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Chemical composition of different morphological parts from 'Dwarf Cavendish' banana plant and their potential as a non-wood renewable source of natural products

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Abstract

The study on chemical composition and structure of components from different morphological parts of 'Dwarf Cavendish' banana plant (petioles/midrib, leaf blades, floral stalk, leaf sheaths and rachis) have been carried out aiming to evaluate their potential as eventual raw materials for the chemical processing. Macromolecular components were analysed using solid-state NMR, ATR-FTIR and wet chemistry methods. Mineral components were assessed by ICP analysis of ashes obtained after raw material calcinations. It was verified that chemical composition of the studied fractions of banana plant varies significantly. The major extremes were found in the contents of cellulose (37.3% in leaf sheaths and only 15.7% in floral stalk), starch (26.3 in floral stalk and 0.4% in petioles/midrib), lignin (24.3% in leaf blades and 10.5% in rachis) and lipophilic extractives (5.8% in leaf blades and 1.2% in petioles/midrib). All morphologic parts of banana plant contained considerable amounts of ashes (from 11.6 to 26.8%) composed mainly by potassium, calcium and silicium salts. The hemicelluloses in banana plant are proposed to be mainly glucuronoxylan and xyloglucan (from 5.5% in floral stalk to 21.5% in petioles/midrib). Rather significant amount of proteins was found in leaf blades (8.3%). Lignin analysis revealed that it is of HGS type with H:G:S proportion ranged of (5–17):(18–54):(35–71). The significant variation of lignin structure among the different morphological parts of banana plant was highlighted. Results of this study allowed some propositions about possible applications of banana plant residues as non-wood renewable source of natural products.
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1. Introduction

Agricultural residues, produced from commercial processing of crop plants, are usually considered of a small inherent value and represent a disposal problem. However, these materials could in many cases represent an abundant, inexpensive and readily available source of renewable lignocellulosic biomass for different purposes. Banana plant is among those raw materials. In the world 4,500,000 ha of cultivated area are occupied by banana plantations (FAO, 2006). The *Cavendish* variety is the most exploited, corresponding to about of 1/3 worldwide production (24,000,000 t/year (FAO, 2006)). After harvesting the single bunch of bananas, a great amount of agricultural residues are produced. These residues are usually left in the soil plantation to be used as organic fertilizer. In terms of dry weight

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material, the *Cavendish* variety produces about 8 t/ha of pseudo-stems, 7.7 t/ha of foliage and ca. 0.5 t/ha of rachis (Soffner, 2001). The development of new applications for these agricultural residues could be an interesting income for banana producers and for a regional economy.

The bibliography covering fundamental aspects of banana plant chemistry is rather scarce and a comprehensive study of its chemistry is certainly missing. Although several studies have been carried out on lignin and polysaccharides structure from leaf sheaths (Oliveira et al., 2006a; Sun et al., 1998a,b, 1999) and on extractives from different parts of banana plant (Oliveira et al., 2005, 2006b), the general chemical composition of all morphological parts of banana plant 'Dwarf Cavendish' (*Musa acuminata* Colla, var. *cavendish*) has not been yet assessed. This knowledge, however, is crucial to define the possible application areas for the rational processing of banana plant residues. Moreover, this information provides fundamentals on eventual possibility of joint or separate processing of banana plant counterparts.

In this paper, the results on the chemical analysis of banana plant 'Dwarf Cavendish' are presented. The banana plant was fractionated into five morphological regions: petioles/midrib, leaf blades, floral stalk, leaf sheaths and rachis. These fractions were chemically and structurally characterised. The chemical composition of macromolecular components in different morphological parts is discussed in the context of their potential applications.

2. Materials and methods

2.1. Sample preparation

Mature banana plants 'Dwarf Cavendish' were randomly selected and harvested from a banana plantation in Funchal (Madeira Island, Portugal). The banana plant was separated firstly in three different morphological regions: pseudo-stems, foliage and rachis. The pseudo-stems were manually separated in leaf sheaths and floral stalk. Foliage was separated in petioles/midrib and leaf blades.

After separation, the five different parts were air dried, during 2 weeks. The humidity of petioles/midrib, leaf blades, floral stalk, leaf sheaths and rachis materials was 89.0, 74.3, 92.9, 91.7 and 93.5%, respectively. All morphological parts were milled in a Retsch AS200 and sieved to 40–60 mesh. These fractions were used in analyses on the chemical composition.

