenol and carbonyl synergically act as antimicrobial. The most acid compounds contained in liquid smoke are derivations of carboxylate acid such as furfural, furan, acetate acid, propionate acid, butyric acid and valerate acid.

Polysyclic aromatic hydrocarbon (PAH) compound can be formed at pyrolysis among others benzo(a)pyren. This compound is a compound which has negative impact as it is carsinogenic in nature. The formation of PAH compound during pyrolysis depends on temperature at prolysis, humidity at production process and also water level in material.

Benzo(a)pyrene has a melting point of 179°C and a boiling point of 495°C in the shape of solid. Crystal with the color of yellow is 5-ring polysyclic aromatic hydrocarbon that resulted from incomplete burning at the temperature range of 300°C and 600°C. Wang. X,co 2007 conducted biomas pyrolysis in a Bed Fluidized reactor with a temperature condition of 250°C-800°C.

Active compound of botany insecticide is taken from plants. Only if the active compound has been determined its chemical structure then can human try to create its derivation. At present, this botany insecticides is starting to be developed especially from pyrethroid group.

Insecticides toxicity will increase when added with another compound become synergical thus the toxicity level increases highly towards the mortality rate of bugs (insects).

The use of agricultural drugs botany insecticide has started since 1690 especially from tobacco plants and in 1874, a synthetic organic insecticide called chlorized hydrocarbon was first used (Baehaki, 2002).

MATERIALS AND METHODS

This study was conducted at the laboratory of Manado State University, Faculty of Mathematics and Sciences, Chemistry major and Gadjah Mada University, Yogyakarta for 3 months starting from February to May 2016.

The material used in this research was liquid smoke from clove tree that infected by stem caterpillar, while the equipment that used were wood drill, gas cromatography syringe, gas cromatography, spectrometer, IR and also several glass tools which support in the laboratory. The pyrolysis of coconut shell was conducted at high temperature reactor of 200°C-400°C with heat rate of 30°C per minute. After reaching the intended temperature, it was left with the interval of 2 hours. The smoke that flowing through the cooling pipe was contained in erlenmeyer. The condensate and charcoal that formed were measured for determination of yield.

The liquid that obtained was liquid smoke with tar. It was left for the 3 days to precipitate the other insoluble compounds and was strained. Tar-free liquid smoke was analyzed for the components using gas cromatography. For the liquid smoke analysis, combination of mass spectrophotometer gas cromatography ionized type was used. EI (Electron Impact) 70 V compound mixture which was passed through a gas cromatography would be separated into individual components, then was analyzed further using mass spectrometer. The types of components of liquid smoke with the help of a computer could be determined after being consulted to the known standard/library.

RESULTS AND DISCUSSION

The result of pyrolysis of 120 kg coconut shells produce an amount of tar charcoal, liquid smoke and uncondensable gas.

Table 2. Pyrolysis Products in Weight, Volume and Yields

Pyrolysis product	Weight (kg)	Volume (L)	Yields (w/w) %
Charcoal	51,00	-	42,50
Liquid smoke	34,20	55,00	45,20
Tar	8,40	7,00	7,00
Uncondensable Gas	6,40	-	5,30

The result of pyrolysis showed that the highest product was liquid smoke. Solid product of shell charcoal of 42,50% and 57,50% were volatile which turned into distillate and uncondensable gas of 5,30%.

The early stage in pyrolysis is released of water, CO and CO_2 gases at temperatures of 100°C-120°C and the second stage is hemicellulose that composed at temperatures of 300°C-350°C which ends at a temperature of 400°C. In order to separate the components of liquid smoke based on differences in boiling point, a column distillation is conducted. In this study, the process of distillation was conducted by collecting distillate at a temperature raise of 20°C with liquid smoke solution of 500 mL. Based on table 3, liquid smoke before distillation was reddish brown in colour which means that the liquid smoke still contained tar, still contained components with high molecule weight which are inseparable either with straining or common distillation.

