scientific reports



OPEN Chemical composition of heartwood and sapwood of Tectona grandis characterized by CG/MS-PY

Vinícius Resende de Castro¹, Paula Gabriella Surdi¹, Sergio Antonio Fernandes¹, Matheus da Silva Berger¹, Antonio José Vinha Zanuncio², José Cola Zanuncio¹ & Solange de Oliveira Araujo³

Teak wood has chemical compounds that can be used for pharmaceutical and textile industries, in addition, this compounds are related to resistance to biodeterioration, color and modification processes. Heartwood and sapwood of T. grandis (teak), 15 years-old, were characterized by Py-CG/MS analysis and syringyl (S)/guaiacyl (G) ratio was evaluated. Heartwood and sapwood were pyrolyzed at 550 °C and 62 and 51 compounds were identified from them, respectively. The acetic acid (10%) and levoglucosan (26.65%) were the most abundant compound in the sapwood and heartwood, respectively. The high acetic acid content enhances the use of teak wood to production of artificial essences for perfumery, paints, dyes. While levoglucosan can be used in the manufacture of epoxy resins, antiparasitic and insecticides. The organic compounds identified include 2-methylanthraquinone as one of the main component responsible for the resistance of the teak wood to biological factors (fungi and termites). The syringyl (S)/quaiacyl (G) ratio of heartwood and sapwood was 0.51 and 0.50, respectively.

The high dimensional stability and natural durability of the Tectona grandis (Verbenaceae) wood characterizes this plant as one of the most important in the world^{1,2}. Native to Southeast Asia (Burma, India, Myanmar, Thailand etc.), T. grandis are introduced and adapted to Central (Belize, Panama and Puerto Rico) and South America (Brazil, Colombia, Guyanas and Venezuela)³.

Brazil has more than 90,000 hm² of planted teak forests, 40% growth in ten years, this wood is mainly used in the naval industry and furniture manufacturing. However, the national market is very restricted, studies on the chemical composition can enable the use of teak wood for other purposes^{4,5}. These compounds are mainly quinones like the anthraquinones group conferring resistance to xylophagous organisms, but with variations in composition and concentration related to age, genetic material, tree position (heartwood and sapwood), silvicultural treatments, soil, climate and management⁶.

Teak extractives can be used as bioproducts, antioxidants and compounds with antitumor activity and teak lignin in adhesives, paints, polymers and resinsand^{3,7}. The large amount of the quinone group, such as 2-methyl-9,10-anthraquinone (tectoquinone), 1,5-dihydroxy-2-methyl-9,10-anthraquinone and lapachol, 2-hydroxy-3-(3 -methyl-2-butenyl)-1, and 4-naphthoquinone potentiate teak wood for natural dyes production⁷. The composition of lignins is alto important, high values of the synringyl/guaiacyl ratio result in lignin with higher reactivity and low resistance to thermal decomposition⁸.

Analytical pyrolysis is a technique to characterize materials in the absence of oxygen by chemical degradation reactions induced by thermal energy⁹. This technique uses a set of small molecular species, separated by gas chromatography and segregating products from pyrolysis¹⁰.

Data obtained from analysis by gas chromatography, coupled with mass spectrometry and analytical pyrolysis (Py-GC/MS), allow to identify and to classify compounds in different samples¹¹.

¹Departamento de Engenharia Florestal, Universidade Federal de Viçosa, Viçosa, MG 36570-900, Brazil. ²Instituto de Ciências Agrárias, Universidade Federal de Uberlândia, Monte Carmelo, MG 38500-000, Brazil. ³Centro de Estudos Florestais, Instituto Superior de Agronomia, Universidade de Lisboa, 1349-017 Lisboa, Portugal. 🗠 email: ajvzanuncio@ufu.br

The objective of the study was to identify, by Py-GC/MS, compounds obtained and the syringyl/guaiacyl ratio of heartwood and sapwood from 15-year-old *Tectona grandis* and use chemical characterization to indicate potential uses for teak wood.

Methods

Three 15-year-old T. grandis trees were harvested in commercial plantations with a spacing of 3×3 m in the municipality of Nova Maringá, Mato Grosso state, Brazil (coordinates of 13° 00' 55.08" S and 57° 05' 52.48" O). This experiment included the collection of plant material, complied with the national laws of Brazil, respecting the Brazilian environmental code. Four discs at the DBH height (1.30 m from the ground) were removed per tree and the heartwood and sapwood regions marked by visual analysis and crushed separately. The 40-60 mesh fraction from these materials was subjected to pyrolysis in Py-GC/MS using the Pyrolyzer Single-Shot "PY-3030S (Frontier Lab Inc, Fukushima, Japan) connected to a GC-2010 Plus system with a GCMS-QP2010 Ultra (Shimadzu, Kyoto, Japan). The temperature of the valve interface was set at 290 °C and the pyrolysis temperature at 500 °C. The GC column used was an Rtx-5MS (Restek), 30 m long, 0.25 mm internal diameter and 0.25 µm thick. The temperature of GC injector was adjusted to 250 °C, the initial oven temperature at 40 °C for 1 min and the heating rate was 6 °C/min until reaching 280 °C with the samples remaining for 15 min at this temperature. Helium was the carrier gas at 1 mL/min flow rate in split mode and then at a split ratio of 20:1. The mass of the samples subjected to pyrolysis was 0.5 mg. The peaks of the compounds, obtained after the pyrolysis of the samples, were identified based on the NIST and Wiley mass spectral data library. The yield of the products formed was obtained dividing the area of each peak by the total area (sum of all areas of the compounds in the chromatogram).

The syringyl/guaiacyl ratio was calculated using the area values of the signals recorded in the pyrogram and compared with the result obtained by the method of alkaline oxidation with nitrobenzene¹². The S/G ratio was obtained by the ratio between the concentration of syringaldehyde and that of vanillin considering the group of markers guaiacol; 4-methyl-1,2-benzenediol; 4-vinyl guaiacol; vanillin; eugenol; isoeugenol; as the guaiacyl type and the methoxyeugenol compounds; cis-4-propenylsyringol; syringaldehyde; 4-vinylsyringol and trans-4-propenylsyringol as the syringyl type.

Results and discussion

The pyrolytic analysis detected 85 compounds in the wood, being 51 in the sapwood and 61 in the heartwood (Table 1). The acetic acid (10%) was the most abundant compound in the sapwood followed by the oxiranemethanol (5.88%), phenol, 4-ethenyl-2-methoxy (7.71%), propanoic acid, 2-oxo (5.51%), levoglucosan (4.47%), 1,2-cyclopentanedione (4.08%) and isoeugenol (4%), with the other compounds representing less than 3.22% of the total. In the heartwood, the most abundant compounds were levoglucosan (26.65%), acetic acid (6.34%), cyclohexanecarboxaldehyde, 4-methoxy (5.1%), squalene (4.85%) and isoeugenol (3. 65%) with less than 2.97% for the others. Two and four compounds from sapwood and heartwood, respectively, were not identified. Acetic acid, the main component of sapwood, can be used in the manufacture of inks, dyes, synthetic silks, cellulose acetate and medicines¹³, while levoglucosan, the main component with heartwood, can be used in the manufacture of epoxy resins, antiparasitic and insecticides¹⁴. Many compounds found are phenolic, these components are fundamental in the resistance against attack by xylophagous agents and can be used in the chemical and food industry³.

The number of compounds identified in the sapwood and heartwood in the 15-year-old teak wood was lower than that reported for this plant with 70-year-old plant, with 127 compounds identified, being 74 and 71% in sapwood and heartwood, respectively¹⁵. In *Quercus* spp. wood, 40 different compounds were found, the acetic acid, levoglucosan, 3/2-furaldehyde and 2,3-dihydro-5-methylfuran-2-one were the main products¹⁶. This may be due to age (15- and 70-year-old) and pyrolysis temperature differences between these works. Compounds with the largest area are mainly derived from carbohydrates and found in the initial part of the pyrogram with shorter retention time, and the lignin and extractives derivates in the middle and at the end of the pyrogram with a smaller area¹⁷. The ion-intensive mass spectra of lignin derivatives correspond, in most cases, to the base peak and the compounds with carbohydrates are more easily fragmented into smaller ones (except levoglucosan) giving, in general, low molecular mass ions and difficult to identify. Some compounds identified in the chromatogram are similar to those obtained from teak wood between 10⁶ and 70¹⁵ years old subjected to a thermochemical process^{18,19}. This similarity of some components is due to the higher concentration of components (lignin derivatives), which are more stable when subjected to the thermochemical process¹⁹.