2.2. Chemical analysis

Ash content was determined by complete incineration of sample in a Nabertherm muffle furnace at $600\,°C$ for 6 h. The analysis of mineral part was performed at the "Laboratories of the Service Central d'Analyse of CNRS" (Vernaison, France). The extractives composition was determined by submitting the samples to successive Soxhlet extractions with dichloromethane, ethanol/toluene (1:2, v/v) mixture and water. Then, the extracted plant fraction was air-dried and used in the analytical work carried out. The lignin content was determined using the Klason method (T 204 om-88). The holocellulose was prepared by the peracetic acid method (Evtuguin et al., 2003) and cellulose was isolated by the Kürschner-Hoffer method (Browning, 1967). Holocellulose was fractionated into hemicellulose A, hemicellulose B and α-cellulose by successive extraction, in nitrogen atmosphere, with 5% and 24% KOH aqueous solutions containing 0.014 g/l of $NaBH_4$, respectively (Browning, 1967). The pentosans content was determined using the bromide/bromate method (Obolenskaya et al., 1991) and the iodine colorimetric method (Humphreys and Kelly, 1961) was used to measure starch in different morphological regions of banana plant. Crude proteins content was calculated by converting the nitrogen content ($N \times 4.4$), determined by the Kjeldahl method in a Kjeldahl Selecta Alcodest still equipment (Yeoh and Wee, 1994; Conklin-Brittain et al., 1999). The neutral sugars of the lignocellulosic samples, extractives in water and isolated hemicelluloses were determined after acid hydrolysis as alditol acetates (Blakeney et al., 1983) by gas chromatography (GC), using a HP 5890 chromatograph equipped with a fused silica capillary column J&W DB-225 (30 m × 0.25 mm i.d.; 0.15 μm film thickness). Before samples injection, calibration curves for rhamnose, fucose, arabinose, xylose, mannose, galactose and glucose were obtained using high purity commercial standards. All chemical analyses and fractionation experiments were carried out, at least, in duplicate, and the presented results are the average of the values obtained for each set with a standard deviation minor than 3%.

The permanganate and nitrobenzene oxidations of "in situ" lignins were performed as previously described (Oliveira et al., 2006a).

^{13}C Solid-State NMR spectra were recorded at 100.6 MHz (9.4 T) on a Bruker Avance 400 spectrometer. A 7-mm double bearing Bruker rotor was spun in air at 5.0 kHz. In all experiments the ^1H and ^{13}C 90° pulses were ca. 4 μs. The CP-MAS spectra were recorded with a 5-s recycle delay and a 2-ms contact time.

ATR-FTIR spectra were recorded on a Bruker IFS-55 spectrometer equipped with a Golden Gate Specac. The spectra resolution was $8\,cm^{-1}$ and 256 scans were averaged.

3. Results and discussion

3.1. Spectroscopic characterisation

A preliminary analysis of non-extracted materials from different morphological regions of banana plant has been carried employing ^{13}C CP-MAS NMR (Fig. 1) and ATR-FTIR (Fig. 2) in order to evaluate the specificity of chemical composition of each morphological region. All morphological regions present several signals between 10 and 40 ppm in ^{13}C CP-MAS NMR spectra (Fig. 1),

