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High valuable compounds from the unripe peel of several *Musa* species cultivated in Madeira Island (Portugal)

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ABSTRACT

The lipophilic extractives of the unripe peel of ten banana cultivars belonging to the *Musa acuminata* and *Musa balbisiana* species (namely 'Giant Cavendish', 'Chinese Cavendish', 'Grand Nain', 'Gruesa', 'Williams', 'Ricasa', 'Eilon', 'Zelig', 'Dwarf Red' and 'Silver') were studied by gas chromatography–mass spectrometry. The extractives content were in the range of 2–3% with substantially higher values for 'Silver' and 'Dwarf Red' (5.7 and 10.7% respectively). Sterols and fatty acids were the major families of compounds identified, with respectively 55.1–87.5% and 10.6–43.2% of total of lipophilic components. Cycloeucalenone was the main component identified in 'Williams' and 'Dwarf Red', with abundances ranging from 806 to 9453 mg Kg^{-1} of dry unripe peels, respectively. The identification of high contents of valuable compounds, can open new strategies for the valorization of the studied banana residues and particularly of those from 'Dwarf Red' followed by 'Silver' and 'Ricasa', as potential sources of high-value phytochemicals.

1. Introduction

Banana and plantain (*Musa spp.*) are major tropical and subtropical sources of food and raw materials. Bananas are cultivated in over 130 countries and grow over a harvested area of approximately 10 million hectares. The annual world production accounts for about 80 million tons, with India as the major producer with about 26 million tons (FAO, 2009).

The genus *Musa* is composed of four sections: Australimusa, Callimusa, Musa and Rhodochlam. Most edible bananas are originated from two species of the section Musa: *M. acuminata* and *M. balbisiana*. The cultivars are either hybrids among subspecies of *M. acuminata* (ploid type A) or between *M. acuminata* and *M. balbisiana* (ploid type B). The most important banana cultivars are triploid AAA and plantains are mostly AAB, ABB or BBB (Ball et al., 2006). Due to the difficulty of breeding infertile plants, only a few cultivars have been introduced in the last 50 years. The advent of clonal propagation, combined with selection programs, led to the singling out of "elite" clones in terms of yield and fruit quality, adapted to the agro-ecological conditions.

Banana crop was introduced in Madeira Island in the sixteenth century and nowadays banana plantations occupy about 11% of agricultural area and represent 20% of the agricultural production and 1/3 of the exports of the Island. Finally, this plantation is currently considered as essential to protect the natural landscape of the region (Ribeiro and Silva, 1998).

The cultivar 'Dwarf Cavendish' is the most important, comprising ca. 60% of the total banana production in Madeira. However, recent changes in European Union Policies prompt farmers to select and grow other varieties (Council Regulation, 2006). As a response, new banana cultivars have been introduced in the region and some of them have already been released to farmers (Ribeiro and Silva, 1998).

After harvesting of the single bunch of bananas, a huge amount of residues are produced (banana plant and unripe banana residues). The banana plant residues (pseudostem, foliage, and rachis) are usually left in the soil plantation and used as fertilizer. The unripe banana residues are produced mainly during their selection process in the collection stations where the bananas too small for shipping or those with damaged or spoiled areas, are removed. These rejected bananas are normally improperly disposed, causing environmental problems. Different strategies have been suggested for the valorization of these wastes such as in flours, dried pulps, jams in animal feed or eventually composted (Zhang

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et al., 2005); for the production of biofuels (Bardiya and Somayaji, 1996; Hammond et al., 1996; Tewari et al., 1986), or as adsorbents for water purification (Annadurai et al., 2002, 2003). Finally, banana peel extracts were also used for phytopharmaceutical applications (Gene, 1999).

In a previous study, we reported a detailed study on the lipophilic extracts from unripe pulp and peel of banana fruit of 'Dwarf Cavendish' (Oliveira et al., 2008), where high amounts of fatty acids and particularly, free sterols, steryl esters, and steryl glucosides were found.

The importance of banana crops in Madeira Island and the detection of valuable compounds in 'Dwarf Cavendish' extracts (Oliveira et al., 2008), lead us to study new varieties introduced in Madeira Island in order to access their potential as sources of high value phytochemicals with nutraceutical applications. Banana peels lipophilic extracts from ten subspecies of *M. acuminata* (AAA) and hybrids from *M. acuminata* and *M. balbisiana* (AAB and ABB), namely 'Giant Cavendish', 'Chinese Cavendish', 'Grand Nain', 'Gruesa', 'Williams', 'Ricasa', Eilon', 'Zelig', 'Dwarf Red' and 'Silver' were surveyed in the present study by gas chromatography–mass spectrometry (GC–MS) analysis.