The highest peak intensity in the sapwood pyrogram (Fig. 1A) correspondes to acetic acid (peak 7), phenol, 4-ethenyl-2-methoxy (peak 43), isoeugenol (peak 50), 3',5'-dimethoxyacetophenone (peak 54) and squalene (peak 85). In the heartwood region (Fig. 1B), the highest peak intensity corresponded to acetic acid (peak 7), cyclohexanecarboxaldehyde, 4-methoxy (peak 26) and squalene (peak 85). The most of these compounds, like acetic acid are derivatives of cellulose and hemicellulose, major components of wood, the degradation of lignins generate phenolic compounds, finally, extractives are not very representative and are divided into several compounds, thus, their derivatives are not very representative in the mass of compounds evaluated¹⁶.

The highest peak intensity corresponding to acetic acid (peak 7), phenol, 4-ethenyl-2-methoxy (peak 43), isoeugenol (peak 50), 3',5'-dimethoxyacetophenone (peak 54) and squalene (peak 85) from the lignin pyrolysis products, which are more abundant and easier to identify than carbohydrate derivatives¹⁵. The mass spectra with more abundant molecular ions are due to the greater thermal stability of the lignin aromatic compounds during pyrolysis and to the impact of electrons from the mass spectrometer¹⁵. It is easier to identify lignin-derived products because its pyrolysis releases a mixture of phenol derivatives preserving the aromatic ring, with the original methoxyl groups and a part or all of the propane side chain²⁰. Furthermore, pyrolysis can cause multiple

