ANALYSIS OF THE CONTENT OF THE HEARTWOOD EXTRACTIVES OF THREE DURABLE NIGERIAN GUNINEA SAVANNAH TIMBERS

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ABSTRACT
Resistance of most wood depend on the toxicity rather than the concentration of the heartwood extractive. However, most studies are not examining the contents of heartwood which are responsible for the resistance of most durable timbers to biological attacks. In this study, the heartwood of Prosopis africana, Burkea africana and Vitellaria paradoxa were extracted with distiled water and absolute ethanol and the extracts were subjected to phytochemical screening. The results showed that B. africana heartwood revealed 42 and 24 bioactive compounds for the ethanolic and aqueous extract. Hexadecanoic acid, methyl ester accounted for 34.82% and 17.38% of the total phyto-constituents in both ethanolic and aqueous extracts respectively. Other compounds occured in trace quantity. P. africana heartwood ethanolic (PHE) extract revealed 11 phyto-constituents while the aqueous (PHA) revealed 24 constituents. 83.36% of PHE was made up of two constitutes; 7,7-Dimethyl-1-oxo-2,3,4,5,6,7-hexahydro-1I (which accounted for 50.16% of the total constituents) and 1,4-methanophthalazine, 1,4,4a,5,6,7,8,8a-oct (33.20%) while the PHA revealed 7 compounds which were in fairly large amount. The major compound in V. paradoxa was (S)-(+)-1,2-Propanediol which accounted for 73.51% out of the 30 compounds revealed in the ethanolic heartwood extract. The aqueous heartwood extract of V. paradoxa however revealed 22 compounds with 7 of the compounds fairly large in proportion. The result showed that extraction medium had influence on the type of bioactive compounds extracted. However, some compounds were similar irrespective of the extraction medium. Extractives from these species could be isolated and utilized to increase the durability of non-durable and non-refractory wood species.

***Keywords**: Phytochemicals; Biocides; Termites, Fungi, (S)-(+)-1,2-Propanediol, Hexadecanoic acid methyl ester*

INTRODUCTION

The destructive effects of insects and decay fungi to structural timbers are enormous. Several efforts is continually being made to complement previous reseraches to control these biodeteroriating organisms. To protect wood and wood-based products against biological agent, preservative treatments is required. However, most conventional preservatives are synthetic and they pose threats to the environment and negatively affect living organisms (Tascioglu et al.,2012). Due to this, attention has been shifted to the use of eco-friendly biocides in the control of wood destructive agents. Wood extractives are a major contributory factor in the natural durability of wood (Roszaini, 2017). Natural durability is undoubtedly derived from and affected by the extractive components (Hillis, 1987; Hon & Minemura 2001). Bioactivity of different parts of wood species against different biological agents of degradation have been reported (Alireza, 2012; Adedeji et al., 2018; Prayitno et al., 2021). Extractives either from the bark, stem or heartwood of most tropical trees are known to possess some bioactivity against varieties of biological agents of degradation. These extractives are of considerable interest for wood protection because of their indigenously known biocidal properties (Ademola et al. 2004, Agbedahunsi et al. 2004).

Many studies have been carried out on the feasibility of using heartwood extractives in preserving wood. Reports of these studies have shown promising results. Adedeji et al. (2018) reported the termicidal activity of *K. ivorensis* stem bark extractives impregnated into *Triplochiton scleroxylon* and *Vitex doniana* against wood-degrading agents under field conditions. Roszaini (2017) reported the toxic effects of selected Malaysian timber heartwood extracts against *Coptotermes gestroi* and *Coptotermes curvignathus* which are two aggressive Asian subterranean termites species. Bald cypress (*Taxodium distichum*) heartwood extract (Scheffrahn et al. 1988), southern catalpa (*Catalpa bibnonioides*) heartwood extract (McDaniel 1992), red louro (*Sextonia rubra*) wood extract (Rodrigues et al. 2011) have all been reportedly utilized to increase natural durability of inferior wood species to biological attack. Tascioglu et al. (2012) concluded that resistance of wood varies depending on many factors including natural durability, density and extractive types and quantities. Of all these factors, the quantity of the extractives and their chemical composition play an important role on wood durability (Anda et al., 2019). Therefore, the durability characteristics of most timbers may be attributed to the toxic content of the extractives rather than the concentration of the total extractive content. Some wood may possess non toxic extractives which may confer little or no level of durability to the wood while some woods may have very toxic extractable materials that were accumulated during the formation of heartwood which are thus responsible for their resistance against different biological agents of degradation.

Wood extractives have shown to have different structures as well as belong to different classes such as flavonoids, steroidal compounds, glycosides, quinones and phenolic acids (Alabi and Oyeku, 2017). Quite a number of bio-compounds in wood extractives are known to inhibit the activities of biological agents. Phenolic compounds, terpenes, carbohydrates, long-chain fatty acids, waxes and other

substances, including steryl esters and sterols are among the main chemical compounds in heartwood extractives (Fengel and Wegener 1989). Ji et al. (2014) reported the bioactivity of limonoids from *K. ivorensis* seed, fruit and stem bark as anti-feeding, anti-fungal, anti-bacterial, anti-trypanosomal and anti-tumor. Sesquiterpenes are known to play a role in plant defense mechanisms against insects and fungi (Fraga, 2003, Wu et al., 2005). Pinosylvin and pinosylvin-monomethyl-ether reported to be toxic to fungi (Hillis and Inoue 1968) as well as quinones (e.g in *Prosopis africana* and *T. grandis*) toxic to termites (Alabi and Oyeku, 2017). Naphthoquinones and anthraquinones have been reported to show remarkable anti-fungal and anti-termitic effects (Guerrero-Vásquez, 2013). Likewise, Bis(2-ethylhexyl)phthalate has also been reported to be toxic to agents of wood degraration (Alabi and Oyeku, 2017).

Although, many studies have been carried out on the anti-termitic and anti-fungal activities of heartwood of many timber species, however, most studies did not examine the content of the heartwood which are responsible for the resistance of most durable timbers to attack by biological agents. According to Tascioglu et al. (2012), extractives isolated from naturally resistant heartwood in some plant species may provide alternatives in pest control because of their bioactive chemicals if their compositions are known to be toxic to biological agents of degradation. In this study, the content of the heartwood extractives of three important and durable timbers species (name them) which are native to the Nigerian Guinea Savannah region were evaluated to know the contents which are likely to be responsible for the enhanced durability of these timbers species. These timber species are some of the prominent timbers of economic value in this region. They have been reported to have high load bearing applications, greater resistance to shock as well as higher resistance to attack by biological agents of degradation by local wood workers. However, to the best of our knowledge, little or no report of the chemical content of the heartwood of these species exists in scientific literature. The present study was with the intent that the extractives from these species could be isolated and utilized to increase the durability of non-durable and non-refractory wood species.

MATERIALS AND METHODS

Collection of Plant Materials

Prosopis africana, *Burkea africana* and *Vitellaria paradoxa* trees were harvested from the natural plantation of the Department of Forest Resources Management, University of Ilorin. Ilorin is located in the transitional zone between the deciduous woodland of the South and dry savannah of North Nigeria (Jimoh 2003) and on latitude 8º 24' N and 83º 6' N and longitude 4º10' E and 4º 36' E. The climate of Ilorin is characterized by both wet and dry seasons. The rainy season begins towards the end of April and last till October while the dry season begins in November and ends in April. The temperature of Ilorin ranges from 33º C to 35º C from November to January while from February to April; the value ranges between 34º C to 37º C. Days are very hot during the dry season. The total annual rainfall in the area ranges from 990.3mm to 1318mm. The rainfall in Ilorin city exhibits the double maximal pattern and greater variability both temporarily and spatially. The relative humidity ranges from 75% to 88% from May to October, while in the dry season it ranges from 35% to 80% (Ajibade and Ojelola 2004). The marchantable lenght of each of the trees were divided into three equal parts. Thereafter, the billets were laterally sawn to separate the heartwood from the sapwood regions. Each of the heartwood portion of the timbers were ground to fine powder. The sawdust were air dried (to avoid the possibility of extracts degradation) to constant weight. They were then sieved using 250 mesh sieve and kept in polythene bags prior to extraction. All reagents used were analytical grades.