Fig. 2. ATR-FTIR spectra of fractions from different morphological regions of 'Dwarf Cavendish': (a) petioles/midrib, (b) leaf blades, (c) floral stalk, (d) leaf sheaths and (e) rachis.
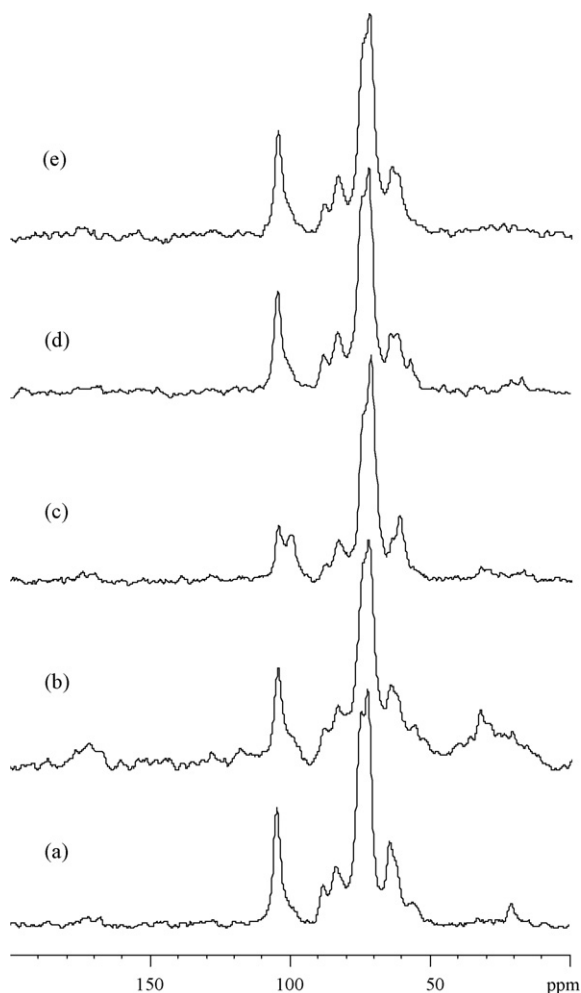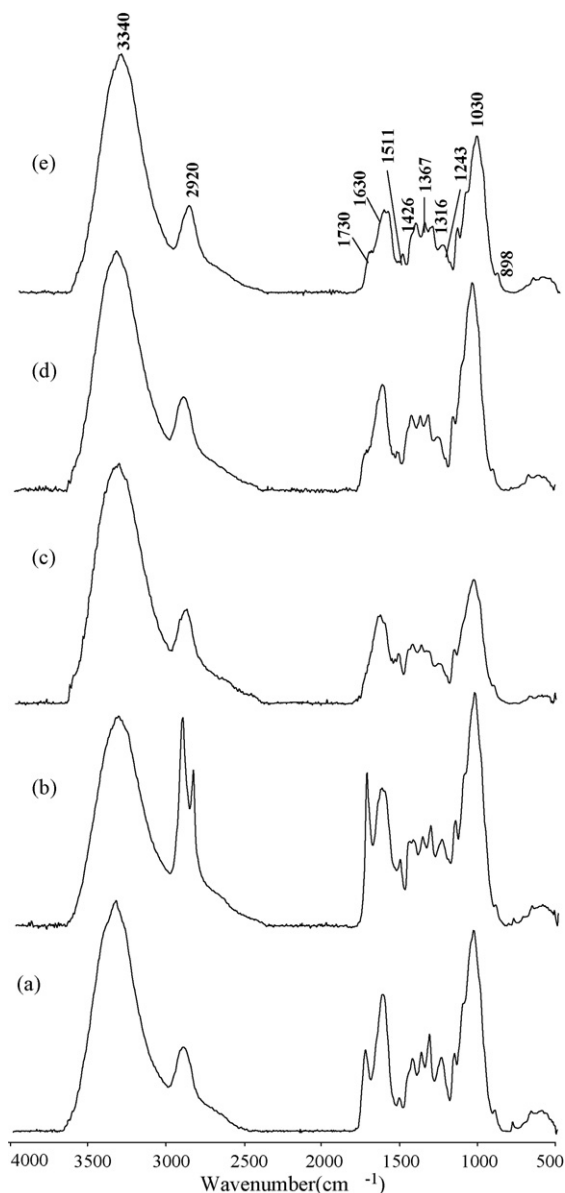
Fig. 1. ^{13}C NMR CP-MAS spectra of fractions from different morphological regions of 'Dwarf Cavendish': (a) petioles/midrib, (b) leaf blades, (c) floral stalk, (d) leaf sheaths and (e) rachis.

which are usually assigned to aliphatic compounds that are easily removed by organic solvent extraction. Indeed, after solvent extraction the intensity of these signals decreased significantly in all fractions (spectra are not shown). However, in the spectrum of leaf blades a set of these signals remained, indicating the eventual presence of aliphatic components covalently bonded to leaf blades cell wall macromolecular components. The group of signals at around 167–170 ppm in ^{13}C solid state NMR spectrum, assigned to the ester groups in aliphatic

components, allows a proposition that leaf blades should be constituted by a cutin/suberin polymer fraction, which is known to appear in the foliage of annual plants and fruits or in tree bark, such as *Quercus suber* L. (Cordeiro et al., 1998). This proposition is corroborated with ATR-FTIR leaf blades spectrum (Fig. 2) showing the strong bands at 2918 and 2850 cm^{-1} (assigned to CH stretching) and the relatively intense band at 1740 cm^{-1} (assigned to C=O in non-conjugated fatty acids) normally present in suberin.

The highly intensive signals at 72–75 and at 103–104 ppm in ^{13}C CP-MAS NMR spectra belongs to C-2,3,5 and C-1, respectively, in hexosans and pentosans (Kolodziejski et al., 1982). The resonance at 63–64 ppm (C-5) indicate the presence of xylans which, probably, are partially acetylated as revealed by the typical signal at 21 ppm in the petioles/midrib spectrum (Fig. 1a), assigned to methyl's resonances in acetate groups of hemicelluloses (Kolodziejski et al., 1982). All ^{13}C CP-MAS NMR spectra showed the presence of cellulose (strong resonances of C-4 at 84 and 89 ppm) that is certainly the major polysaccharide in petioles/midrib, leaf sheaths and rachis (Fig. 1a, d and e). In ATR-FTIR spectra (Fig. 2), the band corresponding to C–H deformation in cellulose at 898 cm^{-1} is very small in floral stalk and leaf blades, which indicates that these morphological parts possess lower cellulose contents. The signal of remarkable intensity at 61 ppm in floral stalk (Fig. 1c) and in leaf sheaths (Fig. 1d) spectra indicates on possibly high amounts of starch (characteristic C-6

resonance, Delval et al., 2004) in these morphological fractions.