1ActivationS14-21.2-Popanelamine-2.792OrinacentelanoloS80974Banoic ad.3-hydraxy187-5Dichoica A.1-hydraxy187-5Dichoica A.1-hydraxy10706.87Actic add10706.347Defaciola 1.4-So damhydra10206.348Propanal.2-Al-Mydray12101.310Dickica 1.4-So damhydra12207.311Dickica 1.4-So damhydra12203.312Defacional.4-Methyl2.153.313Banacial1.53.2142-Pernanoe.4-methyl153.215Methyl provate1201.2162-Furancehaneleydra1.33.217NI0.41.33.2182-Furancehaneleydra1.33.2192-Furancehaneleydra1.33.2102-Furancehaneleydra1.33.210Cataloga1.33.210Cataloga1.33.2121.4-Cyclopertaneelione.3-methyl0.33.213Defacencerbaleydra1.33.214Defacencerbaleydra1.33.215Marcelas1.33.216Defacencerbaleydra1.33.217Natance 2.methyl1.33.218Defacence 2.methyl1.33.219<	Peak	Compound	Sapwood	Heartwood
3Oxinamethanl5.882.974Butanoic acid, 3-hydroxy1.87-5Diethylere onimide3.08-6Propanal, 2.3-dihydroxy-0.687Actic acid10.706.348Propanoic acid, 2-oxo5.510.919D-Glucich, 1.4.3.6-dianhydro0.29-10D-Glucich, 1.4.3.6-dianhydro0.21-11NI-0.59-122.Popanone, 1-hydroxy3.072.3813Butanedial1.55-142.Popanone, 1-hydroxy1.00.9715Methyl pryrute-0.1216Furfunal0.97-17Methyl pryrute-0.11182.Furanceboaldehyde-0.11192.Butanore0.14-202.Furanceboaldehyde-0.1321Octalad0.24-220.Citaldehyde-0.14231.2Cyclopentanedione4.08-24Cyclopentanedione, 2-methyl0.241.3325NI0.2326Nonandehyde-1.0727N0.211.3728Nonandehyde-1.0729Nonandehyde-1.0720Schoprophyclohenand-1.0721Octalad-1.0722Schoprophyclohenand-1.07 <td>1</td> <td>Acetic acid, oxo</td> <td>5.51</td> <td>-</td>	1	Acetic acid, oxo	5.51	-
4Butanoic acid, 3-hydroxy1.87-5Distlylenc oximide308-6Propani, 2.3-dilydroxy-0.687Acetic acid10706.348Popanoic acid, 2-ox5.510.919D-Gluciol, 1.4.3.6-dianlydro0.22-10D-Limonen0.22-11NI-0.59122-Porpanone, 1-hydroxy3.072.3813Butanedia1.5-142-Pentanone, 4-methyl2.15-15Methyl pyrwate-0.1116Furfural0.97-17NI0.95-182-Forrancebocaldehyde-0.11192-Butanone0.24-21Octaladhyde0.24-21Octalachyde0.24-22Octalachyde1.02-23Octalachyde, 4-methyl0.24-24Cyclopertanedione4.08-25NI0.26-26Cyclopertanedione, 5-methyl0.81-27NI0.26-28Nonanidehyde, 4-methyl0.71-29NI0.26-20Silopertanoine, 5-methyl0.81-21Opertanoine, 5-methyl0.81-21Nonanidehyde21Silopertanoine, 5-methyl0.81-21Silopertanoine	2	1,2-Propanediamine	_	2.79
9Dethylene oximide3.08-6Propanic 2.3-dihydroy-0.687Acetic acid10706.348Propanoic acid.2-oxo5.510.919D-Gluciol, 1.4.3.6-dinhydro0.29-10D-Limonen0.22-11NI-0.59122-Porpanone, 1-hydroy3.072.3813Butanedial1.55-142-Pentanone, 4-methyl1.51-15Methyl pyruvate.0.9716Parfaral-0.9717NI0.95-182-Furancebosaldelyde-0.11192-Butanone0.14-202-Furamethanol0.44-21Octanal0.44-21Cidebyeneranothyle0.44-22Octaldehyde-0.81231.2-Cyclopentanedione4.08-24Cyclopentanedione, 3-methyl0.81-25NI0.32-26Cyclopentanedione, 3-methyl0.81-27Nanaldehyde1.021.67281.2-Cyclopentanedione, 3-methyl0.81-29Nonanaldehyde1.02-21Cyclopentanedione, 3-methyl0.81-21Dedecanic acid, 3-hydroxy0.110.35212-speratione, 2-methyl0.81-212-speration, 2-geneyrityl<	3	Oxiranemethanol	5.88	2.97
6Propanal 2.3 dihydroxy-0.6887Acetic acid10.706.348Propanoic acid.2-axo5.510.919D-Guccio,1,4.3.6 dianhydro0.29-10D-Guccio,1,4.3.6 dianhydro0.22-11NI-0.59-122-Propanone,1-hydroxy3.072.8813Butanedial1.55142-Pentanone,4-methyl2.15-0.0715Methyl provate-0.97-16Furfural0.9517NI0.95182-Furanachosalchyde0.16202-Furanachosalchyde0.2421Octalal0.4222Cataluhyde-0.81-231.2 Cyclopentanecione4.0824Cyclopentanecione0.8125NI0.261.53-26NI0.261.53-27NI0.71281.2 Cyclopentanecione1.910.33-29NI0.261.53-20Sciopentanecione1.9221Cyclopentanecione1.9221Cyclopentanecione1.9221Cyclopentanecione1.9221Sciopentanec	4	Butanoic acid, 3-hydroxy	1.87	-
6Propanal 2.3-dihydroxy-0.687Acetic acid10.706.348Propanoic acid.2-coo5.510.919D-Glucciol, 1.4.3.6-dianhydro0.29-10D-Glucciol, 1.4.3.6-dianhydro0.22-11Nil-0.52-122-Propanone, 1-hydroxy3072.8813Butanedial1.55142-Protanone, 4-methyl1.502.1215Methyl provate-0.9716Parfaral0.97-17Ni0.95-182-Foranarchoxaldehyde0.10-202-Foranarchoxaldehyde0.24-21Octalad0.24-22Octaladhyde-0.81231.2-Cyclopentanecione4.08-24Cyclopentanecione1.021.3325Ni0.261.3326Cyclopentanecinone.2-methyl0.31-27Ni0.31-281.2-Cyclopentanecinone1.911.9229Ni0.33-20Ni0.31-21Cyclopentanecinone1.921.9221State1.921.9222Ni0.31-23Ni0.31-24Cyclopentanecinone1.921.9225Ni0.32-26Ni0.31	5		3.08	_
7Acetic acid. 2-∞o10.706.348Propanoic acid. 2-∞o5.510.919D-Gluciol, 1.43.6-dianhydro0.29-10D-Limonene0.22-11NI-0.59122-Propanone, 1-hydroxy3072.3813Butanedial1.55-142-Pentanone, 4-methyl2.15-15Methyl pyruvate-0.9716Furfural0.95-17NI0.95-182-Parancenhoaldehyde-0.11192-Butanone0.12-202-Furanmethanol0.42-21Octanal0.44-22Cacidehyde-0.81231.2-Cyclopertanone, 2-methyl-0.9724Cyclopertanone, 2-methyl0.10-25NI0.24-1.0126NI0.24-27NI0.33-281.2-Cyclopertanoe, 3-methyl0.75.1029NI0.3420Scioleexance add, 3-hydroxy0.81-21Scioleexance add, 3-hydroxy0.81-21Scioleexance add, 3-hydroxy1.071.6721Scioleexance add, 3-hydroxy-1.6722Scioleexance add, 3-hydroxy0.110.3523Phenol, 2-methoxy-4-methyl1.871.6724Dodecan			_	0.68
8Propanoic acid, 2-axo5.510.919D-Clucitol, 1.4.3.6-dianbydro0.29-10D-Limonen0.22-11NI-0.59122-Propanone, 1-bydroxy3072.3813Butandial1.55-142-Pentanone, 4-melyl1.51-15Methyl pruvate-2.1216Methyl pruvate-0.9717NI0.95-182-Furanceboxidebyde-0.11192-Butanone0.15-202-Furanceboxidebyde-0.1321Octaal0.42-22Octadebyde-0.8123Octadebyde-0.8124Octadebyde-0.9725NI0.261.5326Octadebyde-0.9727NI0.161.53281.2-Cyclopertanedione, 3-methyl0.81-29NI0.3320Namaldebyde, 4-methoy-1.6321NI0.3121NI0.3121NI0.3121NI0.3122NI0.3123Nonaldebyde1.9224Nonaldebyde1.9225Ni0.31 <td>7</td> <td></td> <td></td> <td>6.34</td>	7			6.34
9D-Glucitol, 1.4:3.6-dianlydro0.29-10D-Linonene0.22-11NI-0.59122-Propanon, 1-hydroxy3.072.3813Butanedial1.55-142-Pertanone, 4-methyl2.15-15Methyl pyravate-0.2216Furfaral0.972.1217NI0.55-182-Furancarboxaldehyde0.15-202-Furancarboxaldehyde0.15-21Octanal0.42-22Octaldyde-0.81231.2-Cyclopentanedione4.08-24Cyclopentanedione4.08-25NI0.265.1026Cyclopentanedione, 3-methyl0.71-27NI0.33-28Nanaldehyde, 4-methox29NI0.33-20Scaladehyde, 4-methox1.07-21Scaladehyde1.091.8221Scaladehyde1.091.8221Nanaldehyde0.101.3221Scaladehyde1.011.3222Scaladehyde1.0223Penton, 5-Cyclopentanedione, 3-methyl0.8124Nanaldehyde1.021.6225Scaladehyde1.0226Scaladehyde1.0227Scaladehyde1.0228Phenol, 2-me				
10D-Limonene0.22-11NI-0.59122.Propanone.1-hydroxy3.072.3813Butanedial1.55-142.Pentanone,4-methyl2.15-15Methyl pravate-0.9716Furfaral0.97-17NI0.95-182.Furanarboxaldehyde-0.11192.Butanone0.124-202.Furanmethanol0.424-21Octaal0.424-231.2-Cyclopentanedione4.08-24Cyclopentanedione,2-methyl-0.9725NI0.261.5326Cyclopentanedione,3-methyl0.71-27NI0.31-281.2-Cyclopentanedione,3-methyl-0.81-29NI0.3120Saporophyclohexanol1.091.8931Gutacol1.991.8932Pental2.52-33Pental2.52-34Dodecanoic acid,3-hydroxy0.110.3535Pental,5-2-perpynylocy)-1.6736Pental,5-2-perpynylocy)-1.6736Pental,5-2-perpynylocy)-1.6237Saborophylochexanol0.18-38Pental,5-2-perpynylocy)-1.6239Pental,5-2-perpynylocy)0.18-<		-		
11NI-0.59122-Propanone, 1-hydroxy3.072.3813Butandail1.55-142-Prananoe, 4-methyl2.15-15Methyl purvate-2.1216Methyl purvate-0.9717NI0.95-182-Furanarboxaldehyde-0.11192-Butanone0.12-102-Furanarchanol0.14-202-Furanarchanol0.14-21Octadehyde-0.8122Otaldehyde-0.81231.2-Cyclopentanochon408-24Cyclopentanochon0.621.5325NI0.621.5326Valpentanochon0.63-27NI0.33-28Nonanalchyde, 4-methyo0.33-29NI0.33-20Nanalchyde1.81-21Saisof21Nonanalchyde, 4-methyo0.33-21NI0.31-21Niacof2.92-21Niacof1.32-21Niacof1.32-21Niacof1.32-21Niacof1.32-22Niacof1.32-23Pertano1.54-24Niacohytopero1.62-25Pertano<				
122.Propanone, 1-hydroxy3.072.3813Butanedial1.55-142.Pentanone, 4-methyl2.15-14Methyl pyrware-0.2115Methyl pyrware-0.9716Furfural-0.9717NI0.95-182.Furanetbacklehyle-0.112.Butanone0.152.Dutanote0.122.Dutanote0.24- <td></td> <td></td> <td></td> <td></td>				
Butanelial 1.55 - 14 2-Pentanone, 4-methyl 2.15 - 15 Methyl pyruvate - 0.212 15 Methyl pyruvate - 0.95 - 16 Furfural 0.95 - 0.11 17 NI 0.95 - 0.11 18 2-Furannethoxaldehyde - 0.11 0.11 20 2-Furanmethanol 0.24 - 0.11 21 Octanal 0.42 - 0.11 22 Octaldehyde - 0.81 0.21 23 1.2-Cyclopentanelione 4.08 - 0.21 24 Cyclopentanelione, 3-methyl 0.26 1.53 0.21 25 NI 0.31 - 0.21 26 NI 0.01 0.33 - 27 NI 0.31 1.07 1.07 36 1.2-Cyclopentanelione, 3-methyl 0.81 - -				
142.Pentanone, 4-methyl2.15-15Methyl pyruvate-2.1216Furfural-0.9717NI0.95-182.Furancarboxaldehyde-0.11192.Butanone0.15-202.Furanmethanol0.24-21Octaidehyde-0.8122Octaidehyde-0.81231.2-Cyclopentanedione4.08-24Cyclopentanedione, 2-methyl-0.9725NI0.261.5126Cyclopentanedione, 3-methyl0.81-27NI0.71-28N.J0.261.0229NI0.81-30Nonandehyde1091.8931Gualacol2.96-322.5opropylcyclohexanol-1.0733Pentani2.921.0734Dodcanoic acid, 3-hydroxy0.110.3535Phenol, 2-methyl-1.871.67362-methaoty-4-methyl1.871.67373.4.Dimethoxytolene0.40-38Tans-2-Decenal1.122.1739Phenol, 2-methyl-1.811.6739Phenol, 4-isopropyl-1.6730Stanoit, 5-(2-propynyloxy)-1.6731Tans-2-Decenal1.122.1731Bernol, 4-isopropyl0.611.0131<				
15Methyl pyruvate-2.1216Furfural-0.9717NI0.95-182-Furanachoxaldehyde-0.11182-Furanachoxaldehyde0.15-202-Butanone0.12-21Octanal0.42-22Octaldehyde-0.81231.2-Cyclopentanedione4.08-24Cyclopentanoe, 2-methyl-0.9725NI0.261.5326Cyclopentanoe, 2-methyl0.81-27NI0.261.53281.2-Cyclopentanedione, 3-methyl0.81-29NI0.33-29NI0.33-30Nonanaldehyde1.091.8931Gualacol2.96-34Dodecanoic acid, 3-hydroxy0.110.3534Dodecanoic acid, 3-hydroxy0.110.3534Dimethoxytoluere0.20-34Dimethoxytoluere0.20-34Dimethoxytoluere0.120.3534 <td< td=""><td></td><td></td><td></td><td></td></td<>				
