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Abstract: Analytical pyrolysis (Py-GC/MS) at 500 °C was applied to study wood composition of Eucalyptus species (*E. grandis*, *E. dunnii* and *E. benthamii*) which are relevant for pulping in Uruguay. Multivariate data treatments mainly principal component analysis and discriminant analysis with automatic backwards variable selection were used to explore differences between the original wood cultivars. Multivariate analyses with automatic backwards variable selection indicated that simplified methoxyphenol patterns (up to 10 compounds) are sufficient for wood discrimination in terms of species and geographical origin but also with purposes of forecasting the ease of delignification of the resulting pulps measured as active alkali. No additional chemotaxonomical accuracy was achieved when the data sets were enlarged with carbohydrate-derived products. On the other side, discriminant or forecasting models were much less significant when based on individual diagnostic compounds, groups of compounds, or the classical syringyl-to-guaiacyl (SG) ratio. Principal component analysis indicated that the variability in lignin composition due to bioclimatic variations (spatial replications) was more significant than that due to phylogenetic differences (species and cultivars).

Chemometric appraisal of lignin pyrolytic assemblages from

Eucalyptus woods relevant for pulping in Uruguay

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Abstract

Analytical pyrolysis (Py-GC/MS) at 500 °C was applied to study wood
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which are relevant for pulping in Uruguay. Multivariate data treatments mainly
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Keywords: Analytical pyrolysis; chemometry; discriminant analysis; *Eucalyptus* ssp.; multiple regression models; partial least squares regression; principal components analysis; lignin methoxyphenols.

1. Introduction

Current total forest area in Uruguay is 1,721,658 ha, from which 43% corresponds to natural forests and 57% to plantations [1]. About 70% of this area is forested with *Eucalyptus* species, the predominant ones being *E. globulus*, *E. grandis* and *E. dunnii*, although *E. benthamii* was recently introduced in breeding programs. More than half of the total extraction of eucalyptus wood in Uruguay is for pulping industries and this utilization will increase in the next future.

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51 It is clear that effective utilization of wood for pulping or the production of
52 chemicals can be increased by appropriate analyses of the raw materials [2] in
53 particular concerning the concentration and chemical composition of its lignin
54 fraction [3]. In fact, different wood species or clones from the same species
55 might require different pulping conditions depending on the amount of lignin and
56 its structural features [4,5]. The large variety of lignins is well known since a
57 long time [6] and the supramolecular architecture of the cell wall with regard of
58 lignin composition within the 3D-lignin-polysaccharide matrix has been reviewed
59 [7].

60 Lignin isolation is time-consuming, e.g. by the method by Björkman [8],
61 thus analytical techniques for direct lignin analysis using intact plant material
62 have been developed. The up-to dated methods based on NMR [9], Raman
63 spectroscopy [10] or UMSP [11] are expensive and better suited for research
64 purposes than for routine analysis. We still consider that methods involving
65 analytical pyrolysis (Py-GC/MS) are better suited to this purpose [12–15]:
66 sample preparation is restricted to drying and milling; the GC separation needs
67 ca. one hour and, in case of routine data evaluation, the results are available
68 within the next hour.

69 Various aspects of lignin pyrolysis are well discussed in the literature
70 [14,16–18] since lignin cleavage compounds retain their methoxyl substitution
71 patterns, and it is easy to identify stoichiometric changes defined by the yields
72 of *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) type subunits, expressed
73 by the H/G/S ratios. On the other hand, these data are also relevant as regards
74 the pulpability of various wood species, and the S/G ratio is frequently used in
75 the context of delignification during pulping processes [19].

As suggested by previous studies with *E. globulus* [5,21] and *E. camaldulensis* [22], the aim of the present work is comparing by means of Py-GC/MS the structural variability amongst eucalypt species and its role on pulping efficiency using wood samples from *E. grandis*, *E. dunnii* and *E. benthamii*, which are important species for pulping in Uruguay [20],

Materials and Methods

2.1. Wood samples

The samples were collected from representative plantations for paper pulp production in Uruguay (Table 1). Eucalypt trees were 6–17-year old, and sampling was carried out at about 6-months after felling. Combined wood samples were prepared by mixing up to 5 subsamples of wood collected in progressive transversal sections of commercial boles 0, 25, 50, 75 and 100%. Chips were debarked, air-dried and milled to 40–60 mesh. *Eucalyptus* woods planted in Uruguay were previously analyzed in terms of pulping by Backman and García de León [23].