The strong peak at 56 ppm, assigned to carbon atom in methoxyl groups of lignin, is present in all ^{13}C CP-MAS NMR spectra, excepting for floral stalk and rachis. This indicates lower lignin content in the latter morphological parts of the banana plant. Resonances at 110–162 ppm, assigned to aromatic carbons from lignin, are rather weak (excluding leaf blades), when compared to polysaccharides signals, indicating on the relatively low lignin contents. Small resonances at 158–162 ppm indicate the presence of *p*-hydroxyphenyl type structures (H type structures) in lignins. Part of these structures belongs to coumarates and/or ferulates as follow from the shoulder at 1630 cm^{-1} in ATR-FTIR spectra, assigned to stretching of conjugated C=C bonds to aromatic ring (Herbert, 1971). The bands at 1367 and 1243 cm^{-1} in ATR-FTIR spectra, assigned to Ar-OCH$_3$ stretching in syringyl and guaiacyl aromatic rings, respectively, indicate that practically in all samples guaiacyl (G) and syringyl (S) type structures are presented simultaneously. Therefore, more likely, lignin in all morphological parts of the banana plant is of HGS type.

3.2. General chemical composition

The results on general chemical composition of different morphological parts of 'Dwarf Cavendish' are presented in Table 1. Practically all fractions of banana plant contained rather notable amounts of ashes

Table 1
Chemical composition of different morphological regions of 'Dwarf Cavendish' (%, w/w of o.d. material)

Components	Petioles/midrib	Leaf blades	Floral stalk	Leaf sheaths	Rachis
Ash	11.6	19.4	26.1	19.0	26.8
Extractives[a]	5.9	16.1	17.6	12.6	17.6
Dichloromethane	1.2	5.8	1.4	1.4	1.5
Ethanol/toluene	0.9	2.6	1.1	2.1	1.4
Water[b]	3.8	7.7	15.1	9.1	14.7
Lignin	18.0	24.3	10.7	13.3	10.5
Insoluble[a]	16.8	22.0	9.8	12.6	9.6
Soluble	1.2	2.3	0.9	0.7	0.9
Holocellulose[a]	62.7	32.1	20.3	49.7	37.9
Hemicellulose A[a]	14.8	6.7	2.8	7.2	3.9
Hemicellulose B[a]	6.7	1.9	2.7	4.2	3.6
α-Cellulose[a]	39.5	20.7	14.4	37.1	28.4
Cellulose[a]	31.0	20.4	15.7	37.3	31.0
Pentosanes[a]	16.2	12.1	8.0	12.4	8.3
Starch	0.4	1.1	26.3	8.4	1.4
Proteins	1.6	8.3	3.2	1.9	2.0

[a] Corrected for ashes content.

[b] Corrected for starch content.

Table 2
Elemental composition of ashes from banana plant fractions (% of ash content)

Elements	Petioles/ midrib	Leaf blades	Floral stalk	Leaf sheaths	Rachis
Si	7.0	24.9	7.8	2.7	1.2
Ca	32.3	8.0	0.6	5.5	0.6
K	9.4	11.6	23.1	21.4	28.0
P	0.7	0.7	0.7	0.9	1.7
Mg	2.9	1.1	0.5	1.9	0.3

(12–27%), which are considerably high when compared with other fast growing plants and which usually vary from about 3% in alpha (*Stipa tenacissima*) (Belgacem et al., 1986) to about 10% in kenaf (*Hibiscus cannabinus*) (Pascoal Neto et al., 1996). The high ash content in floral stalk and rachis (about 27%) is, probably, due to their important function in nutrient transport. The value obtained for ashes in rachis is similar to that found in 'Giant Cavendish' (23%) (Roja and Neves, 2002). SEM microscopy analysis showed small salt crystals over the fibrils of the several fractions (Cordeiro et al., 2006). Elemental analysis of ashes revealed mainly the presence of potassium, calcium and silicium salts (Table 2). Inorganic elements have a negative effect on the kraft pulping (Ilvessalo-Pfäffli, 1995; Obernberger et al., 1997), on chemicals and energy recovery (Keitaanniemi and Virkola, 1982) and paper quality and yield (Jeyasingam, 1988); thus, their high content in banana plant deserves a special attention, especially when applied to pulping. This point may be considered as a serious disadvantage of banana plant as a raw material for pulp and paper production.

As was already discussed based on ^{13}C CP-MAS NMR data, floral stalk and rachis (younger regions with nutrient transport function) present the highest

amount of extractives, ca. 18% (Table 1), whereas, petioles/midrib represented the lowest value (5.9%). These extractive amounts are relatively high when compared with those in wood and annual plants (Atchison, 1993). It is worth notably that in some cases the amount of extractives components can be very high as, for example, for *Cynara cardunculus* and *Arundo donax* (between 12 and 23%) (Pascoal Neto et al., 1997a; Antunes et al., 2000).