16Furfural-0.9717NI0.95-182-Furancarboxaldehyde-0.11192-Butanone0.15-202-Furannethanol0.24-21Octanal0.42-22Octaldehyde-0.81231.2-Cyclopentance, 2-methyl-0.9724Cyclopentance, 2-methyl-0.9725NI0.261.5326Cyclopentance, 2-methyl-5.1027NI0.21-281.2-Cyclopentanceine, 3-methyl-0.8129NI0.33-29NI0.33-20Nanaaldehyde1.091.8930Nonaaldehyde2.96-31Guniacol2.96-322-Isopropylcyclohexanol2.96-34Dodecanoic acid, 3-hydroxy0.110.3534Dodecanoic acid, 3-hydroxy0.110.3535Phenol, 2-methoxy-4-methyl1.871.67362-Pentanol, 5-(2-propnyloxy)-1.76373-4-Direnthoxy-4-methyl1.81-362-Pentanol, 5-(2-propnyloxy)-1.3636Phenol, 4-thenyl-2-methoxy0.110.11373-Dicenal0.20-38Tans-2-Decenal1.311.78414-Ethylcyclohexanol0.81-422-Decadenal0.611				
17NI0.95-182-Furancarboxaldehyde-0.11192-Butanone0.15-202-Furanmethanol0.24-21Octaal0.42-22Octaldehyde-0.81231.2-Cyclopentanecione4.08-24Cyclopentanoe. 2-methyl-0.9725NI0.261.5326Cyclopentancearboxaldehyde, 4-methoxy27NI0.265.10281.2-Cyclopentanedione, 3-methyl-0.81-29NI0.33-20Ni0.33-21Outaicol2.96-31Guaicol2.96-322-Isoprophyclohexanol1.091.8933Pentanal2.52-34Obdecanoi acid, 3-hydroxy0.110.3535Pentanol, 5-(2-prophyploxy)-1.76362-Pentanol, 5-(2-prophyploxy)-1.76373.4-Dimethoxy-4-methyl1.87-362-Pentanol, 5-(2-prophyploxy)-1.67373.4-Dimethoxytoluene0.20-38Trans-2-Decenal1.212.1739Pethylguaicol0.411.3140Cyclohexanol1.811.78414-Ethylcyclohexanol0.111.31422-Indecenal1.311.7843Phenol, 4-ethenyl-2-methoxy <td< td=""><td></td><td></td><td></td><td></td></td<>				
182-Furancaboxaldehyde-0.11192-Butanone0.15-202-Furanmethanol0.24-21Octanal0.42-22Octaldehyde-0.81231.2-Cyclopentanedione4.08-24Cyclopentanone, 2-methyl-0.9725NI0.261.5326Cyclohexacarboxaldehyde, 4-methoxy27NI0.71-281.2-Cyclopentanedione, 3-methyl-0.81-29NI0.33-30Nonanaldehyde1.091.8931Guaicol2.96-322-Isopropicyclohexanol34Dodecanoic acid, 3-hydroxy0.110.3535Pentonal. 5-(2-propinycloy)-1.76362-Pertanol. 5-(2-propinycloy)-1.76373.4-Dimethoxytoluene0.20-38Tans-2-Decenal1.212.1739Pethylgeaiacol0.410.35414-Ethylcyclohexanol0.18-422.4-Decandinal1.311.7843Pienol, 4-ethenyl-2-methoxy4.711.45442.14-Decadienal0.610.1745Eugonol0.610.1746Syringol0.39-47Dodecanoic acid, 3-hydroxy0.39-48Phenol, 4-ethenyl-2-methoxy0.310.3549<				
192-Butanone0.15-202-Furanmethanol0.24-21Octanal0.42-22Octaldehyde-0.81231.2-Cyclopentanedione4.08-24Cyclopentanone, 2-methyl-0.9725NI0.261.5326Cyclohexanecarboxaldehyde, 4-methoxy-5.1027NI0.71-281.2-Cyclopentanedione, 3-methyl0.81-29NI0.33-30Nonanaldehyde1.091.8931Guaiacol2.96-322-lsopropylcyclohexanol-1.0734Dodecanoic acid, 3-hydroxy0.110.3535Phenol, 2-methoxy-4-methyl1.871.67362-Pentanol, 5-(2-propynyloxy)-1.76373.4-Dimethoxy10uene0.20-38Trans-2-Decenal1.212.1739p-Ethylguaicol0.45-414-Ethylcyclohexanol0.18-422.4-Decenal1.310.1743Defocanic acid, 3-hydroxy0.110.35442-Undecenal0.611.0145Eugenol0.611.0146Syringol2.380.7247Dodecanoic acid, 3-hydroxy0.110.2148Phenol, 4-methoxy-5-(1-propenyl)0.39-49Vanilin0.720.6250 <td></td> <td></td> <td></td> <td></td>				
202-Furamethanol0.24-21Octanal0.42-22Octaldehyde-0.81231,2-Cyclopentanedione4.08-24Cyclopentanedione, 2-methyl-0.9725NI0.261.5326Cyclopentance, 2-methyl-5.1027NI0.71-281,2-Cyclopentanedione, 3-methyl-0.81-29NI0.33-20NI0.33-30Nonanaldehyde296-31Guaicol2.96-322-Isopropicyclohexanol-1.0734Dodecancic acid, 3-hydroxy0.110.3535Pentanal2.52-362-Pentanol, 5-(2-propynloxy)1.871.67362-Pentanol, 5-(2-propynloxy)1.871.67373.4-Dimethoxy-4-methyl1.871.6738Trans-2-Decenal1.212.1739p-Ethylguaicol0.45-414-Ethylcychokxanol0.18-422-Occadienal0.18-43Penol, 4-ethenyl-2-methoxy4.711.45442-Undecenal0.311.7845Eugenol0.610.1746Syringol2.380.7247Dodecancic acid, 3-hydroxy0.110.2148Phenol, 2-methoxy-5-(1-propenyl)0.39-49Vanilin<				
21Octaal0.42-22Octaldehyde-0.81231,2-Cyclopentanedione4.08-24Cyclopentanec, 2-methyl-0.9725NI0.261.5326Cyclobexanecarboxaldehyde, 4-methoxy-5.1027NI0.71-281,2-Cyclopentanedione, 3-methyl-0.81-29NI0.33-30Nonanaldehyde1.091.8931Guaiacol2.96-322-Isopropylcyclohexanol-1.0734Dodecanoic acid, 3-hydroxy0.110.3534Dodecanoic acid, 3-hydroxy0.110.3534Dodecanoic acid, 3-hydroxy0.110.3534Dodecanoic acid, 3-hydroxy0.110.3536Phenol, 2-methoxy-4-methyl1.871.67362-Pentanol, 5-(2-propynyloxy)-1.763734-Direthoxytoluene0.20-38Trans-2-Decenal1.212.1739p-Ethylguaicol0.411.4540Cyclohexanol, 4-isopropyl-0.35414-Etheryl-2-methoxy4.711.45422-Undecenal0.610.1745Eugenol0.610.1746Syringol2.380.7247Dodecanoic acid, 3-hydroxy0.110.2148Phenol, 2-methoxy-5-1-propenyl0.39-49Vanillin<				
22Octaldehyde-0.81231,2-Cyclopentanedione4.08-24Cyclopentanone, 2-methyl-0.9725NI0.261.5326Cyclohexnaccarboxaldehyde, 4-methoxy-5.1027NI0.71-281,2-Cyclopentanedione, 3-methyl0.81-29NI0.33-20Nonanaldehyde1.091.8931Guaiacol2.96-322-Isopropicyclohexanol-1.0734Dodecanoic acid, 3-hydroxy0.110.3535Phenol, 2-methoxy-4-methyl1.871.67362-Pentanol, 5-(2-propynyloxy)-1.763734-Dimethoxytoluene0.20-38Tans-2-Decenal1.212.1739p-Ethylguaiacol0.45-414-Ethylcyclohexanol1.81-4224-Decadienal1.311.78442-Undecenal1.311.7845Eugenol0.610.1746Syringol2.380.7247Dodecanoic acid, 3-hydroxy0.110.2148Phenol, 4-ethenyl-2-methoxy4.711.4549Vardenoide acid, 3-hydroxy0.610.17414-Ethylcyclohexanol1.311.784224-Decadienal0.610.1743Deceanoic acid, 3-hydroxy0.110.2144Dodecanoic acid, 3-hydr				
23 1.2-Cyclopentanone, 2-methyl - 0.97 24 Cyclopentanone, 2-methyl - 0.97 25 NI 0.26 1.53 26 Cyclohexanecarboxaldehyde, 4-methoxy - 5.10 27 NI 0.71 - - 28 1.2-Cyclopentanedione, 3-methyl- 0.81 - 29 NI 0.33 - - 30 Nonanaldehyde 1.09 1.89 - 31 Guaiacol 2.96 - - - 32 2-Isopropylcyclohexanol - 1.07 - 34 Dodecanoic acid, 3-hydroxy 0.11 0.35 - 35 Phenol, 2-methoxy-4-methyl 1.87 1.67 36 2-Pentanol, 5-(2-proprynloxy) - 1.76 37 3,4-Dimethoxytoluene 0.20 - 38 Trans-2-Decenal 1.21 2.17 39 p-Ethylguaicol 0.45 - 40				
24 Cyclopentanone, 2-methyl - 0.97 25 NI 0.26 1.53 26 Cyclohexanecarboxaldehyde, 4-methoxy - 5.10 27 NI 0.71 - 28 1,2-Cyclopentanedione, 3-methyl- 0.81 - 29 NI 0.33 - 30 Nonanaldehyde 1.09 1.89 31 Guaicol 2.96 - 32 2-Isopropylcyclohexanol - 1.07 33 Pentanal 2.52 - 34 Dodecanoic acid, 3-hydroxy 0.11 0.35 35 Phenol, 2-methoxy-4-methyl 1.87 1.67 36 2-Pentanol, 5-(2-propynyloxy) - 1.76 37 3,4-Dimethoxytoluene 0.20 - 38 Trans-2-Decenal 1.21 2.17 39 p-Ethylguaiacol 0.45 - 41 4-Ethylcyclohexanol 1.88 - 42 2,4-Decadienal		,		
25 NI 0.26 1.53 26 Cyclohexanecarboxaldehyde, 4-methoxy - 5.10 27 NI 0.71 - 28 1,2-Cyclopentanedione, 3-methyl- 0.81 - 29 NI 0.33 - 30 Nonanaldehyde 1.09 1.89 31 Guaiacol 2.96 - 32 2-Isopropylcyclohexanol - 1.07 33 Pentanal 2.52 - 34 Dodecanoic acid, 3-hydroxy 0.11 0.35 35 Phenol, 2-methoxy-4-methyl 1.87 1.67 36 2-Pentanol, 5-(2-propynyloxy) - 1.76 37 3,4-Dimethoxytoluene 0.20 - 38 Trans-2-Decenal 1.21 2.17 39 p-Ethylguaicol 0.45 - 41 4-Ethylcyclohexanol 0.18 - 42 2,4-Decadienal 0.61 1.01 43 Phenol, 4-ethenyl-2-methoxy <td></td> <td></td> <td></td> <td></td>				
26Cyclohexanecarboxaldehyde, 4-methoxy-5.1027NI0.71-281,2-Cyclopentanedione, 3-methyl-0.81-29NI0.33-30Nonanaldehyde1.091.8931Guaicol2.96-322-Isopropylcylohexanol-1.0733Pentanal2.52-34Dodecanoic acid, 3-hydroxy0.110.3535Phenol, 2-methoxy-4-methyl1.871.67362-Pentanol, 5-(2-propynyloxy)-1.76373,4-Dimethoxytoluene0.20-38Trans-2-Decenal1.212.1739p-Ethylguaiacol0.45-414-Ethylcyclohexanol0.18-422,4-Decadienal0.13-43Phenol, 4-ethenyl-2-methoxy4/11.45442-Undecenal0.610.1745Eugenol0.610.1746Syringol2.380.7247Dodecanoic acid, 3-hydroxy0.110.2148Phenol, 2-methoxy-5-(1-propenyl)0.39-49Vanillin0.770.6250Toluene, 3,45-trimethoxy0.43-51Guaiacylacetone0.68-52Toluene, 3,45-trimethoxy0.43-53Guaiacylacetone0.68-54Syr-Dimethoxylacetophenone3.220.8655Tiolecanaldehyde<				
27NI0.71-281,2-Cyclopentanedione, 3-methyl-0.81-29NI0.33-30Nonanaldehyde1.091.8931Guaiacol2.96-322-Isopropylcyclohexanol-1.0733Pentanal2.52-34Dodecanoic acid, 3-hydroxy0.110.3535Phenol, 2-methoxy-4-methyl1.871.67362-Pentanol, 5-(2-propynyloxy)-1.76373.4-Dimethoxytoluene0.20-38Trans-2-Decenal1.212.1739p-Ethylguaiacol0.45-414-Ethylcyclohexanol0.18-422,4-Decadienal0.611.0143Phenol, 4-ethenyl-2-methoxy4.711.45442-Undecenal1.311.7845Eugenol0.610.1746Syringol2.380.7247Dodecancia ci, 3-hydroxy0.110.2148Phenol, 2-methoxy-5-(1-propenyl)0.39-49Naillin0.770.6250Isoeugenol4.003.6551Tetradecane0.16-52Toluene, 3,4,5-trimethoxy0.43-53Guaiaylacetone0.68-543,5'-Dimethoxyacetophenone3.222.0855Tridecanaldehyde2.730.46				
281.2-Cyclopentanedione, 3-methyl-0.81-29NI0.33-30Nonanaldehyde1.091.8931Guaiacol2.96-322-Isopropylcyclohexanol-1.0733Pentanal2.52-34Dodecanoic acid, 3-hydroxy0.110.3535Phenol, 2-methoxy-4-methyl1.871.67362-Pentanol, 5-(2-propynloxy)-1.76373.4-Dimethoxytoluene0.20-38Trans-2-Decenal1.212.739p-Ethylguaiacol0.45-40Cyclohexanol, 4-isopropyl-0.35414-Ethylcyclohexanol0.18-422.4-Decadienal0.611.0143Phenol, 4-ethenyl-2-methoxy4.711.45442-Undecenal1.311.7845Eugenol0.610.1746Syringol2.380.7247Dodecanci acid, 3-hydroxy0.110.2148Phenol, 2-methoxy-5-(1-propenyl)0.39-49Naillin0.770.6250Isougenol4.003.6551Tetradecane0.16-52Toluene, 3.4,5-trimethoxy0.43-53Guaiaylacetopenone3.222.0854Levoglucosan4.472.65				5.10