2. Material and methods

2.1. Chemicals

Dichloromethane (99% purity), pyridine (99% purity), *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (99% purity), trimethylchlorosilane (99% purity), stigmasterol (95% purity), octadecanoic acid (99% purity), nonadecanol (99% purity), coniferyl alcohol (98% purity) and tetracosane (99% purity) were supplied by Sigma Chemicals Co. (Madrid, Spain).

2.2. Samples preparation

Ten varieties of unripe bananas from the Bananiculture Center of the Regional Government, Lugar de Baixo, in the Madeira Island, were selected: 'Chinese Cavendish', 'Giant Cavendish', 'Dwarf Red', 'Grand Nain', 'Eilon', 'Gruesa', 'Silver', 'Ricasa', 'Williams' and 'Zelig'. For each variety a minimum of 50 unripe fruits were collected. Peels were separated from the fruit, cut, lyophilized and milled to pass through a 40–60 mesh sieve.

2.3. Extraction

Three powdered samples (20 g) of each cultivar were Soxhlet extracted with dichloromethane (600 mL) for 6 h. The solvent was evaporated to dryness, the lipophilic extracts were weighed and the results were expressed in percent of dry material. Dichloromethane was selected as a fairly specific solvent for lipophilic extractives isolation for analytical purposes.

2.4. GC–MS analysis

Before GC–MS analysis, two aliquots of each dried extract (20 mg each) and an accurate amount of internal standard (tetracosane, 0.25–0.50 mg) were dissolved in 250 μl of pyridine. The compounds containing hydroxyl and carboxyl groups were converted into trimethylsilyl (TMS) ethers and esters, respectively, by adding 250 μl of *N*,*O*-bis(trimethylsilyl)trifluoroacetamide and 50 μl of trimethylchlorosilane, standing the mixture at 70 °C for 30 min (Freire et al., 2002a). The derivatized extracts were analyzed by GC–MS following previously described methodologies (Freire et al., 2002a; Oliveira et al., 2008) on a Trace Gas Chromatograph 2000 Series, equipped with a Thermo Scientific DSQII single-quadrupole mass spectrometer and a DB-1 J&W capillary column (30 m × 0.32 mm inner diameter, 0.25 μm film thickness). The chromatographic conditions were as follows: initial temperature, 80 °C for 5 min; temperature gradient, 4 °C/min; final temperature, 260 °C; temperature gradient, 2 °C/min; final temperature, 285 °C for 8 min; injector temperature, 250 °C; transfer-line temperature, 290 °C; split ratio, 1:33.

To check the presence of esterified structures, samples were also analyzed with a DB-1 J&W capillary column (15 m × 0.32 mm inner diameter, 0.25 μm film thickness); the chromatographic conditions were as follows: initial temperature, 100 °C for 3 min; temperature gradient, 5 °C/min; final temperature, 340 °C for 12 min; injector temperature, 290 °C; transfer-line temperature, 290 °C; split ratio, 1:33.

Compounds were identified as TMS derivatives by comparing their mass spectra with the GC–MS spectral library (Wiley-NIST Mass Spectral Library, 1999), their characteristic retention times obtained under the described experimental conditions (Oliveira et al., 2006, 2008), by comparing their fragmentation profiles with published data (Freire et al., 2002a; Oliveira et al., 2006, 2008; Villaverde et al., 2009 and references therein) and by injection of standards.

For semi-quantitative analysis, GC–MS was calibrated with pure reference compounds, representative of the major lipophilic extractive families (stigmasterol, octadecanoic acid, ferulic acid and nonadecan-1-ol), relative to tetracosane. The respective response factors were calculated as an average of six GC–MS runs. For tocopherols the response factor of stigmasterol was used. Each aliquot was injected in triplicate. The presented results are the average of the concordant values obtained for the six aliquots (less than 5% variation between injections of the same aliquot and between aliquots of the same banana variety extracts).

3. Results and discussion

The lipophilic extractives yields obtained for the banana peels from the different studied cultivars (Fig. 1) are in general very similar between them accounting for around 3% of the dry material weight, with the exception of 'Williams', 'Silver' and 'Dwarf Red' cultivars that presented 2.0, 5.7 and 10.7% of lipophilic extractives, respectively. These values are generally in good agreement with those previously reported for other *Musa* varieties (Goldstein and Wick, 1969; Oliveira et al., 2006, 2008), although the high extractives content of 'Dwarf Red' is particularly worth of note in the context of this study.

The GC–MS analysis of the lipophilic extracts of the banana peels from the different cultivars shows that they are composed mainly by sterols, followed by fatty acids, aliphatic alcohols and α-tocopherol (Fig. 2 and Table 1). Minor amounts of *trans*-ferulic acid were also detected in all samples. This composition and relative abundances are concordant with that reported for 'Dwarf Cavendish' (Oliveira et al., 2008). The relative abundance of the identified compounds and their families is in general very similar between all samples, except for 'Dwarf Red', Silver' and 'Ricasa' that presented higher sterols contents. Therefore, these results indicated that the *Musa balbisiana* cultivars ('Dwarf Red' and 'Silver') are richer in sterols than the *Musa acuminata* counterparts (the rest of studied species).