2.2. Pulping parameters. Wood samples of 250 g were cooked at 170°C (25% sulfidity; time to reach maximum temperature: 90 min; time at maximum temperature: 50 min; 3.5 liquor/wood ratio). The variable condition used to reach a final Kappa number of 18 ± 1 was referred to as alkali charge (TAPPI Test Method T 236cm-85). In order to obtain the same Kappa, different alkali charges were tried in the same samples.

2.3. Pyrolysis experiments

Pyrolysis was performed using a vertical micro-furnace type double-shot pyrolyzer PY2020iD (Frontier Laboratories Ltd., Fukushima, Japan) attached to a GC/MS system (Agilent 6890 GC attached to an Agilent 5973 MS system). Homogenized and lyophilized eucalypt wood samples (ca. 100 μg) were introduced in the pre-heated micro-furnace at a pyrolysis temperature of 500 $^{\circ}\text{C}$ for 1 min. The evolved gases from pyrolysis were transferred, through a capillary transfer line interfase heated at 350 $^{\circ}\text{C}$, to the gas chromatograph inlet (splitless mode and 250 $^{\circ}\text{C}$). The gas chromatograph was equipped with a low-to-mid polarity-fused silica capillary column (J&W Scientific) of 30 m $\times$ 250 μm $\times$ 0.25 μm film thickness (Ref. DB-1701). The oven temperature was held at 50 $^{\circ}\text{C}$ for 1 min and then increased to 100 $^{\circ}\text{C}$ at 30 $^{\circ}\text{C min}^{-1}$, from 100 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$, and stabilized at 300 $^{\circ}\text{C}$ for 10 min using a heating rate of 20 $^{\circ}\text{C min}^{-1}$ in the scan mode. The carrier gas was helium at a controlled flow of 1 mL min^{-1} . The detector consisted of an Agilent 5973 mass selective detector and electron ionisation mass spectra were acquired with 70 eV ionizing energy. The identification of individual compounds was carried out by using the extracted ion chromatograms for different homologous series, low resolution mass spectrometry, and comparison with stored data (NIST and Wiley libraries) and with previously published mass spectra [13–14].

Compound quantification was based on percent peak areas of the total ion chromatogram trace (total integral of pyrolysis products identified equal to 100). Cumulative values for different compound families were calculated, and the S/G ratio was determined as the ratio of the sum of the percent peaks areas of S and G-type compounds.

126 *2.4. Data treatments:* Pyrolytic data were subjected to several multivariate data
127 treatments with the Statistica software [24]. The total abundances of pyrolysis
128 compounds calculated from the total area of the ion chromatographic trace
129 served as variables and the different woods, as samples. In the case of
130 supervised chemotaxonomical treatments, a ‘classification factor’ consisting of
131 five states was considered, corresponding to wood origin (spatial replications of
132 samples collected in different locations and/or from different species, referred to
133 as Rio Negro (I–IV) and Cerro Largo (Table 1)).

134 *Discriminant analysis* was used with automatic backward variable
135 selection. As known, one of essential step is the simplification of the models by
136 removing variables with poor discriminating potential.

137 *Principal component analysis* was carried out for unsupervised
138 classification of wood samples as well as to describe the pyrolysis compounds
139 more characteristic for the different groups of samples.

140 *Partial Least Squares (PLS)* was used to forecast technical pulping
141 parameters (in this case active alkali) from the pyrolytic data. This classical
142 statistical procedure leads to a model relating multiple independent variables to
143 one or more dependent variables. The use of PLS was also justified as
144 exploratory treatment because it is especially suitable when there are large
145 number or factors (an usual situation in Py-GC-MS, releasing large number of
146 compounds) as regards the comparatively lower number of samples used to
147 forecast the response variable.