29NI0.33-30Nonanaldehyde1.091.8931Guaiacol2.96-322-Isopropylcyclohexanol-1.0733Pentanal2.52-34Dodecanoic acid, 3-hydroxy0.110.3535Phenol, 2-methoxy-4-methyl1.871.67362-Pentanol, 5-(2-propynyloxy)-1.76373.4-Dimethoxytoluene0.20-38Trans-2-Decenal1.212.1739p-Ethylguaiacol0.45-40Cyclohexanol, 4-isopropyl-0.35414-Ethylcyclohexanol0.611.0143Phenol, 4-ethenyl-2-methoxy4.711.45442-Undecenal0.611.0145Eugenol0.610.1746Syringol2.380.7247Dodecanoic acid, 3-hydroxy0.110.2148Phenol, 2-methoxy-5-(1-propenyl)0.39-49Vanillin0.770.6250Isoeugenol4.003.6551Tetradecane0.16-52Toluene, 3.4,5-trimethoxy0.43-53Guaiaylacetopehone3.222.0854Kyridylacetophone3.220.46				
30Nonanaldehyde1.091.8931Guaiacol2.96-322.1sopropylcyclohexanol-1.0733Pentanal2.52-34Dodecanoic acid, 3-hydroxy0.110.3535Phenol, 2-methoxy-4-methyl1.871.67362.Pentanol, 5-(2-propynyloxy)-1.76373,4-Dimethoxytoluene0.20-38Trans-2-Decenal1.212.1739p-Ethylguaiacol0.45-40Cyclohexanol, 4-isopropyl-0.35414-Ethylcyclohexanol0.611.01422.4-Decadienal0.611.0143Phenol, 4-ethenyl-2-methoxy4.711.45442-Undecenal1.311.7845Eugenol0.610.1746Syringol2.380.7247Dodecanoic acid, 3-hydroxy0.110.2148Phenol, 2-methoxy-5-(1-propenyl)0.39-49Vanillin0.770.6250Isoegenol4.003.6551Tetradecane0.16-52Toluene, 3,4,5-trimethoxy0.43-53Guaiaylacetopehone3.222.0854SyriDimethoxyacetophenone3.220.46	28	1,2-Cyclopentanedione, 3-methyl-	0.81	-
31 Guaiacol 2.96 - 32 2.1sopropylcyclohexanol - 1.07 33 Pentanal 2.52 - 34 Dodecanoic acid, 3-hydroxy 0.11 0.35 35 Phenol, 2-methoxy-4-methyl 1.87 1.67 36 2-Pentanol, 5-(2-propynyloxy) - 1.76 37 3.4-Dimethoxytoluene 0.20 - 38 Trans-2-Decenal 1.21 2.17 39 p-Ethylguaicol 0.45 - 40 Cyclohexanol, 4-isopropyl - 0.35 41 4-Ethylcyclohexanol 0.18 - 42 2.4-Decadienal 0.61 1.01 43 Phenol, 4-ethenyl-2-methoxy 4.71 1.45 44 2-Undecenal 1.31 1.78 45 Eugenol 0.61 0.17 46 Syringol 2.38 0.72 47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phen	29	NI	0.33	-
322-Isopropylcyclohexanol-1.0733Pentanal2.52-34Dodecanoic acid, 3-hydroxy0.110.3535Phenol, 2-methoxy-4-methyl1.871.67362-Pentanol, 5-(2-propynyloxy)-1.76373.4-Dimethoxytoluene0.20-38Trans-2-Decenal1.212.1739p-Ethylguaicol0.45-40Cyclohexanol, 4-isopropyl-0.35414-Ethylcyclohexanol0.18-422.4-Decadienal0.611.0143Phenol, 4-ethenyl-2-methoxy4.711.45442-Undecenal1.311.7845Eugenol0.610.1746Syringol2.380.7247Dodecanoic acid, 3-hydroxy0.110.2148Phenol, 2-methoxy-5-(1-propenyl)0.39-49Vanillin0.770.6250Isoeugenol4.003.6551Tetradecane0.16-52Toluene, 3.4,5-trimethoxy0.43-53Guaicylacetone0.68-543,5'-Dimethoxyacetophenone3.222.0855Tridecanaldehyde2.730.46			1.09	1.89
33 Pentanal 2.52 - 34 Dodecanoic acid, 3-hydroxy 0.11 0.35 35 Phenol, 2-methoxy-4-methyl 1.87 1.67 36 2-Pentanol, 5-(2-propynyloxy) - 1.76 37 3,4-Dimethoxytoluene 0.20 - 38 Trans-2-Decenal 1.21 2.17 39 p-Ethylguaiacol 0.45 - 40 Cyclohexanol, 4-isopropyl - 0.35 41 4-Ethylcyclohexanol 0.18 - 42 2,4-Decadienal 0.61 1.01 43 Phenol, 4-ethenyl-2-methoxy 4.71 1.45 44 2-Undecenal 1.31 1.78 45 Eugenol 0.61 0.17 46 Syringol 2.38 0.72 47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 51	31		2.96	-
34Dodecanoic acid, 3-hydroxy0.110.3535Phenol, 2-methoxy-4-methyl1.871.67362-Pentanol, 5-(2-propynloxy)-1.76373,4-Dimethoxytoluene0.20-38Trans-2-Decenal1.212.1739p-Ethylguaiacol0.45-40Cyclohexanol, 4-isopropyl-0.35414-Ethylcyclohexanol0.18-422,4-Decadienal0.611.0143Phenol, 4-ethenyl-2-methoxy4.711.45442-Undecenal1.311.7845Eugenol0.610.1746Syringol2.380.7247Dodecanoic acid, 3-hydroxy0.110.2148Phenol, 2-methoxy-5-(1-propenyl)0.39-49Vanillin0.770.6250Isoeugenol4.003.6551Tetradecane0.68-52Toluene, 3,4,5-trimethoxy0.43-53Guaicylacetone0.68-543,5'-Dimethoxyacetophenone3.222.0855Tridecanaldehyde2.730.46	32		-	1.07
35 Phenol, 2-methoxy-4-methyl 1.87 1.67 36 2-Pentanol, 5-(2-propynyloxy) - 1.76 37 3,4-Dimethoxytoluene 0.20 - 38 Trans-2-Decenal 1.21 2.17 39 p-Ethylguaiacol 0.45 - 40 Cyclohexanol, 4-isopropyl - 0.35 41 4-Ethylcyclohexanol 0.18 - 42 2,4-Decadienal 0.61 1.01 43 Phenol, 4-ethenyl-2-methoxy 4,71 1.45 44 2-Undecenal 1.31 1.78 45 Eugenol 0.61 0.17 46 Syringol 2.38 0.72 47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone <td>33</td> <td></td> <td>2.52</td> <td>-</td>	33		2.52	-
36 2-Pentanol, 5-(2-propynyloxy) - 1.76 37 3,4-Dimethoxytoluene 0.20 - 38 Trans-2-Decenal 1.21 2.17 39 p-Ethylguaiacol 0.45 - 40 Cyclohexanol, 4-isopropyl - 0.35 41 4-Ethylcyclohexanol 0.18 - 42 2,4-Decadienal 0.61 1.01 43 Phenol, 4-ethenyl-2-methoxy 4.71 1.45 44 2-Undecenal 1.31 1.78 45 Eugenol 0.61 0.17 46 Syringol 2.38 0.72 47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacyl	34	Dodecanoic acid, 3-hydroxy	0.11	0.35
37 3,4-Dimethoxytoluene 0.20 - 38 Trans-2-Decenal 1.21 2.17 39 p-Ethylguaiacol 0.45 - 40 Cyclohexanol, 4-isopropyl - 0.35 41 4-Ethylcyclohexanol 0.18 - 42 2,4-Decadienal 0.61 1.01 43 Phenol, 4-ethenyl-2-methoxy 4,71 1.45 44 2-Undecenal 1.31 1.78 45 Eugenol 0.61 0.17 46 Syringol 2.38 0.72 47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 3.68 - 54 3',5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde	35	Phenol, 2-methoxy-4-methyl	1.87	1.67
38 Trans-2-Decenal 1.21 2.17 39 p-Ethylguaiacol 0.45 - 40 Cyclohexanol, 4-isopropyl - 0.35 41 4-Ethylcyclohexanol 0.18 - 42 2,4-Decadienal 0.61 1.01 43 Phenol, 4-ethenyl-2-methoxy 4.71 1.45 44 2-Undecenal 1.31 1.78 45 Eugenol 0.61 0.17 46 Syringol 2.38 0.72 47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 3.68 - 54 3,5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldeh	36	2-Pentanol, 5-(2-propynyloxy)	-	1.76
39 p-Ethylguaiacol 0.45 - 40 Cyclohexanol, 4-isopropyl - 0.35 41 4-Ethylcyclohexanol 0.18 - 42 2,4-Decadienal 0.61 1.01 43 Phenol, 4-ethenyl-2-methoxy 4.71 1.45 44 2-Undecenal 1.31 1.78 45 Eugenol 0.61 0.17 46 Syringol 2.38 0.72 47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 0.68 - 54 3',5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46	37	3,4-Dimethoxytoluene	0.20	-
40 Cyclohexanol, 4-isopropyl - 0.35 41 4-Ethylcyclohexanol 0.18 - 42 2,4-Decadienal 0.61 1.01 43 Phenol, 4-ethenyl-2-methoxy 4.71 1.45 44 2-Undecenal 1.31 1.78 45 Eugenol 0.61 0.17 46 Syringol 2.38 0.72 47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 0.68 - 54 3',5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46	38	Trans-2-Decenal	1.21	2.17
41 4-Ethylcyclohexanol 0.18 - 42 2,4-Decadienal 0.61 1.01 43 Phenol, 4-ethenyl-2-methoxy 4.71 1.45 44 2-Undecenal 1.31 1.78 45 Eugenol 0.61 0.17 46 Syringol 2.38 0.72 47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 0.68 - 54 3,5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46	39	p-Ethylguaiacol	0.45	-
42 2,4-Decadienal 0.61 1.01 43 Phenol, 4-ethenyl-2-methoxy 4.71 1.45 44 2-Undecenal 1.31 1.78 45 Eugenol 0.61 0.17 46 Syringol 2.38 0.72 47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 0.68 - 54 3,5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46	40	Cyclohexanol, 4-isopropyl	-	0.35
43 Phenol, 4-ethenyl-2-methoxy 4.71 1.45 44 2-Undecenal 1.31 1.78 45 Eugenol 0.61 0.17 46 Syringol 2.38 0.72 47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 0.68 - 54 3,5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46	41	4-Ethylcyclohexanol	0.18	-
44 2-Undecenal 1.31 1.78 45 Eugenol 0.61 0.17 46 Syringol 2.38 0.72 47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 3.68 - 54 3,5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46 56 Levoglucosan 4.47 26.65	42	2,4-Decadienal	0.61	1.01
45 Eugenol 0.61 0.17 46 Syringol 2.38 0.72 47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 0.68 - 54 3,5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46 56 Levoglucosan 4.47 26.65	43	Phenol, 4-ethenyl-2-methoxy	4.71	1.45
46 Syringol 2.38 0.72 47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 0.68 - 54 3',5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46 56 Levoglucosan 4.47 26.65	44	2-Undecenal	1.31	1.78
47 Dodecanoic acid, 3-hydroxy 0.11 0.21 48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 0.68 - 54 3',5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46 56 Levoglucosan 4.47 26.65	45	Eugenol	0.61	0.17
48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 0.68 - 54 3,5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46 56 Levoglucosan 4.47 26.65	46	Syringol	2.38	0.72
48 Phenol, 2-methoxy-5-(1-propenyl) 0.39 - 49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 0.68 - 54 3,5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46 56 Levoglucosan 4.47 26.65	47	Dodecanoic acid, 3-hydroxy	0.11	0.21
49 Vanillin 0.77 0.62 50 Isoeugenol 4.00 3.65 51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 0.68 - 54 3,5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46 56 Levoglucosan 4.47 26.65	48		0.39	-
51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 0.68 - 54 3,5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46 56 Levoglucosan 4.47 26.65	49		0.77	0.62
51 Tetradecane 0.16 - 52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 0.68 - 54 3,5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46 56 Levoglucosan 4.47 26.65	50	Isoeugenol	4.00	3.65
52 Toluene, 3,4,5-trimethoxy 0.43 - 53 Guaiacylacetone 0.68 - 54 3,5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46 56 Levoglucosan 4.47 26.65	-			-
53 Guaiacylacetone 0.68 - 54 3;5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46 56 Levoglucosan 4.47 26.65				
54 3,5'-Dimethoxyacetophenone 3.22 2.08 55 Tridecanaldehyde 2.73 0.46 56 Levoglucosan 4.47 26.65		· · ·		
55 Tridecanaldehyde 2.73 0.46 56 Levoglucosan 4.47 26.65		-		
56 Levoglucosan 4.47 26.65				
		· ·		
		Levogneosan	1. 1/	20.03