Extraction and isolation of Extractives

About 1000 g of sawdust from each of the wood was extracted with de-ionised water and absolute ethanol (EtOH) for 48 hours on an orbital shaker (Gallenkamp, UK). Thereafter, the extracts were concentrated under pressure at 45ºC, using a rotary evaporator (EYELA, SB-651, Rikakikai Co. Ltd. Tokyo, Japan). After extract concentration, the extracts were stored in glass vials and refrigerated at a temperature of -4ºC prior to analyses.

Gas Chromatography Mass Spectra Analysis

The bioactive compounds analysis of the heartwood extracts of the three timber species was done by GC-MS analysis of the aqueous and ethanolic extracts. Breifly, the extracts were subjected to GC-MS analysis to identify the various bioactive compounds present. Each of the samples was analyzed in Perkin Elmer-Clarus-600 instrument using software Turbomass 5.2 version. Capillary standard non-polar column (30 m x 0.25 mm, 0.25 mm film thickness) was used. The volume of injected specimen was 1 L of ethanol extract, injector temperature (temp.) of. 220°C with a split ratio of 25:1 Carrier gas Helium, Solvent Delay=3.00 min, source Temp=180°C, oven temperature program initial temp. of 60°C for 5 min, ramp7°C/min to 300°C, hold 15 min, Scan: 50 to 600Da, ionization energy 70 eV, in the electronic ionization mode.

Identification of Compounds

The identification of compounds was done using computer matching of mass spectra with those of standards (NIST library). The spectrum of the unknown component was compared with the spectrum of the known components stored in the NIST library. The Name, Molecular weight and structure of the components of the test materials were ascertained. The test was run in triplicate.

RESULT

Bioactive Compounds in *Burkea africana* Heartwood

B. africana Heartwood Ethanolic Extract revealed 42 phyto-constituents. The constituents which occured in fairly large amount was hexadecanoic acid, and methyl acid. This accounted for 34.82% of the total phyto-constituents. Others include Dibutyl phthalate (5.38%), 9-Octadecenoic acid, methyl ester (E)- (9.01%); Methyl stearate 7.6% and Squalene (4.86%) (Table 1). However, aqeouos extract revealed 24 constituents which included 6 compounds which occured in fairly large amount, like the ethanolic extract, Hexadecanoic acid, and methyl ester were the major constutuent in *B. africana* aqeuous extract accounting for 17.38% of the total phytochemicals present. Other constituents included; 1H-Pyrido [3,4-b]indole 2,3,4,9-tetrahydro-1-1 (11.46%); 9-Octadecenoic acid (Z)- methyl ester (6.97%); Stigmasterol (14.38%); Resorcinol (6.98%) and Campesterol (7.51%) (Table 2). The remaining 18 were in minute quantities.

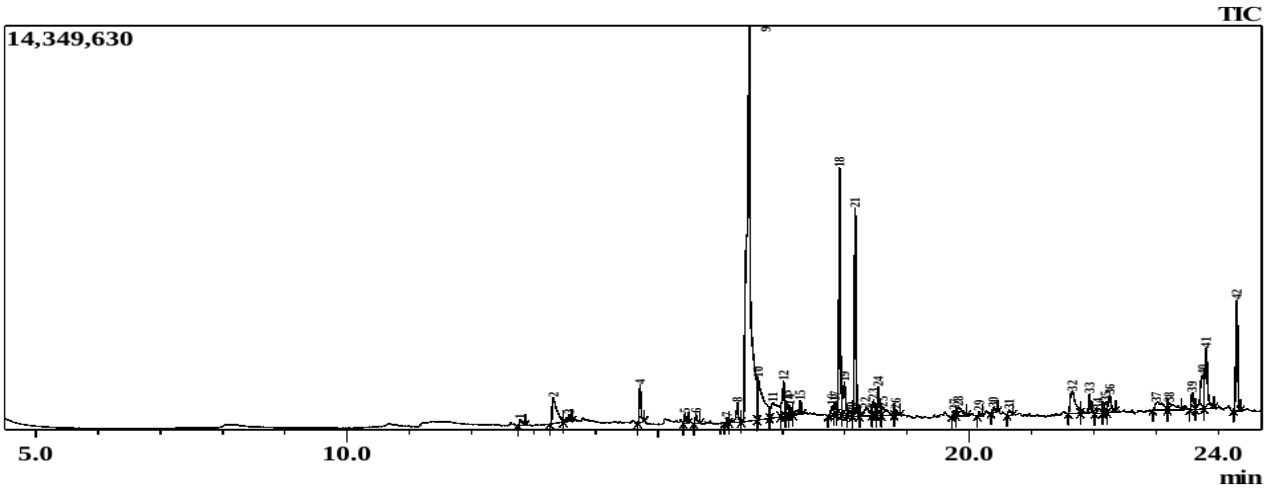

Figure 1: Chromatogram of *B. africana* Heartwood Ethanolic Extract

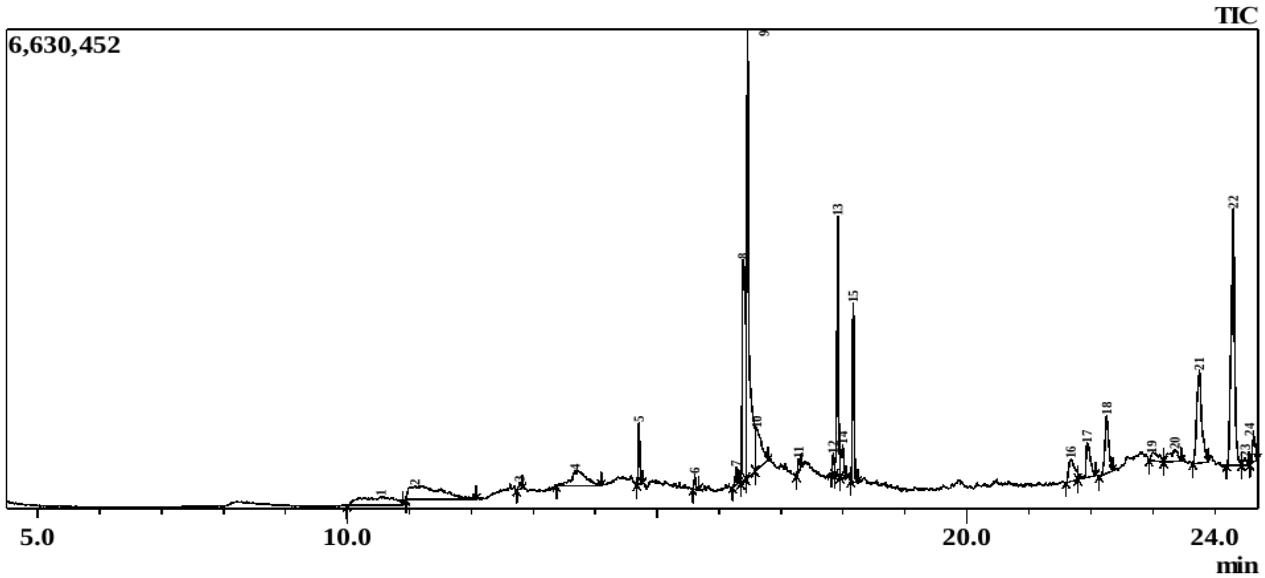

Figure 2: Chromatogram of *B. africana* Heartwood Aqueous Extract

Although, extraction medium had great influence on the type as well as the concentration of bioactive compounds extracted from *B. africana*, 8 compounds were similarly revealed in both extracts. The compounds were Methyl tetradecanoate, Pentadecanoic acid methyl ester, Hexadecanoic acid methyl ester, 9-12-Octadecadienioc acid methyl ester, 9-Octadecenoic acid methyl ester, Methyl stearate, 1,4-Di-O-acetyl-2,3,5-tri-O-methylribitol and Bis(2-ethylhexyl) phthalate (Table 1 and 2). *B. africana* could be a source for the extraction of hexadecanoic acid, methyl ester, because this compound occured in large amount representing 34.82% of the total constituents while others occured in fairly large to minute quantities.