Leaf blades presented the highest content of lipophilic extractives (5.8%), which can be problematic if this raw material is used for the pulp and paper production (Back and Allen, 2000). An exhaustive work on the lipophilic extractives composition, recently realized in our laboratory (Oliveira et al., 2005, 2006b), showed high contents of steryl glycosides together with other compounds such as sterol type structures, saturated and unsaturated fatty acids, long chain aliphatic alcohols and cinnamic type acids. Many of these components may be considered as a good source of valuable phytochemicals, which can be used, for example, in functional foods. In this way, extractives can contribute to the valorisation of 'Dwarf Cavendish' plant residues.

A very significant proportion of extractives in different morphologic regions of 'Dwarf Cavendish' are water-soluble compounds, representing totally more than 50% of extractives. The analysis of water-soluble extractives revealed that these are mainly composed of carbohydrates: from 6.4% in rachis to 33.3% in leaf sheaths (Table 3). Among the water-extracted carbohydrates, glucose is the most abundant one in leaf blades (42%), floral stalk (45%) and in leaf sheaths (85%). The high content of glucose in leaf sheaths and floral stalk can also be explained by the presence of starch in these morphological regions in high amounts, as will be discussed below. Uronic moieties and water-soluble tannins

Table 3
Composition of water-soluble extractives from different morphological regions of 'Dwarf Cavendish'

Components	Petioles/midrib	Leaf blades	Floral stalk	Leaf sheaths	Rachis
Ash (%)	68.1	42.7	56.1	49.2	63.9
Sugars (%)	14.9	16.0	14.1	33.3	6.4
Monosaccharides (% molar)					
Rhamnose	1.1	3.0	0.8	0.1	0.3
Fucose	<0.1	<0.1	<0.1	nd	nd
Arabinose	3.8	2.1	2.2	1.2	1.2
Xylose	1.2	0.3	1.3	0.4	0.4
Mannose	1.5	0.5	0.6	1.9	0.6
Galactose	3.6	3.3	2.9	1.5	1.9
Glucose	3.7	6.8	6.3	28.3	1.9
Others (%)	17.0	41.3	29.8	17.5	29.7

(%): based on total water extract; nd: non detected.

were not assessed in this study and designated in Table 3 as others water-soluble extractives.

The values for the lignin content found in banana plant, 11–24%, are those typically reported for a large variety of gramineaceous species and very similar to values found in other annual plants (9–26%) (Pascoal Neto et al., 1996, 1997a; Antunes et al., 2000) or in non-wood fibres (12–24%) (Atchison, 1993). Interestingly, the lignin content varied significantly in different fractions of the banana plant (Table 1). Confirming the previous observations based on ^{13}C CP-MAS NMR spectra, the highest amount of lignin was determined in leaf blades and the lowest in rachis and floral stalk. Due to the small lignin amounts in pseudo-stem (leaf sheaths and floral stalk), this massive part of banana plant is especially interesting for the pulp and paper applications. This was confirmed in our recent studies showed that leaf sheaths can be pulped under relatively soft conditions, with good pulp yield and sufficiently high pulp strength properties (Cordeiro et al., 2004, 2005). It was also proposed that banana plant pulp could be used in papermaking applications alone or in combination with other pulps including recycled fibres (Cordeiro et al., 2005).

The amount of polysaccharides in the studied fractions was estimated based on the holocellulose determination. Thus, petioles/midrib, leaf sheaths and rachis contained the highest amount of holocellulose (62.7, 49.7 and 37.9%, respectively) in contrast to floral stalk containing only 20.3% of holocellulose (Table 1). Roja and Neves (2002) estimated the holocellulose content in rachis from 'Giant Cavendish' of about 33%, which is slightly lower to that obtained in the present work (37.9%). In spite of the low holocellulose content in rachis, its unmodified and modified fibres could find some interesting applications (Faria et al., 2006). The chemical modification of rachis surface with grafting agents allowed the diminishing of surface hydrophilicity, which improved the intersurface interaction with macromolecular matrices possessing a predominantly

dispersive character, such as polypropylene (PP) and maleic anhydride polypropylene (MAPP), natural rubber or lattices (Faria et al., 2006; Cordeiro et al., 2006).

The pentosans content, determined by the bromide/bromate method, showed that petioles/midrib is the morphological region containing the highest amount of pentoses (16.2%), followed by leaf sheaths (12.4%) and leaf blades (12.1%). These results are in agreement with neutral sugars (xylose and arabinose) analysis of the extracted materials summarised in Table 4.