148 Because the large potential of PLS to yield significant models in the above
149 situations where the data matrices have very large number of variables as
150 regards the number of observations, the fitted models must be carefully

validated. Apart from the standard cross-validation with the strategy 'leave out one at a time' (the missing observation is predicted with the model from which it was removed), a total of 10 PLS models were compared after random permutation of the values of the dependent variable (active alkali) of the different samples. The models were discarded as spurious when not only the experimental data set but at least one of the randomized data sets led to significant ($P < 0.05$, observed vs predicted) fitting with the variable assemblages considered for each model.

Multiple regression was also used to refine forecasting models for active alkali using the reduced variable sets after the data reduction suggested by the above treatments. This procedure, yielding a statistical model describing the impact of several quantitative factors (pyrolysis compounds) on a dependent variable (active alkali), was also used with the option of stepwise backward variable selection, in which compounds with low forecasting potential are removed from the model.

3. Results

The pyrograms of sample 22 (Cerro Largo site, *E. grandis*) is presented in Figure 1. The corresponding pyrolysis compounds and its semiquantitative amounts are listed in Table 2.

The peaks can be easily classified as originating from polysaccharides or lignins and, in the latter case, the monomethoxy- and dimethoxy-type degradation products (i.e., G- and S-type, respectively) can be differentiated. The major compounds are guaiacol (No. 37), 4-vinylguaiacol (55), syringol (59),

1 176 4-methylsyringol (64), 4-vinylsyringol (73), *trans*-4-propenylsyringol (78), and
2 177 syringaldehyde (84). All these products are well known and described in the
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4 178 literature. In addition, several less specific compounds may derive from
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6 179 polysaccharide (8) or H-lignin units, such as phenol (36), methylphenols (38),
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8 180 and dimethylphenol (46). As stated by Sarkanen and Hergert [25], degradation
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10 181 techniques release more easily S-type products, because S-units are less
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12 182 cross-linked in the native lignin [6,26,27].
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16 183 Figure 2 illustrates the yields of the major groups of pyrolysis products as well
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18 184 as the variability in the S/G ratio of different wood samples, in both cases
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20 185 showing as error bars the standard deviations calculated from replicated
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22 186 analyses of independent wood samples (two to four).
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30 188 3.1. Data analyses

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32 189 Multivariate data treatments used for unsupervised and supervised
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34 190 classification purposes (principal component analysis and discriminant analysis,
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36 191 respectively) were carried out from standardized matrices (i.e., total
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38 192 abundances considering 100% volatile products, where peak area for
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40 193 levoglucosan was not computed with the total of polysaccharide-derived
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42 194 products, and was not considered in the multivariate data treatments.
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49 196 Large number of exploratory, preliminary treatments (not shown) comparing
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51 197 decreasingly complex matrices of pyrolytic compounds processed by principal
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53 198 component analysis and multidimensional scaling on the whole data matrix
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55 199 coincided in suggesting that the wide chemical diversity provided by analytical
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57 200 pyrolysis was not, by itself, appropriate for optimum differentiation between
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eucalypt samples. On the contrary, a reduced number of diagnostic variables was always better suited for accurate discrimination between wood types.

This fact could be explained as most wood aliphatic pyrolysis compounds—mainly those from carbohydrate—consist of secondary products (alkyl acids, furans, anhydrosugars, etc.) not pre-existing in the wood, i.e., a situation in which the pyrolysis lead to an effect of increasing the complexity of the data matrix without an increase of the information supplied. In fact, in all the models, variables corresponding to carbohydrate-derived products represented spurious information producing a ‘noise’ effect, and final processed data matrix consisted of guaiacol (GU), methylguaiacol (MG), ethylguaiacol (EG), vinylguaiacol (VG), vanillin (VAN), methysyringol (MS), ethysyringol (ES), vinsyringol (VS), acetosyringone (AS) and syringaldehyde (SA). The values in the reduced data set were recalculated as relative abundances (considering 100% methoxyphenols) of selected methoxyphenols.