Table 1: Biochemical Compounds in *B. africana* Ethanolic extract

Peak No.	R_{time}	Area (%)	Compound
1	12.781	0.33	Dodecanoic acid, methyl ester
2	13.317	2.79	Diethyl Phthalate
3	13.568	0.40	1-Hexadecanol
4	14.708	1.40	Methyl tetradecanoate
5	15.433	0.35	9-Eicosene, (E)-
6	15.609	0.39	Pentadecanoic acid, methyl ester
7	16.108	0.22	n-Nonadecanol-1
8	16.274	1.08	7-Hexadecanoic acid, methyl ester, (Z)
9	16.463	34.82	Hexadecanoic acid, methyl ester
10	16.608	5.38	Dibutyl phthalate
11	16.842	2.59	8-Methyl-6-nonenamide
12	17.02	1.80	Hexadecanoic acid, methyl ester
13	17.06	0.75	Tetradecanoic acid, 12-methyl-, methyl ester
14	17.12	0.46	1-Heneicosanol
15	17.28	0.58	Hexadecanoic acid, 14-methyl-, methyl ester
16	17.8	0.5	n-Pentadecanol
17	17.84	0.48	9,12-Octadecadienoic acid, methyl
18	17.92	9.01	9-Octadecenoic acid, methyl ester, (E)
19	17.99	1.86	11-Octadecenoic acid, methyl ester
20	18.1	0.42	Trans-2,3-Epoxynonane
21	18.17	7.80	Methyl stearate
22	18.33	0.97	2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undeca
23	18.46	0.7	Ethyl 9,12-hexadecadienoate
24	18.54	1.31	(E)-9_Octadecenoic acid ethyl ester
25	18.61	0.92	Decanamide-
26	18.82	0.31	Octadecanoic acid, 17-methyl-, methyl ester
27	19.76	0.29	Octadecanoic acid, 2,3-dihydroxypropyl ester
28	19.83	0.94	1,4-Di-O-acetyl-2,3,5-tri-O-methylribitol
29	20.16	0.18	Methyl 18-methylnonadecanoate
30	20.39	0.26	9-Octadecenamide
31	20.64	0.36	Tetradecanamide
32	21.66	2.62	Hexadecanoic acid, trimethylsilyl ester
33	21.93	0.88	Bis(2-ethylhexyl) Phthalate
34	22.07	0.49	Tetracosanoic acid, methyl ester
35	22.19	0.73	6,8-Dioxapentadecane
36	22.26	1.07	Octane, 1,1'-oxybis-

Peak No.	R_{time}	Area (%)	Compound
37	23.01	1.43	Cis, 6-Octadecenoic acid, trimethylsilyl ester
38	23.21	1.12	1,4-Di-O-acetyl-2,3,5-tri-O-methylribitol
39	23.58	0.93	1,3-Benzenedicarboxylic acid, bis(2-ethylhexy)
40	23.75	2.97	Hexanoic acid, 2-ethyl-, nonyl ester
41	23.81	3.48	Oxalic acid, decyl neopentyl ester
42	24.3	4.86	Squalene

Table 2: Biochemical Compounds in *B. africana* Aqeous extract

Peak No.	R_{time}	Area (%)	Compound
1	10.543	4.76	1-Oxaspiro[3.5]nona-5,8-dien-7-one, 3-methyl
2	11.090	6.98	Resorcinol
3	12.781	0.23	Undecanoic acid, 10-methyl-, methyl ester
4	13.679	3.56	Hydrazinecarboxylic acid, butylidene-, methyl
5	14.704	1.64	Methyl tetradecanoate
6	15.608	0.37	Pentadecanoic acid, methyl ester
7	16.274	0.52	13-Methyltetradec-9-enoic acid methyl ester
8	16.388	11.46	1H-Pyrido[3,4-b]indole, 2,3,4,9-tetrahydro-1-
9	16.460	17.83	Hexadecanoic acid, methyl ester
10	16.608	3.91	2-(Heptyloxycarbonyl)benzoic acid
11	17.286	0.38	Hexadecanoic acid, methyl ester
12	17.840	0.57	9,12-Octadecadienoic acid, methyl ester
13	17.915	6.97	9-Octadecenoic acid (Z)-, methyl ester
14	17.994	1.47	9-Octadecenoic acid (Z)-, methyl ester
15	18.165	4.69	Methyl stearate
16	21.678	2.14	1,4-Di-O-acetyl-2,3,5-tri-O-methylribitol
17	21.940	2.47	Bis(2-ethylhexyl) Phthalate
18	22.255	3.54	Vitamin E
19	22.983	1.07	Ocadecane, 1-isocyanato-
20	23.355	1.72	3-Methoxy-D-homoesta-1,3.5(10)-trien-14-.b
21	23.751	7.51	Campesterol
22	24.298	14.38	Stigmasterol
23	24.492	0.45	Cholestan-3-one, 4,4-dimethyl-,(5.alpha)-
24	24.627	1.37	Campesterol

Bioactive Compounds in *Prosopis africana* Heartwood

P. africana Heartwood Ethanolic Extract revealed 11 phyto-constituents. The most prevailing compounds in the ethanolic extract of *P. africana* were two namely; (7,7-Dimethyl-1-oxo-2,3,4,5,6,7-hexahydro-1) (50.16%) which accounted for more than half of the total constituents contained in *P. africana* and 1,4-Methanophthalazine, 1,4,4a,5,6,7,8,8a-oct with peak area of 33.20% (Table 3). The two

compounds represented 83.36% of the total phytochamicals in ethanolic extract of *P. africana*. *P. africana* aqeuous extract had 5 constituents which occured in fairly large quantities, however, 14.alpha.-Methyl-5.alpha.-ergosta-8,24(28)-di was the major constituent with peak area of 17.95%