As proposed in the ^{13}C CP-MAS NMR analysis, 'Dwarf Cavendish' should contain starch. The starch presence in floral stalk and leaf sheaths was observed by optical microscopy by lugol coloration of the plant tissues. This was confirmed also by wet chemistry analyses (Table 1). In petioles/midrib, leaf blades and rachis, starch was detected in a very small amount (c.a. 1%), whereas, in floral stalk and leaf sheaths its abundance was rather significant (26.3 and 8.4%, respectively).

Proteins were also detected in banana plant. The results presented in Table 1 were calculated in base of organic N (Kjeldahl N) through a conversion factor of 4.4, determined for several taxonomic groups as a good estimate of the protein content in plants (Yeoh and Wee, 1994; Conklin-Brittain et al., 1999). As expected, leaf blades presented the highest protein content (8.3%), followed by floral stalk (3.2%). The protein content obtained for leaf blades are similar with that presented by other leaf plants (Conklin-Brittain et al., 1999).

3.3. Isolation and characterisation of polysaccharides

The monosaccharides composition in different morphological regions of 'Dwarf Cavendish' is presented in Table 4. The neutral sugars analysis showed that proportion of glucose and xylose ranged from 9–24 to 60–80%, respectively, of total sugars. Arabinose was the third most abundant sugar in almost all the morphological regions, with highest contents in leaf blades (5.3% in

Table 4
Monosaccharides composition (%) in different morphological regions of 'Dwarf Cavendish'

Monossacharide	Petioles/midrib	Leaf blades	Floral stalk	Leaf sheaths	Rachis
Rhamnose	0.4 (0.8)	0.3 (0.9)	0.3 (0.7)	0.4 (0.8)	0.3 (0.7)
Arabinose	2.6 (4.9)	5.3 (15.5)	2.3 (5.1)	4.0 (7.5)	1.7 (4.1)
Xylose	12.4 (23.6)	6.0 (17.5)	4.2 (9.3)	7.3 (13.8)	5.8 (14.0)
Mannose	0.8 (1.5)	0.8 (2.3)	1.0 (2.2)	0.8 (1.5)	1.2 (2.9)
Galactose	0.6 (1.1)	1.3 (3.8)	1.3 (2.9)	1.2 (2.2)	0.7 (1.7)
Glucose	35.8 (68.1)	20.5 (60.0)	36.0 (79.8)	39.4 (74.2)	31.8 (76.6)
Total	52.6	34.2	45.1	53.1	41.5

The values in parentheses are the molar proportions.

raw material). Mannose, galactose and rhamnose are also present of about 1%, whereas, fucose has been detected in trace amounts. Overall, these data evidence that xylose and glucose are the most abundant monosaccharides though cellulose is not a unique source of glucose, i.e. several hemicelluloses can also give glucose in monosaccharide analysis.

In order to estimate the proportion of different hemicelluloses, the rough fractionation has been carried out to separate acidic and neutral hemicelluloses. Table 1 summarises the results on polysaccharides fractionation by sequential extraction of holocellulose with 5% KOH aqueous solution (Hemicellulose A or HA) and 24% KOH aqueous solution (Hemicellulose B or HB). Normally, the amount of Hemicellulose A corresponds to the abundance of acidic glucuronoxylan in the plant material and the amount of Hemicellulose B indicates predominantly the contribution of glucomannan or other neutral hemicelluloses.

The fraction of HA was predominant (ca. 3–15% o.d. material), representing 51–71% of the total amount of the extracted hemicelluloses, and composed, probably, with acidic glucuronoxylans as the most abundant hemicelluloses. At the same time, the ratio HA/HB varied significantly in different morphological parts of banana plant indicating a notable change in hemicelluloses composition. Thus, HA/HB ratio was rather high in petioles/midrib, leaf blades and leaf sheaths fractions and practically close to 1 in floral stalk and rachis. The analysis of monosaccharide composition of HA and HB fractions (Table 5) allowed some propositions about hemicellulose composition. Thus, HA fraction of leaf blades and leaf sheaths contain remarkable proportion of arabinose, which may be tentatively explained by the presence of pectic compounds in these fractions. Indirectly, the significant amounts of pectin in these morphological parts of banana plant, mainly in leaf blades, are evidenced by strong signals at 170–172 ppm of ^{13}C CP-MAS spectra. However, the presence of unusual

arabinoglucuronoxylan with high proportion of arabinofuranose substitutes to xylan backbone is not also excluded. The relatively high proportion of xylose in HB fractions may be, at least partially, due to incomplete xylan extraction during HA isolation. However, rather high proportion of glucose allows the proposition about the presence of significant amounts of xyloglucans in all HB fractions, excepting in petioles/midrib. The chemical structure of HA and HB, however, should be studied in more details and this work is in progress.

The content of α-cellulose varies from 14 to 40% in the different fractions of banana plant showing the highest values for petioles/midrib, leaf sheaths and rachis (39.5, 37.1 and 28.4%, respectively). These values are coherent with those obtained for Kürschner-Hoffer cellulose (Table 1).