Table 3. Volume, yields, color, and pH of coconut shell liquid smoke distillate at each temperature increase of 20°C

Fraction	Temperature of liquid smoke (°C)	pH	Volume (mL)	Color	Yields
I	< 100	3,86	8	Greenish yellow	1,60
II	101-120	2,24	335	Dark brownish yellow	67,00
III	121-140	1,96	35	Dark brownish yellow	7,00
IV	141-160	2,01	30	Brownish yellow	6,00
V	161-180	1,81	26	Brownish yellow	5,20
VI	181-200	1,87	13	Brownish	2,60
VII	Residue	1,62	40	Blackish brown	8,00

Value of pH is one of the parameters of liquid smoke quality in which if pH from liquid smoke is low, it shows a high liquid smoke quality because as a whole it has an effect on storability and durable organoleptic value. From the pH data, the result of liquid smoke distillation shows number between 2,24-1,62, showing that the result of pyrolysis and distillation from coconut shell studied is that coconut shell liquid smoke has a high level of acidity.

The value of pH becomes low as the raise in temperature since the water content component decreases (becomes less) and the increase in distillized organic acids such as at boiling point of 118°C is acetate acid boiling point, while 122°C is the boiling point of butanoic acid and the content of phenol in each distillate distillized is predicted to be able to cause pH decrease or increase liquid smoke acidity.

F_1 fraction of coconut shell liquid smoke gas cromatogram showed 7 peaks which can be implied that F_1 fraction of liquid smoke has 7 compounds as shown in the table below.

Table 4. Data of KG and SM from coconut shell liquid smoke chromatogram F_1 fraction peak number, retention time, area, molecule weight, compound prediction

Peak number	Retention time (minute)	Area %	Molecule weight	Compound prediction
1	2,004	0,78	44	Nitrogen oxide
2	2,140	0,47	58	Dimetyl ketones
3	2,191	0,34	74*	Metyl acetate
4	2,283	2,32	46	Metanoate acid
5	2,714	87,35	74	1 hydroxy – 2 propanone
6	3,602	3,40	88*	1 hydroxy – 2 butanone
7	9,114	5,34	94	Phenyl alcohol

**assumed that compound peak as pesticide*

Compound of peak 3 has the same peaks as compound shown by library data wiley 229 LIB at m/z = 43. Both spectra show the same molecule ion peak at m/z = 74 stated molecule weight of compound. The presence of electron release at molecule m/z = 74 results molecule ion fragment m/z = 74 releases $-CH_3$ (15) at molecule m/z = 59. Release –O(16) at molecule m/z = 59. Release –O(16) at molecule m/z = 59 results molecule ion fragment m/z = 43 (100%) and molecule ion acidity of M^+ = 74 also the presence of acidity of compound fragment pattern thus it can be concluded that peak 3 means acetate methyl compound with molecule weight of 74 and has a molecule formula of $C_3H_6O_2$. Peak 3 compound fragment can be seen in figure 1.