Peak	Compound	Sapwood	Heartwood
57	Phenol, 2,6-dimethoxy-4-(2-propenyl)	0.27	-
58	Syringaldehyde	0.78	1.05
59	Methoxyeugenol	2.60	2.63
60	Acetosyringone	0.56	1.20
61	4-Hydroxy-2-methoxycinnamaldehyde	1.03	
62	Desaspidinol	0.53	0.37
63	Ethanone, 1-[2-(5-hydroxy-1,1-dimethyl- hexyl) -3-methyl-2-cyclopropen-1-yl]	-	0.55
64	2(3H)-Benzofuranone, hexahydro-4,4,7a- trimethyl-	-	0.19
65	Pentadecanoic acid	-	0.36
66	Oleylaldehyde	0.16	0.23
67	Octadecanal	0.15	-
68	Oleic Acid	0.26	-
69	Myristaldehyde	-	0.94
70	Palmitic acid	1.20	1.43
71	Cyclopentadecanone, 2-hydroxy	-	2.56
72	Heneicosane	0.14	-
73	NI	0.86	-
74	3,5-Dimethoxy-4-hydroxycinnamaldehyde	-	0.12
75	Hexacosane	0.10	-
76	Vinyl myristate	-	0.22
77	Anthraquinone, 2-methyl	-	1.63
78	Octadecanoic acid	3.07	0.47
79	2-Hydroxycyclopentadecanone	-	2.88
80	Stearic acid	0.30	-
81	Octadecanal	0.15	-
82	Stearaldehyde	0.14	-
83	Benzylidenepinacolone	-	0.55
84	1,1'-Biphenyl-3,4,4'-trimethoxy-6'-formyl	0.97	0.56
85	Squalene	1.87	4.85