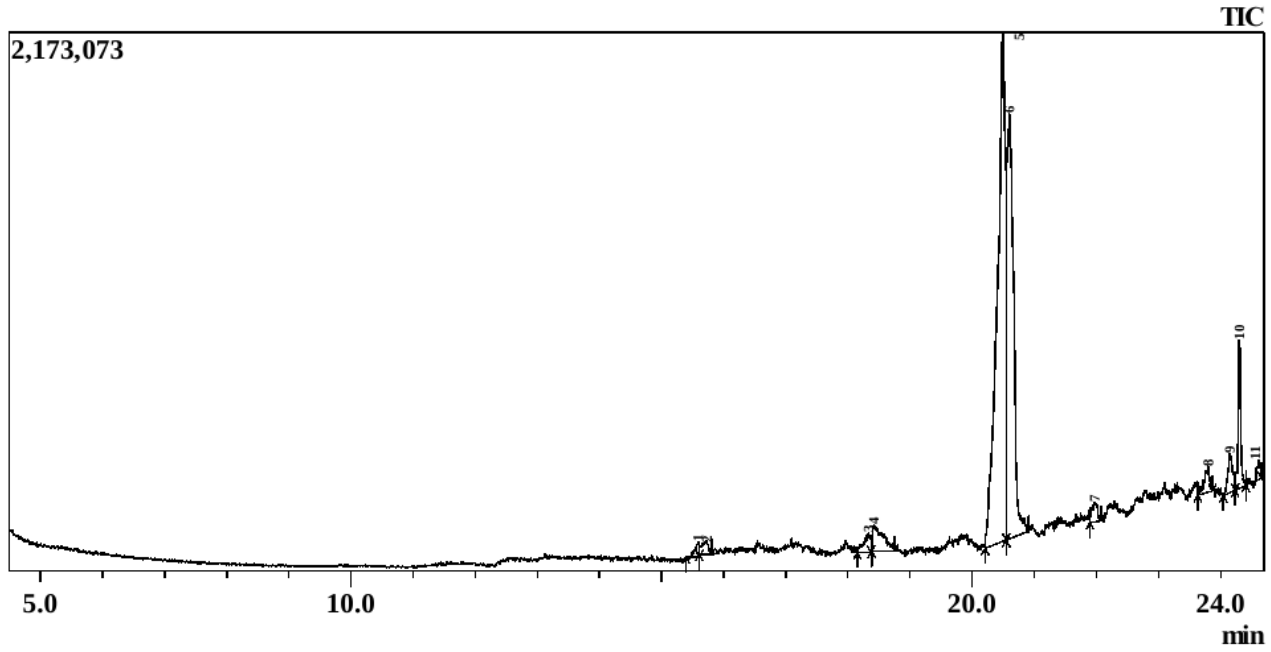

Figure 3: Chromatogram of *P. africana* Heartwood Ethanolic Extract

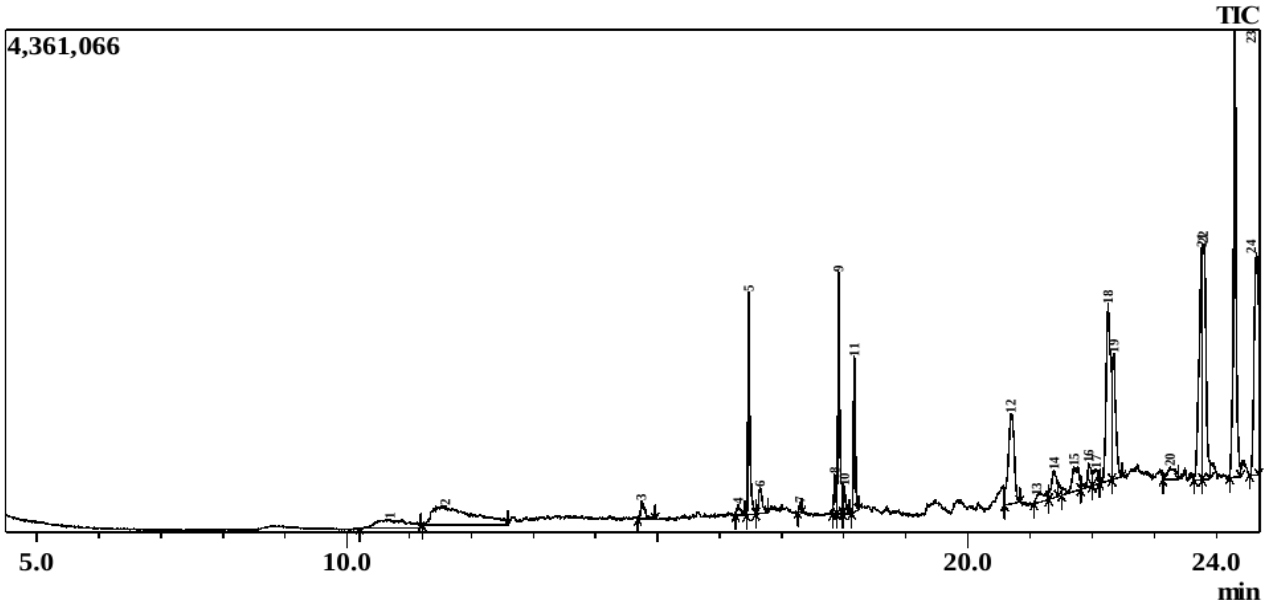

Figure 4: Chromatogram of P. *africana* Heartwood Aqueous Extract

The aqueous *P. africana* heartwood extract revealed 24 constituents out of which 5 compounds are considered to occur in fairly large amount. They include; tetracosapentaene 2,6,10,15,19,23-hexamethyl (13.74%); Campesterol (10.96%); 14.alpha.-methyl-5.alpha.-ergosta-8,24(28)-dis (17.95%); dl-.alpha.-Tocopherol (9.26%) and hydroquinone (8.70%) (Table 4). There were no compounds similar to both aqueous and ethanolic extracts of *P. africana*. The compounds that were revealed in the ethanolic extract were quite different from the aqeouos extract. This showed that extraction medium has great influence on the type of bioactive compounds extracted. This

further corroborated the findings in earlier studies (Naczk and Shahidi 2004, Spigno et al. 2007, Kajdžanoska et al. 2011, Lolita et al. 2012) that different solvents extract different compounds.

Table 3: Biochemical Compounds in *P. africana* Ethanolic extract

Peak No.	R_{time}	Area (%)	Compound
1	15.591	0.63	(.+/-.)-Lavandulol, pentafluoropropionate
2	15.733	0.99	1,3,3-Trimethyl-2-(2-methyl-cyclopropyl)-cyclo
3	18.334	1.54	P-Mentha-6,8-dien-2-one, semicarbazone
4	18.417	3.29	Tetrahydroabietic acid
5	20.492	50.16	(7,7-Dimethyl-1-oxo-2,3,4,5,6,7-hexahydro-1)
6	20.600	33.20	1,4-Methanophthalazine, 1,4,4a,5,6,7,8,8a-oct
7	21.973	1.24	7,7-Dimethyl-9-oxatricyclo[6.2.2.0(1,6)dodec]
8	23.800	1.62	Thiositosteroldisulfide
9	24.150	2.24	9,19-cyclolanostan-3-ol, acetate, (3.beta.)-
10	24.304	4.41	Squalene
11	24.617	0.69	2-(4a,8-dimethyl-1,2,3,4,4a,5,6,7-octahydro-r)

Table 4: Biochemical Compounds in *P. africana* Aqeous extract

Peak No.	**R_{time}**	**Area (%)**	**Compound**
1	10.691	2.92	1,3-Diethoxybenzene
2	11.583	8.70	Hydroquinone
3	14.742	0.87	Tridecanoic acid, methyl ester
4	16.299	0.38	6-Octadecenoic acid, methyl ester, (Z)-
5	16.468	4.71	Hexadecanoic acid, methyl ester
6	16.651	1.08	Dibutyl phthalate
7	17.293	0.14	Methyl 8-methyl-nonanoate
8	17.852	0.82	9,12-Octadecadienoic acid, mthyl ester
9	17.918	5.52	10-Octadecenoic acid, methyl ester
10	18.008	0.84	Cyclopropanenonanoic acid, methyl ester
11	18.170	3.22	Methyl stearate
12	20.694	6.05	trans-Geranylgeraniol
13	21.108	0.96	Comarin, 3,4,4a,5,6,8a-hexahydro-6,8a-epidio
14	21.392	1.64	Dimethyl(bis{[(2E,6E)-3,7,11-trimethyldodec
15	21.706	2.06	Hexadecanoic acid, trimethylsilyl ester
16	21.944	1.10	Bis(2-ethylhexyl) Phthalate
17	22.067	0.91	2,2,4-Trimethyl-3-(3,8,12,16-tetramethyl-hept)
18	22.257	9.26	dl-.alpha.-Tocopherol
19	22.347	4.98	Oxirane, 2,2-dimethyl-3-(3,7,12,16,20-pentan)

Peak No.	R_{time}	Area (%)	Compound
20	23.256	1.20	3-Trimethylsilyloxystearic acid, trimethylsilyl
21	23.767	8.92	14.alpha. -Methyl-5. alpha. -ergosta-8,24(28)-di
22	23.785	9.03	14.alpha. -Methyl-5. alpha.-ergosta-8,24(28)-di
23	24.299	13.74	Tetracosapentaene, 2,6,10,15,19,23-hexamethyl
24	24.647	10.96	Campesterol

Bioactive Compounds in *Vitellaria paradoxa* Heartwood

The ethanolic heartwood extract of *V. paradoxa* wood contained 30 phyto-constituents, of these the most important is (S)-(+)-1,2-Propanediol which accounted for 73.51% of the heartwood constituent. However, Silane, [[(3.beta.)-lanosta-9(11), 24-dien-3yl]o only accounted for 5.23%. Other constituents occured in minute amount (Figure 5 & Table 5).