3.4. Characterisation of "in situ" lignins by degradation methods

The preliminary data about the presence of H, G and S units in banana plant obtained by ^{13}C CP-MAS NMR and ATR-FTIR spectroscopy were confirmed by degradation chemical techniques (nitrobenzene and permanganate oxidation). The molar ratios (H:G:S) were found to be 5:36:59, 6:54:40, 17:48:35, 12:25:63 and 11:18:71 for petioles/midrib, leaf blades, floral stalk, leaf sheaths and rachis, respectively, as assessed by nitrobenzene oxidation (NO). Hence, petioles/midrib, leaf sheaths and rachis fractions are especially rich in S units.

The analysis of permanganate oxidation (PO) products arisen from lignin of the different banana plant morphological fractions allowed the identification and quantification of several substructures (Table 6 and Fig. 3). Products **1**, **2** and **3** arise from non-condensed lignin of H, G and S type units, respectively. The notable proportion of H units giving product **1** is probably due to the presence of *p*-coumaric acid type structures detected by ATR-FTIR (see discussion above). A small proportion

Table 5

Monossacharides composition in hemicelluloses A and B (HA and HB, respectively) from different morphological regions of 'Dwarf Cavendish' (molar proportions, %)

Monosaccharide	Petioles/midrib		Leaf blades		Floral stalk		Leaf sheaths		Rachis	
	HA	HB	HA	HB	HA	HB	HA	HB	HA	HB
Rhamnose	0.6	0.6	0.4	0.5	0.8	0.4	0.5	0.4	1.5	0.4
Arabinose	16.2	8.7	31.7	5.4	4.2	0.9	27.5	4.1	6.3	1.2
Xylose	77.7	68.8	52.5	40.4	35.1	29.8	57.0	52.3	72.6	50.4
Mannose	<0.1	2.0	1.1	6.4	1.6	4.4	0.2	0.9	1.0	2.1
Galactose	2.9	2.9	5.2	2.8	2.3	3.0	6.9	4.1	2.9	4.4
Glucose[a]	2.6	17.0	9.1	44.5	56.0	61.5	7.9	38.2	15.7	41.5

[a] Corrected for starch content.

Table 6
Molar proportions (%) of permanganate oxidation products from different morphological regions of 'Dwarf Cavendish'[a]

Compound	Petioles/midrib	Leaf blades	Floral stalk	Leaf sheaths	Rachis
1	25	18	31	46	53
2	53	54	40	31	24
3	7	6	4	6	10
4	5	7	8	6	4
5	2	1	1	<0.5	1
6	1	5	7	2	1
7	4	6	8	7	4
8	1	1	1	1	1
9	2	2	<0.5	1	2
H:G:S	25:66:9	18:70:12	31:58:11	46:46:8	53:35:12

[a] See Fig. 3 for structure assignments.

of terminal phenolic S units may explain a rather small proportion of product **3**, when compared to NO data, since only free phenolic lignin units are accessible for PO (Gellerstedt, 1992; Chen, 1992). Among condensed structures those giving products **4** (β-5′ structures), **6** (presumably of phenylisochroman type) and **7** (biphenyl 5-5′ type) in PO analysis were the most abundant (Table 6). Products **4**, **6**, and **7** were especially abundant in lignin of leaf sheaths, leaf blades and floral stalk. The abundance of diaryl ether structures of 4-*O*-5′ type (product **9**) in all fractions of banana plant was

rather small (1–2 mol%). The frequency of occurrence of condensed structures, defined as sum of products **4**–**9**, was highest in leaf blades and floral stalk and lowest in rachis and petioles/midrib.