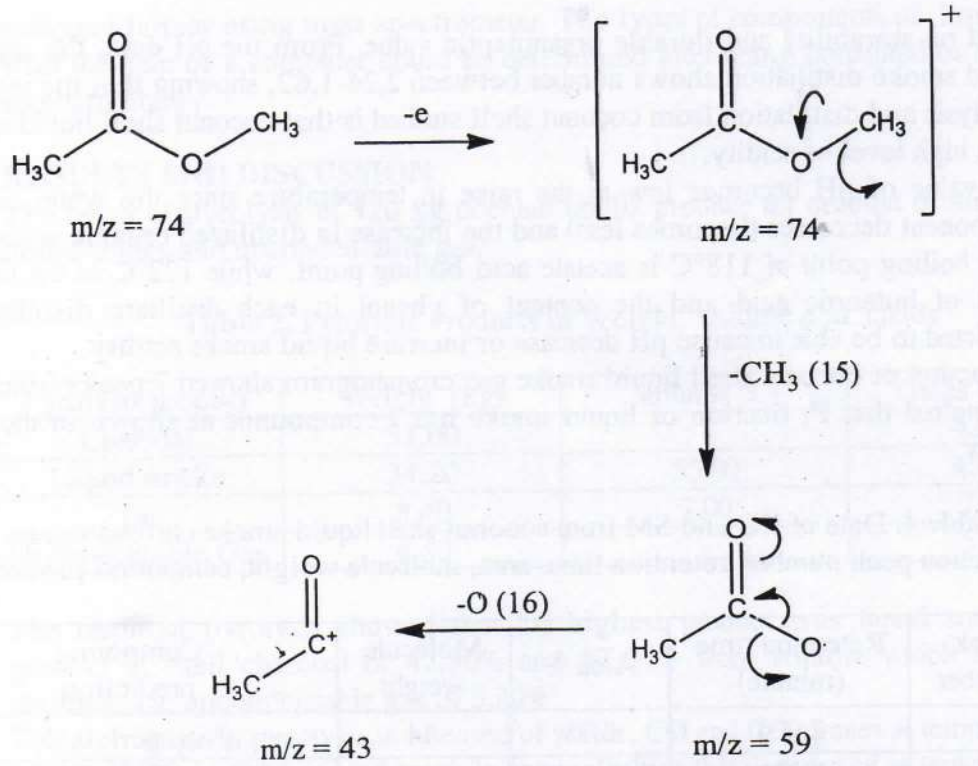

Figure 1. Prediction of ion release fragmentation pattern or peak 3 compound molecule or methyl acetate.

Peak 6 compound has rough peak similar to that shown by library data wiley 229 LIB at m/z = 57, both spectra show the same molecule ion peak at m/z = 88 which states molecule weight of peak 6 compound fragmentation pattern (figure 2).