3.2. Principal components analysis

Principal components analysis applied as exploratory method to assess the origin of the variability between relative abundances of lignin-derived pyrolysis compounds is shown in Fig 3. In order to simplify the scatter diagram, the plots for the sample scores (1) exclusively show centroids calculated as the averages for the five pre-defined sample groups, with error bars in this case showing variability between spatial replications (two to four) of the sample scores in the factorial plane. Principal components explained ca. 38% of the total variance for PC1 and 30% for PC2. Since PC1 and PC2 together explain ca. 70% of the

total variance, it is possible to obtain a reliable representation plotting both variables [28].

The resulting scatterdiagram (Fig. 3a) suggests clear trends, but no sharp sample clusters, mainly reflecting differences between samples of *E. grandis*, and another group including samples of *E. dunnii* and *E. benthamii*.

The compounds more frequent in each group of wood samples are shown as formulae in the plots for component weights (Fig. 3b). For instance, the clearly different group of wood samples from Cerro Largo tends to release after pyrolysis higher yields of VG and AG whereas, in the opposed side, woods from Rio Negro tend to release VS, its highest yields corresponding to Rio Negro I.

3.3. Discriminant analysis

Discriminant analysis suggests successful classification of the wood samples according to the pre-established groups (Fig. 4) since 100% samples were correctly classified. In all cases the best differentiation was between Cerro Largo woods and the other samples, with Rio Negro III woods showing intermediate methoxyphenol signature as regards the remainder samples (Rio Negro I, II and IV).

3.4. Forecasting Models

Apart from the interest of pyrolytic data for chemotaxonomic purposes, the variable importance of the pyrolysis products to forecast pulping efficiency (alkali loading) was examined by simple, multiple and partial least squares regression models.

In a first step, we intended to predict the alkali loading with simple models based on individual compounds which could expectedly behave as proxies for wood composition or lignin condensation, with a presumptive role on the ease to delignification. We also examined variables corresponding to cumulative pyrolysis data for compound families, or ratios between groups of compounds, such as the classical S/G ratio. All these simple models were examined after calculating the correlation matrix with up to 90 variables, followed by supervised examination of the individual regression plots to check for the presence of outliers. Nevertheless, all these simple models displayed a very poor forecasting potential. For instance, the S/G ratio show a weak correlation with the active alkali ($P= 0.049$) after removing two outliers.

These previous results lead to suggest that the ease to delignification behaves as an emergent property which is probably not governed by a principal wood property, but by the synergistic participation of a variable set of structural factors any of them having a decisive influence by itself. Consequently, multivariate models could be superior as regards taking advantage of the large information provided by Py-GC/MS.

In the second step, PLS was used to manage simultaneously the above 90 pyrolytic variables (individual compounds, compound families and and/or ratios) vs the active alkali. Nevertheless, the exploratory models obtained by PLS when using very large sets of variables confirmed the previous results by discriminant analysis with backward variable selection: the best forecasting success was obtained by using the reduced data set consisting of lignin-derived methoxyphenols, with no carbohydrate-derived product. One out of the most significant models (observed vs predicted, P value= 0.0111) is shown in Fig. 5a,

while Fig. 5b shows the variable importance for prediction (VIP) of the compounds introduced in the model. The VIPs highlight the importance of the yields of GU, MS and VS, the coefficients of which in the PLS function explaining most of the variability of the active alkali.

The above results are confirmed and refined by multiple linear regression models, using the variable set suggested by the previous treatments and the backwards automatic variable selection. The significant ($P < 0.05$) model describing the relationship between active alkali and 9 independent variables was $\text{Active_alkali} = 17,53 + 7,21 \cdot \text{GU} - 1,03 \cdot \text{MG} - 3,67 \cdot \text{EG} - 3,46 \cdot \text{VG} + 1,42 \cdot \text{MS} - 0,969724 \cdot \text{ES} - 0,990 \cdot \text{VS}$, which explains 98,9967% of the variability in the dependent variable. As expected, the coefficients and signs of the multiple regression function agree with the VIPs calculated by PLS.