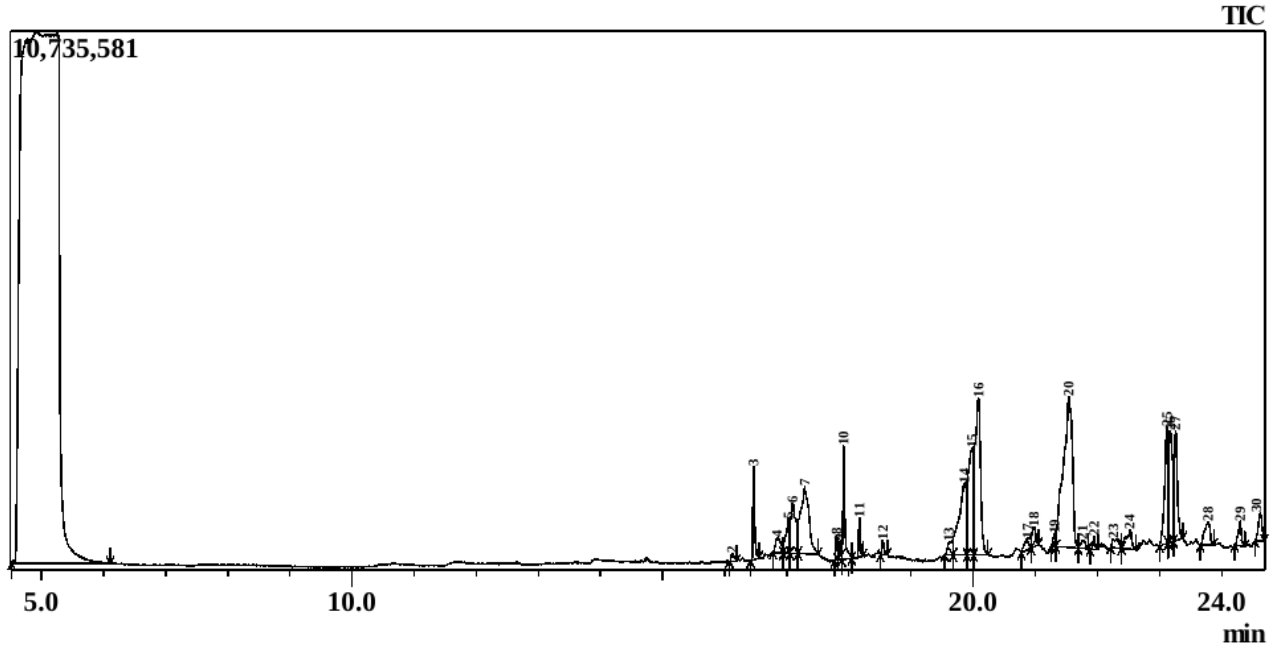

Figure 5: Chromatogram of V. *paradoxa* Heartwood Ethanolic Extract

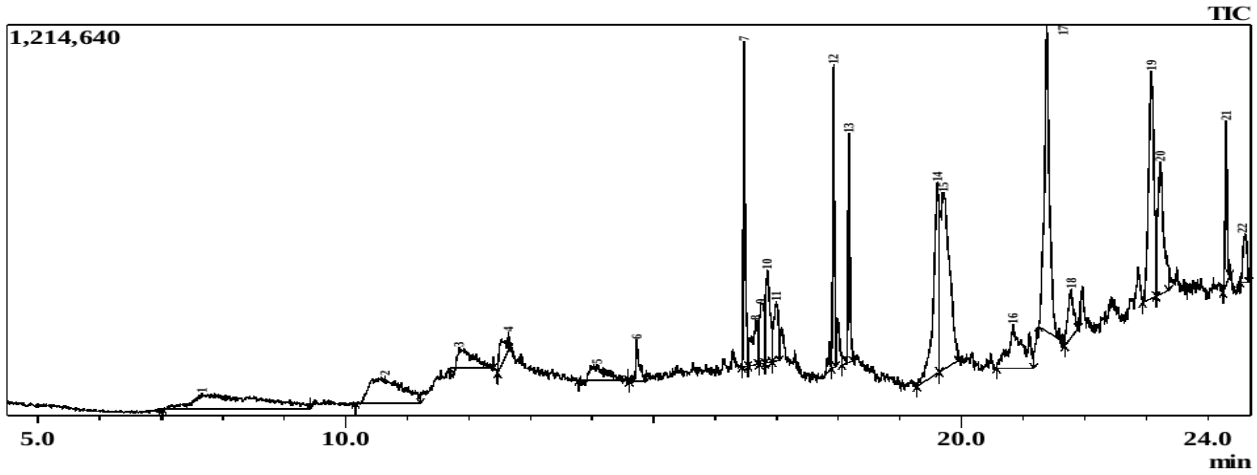

Figure 6: Chromatogram of *V. paradoxa* Heartwood Aqueous Extract

In the case of the aqueous extract, 22 compounds were revealed. Seven of the compounds were fairly large in proportion. 9,19-cyclchloestene-3,7-diol,4,14-dimethyl had the largest concentration of 12.21%; Acetic acid, 2-(4-cyclohexylphenoxymethyl)-4 had 8.24%. 4-Butoxyphenoxycarbonylamino acetic acid, Cyclohexanol, 3,5-dimethoxy-, stereoisomer, 9,19-cyclo-9.beta. -Ianostane-3.beta.,25-diol, 9,19-Cycloianostan-3-ol, 24-methylene-3.beta and Pregnan-17,21-diol-9,11-epoxy-3,20-dione accounted for 8.24%, 6.32%, 7.67%, 11.76%, 9.22% and 6.00% respectively (Table 6 and Figure 6).

Similarly as recorded for *B. africana*. 5 compounds were similarly revealed in both ethanolic and aqeouos extracts of *V. paradoxa*. The compounds were Hexadecanoic acid methyl ester; .gamma.-Sitosterol; .beta.-Sitosterol; 9-Octadecenoic acid methyl ester and Methyl stearate. These compounds are almost similar to those of *B. africana* except for a few of the compounds. From the result, *V. paradoxa* could serve as a raw material for the extraction of (S)-(+)-1,2-Propanediol owing to the concentration (73.51%) of the compound which occured in very large amount.

Table 5: Biochemical Compounds in *V. paradoxa* Ethanolic Extract

Peak No.	R_{time}	Area (%)	Compound
1	4.909	73.51	(S)-(+)-1,2-Propandiol
2	16.120	0.08	1-Tetradecanol
3	16.466	0.61	Hexadecanoic acid, methyl ester
4	16.842	0.32	.beta.-Sitosterol
5	17.026	0.49	Ethyl 14-methyl-hexadecanoate
6	17.094	0.98	.beta.-Sitosterol
7	17.288	2.13	.gamma.-Sitosterol
8	17.803	0.17	1-Hexadecanol
9	17.846	0.08	7,10-Hexadecadienoic acid, methyl ester
10	17.917	0.83	9-Octadecenoic acid (Z)-, methyl ester
11	18.170	0.25	Methyl stearate
12	18.545	0.11	Ethyl Oleate
13	19.608	0.27	9,19-Cycloergost-24(28)-en-3-ol, 4,14-dimethy
14	19.858	2.13	9,19-Cycloergost-24(28)-en-3-ol, 4,14-dimethy
15	19.983	2.13	Ergosta-5,22-dien-3-ol, acetate, (3.beta,22E)-