The detection of product **A** (Fig. 3) among PO products indicates the presence of condensed tannins of catechin type in the banana plant, mainly in leaf blades and floral stalk. The presence of this structure shows that the exhaustive water extraction was not completely efficient to remove the polyphenolic compounds. In order to remove them, banana plant fractions should be submitted
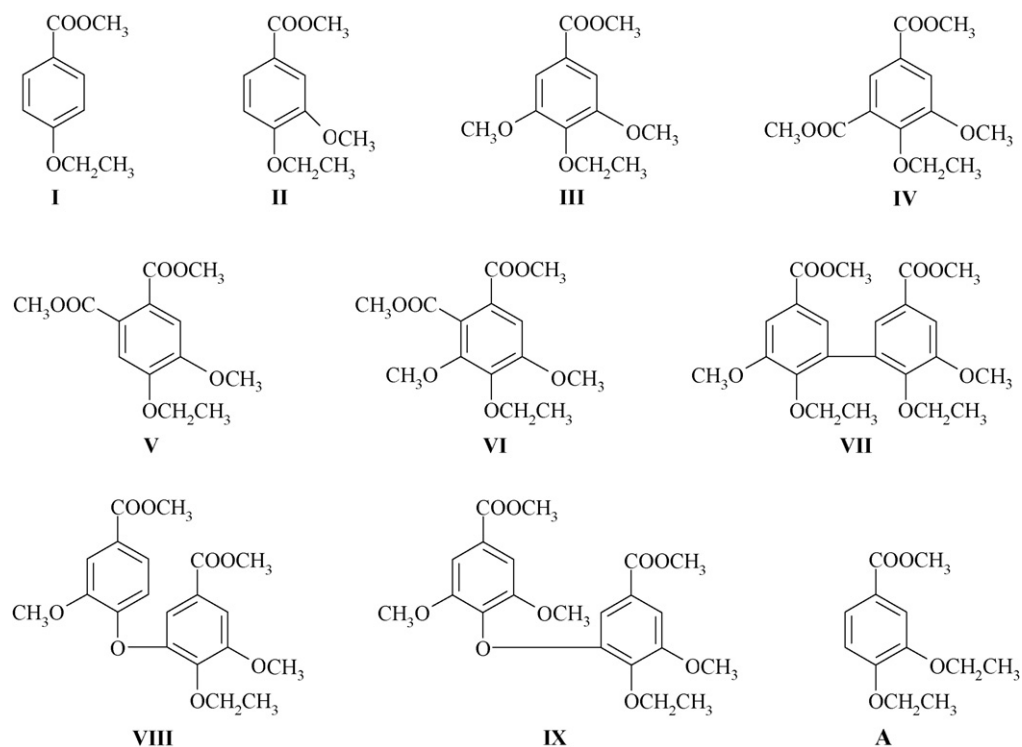

Fig. 3. Permanganate oxidation products from different morphological fractions of banana plant.

previously to an alkaline pre-extraction, as it is applied for wood and annual plants containing condensed tannins (Pascoal Neto et al., 1997b; Evtuguin et al., 2001).

Data obtained on lignin structure in different morphological regions of the banana plant allows the proposition about their different responses in the chemical processing, especially as the pulping is concerned. Among the several parameters that may affect pulp production and the quality of the final products of the pulping process, the composition of lignin is relevant. In general, the efficiency of pulping is directly proportional to the amount of syringyl (S) units in lignin, whereas, the increase of proportion of guaiacyl (G) units having a free C-5 position available for carbon-carbon interunit bonds makes them fairly resistant to lignin depolymerization in pulping (Sun et al., 2003; Gutierrez et al., 2004). In this context the envelopment of leaf sheaths and rachis in pulping processes looks attractive, whereas, the pulping of leaf blades and floral stalk should be much more problematic. In contrast, the presence of high lignin concentrations is beneficial regarding, for example, the fibreboard production. The lignin has excellent compatibility with the thermosetting resins commonly used in product manufacture and contributes itself as an adhesive material (Donaldson et al., 2001). Hence, petioles/midrib and leaf blades possessing additionally long fibres may be good candidates for this application.

4. Conclusion

The chemical composition of the different morphologic regions of banana plant 'Dwarf Cavendish' (*Musa acuminata* Colla, var. *cavendish*) has been evaluated aiming to estimate their potential applications. All fractions (petioles/midrib, leaf blades, floral stalk, leaf sheaths and rachis) were characterised on carbohydrates, lignin, extractives, proteins and ash content. The results of analyses showed a remarkable variability in structure and the amounts of the main macromolecular constituents. It was suggested that the rather high content of mineral elements in different morphological parts of the banana plant (from 11.6 to 26.8%) could create problems for their chemical processing. Previous successful kraft pulping of pseudo-stem was explained by relatively low content (about 13%) and particular structure of lignin (high content of S units and low condensation degree) in leaf sheaths of the banana plant as well as by relatively high cellulose content (>37%). On the other hand, floral stalk, the other counterpart of pseudo-stem, differs significantly from leaf sheaths and contains a high proportion of condensed G-type lignin, starch and a low proportion of cellulose. Therefore, the joint cooking of floral stalk and leaf sheaths can lead to the deterioration of the pulping efficiency indicating that these two parts of pseudo-stem (leaf sheaths and floral stalk) should be separated before the pulping. For the same reasons petioles/midrib and leaf blades should be separated from the material to be submitted for the pulping. The latter banana plant fractions, however, may find interesting applications in biocomposites. Floral stalk contains rather impressive amounts of starch (>26%) and is potentially an interesting source for different food and technical needs. Leaf blades contain, according to recently published results, unusual high amounts of lipophilic extractives, namely steryl glycosides that are valuable additives in functional food products. Most of banana plant fractions contained also remarkable amounts (up to about 22%) of structural hemicelluloses (probably xylan and xyloglucan), which structure was not been yet assessed. More structural studies are in progress in order to find better/new applications for this non-wood renewable source.

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