The above fact that only seven phenols, and no carbohydrate-derived product, were sufficient for discriminating between wood types, as well as to forecast the ease of delignification is the line, of studies considering that the 'methoxyphenol pattern' is largely responsive for the origin, transformation extent and presumptive resilience of the material under study [29–32]. To some extent, this may be explained by the distinct origin of the pyrolysis products, i.e., 'primary pyrolytic fragments' in the case of methoxyphenol compounds (reflecting with their structure the original 'building blocks' of the lignin macromolecule), whereas the carbohydrate-derived compounds comparatively consist of 'secondary pyrolysis products' coming from severe pyrolytic cleavage, defunctionalization and rearrangement leading to acetic acid, anhydrosugars, cyclic ketones, furans and other aromatic pyrolysis compounds, in some cases meaningless as biomarkers or signature compounds. This is illustrated with the

classical example that a simple macromolecule such as cellulose, exclusively consisting of β -glucose may yield, under pyrolysis conditions, about hundred pyrolytic compounds [33,34] a situation that, for the present study, is not favorable to gain chemotaxonomic information on pre-existent differences in the wood chemistry of the different eucalypt samples.

4. Conclusions

Levogluconan was in all the cases the most abundant product from woods, followed by lignin pyrolysis fragments (i.e., methoxyphenols) and additional polysaccharide derivatives (furans and cyclic ketones).

Exploratory chemotaxonomical analyses based on the whole pyrolysis compound assemblages showed large internal redundancy, then were found suitable for chemotaxonomic purposes only after suitable data reduction achieved by automatic backward variable selection implemented in multiple correlation and discriminant analyses. In fact, carbohydrate-derived pyrolysis compounds did not supply additional chemotaxonomic information, and in most cases behave as spurious variables.

As regards multivariate forecasting models applied to pyrolysis data from wood samples being very similar each to other, data reduction (instead of managing the maximum number of variables from complex molecular pyrolytic assemblages) was considered the most successful strategy: both the multiple regression models with backwards variable selection as well as the partial least squares regression, led to significant prediction of technical pulping parameters (i.e., active alkali) through models mainly based on the yields of MS, VS, G and EG. Conversely, reliable forecasting (after cross validation) was not possible

with models including much greater number of variables (up to 83 major pyrolysis products). An intermediate situation with only weakly significant forecasting success was using individual compounds—presumptively source origin indicators—or compound ratios such as the classical S/G.

Concerning numerical taxonomy models, the lignin signature expressed as 10 index methoxyphenols (i.e., GU, MG, EG, VG, VAN, MS, ES, VS, AS and SA) suggests that the sources of variability among wood samples were (i) biogeographical differences (probably environmental) between woods, followed by (ii) varietal differences between woods from the same species in different plantations and, finally (iii) differences between eucalypt species.

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TABLES AND FIGURES CAPTIONS

Table 1. Origin of the wood samples studied

Table 2. Main products of wood pyrolysis

Fig. 1. Example of *E. grandis* wood pyrogram (total ion current chromatogram).

The main pyrolysis compounds are labelled on the peaks. Numbers on the peaks correspond to those in Table 2. Major methoxyphenols are also indicated: guaiacol (GU), methylguaiacol (MG), ethylguaiacol (EG), vinylguaiacol (VG), vanillin (VAN), methysyringol (MS), ethysyringol (ES), vinsyringol (VS), acetosyringone (AS) and syringaldehyde (SA).

Fig. 2. Cumulative yields of the major groups of pyrolysis compounds (total abundance as regards total ion chromatographic area), average S/G ratios and the corresponding standard deviations.

Fig. 3. Principal component analysis applied to the classification of wood samples (a). The loading factors of the different variables (methoxyphenols) on the space defined by the two first principal components are shown below (b).

Fig. 4. Sample grouping suggested by discriminant analysis exclusively using as variables pyrolytic methoxyphenols. Circles show group centroids and

whiskers indicate variability limits between spatial replications of each group.

The functions defining the discriminant space are shown in the axes.

Fig. 5. Forecasting pulping parameters (active alkali) by partial least squares regression. Significant ($P= 0.0111$) model based on the pyrolytic yields of guaiacol (GU), methylguaiacol (MG), ethylguaiacol (EG), vinylguaiacol (VG), methysyringol (MS), ethysyringol (ES), vinsyringol (VS), acetosyringone (AS) and syringaldehyde (SA). Plot of average data showing observed vs predicted values (a). Error bars indicate variability limits between replications; (b) bar plot showing the variable importance for prediction (VIP) of the compounds considered in the models (solid bars: positive loadings, dashed bars: negative loadings).