16	20.084	3.26	9,19-Cycloergost-24(28)-en-3-ol, 4,14-dimethy
17	20.875	0.28	.beta.-Sitosterol
18	20.978	0.28	.beta.-Sitosterol
19	21.308	0.14	Acetic acid, 3-hydroxy-6-isopropenyl-4,8a-din
20	21.541	5.23	Silane, [[(3.beta.)-Ianosta-9(11),24-dien-3-yl]o
21	21.765	0.13	Stigmastan-3,5-diene
22	21.947	0.11	Bis(2-ethylhexyl) Phthalate
23	22.256	0.24	dl-.alpha.-Tocopherol
24	22.520	0.42	Obtusifoliol
25	23.122	1.62	9,19-CycloIanost-25-en-3-ol, 24-methy-, (3.b)
26	23.175	1.67	9,19-CycloIanost-25-en-3-ol, 24-methy-, (3.b)
27	23.260	1.36	17.beta.-Methyl-18-nor-17-isopregna-4,13-die
28	23.783	0.50	14.alpha.-Methyl-5.alpha.-ergosta-8,24(28)-di
29	24.299	0.29	Stigmasten-3-one
30	24.622	0.40	Stigmasta-5,22-dien-3-ol, acetate, (3.beta.)-

Table 6: Biochemical Compounds in *V. paradoxa* Aqeuous Extract

Peak No.	R_{time}	Area (%)	Compound
1	7.666	7.67	Cyclohexanol, 3,5-dimethoxy-, stereoisomer
2	10.640	6.32	(4-Butoxyphenoxycarbonylamino) acetic acid
3	11.842	2.07	Phenol, 2-propyl
4	12.642	1.32	.beta.-D-Glucopyranose, 1,6-anhydro
5	14.085	1.60	Phenol, 3,4,5-trimethoxy-
6	14.726	1.12	Methyl tetradecanoate
7	16.468	4.65	Hexadecanoic acid, methyl ester
8	16.658	2.01	1,2-benzenedicarboxylic acid, bis(8-methylno)
9	16.742	2.05	5.beta., 6.beta.-Epoxy-7-bromocholestan-3-one
10	16.846	2.99	.gamma.-Sitosterol
11	16.991	2.12	.beta.-Sitosterol
12	17.922	4.19	9-Octadecenoic acid, methyl ester (E)-
13	18.171	3.48	Methyl stearate
14	19.608	8.24	Acetic acid, 2-(4-cyclohexylphenoxymethyl)-4
15	19.709	12.21	9,19-Cyclochloestene-3,7-dol, 4,14-dimethyl-
16	20.837	4.97	.beta.-Sitosterol
17	21.385	11.76	9,19-Cyclo-9.beta.-Ianostane-3.beta,25-diol
18	21.738	2.08	6,9-Octadecadiynoic acid, methyl ester
19	23.084	9.22	9,19-CycloIanostan-3-ol, 24-methylene-, (3.be
20	23.226	6.00	Pregnan-17,21-diol-9,11-epoxy-3,20-dione, ac

21	24.297	2.48	Squalene
22	24.604	1.47	2(3H)-Naphthalenone, 4,4a,5,6,7,8-hexahydro

Table 7: Dominant compounds present in the Heartwood Extractives of Three Nigerian Guinea Savannah Species.

Extract	Compound	Conc.(%)	MW (g/mol)	Formula	CAS No.
VHE	(S)-(+)-1,2-Propandiol (Polyols; Aliphatic acyclic compounds)	73.51	76.09	$C_3H_8O_2$	4254-15-3
VHA	9,19-Cyclochloestene-3,7-diol, 4,14-dimethyl-, 3-acetate	12.21	472.8	$C_{31}H_{52}O_3$	4254-15-3
	9,19-Cyclo-9β.-Ianostane-3β.,25-diol	11.76	444.7	$C_{30}H_{52}O_2$	26525-84-8
BHE	Hexadecanoic acid, methyl ester (Palmitic acid)	34.82	270.45	$C_{17}H_{34}O_2$	112-39-0
BHA	Hexadecanoic acid, methyl ester (Palmitic acid)	17.38	110.11	$C_6H_6O_2$	123-31-9
	1H-Pyrido [3,4-b]indole 2,3,4,9-tetrahydro-1-methyl	11.46	228.33	$C_{15}H_{20}N_2$	
	Stigmasterol (Sterol)	14.38	412.7	$C_{29}H_{48}O$	83-48-7
PHE	7,7-Dimethyl-1-oxo-2,3,4,5,6,7-hexahydro-1) (Bicyclic monoterpenoids)	50.16	250.34	$C_{15}H_{22}O_3$	139571-20-3
	1,4-Methanophthalazine, 1,4,4a,5,6,7,8,8a-oct	33.20	178.27	$C_{11}H_{18}N_2$	
PHA	14.alpha.-Methyl-5.alpha.-ergosta-8,24(28)-di (Triterpene)	17.95	412.7	$C_{29}H_{48}O$	10191-41-0
	Campesterol (Sterol)	10.96	400.68	$C_{28}H_{48}O$	474-62-4
	Tetracosapentaene, 2,6,10,15,19,23-hexamethyl (Triterpenoid)	13.74	414.4	$C_{30}H_{52}$	26266-08-0

MW = Molecular weight

Hit#:1 Entry:445 Library:NIST11.libSI:97 Formula:C3H8O2 CAS:4254-15-3 MolWeight:76 RetIndex:724

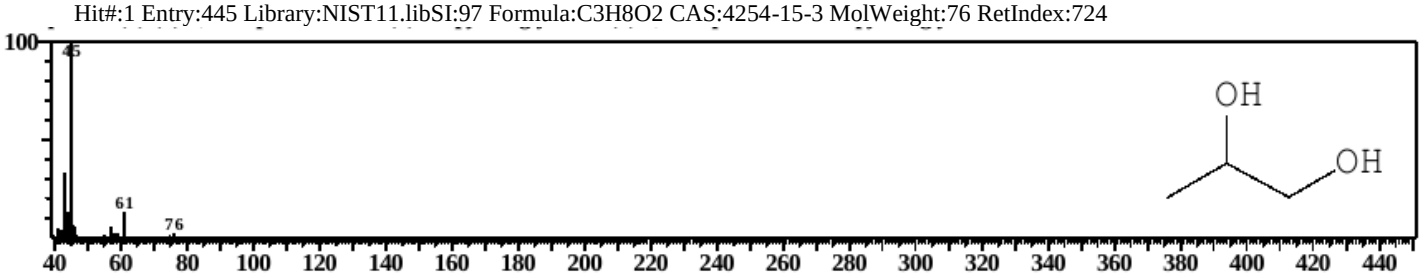

Fig. 7. Chromatogram of compound S)-(+)-1,2-Propanediol.

Hit#:1 Entry:201003 Library:NIST11.libSI:63 Formula:C31H52O3 CAS:0-00-0 MolWeight:472 RetIndex:3022

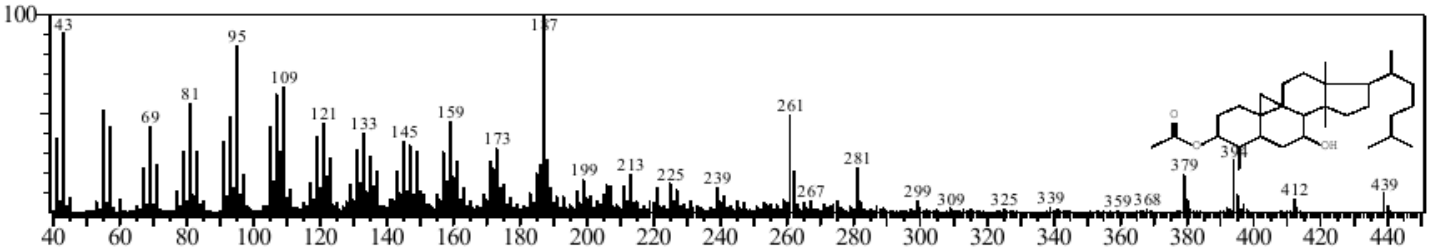

Fig. 8. Chromatogram of compound 9,19-Cyclochloestene-3,7-diol, 4,14-dimethyl-, 3-acetate

Hit#:4 Entry:24299 Library:NIST11s.libSI:88 Formula:C17H34O2 CAS:112-39-0 MolWeight:270 RetIndex:1878