Table 1. Area of the pyrolytic compounds peaks (percentage of the total chromatogram area) of the teak sapwood and heartwood. *NI* The compound was not identified.

rearrangements in the carbohydrates resulting in isomers lacking molecular ions and, therefore, difficult to interpret 21 .

Levoglucosan was the main pyrolytic product formed from the heartwood sample (26.65%).

The formation of levoglucosan is due to the conversion of cellulose, hemicellulose, lignin and extractives from biomass into sugar, acids and furans, compounds with larger areas⁷. Sugars can be used as a carbon source, in fermentation, to produce compounds of industrial interest, such as citric acid, ethanol, 5-hydroxymethylfurfural, furans, aromatic hydrocarbons and lipids^{22,23}.

The biphenyl compounds (1,1'-biphenyl-3,4,4'-trimethoxy-6'-formyl) and anthraquinone, 2-methyl, from the naphthoatraquinone group were identified at the end of the chromatogram of the sapwood and heartwood (Fig. 1).

The identification of biphenyl (1,1'-biphenyl-3,4,4'-trimethoxy-6'-formyl) and anthraquinone, 2-methyl compounds from the naphthoatraquinone group, at the end of the chromatogram for the sapwood and heartwood are due to the difficulty of fragmentation into small components and because they are derivatives of lignin. This compound, during pyrolysis, releases a mixture of phenolic derivatives preserving the aromatic ring, with the original methoxyl groups, and a part, or all, of the side chain of propane²⁰. These components, with antifungal and bactericidal properties, protect the plant against xylophagous organisms, increasing the durability of its wood^{24,25}. In addition, anthraquinones can replace synthetic dyes^{26–28}.

Syringyl/guaiacyl ratio. The syringyl/guaiacyl (S/G) ratio was 0.51 ± 0.010 and 0.50 ± 0.012 for the sapwood and heartwood respectively. The 4-vinylsyringol, trans-coniferyl alcohol and coniferaldehyde, 4-vinyl-guaiacol, 4-methylguaiacol, vanillin and sinapinaldehyde were the main compounds derived from lignin.

The S/G ratio of the *T. grandis* heartwood and sapwood was lower than that of the 70-year-old teak wood from the DBH position, 0.8 for heartwood and sapwood with total lignin content of 35.4% for the sapwood and 37.3% for the heartwood¹⁵ and for the 12 years old teak trees with a total lignin content of 31% and a S/G ratio of 0.72²⁹



Figure 1. Py-GC/MS chromatogram of the sapwood (A) and heartwood (B) of the Tectona grandis wood.

and of *Eucalyptus* spp. used for Kraft Pulp production, with an S/G from 2.0 to 3.2³⁰. Differences between the S/G ratio values may be due to the growth stage (age), climatic factors and exposure to microorganisms, insects and pests³¹. The S/G ratio is important for the pulp industry, as the alkaline hydrolysis reactions of lignin fragmentation vary with the ratio between syringyl units²⁹. The chemical structure of syringyl lignin is less condensed and more favorable to delignification by Kraft cooking liquor due to the absence of the C5 reactive carbon available for reaction in the polymerization step of lignin biosynthesis³². In addition, the high content of guaiacyl units indicates a more condensed lignin (greater number of bonds between C–C units), increasing the thermal resistance of the wood³¹. The characterization of lignin by pyrolysis (Py-GC/MS) is an effective, faster and cheaper method with lower consumption of reagents, analysis time and higher precision compared to traditional ones¹².

Conclusion

A total of 85 compounds, 51 in sapwood and 62 in heartwood, were identified in the pyrolyzed of teak wood samples. The area and retention time of carbohydrate-derived compounds were lower with lignin derivatives and extractives appearing at the middle and at the end of the pyrogram. The highest intensity peaks in the sapwood pyrogram corresponded to acetic acid, phenol, 4-ethenyl-2-methoxy, isoeugenol, 3,5'-dimethoxyacetophenone and squalene and those in the heartwood to acetic acid, cyclohexanecarboxaldehyde, 4-methoxy and squalene. The compounds found can be used in the manufacture of paints, dyes, synthetic silks, cellulose acetate, enhancing the use of teak wood. The syringyl (S)/guaiacyl (G) ratio of heartwood and sapwood were 0.51 and 0.50, respectively. Gas chromatography with mass spectrometry is a useful, cheaper and fast methodology, and can be applied with small quantities of material.