Highlights:

- ⊙ Exploratory chemometric research on the sources of variability in wood composition.
- ⊙ Data reduction strategies removed redundant, spurious and meaningless information.
- ⊙ Ease of delignification can be predicted from a reduced set of 4-10 methoxyphenols.

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Table 1

Origin of the wood samples studied

Sample reference	Species	Age (years)	Origin Location (Uruguay)
1,2,3	<i>E. grandis</i>	10	Rio Negro I
4,5,6	<i>E. grandis</i>	10	Rio Negro I
7,8	<i>E. grandis</i>	10	Rio Negro I
10	<i>E. grandis</i>	10	Rio Negro I
13	<i>E. grandis</i>	10	Rio Negro II
16	<i>E. grandis</i>	10	Rio Negro III
19	<i>E. grandis</i>	10	Rio Negro IV
22	<i>E. grandis</i>	17	Cerro Largo
23	<i>E. dunnii</i>	17	Cerro Largo
24	<i>E. benthamii</i>	6	Cerro Largo

Products of wood pyrolysis

[illegible]

21	1,2-cyclopentanedione	S	☐	☐	☐	☐	☐	☐	-	☐	☐	☐	☐	☐	☐	-
22	2(3 <i>H</i>)-Furanone, 5-methyl-	S	-	-	-	-	-	-	☐	-	-	☐	-	-	-	☐
23	2-Furancarboxaldehyde, 5-methyl-	S	☐	-	-	☐	-	☐	☐	-	☐	-	☐	☐	☐	☐
24	Cyclic ester [caprolactone]	S	-	■	☐	-	-	☐	-	-	-	-	-	-	-	-
25	Cyclopentanone, 2,5-dimethyl-	S	-	-	-	-	-	-	-	-	-	-	-	-	-	-
26	2-Cyclopenten-1-one, 3 methyl-	S	☐	-	-	-	☐	☐	-	-	☐	-	☐	☐	-	-
27	2(5 <i>H</i>)-Furanone	S	☐	☐	☐	☐	☐	-	☐	☐	-	☐	☐	☐	☐	☐
28	1,3-Benzenediol	Ai	-	-	-	-	-	-	-	-	-	-	-	-	-	-
29	2,4-Imidazolidinedione, 3-methyl-	P	☐	☐	☐	☐	-	☐	☐	☐	☐	☐	☐	☐	☐	☐
30	Benzaldehyde, 2-hydroxy-	Ai	-	-	-	-	☐	-	-	-	-	-	-	-	-	-
31	Alkylcyclopentenone	S	-	-	-	☐	-	-	-	-	-	-	-	☐	-	-
32	Alkylcyclopentenone	S	☐	☐	☐	-	☐	☐	☐	☐	☐	☐	☐	-	☐	☐
33	Alkylcyclopentenone	S	-	-	-	-	-	-	-	-	-	-	-	-	-	-
34	Alkylcyclopentenone	S	-	-	-	-	-	-	-	-	-	-	-	-	-	-
35	Alkylcyclopentenone	S	-	-	-	-	-	-	-	-	-	-	-	-	-	-
36	Phenol	Ai	-	-	-	-	-	-	-	-	-	-	-	-	-	-
37	Phenol, 2-methoxy	L-G	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
38	Phenol, 2-methyl	Ai	-	-	-	-	-	-	-	-	-	-	-	-	-	-
39	Alkylcyclopentenone	S	-	-	-	-	-	-	-	-	-	-	-	-	-	-
40	Maltol	S	-	-	-	-	-	-	-	-	-	☐	☐	☐	☐	-
41	2,5-Furandicarboxaldehyde	S	-	-	☐	-	-	-	☐	-	-	-	-	-	☐	-
42	Phenol, 4-methyl	Ai	-	-	-	-	-	-	-	-	-	-	-	-	-	-
43	Phenol, 2-methoxy, 3-methyl	L-G	☐	-	☐	-	☐	☐	☐	-	☐	-	-	-	-	-
44	2(3 <i>H</i>) Furanone (5-butylidihydro-)	S	☐	☐	☐	☐	-	☐	☐	☐	☐	☐	☐	☐	☐	-
45	Phenol, 2-methoxy, 4-methyl	L-G	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
46	Phenol, 2,4-dimethyl	Ai	-	☐	-	☐	☐	-	☐	☐	☐	-	-	-	☐	-
47	3(2 <i>H</i>)-Furanone, 4-methoxy-2,5-dimethyl-	S	☐	☐	☐	☐	-	-	☐	-	☐	☐	☐	☐	-	-
48	4 <i>H</i> -Pyran-4-one-3,5-dihydroxy-2-methyl-	S	☐	☐	☐	☐	-	☐	-	-	☐	-	☐	☐	-	-