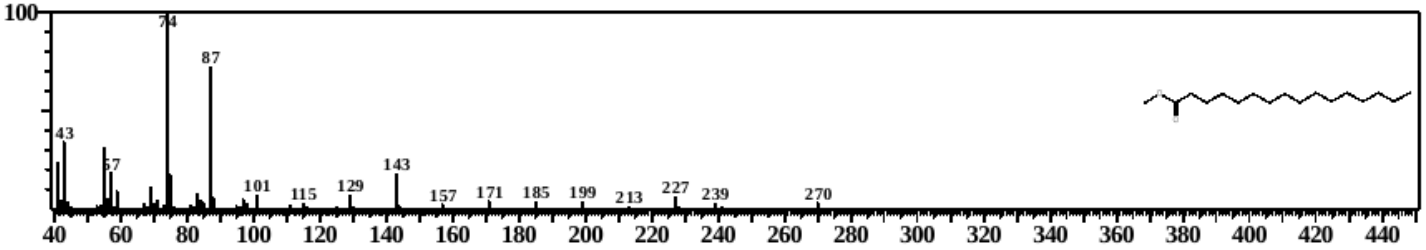

Fig. 9. Chromatogram of compound Hexadecanoic acid, methyl ester

Hit#:1 Entry:15456 Library:NIST11s.libSI:92 Formula:C12H14N2 CAS:2506-10-7 MolWeight:186 RetIndex:1820

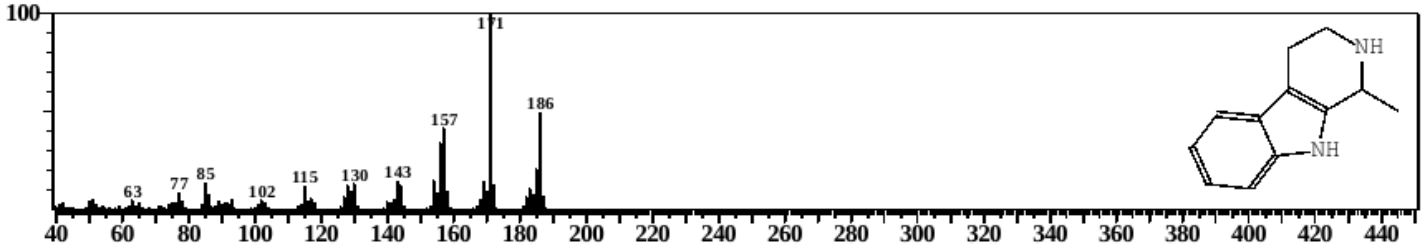

Fig. 10. Chromatogram of compound 1H-Pyrido[3,4-b]indole, 2,3,4,9-tetrahydro-1-methyl-

Hit#:1 Entry:79662 Library:NIST11.libSI:75 Formula:C15H22O3 CAS:139571-20-3 MolWeight:250 RetIndex:1853

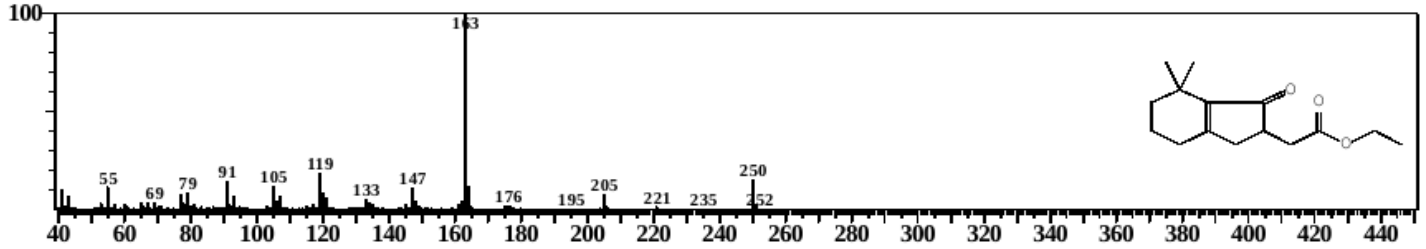

Fig. 11. Chromatogram of compound (7,7-Dimethyl-1-oxo-2,3,4,5,6,7-hexahydro-1H-inden-2-yl)acetic acid, ethyl ester

Hit#:2 Entry:47968 Library:NIST11.libSI:74 Formula:C13H22N2 CAS:109746-14-7 MolWeight:206 RetIndex:0

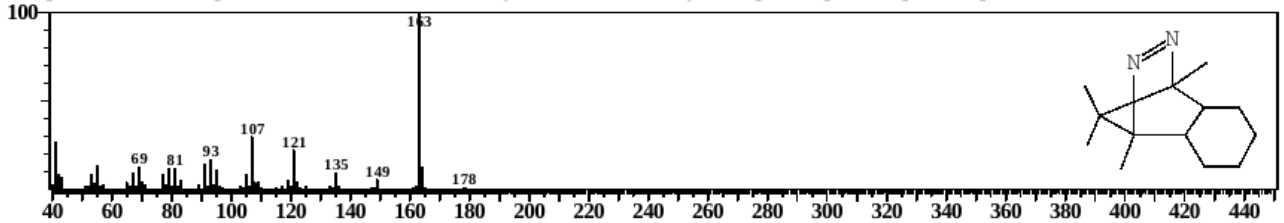

Fig. 12. Chromatogram of compound 1,4-Methanophthalazine, 1,4,4a,5,6,7,8,8a-octahydro-1,4,9,9-tetramethyl-, (1.alpha.,4.alpha.,4a.alpha.,8a.alpha100

Hit#:1 Entry:186839 Library:NIST11.libSI:72 Formula:C29H48O CAS:84693-05-0 MolWeight:412 RetIndex:2765

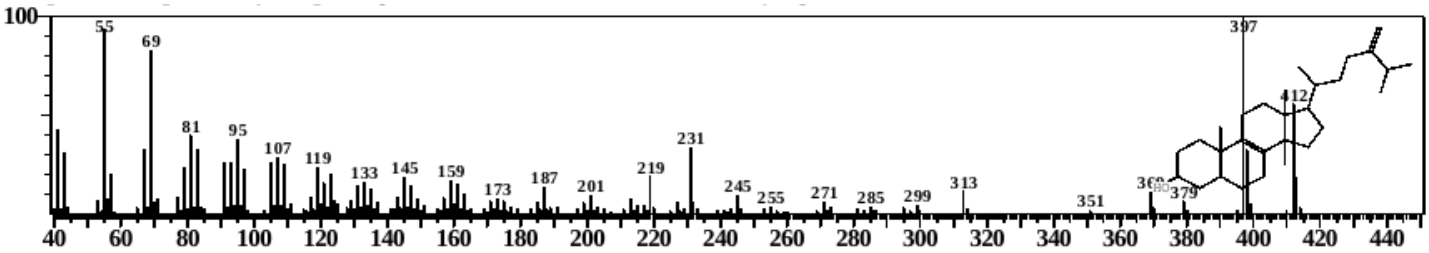

Fig. 13. Chromatogram of compound 14.alpha.-Methyl-5.alpha.-ergosta-8,24(28)-dien-3.beta.-ol $$ 14-Methylergosta-8,24(28)-dien-3-ol # 100

Hit#:1 Entry:182675 Library:NIST11.libSI:75 Formula:C28H48O CAS:474-62-4 MolWeight:400 RetIndex:2632