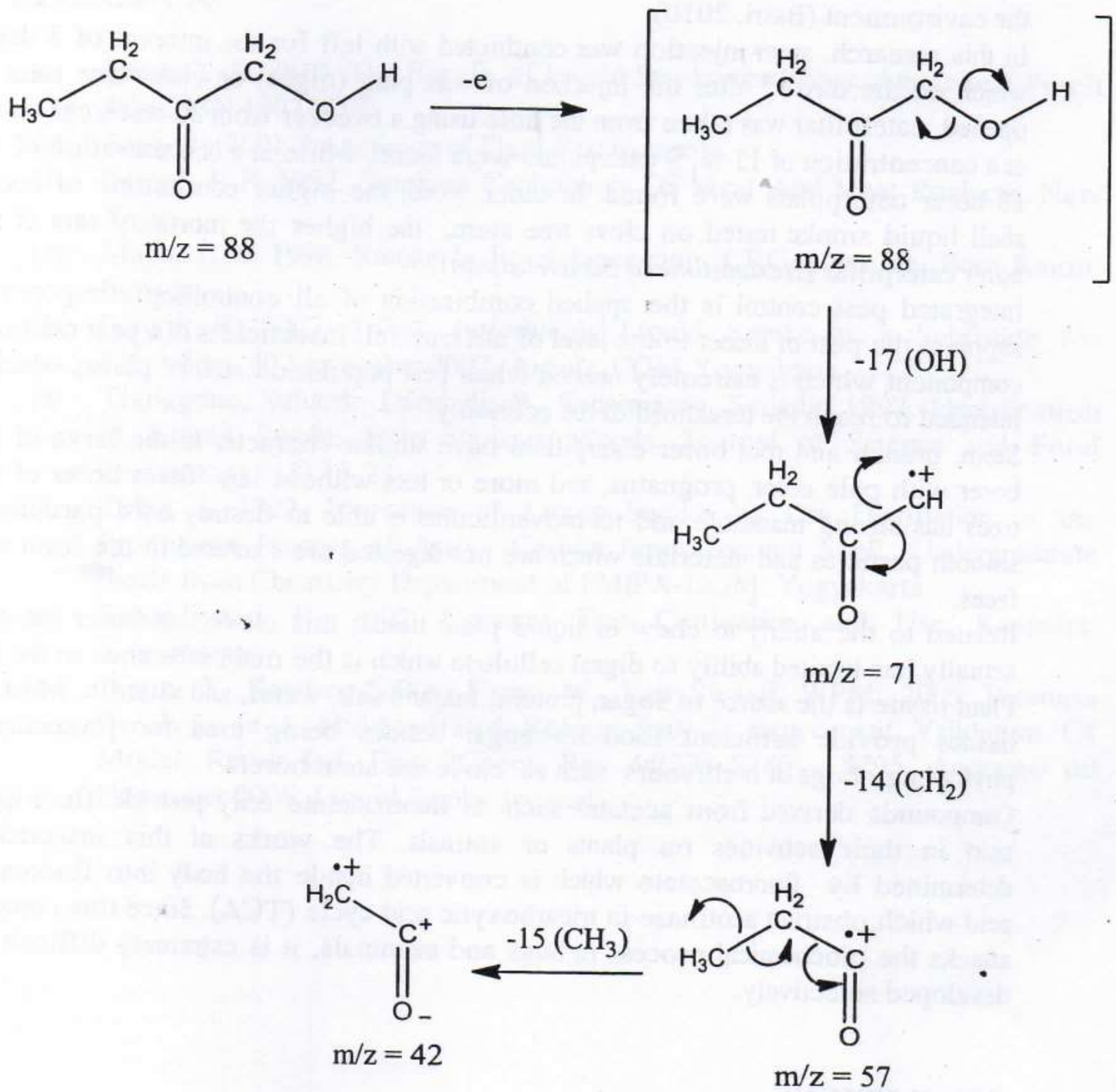

Figure 2. Prediction of compound fragmentation pattern peak 6 or 1 hydroxy 2 butanone.

At m/z = 88 with a retention time of 3,602 minute and abundance of 3,40 % the first break there is a release of OH(17) and forming molecule ion fragment of m/z = 71 and followed by a release of $-CH_2$ (14) and a release of CH_3 (15) thus forming molecule of m/z = 57 and molecule ion of m/z = 42. From the fragmentation pattern that has explained, it can be seen that peak 6 compound has the same base peak as compound of 1-hydroxy 2 butanone shown by library fragment Wiley 299 LB at m/z = 57.

In agriculture sector, liquid smoke is used to increase the quality of soil and neutralize soil acidity, kill plant pests (pesticide) and control plant growth, accelerate growth in the root, stem, bulb, leaves, root and fruit. Liquid smoke is believed to be able to replace the function of chemical pesticides which are highly dangerous for health and the environment (Basri, 2010).

In this research, stem injection was conducted with left for the interval of 3 days in which on the day 4th after the injection of wax plug (night) on clove tree stem was opened, caterpillar was taken from the hole using a tweezer from 30 test trees on field at a concentration of 15 %, 9 caterpillars were found, while at a concentration of 20%, 18 borer caterpillars were found. In other word, the higher concentrate of coconut shell liquid smoke tested on clove tree stem, the higher the mortality rate of stem borer caterpillar *(Hexamitodera Semivelutinia).*

Integrated pest control is the applied combination of all controlling components to suppress the pest of insect to the level of not harmful. Insecticides is a pest controlling component which is extremely needed when pest population attacks plants which are intended to reach the threshold of the economy.

Stem, branch and root borer caterpillars have similar character to the larva of leave borer with pale color, prognatus, and more or less without legs. Stem borer of clove trees has strong mandible and its proventiculus is able to destroy hard particles into smooth particles and materials which are not digested are excreted in the form of dry feces.

Related to the ability to chew or liquid plant tissue, this clove tree borer caterpillar actually has limited ability to digest cellulose which is the main substance in the plant. Plant tissue is the source of sugar, protein, fat, and salt, water, and vitamin. Most plant tissues provide sufficient food for bugs, besides being used for protection for phytophagy bugs or herbivours such as clove tree stem borers.

Compounds derived from acetates such as fluoroacetate only provide fluoroacetate acid in their activities on plants or animals. The works of this insecticide is determined by fluoroacetate which is converted inside the body into fluoroacetate acid which obstruct acotinase in tricarboxylic acid cycle (TCA). Since this compound attacks the biochemical process in bugs and mammals, it is extremely difficult to be developed selectively.

CONCLUSION

The result of pyrolysis and distillation of coconut shell has high acidity pH level of 2,24 - 1,62 which will increase organic acids which are distilled. The higher concentration of coconut shell liquid smoke solution, then the mortality rate of stem borer caterpillar also higher and the death period also shorter.

Chemical compound from coconut shell liquid smoke fraction F, which is predicted to be potential as pesticide is the methyl acetate compound, and compound of 1-hydroxy 2 butanones which is toxic has the ability to kill clove tree stem borer caterpillars *(Hexamitodera Semivelutinia).*

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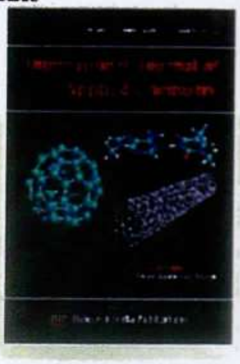

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