[illegible]

77	Propane, 3-methoxy-4 hydroxyphenone	L-G	-	-	-	-	-	-	-	-	-	-	-	-	-	-
78	2,6-Dimethoxy-4-propenylphenol	L-S	-	-	-	-	-	-	-	-	-	-	-	-	-	-
79	2,5-Dihydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one	Ai	□	□	-	□	□	-	-	□	-	□	□	-	□	-
80	Isomer of 75 [methoxyeugenol]	L-G	■	■	■	■	□	□	■	□	□	□	□	□	□	□
81	5,6-Dimethoxy-1-indane	L-S	□	□	□	□	□	□	-	□	□	□	□	□	□	□
82	2-Allyl-1,4-dimethoxy-3-methylbenzene	L-S	□	□	-	-	□	□	□	-	-	□	-	-	-	-
83	2,6-Dimethoxy-4-prop-1-enylphenol	L-S	■	■	■	■	■	■	■	■	■	■	■	■	■	■
84	Benzaldehyde, 4-hydroxy-3,5-dimethoxy- [syringaldehyde]	L-S	■	■	■	■	■	■	■	■	■	■	■	■	■	■
85	Coniferaldehyde	L-G	□	□	□	□	■	□	-	□	□	□	□	□	-	-
86	Carbohydrate-derived (m/z 60)	S	□	-	-	□	-	-	-	□	□	□	-	□	□	-
87	Homosyringaldehyde	L-S	□	□	□	□	■	■	□	□	□	■	■	□	■	■
88	Benzene, 1,2,3-trimethoxy-5-(2-propenyl)-	L-S	□	□	□	□	-	-	-	-	□		□	-	-	□
89	Benzoic acid, 4-hydroxy-3,5-dimethoxy-, methyl ester	L-S	□	□	□	□	□	-	-	-	-	□	□	□	□	-
90	1(3 <i>H</i>) Isobenzofuranone-7-phenyl	S	-	-	-	-	□	-	□	-	-	-	-	□	-	□
91	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	L-S	□	■	□	□	■	■	□	□	■	■	■	■	■	■
92	Syringylacetone	L-S	■	■	□	□	■	■	■	■	■	■	■	■	■	■
93	Propiosyringone	L-S	□	□	-	□	-	-	□	□	□	□	□	□	-	□
94	Synapyl alcohol	L-S	□	□	□	□	□	□	□	□	□	□	□	□	□	□
95	Lipid-derived	Lp	□	-	-	-	-	-	-	-	-	□	□	-	-	-
96	Dihydrosinapyl alcohol	L-S	□	-	-	-	□	□	□	□	□	□	□	□	-	□
97	1,1'-Biphenyl, 5-hydroxy-3,4'-dimethoxy-	L-S	-	-	-	-		-	-	-	-	-	-	-	-	-
98	3,5-Dimethoxy-4-hydroxycinnamaldehyde	L-S	■	-	□	□	□	□	□	□	□	■	■	■	■	■

Origin: L: lignin; (-G: guaiacyl, -S: syringyl), S: carbohydrate; L: lipid; Ai: unspecific aromatic (methoxyl-lacking); P: peptides.
Total abundances referred to total volatile compounds, excluding levoglucosan: - = 0 %; □ = 0–2 %; ■ = >2 %.