Data availability

The datasets generated and analysed during the current study are available from the corresponding author on reasonable request.

Received: 18 August 2022; Accepted: 19 October 2022 Published online: 02 November 2022

References

- 1. Nidavani, R. B. & Am, M. Teak (Tectona grandis Linn.): A renowned timber plant with potential medicinal values. *Int. J. Pharm. Pharm. Sci.* 6, 48–54 (2014).
- Lengowski, E. C., Júnior, E. A. B., Nisgoski, S., de Muñiz, G. I. B. & Klock, U. Properties of thermally modified teakwood. *Maderas Cienc. Tecnol.* 23, 1–16 (2020).

- 3. Vyas, P., Yadav, D. K. & Khandelwal, P. Tectona grandis (teak)–A review on its phytochemical and therapeutic potential. *Nat. Prod. Res.* **33**, 2338–2354 (2019).
- 4. Mascarenhas, A. R. P. et al. Quality assessment of teak (Tectona grandis) wood from trees grown in a multi-stratified agroforestry system established in an Amazon rainforest area. *Holzforschung* 75, 409–418 (2021).
- 5. IBA, Indústria brasileira de árvores, I. Relatório annual de sustentabilidade (2021).
- 6. Brocco, V. F., Paes, J. B., da Costa, L. G., Brazolin, S. & Arantes, M. D. C. Potential of teak heartwood extracts as a natural wood preservative. J. Clean. Prod. 142, 2093–2099 (2017).
- Rodríguez Anda, R. *et al.* Formation of heartwood, chemical composition of extractives and natural durability of plantation-grown teak wood from Mexico. *Holzforschung* 73, 547–557 (2019).
- Evstigneyev, E. I. & Shevchenko, S. M. Structure, chemical reactivity and solubility of lignin: A fresh look. Wood Sci. Technol. https://doi.org/10.1007/s00226-018-1059-1 (2019).
- 9. Wang, T., Zhang, R., Peng, L., Ai, Y. & Lu, Q. Pyrolysis characteristic changes of poplar wood during natural decay. J. Anal. Appl. Pyrolysis 128, 257–260 (2017).
- 10. David, G. F. *et al.* Fast pyrolysis as a tool for obtaining levoglucosan after pretreatment of biomass with niobium catalysts. *Waste Manag.* **126**, 274–282 (2021).
- 11. Okoffo, E. D. *et al.* Identification and quantification of selected plastics in biosolids by pressurized liquid extraction combined with double-shot pyrolysis gas chromatography-mass spectrometry. *Sci. Total Environ.* **715**, 136924 (2020).
- 12. Lin, S. Y. & Dence, C. W. Methods in Lignin Chemistry (Springer, 1992).
- Martín-Espejo, J. L., Gandara-Loe, J., Odriozola, J. A., Reina, T. R. & Pastor-Pérez, L. Sustainable routes for acetic acid production: Traditional processes vs a low-carbon, biogas-based strategy. Sci. Total Environ. 840, 156663 (2022).
- Itabaiana, I. Jr., Do Nascimento, M. A., de Souza, R. O., Dufour, A. & Wojcieszak, R. Levoglucosan: A promising platform molecule?. Green Chem. 22, 5859–5880 (2020).
- Lourenço, A., Neiva, D. M., Gominho, J., Marques, A. V. & Pereira, H. Characterization of lignin in heartwood, sapwood and bark from Tectona grandis using Py–GC–MS/FID. Wood Sci. Technol. 49, 159–175 (2015).
- Traoré, M., Kaal, J. & Cortizas, A. M. Variation of wood color and chemical composition in the stem cross-section of oak (*Quercus* spp.) trees, with special attention to the sapwood-heartwood transition zone. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 285, 121893 (2023).
- Silveira Junior, E. G. et al. Fast pyrolysis of elephant grass: Intensification of levoglucosan yield and other value-added pyrolytic by-products. J. Energy Inst. 101, 254–264 (2022).
- Balogun, A. O., Lasode, O. A. & McDonald, A. G. Devolatilisation kinetics and pyrolytic analyses of Tectona grandis (teak). Bioresour. Technol. 156, 57–62 (2014).
- 19. Lasode, O. A., Balogun, A. O. & McDonald, A. G. Torrefaction of some Nigerian lignocellulosic resources and decomposition kinetics. J. Anal. Appl. Pyrolysis 109, 47–55 (2014).
- 20. Zadeh, Z. Hardwood and softwood lignin. Energies 1-14 (2020).
- Nonier, M. F. et al. Pyrolysis-gas chromatography/mass spectrometry of Quercus sp. wood: Application to structural elucidation of macromolecules and aromatic profiles of different species. J. Anal. Appl. Pyrolysis 75, 181–193 (2006).
- 22. Mullen, C. A. & Boateng, A. A. Production of aromatic hydrocarbons via catalytic pyrolysis of biomass over fe-modified HZSM-5 zeolites. ACS Sustain. Chem. Eng. 3, 1623–1631 (2015).
- 23. Hu, X. *et al.* Mediating acid-catalyzed conversion of levoglucosan into platform chemicals with various solvents. *Green Chem.* 14, 3087–3098 (2012).
- 24. Moreira, R. Y. O. *et al.* Antraquinonas e naftoquinonas do caule de um espécime de reflorestamento de Tectona grandi (Verbenaceae). *Rev. Bras. Farmacogn.* 16, 392–396 (2006).
- Dungani, R., Bhat, I. U. H., Abdul Khalil, H. P. S., Naif, A. & Hermawan, D. Evaluation of antitermitic activity of different. *BioResources* 7, 1452–1461 (2012).
- Duval, J., Pecher, V., Poujol, M. & Lesellier, E. Research advances for the extraction, analysis and uses of anthraquinones: A review. Ind. Crops Prod. 94, 812–833 (2016).
- Challinor, J. M. Characterisation of wood extractives by pyrolysis-gas chromatography/mass spectrometry of quaternary ammonium hydroxide extracts. J. Anal. Appl. Pyrolysis 37, 1–13 (1996).
- Aguinaldo, A. M., Ocampo, O. P. M., Bowden, B. F., Gray, A. I. & Waterman, P. G. Tectograndone, an anthraquinone-naphthoquinone pigment from the leaves of Tectona grandis. *Phytochemistry* 33, 933–935 (1993).
- Chagas, S. F., Evangelista, W. V., Silva, J. C. & Carvalho, A. M. M. L. Caracterização anatômica, física e química da madeira de clones de Eucalyptus cultivados em áreas sujeitas à ação de ventos. *Rev. Ciência Madeira RCM* 5, 138–150 (2014).
- Zanuncio, A. J., Carvalho, A. G., Carneiro, A. D., Colodette, J. L. & Rocha, M. F. Chemical and energetic characterization of Eucalyptus grandis × Eucalyptus urophylla clones subject to wind damage. *Rev. Arvore* 43, 1–7 (2019).
- Prasad, L., Salvi, B. L. & Kumar, V. Thermal degradation and gasification characteristics of Tung Shells as an open top downdraft wood gasifier feedstock. *Clean Technol. Environ. Policy* 17, 1699–1706 (2015).
- Varfolomeev, M. A. et al. Thermal analysis and calorimetric study of the combustion of hydrolytic wood lignin and products of its pyrolysis. Chem. Technol. Fuels Oils 51, 140–145 (2015).

Acknowledgements

This work was supported by the Brazilian agencies "Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq)" and "Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES)", and by the Portuguese agency "Fundação para a Ciência e a Tecnologia (FCT)" through funding of the Forest Research Centre (Grant No. UID/AGR/00239/2019 and Grant No. UIDB/00239/2020) and CLEANPELL (Grant No. EXPL/ CTM-PAM/0850/2021). Solange Araújo acknowledges funding from the FCT for their research contracts (DL 57/2016/CP1382/CT0018).

Author contributions

All authors perform the experiment and reviewed the manuscript. V.R.C.; P.G.S. and A.J.V.Z. wrote the manuscripts. S.A.F. and M.S.B. prepared the figure. J.C.Z. and S.O.A. reviewed the results.

Competing interests

The authors declare no competing interests.

Additional information

Correspondence and requests for materials should be addressed to A.J.V.Z.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2022