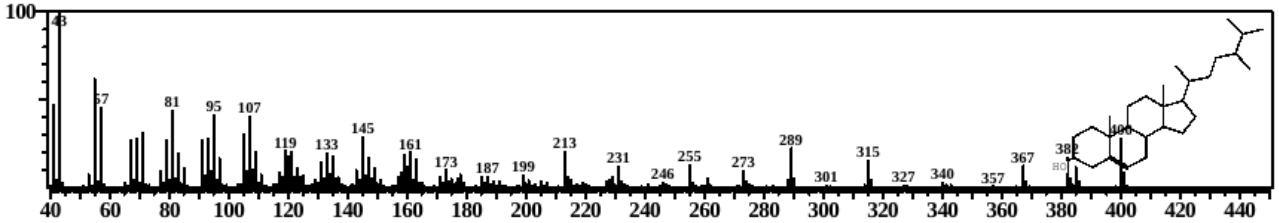

Fig. 14. Chromatogram of compound Campesterol

Hit#:1 Entry:186858 Library:NIST11.libSI:74 Formula:C30H52 CAS:26266-08-0 MolWeight:412 RetIndex:2865

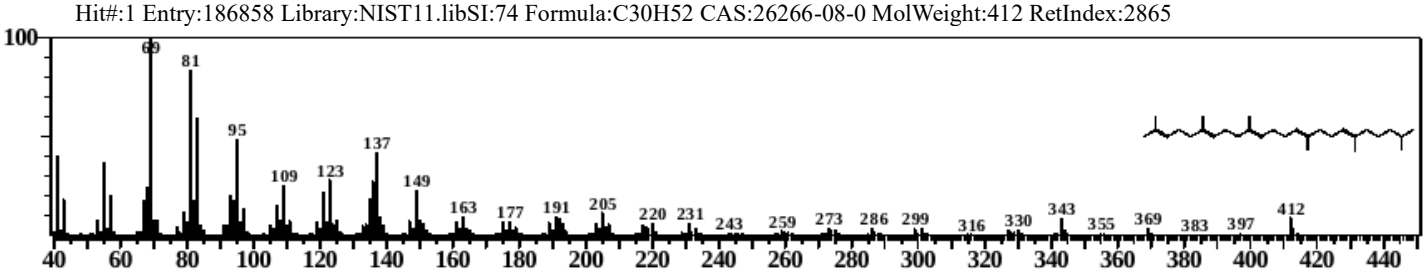

Fig. 15. Chromatogram of compound Tetracosapentaene, 2,6,10,15,19,23-hexamethyl-

DISCUSSION

The quantitative analysis of the chemical content in the ethanolic and aqeous extractives detected by GC-MS analysis of the heartwood extractives of the selected timber species are presented in Figures 1 to 19 and Table 1 to 6 while the principal compounds are presented in Tables 7. The GC-MS analysis of the selected timber species confirmed the presence of various pharmacologically active compounds. The heartwood of the selected timber species revealed the presence of fatty acids, coumarin, sesquiterpenes, flavonoids, alcohols, lignans, phenols, aldehyde, and ketone, etc (Table 1 to 5). The principal leading compound identified was (S)-(+)-1,2-Propandiol a polyol. This compound represented 73.51% of the total ethanolic extract of *V. paradoxa.* The remaining principal components were; 9,19-Cyclochloestene-3,7-diol, 4,14-dimethyl-, 3-acetate (12.21%) in VHA; Hexadecanoic acid, methyl ester (34.82% and 17.38%) in BHE and BHA respectively; 7,7-Dimethyl-1-oxo-2,3,4,5,6,7-hexahydro-1) (50.16%) in PHE and 14.alpha.-Methyl-5.alpha.-ergosta-8,24(28)-di (17.95%) in PHA (Table 6).

The phytochemicals in wood consist of fats, waxes, alkaloids, proteins, simple and complex phenolics, simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins and fatty acids which occur in minute quantities. According to Alireza (2012), main functions of these chemical components are to conserve energy in the tree metabolism, and protect against microbial attacks such as fungi, and/or insects [5,16] through the free radical scavenging and metal chelation activities of the wood extractives; wood are given enhanced protection against fungi degradation (Alireza (2012; Prayitno et al., 2021).

Generally, ethanol extract had more phytochemicals than water as revealed in the GC-MS result except in the case of *V. paradoxa* in tables …. . Likewise, the concentration of the phytochemicals that were revealed were more from ethanolic extracts compared to aqeuous extracts. This clearly shows that extraction media has great influence on the extraction of phytochemicals (Roszaini, 2017). Ethanol extraction led to the identification of 42 and 30 known compounds from the heartwood of *B. africana* and *V. paradoxa*. The ethanol extractives in heartwood were higher in composition and content than those of aqeuous for *B. africana* and *V. paradoxa* while they were low in *P. africana.* Due to the different species, the content of each component in each extract and species were different. However, some of the chemicals were common to all the species. According to (Qiu et al., 2019), the proportion of extractives in wood

is small, but they play an important role in dictating some of the characteristics such as the color and smell of the wood as well as their resistance to bio-degrading agents. All the three timbers have brown to reddish-brown colours in their heartwood. These colours are as a result of these extractives in them which contains chromatic substances such as pigments, tannins and resins (Qiu et al., 2019. Most of these color-related components have been reported by (Qiu et al., 2019) to contain phenols, quinones, and ketones etc.

From the differences in compositions, it can be assumed that Hexadecanoic acid, methyl ester, and 1H-Pyridol[3,4-b]indole, 2,3,4,9-tetrahydro-1-; Stigmasterol could be responsible for the enhanced durability of *B. africana* because of their high concentrations in the extracts. Similalry, the enhanced durability of *P. africana* as claimed by local wood workers may be attributed to the concentration of 7,7-Dimethyl-1-oxo-2,3,4,5,6,7-hexahydro-1-methyl which represented more than half (50.16%) of the total constituents and in combination with 1,4-Methanophthalazine 1,4,4a,5,6,7,8,8a-oct which also represented 33.20% of the total constituents in *P. africana*. Other constituents of importance are 14.alpha.-Methyl-5.alpha.-ergosta-8,24(28)-di (a triterpene) Tetracosapentaene, 2,6,10,15,19,23-hexamethyl and campesterol may further contribute to the enhanced durability of *P. Africana*. Sadiku et al. (2021), reported *V. paradoxa* to be resistant to white (*Lentinus sajor-caju*) and brown rot (*Sclerotium rolfsii*) fungi and highly resistant to subterranean termite. (S)-(+)-1,2-Propanediol which occured in large amount (73.51%) is likely responsible for the resistance against these bio-degradingagents. Although, this may be in combination with 9,19-cyclchloestene-3,7-diol,4,14-dimethyl and 9,19-cyclo-9.beta. -Ianostane-3.beta.,25-diol. because these two compounds occured in fairly large amount in the heartwood of *V. paradoxa*.
Although, the principal compounds revelaed in the heartwood of these three timbers are assumed to provides the scientific evidences for their enhanced durabilty to biological agents of degradation, further studies will substantiate these claims. Therefore, isolation and investigation on the inhibitory activities of these principal components against various bio-digrading agents of wood is recommended.

CONCLUSION

The difference in content of the ethanolic and aqeuous heart wood extracts from each of the three timbers were distinct, the content of each component in each extract and species was different. The contents were obviously different based on extraction medium and from species to species. However, 5 compounds were similarly revealed in both ethanolic and aqeouos extracts of each of *V. paradoxa* and *B. africana*. Likewise, some compounds were common to *V. paradoxa and B. africana.* Generally, ethanol extract had more phytochemicals than water and the concentration of the phytochemicals were higher for ethanolic extracts compared to aqeuous extracts. This clearly shows that extraction media has great influence on the extraction of phytochemicals. The presence of some principal constituents in the heartwood of these species such as (S)-(+)-1,2-Propandiol which accounted for 73.51% of the total constituents in *V. paradoxa* ethanolic extract as well as 7,7-Dimethyl-1-oxo-2,3,4,5,6,7-hexahydro-1) and 1,4-Methanophthalazine, 1,4,4a,5,6,7,8,8a-oct which accounted for 50.16%, and 33.20% respectively in *P. africana* ethanolic extract and Hexadecanoic acid, methyl ester with concentration of 34.82% of the total constituents of *B. africana* Ethanolic extract could be responsisble for the enhanced resistance and durabilty of the three timbers to biological agents of degradation. The principal constituents may be isolated and investigate their termicidal as well as fungicidal activities..

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