As already referred, sterols (Table 1 and Fig. 2) are the main class of compounds present in the unripe banana peels, with total contents between 55.1 and 87.5% of the total lipophilic extractives identified (2.8–12.4 g/kg of dry material), with the extreme values recorded for 'Giant Cavendish' and 'Dwarf Red', respectively. Cycloeucalenone (Fig. 3) is the major component of this family identified in all peel samples, representing between 46.8 ('Gruesa') and 76.4% ('Dwarf Red') of total sterols contents and

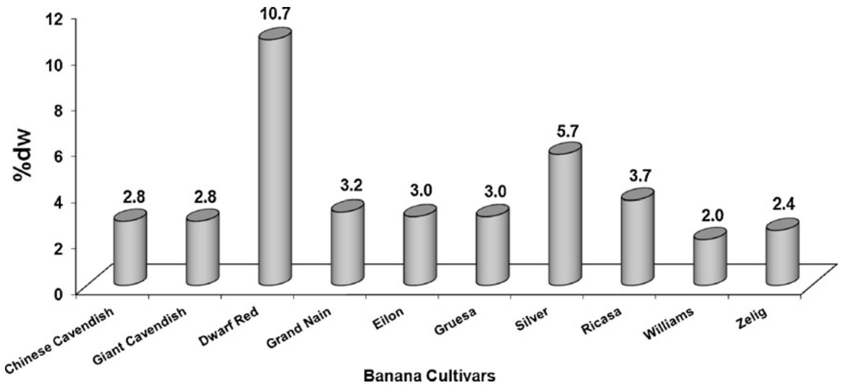

Fig. 1. Dichloromethane extractive yields in dry material % for each unripe peel, from the studied cultivars.

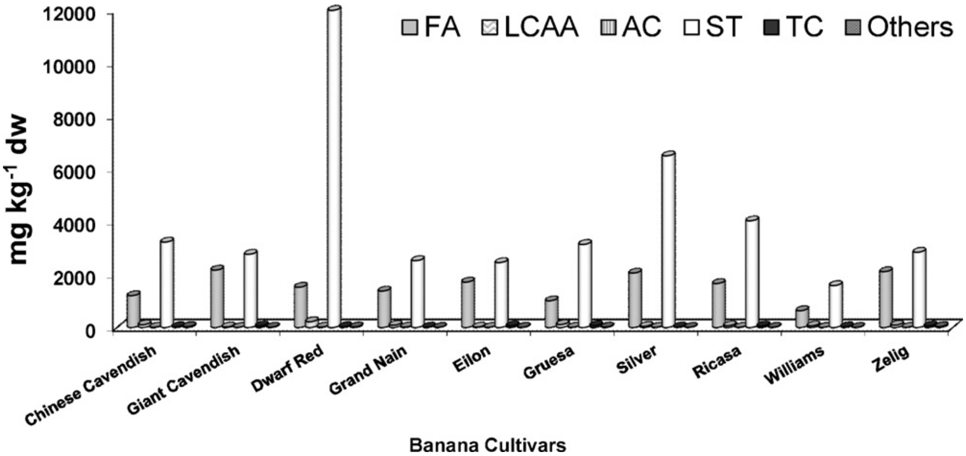

Fig. 2. Families of compounds identified in the dichloromethane extracts. FA, fatty acids; LCAA, long-chain aliphatic alcohols; AC, aromatic compounds; ST, sterols; TC, tocopherols.

between 26.8 ('Zelig') and 65.8% ('Dwarf Red') of the total lipophilic extractives (Table 1). Other abundant identified sterols included 31-norcyclolaudenone (199–1975 mg kg^{-1} of extracts), stigmasterol (194–373 mg kg^{-1} of extracts), β-sitosterol (269–601 mg kg^{-1} of extracts), campesterol (110–741 mg kg^{-1} of extracts) and smaller amounts of cycloeucalenol and cycloartenol (Fig. 3).

Cycloeucalenone and 31-norcyclolaudenone are two isomeric steroid ketones previously identified in banana peel, pulp, flowers, petioles/midrib, leaf blades/sheaths, floral stalk and rachis of some *Musa* species (Akihisa et al., 1986; Banerji et al., 1982; Knapp and Nicholas, 1969; Oliveira et al., 2006, 2008). In fact, these two compounds have been detected in the unripe peel of 'Dwarf Cavendish', as the most important exploitable compounds, with 6.5 and 2.1 g/kg of dry material (Oliveira et al., 2008). β-sitosterol, stigmasterol and campesterol are also abundant sterols in all the studied banana peels (Table 1). These sterols are frequently found in tissues and

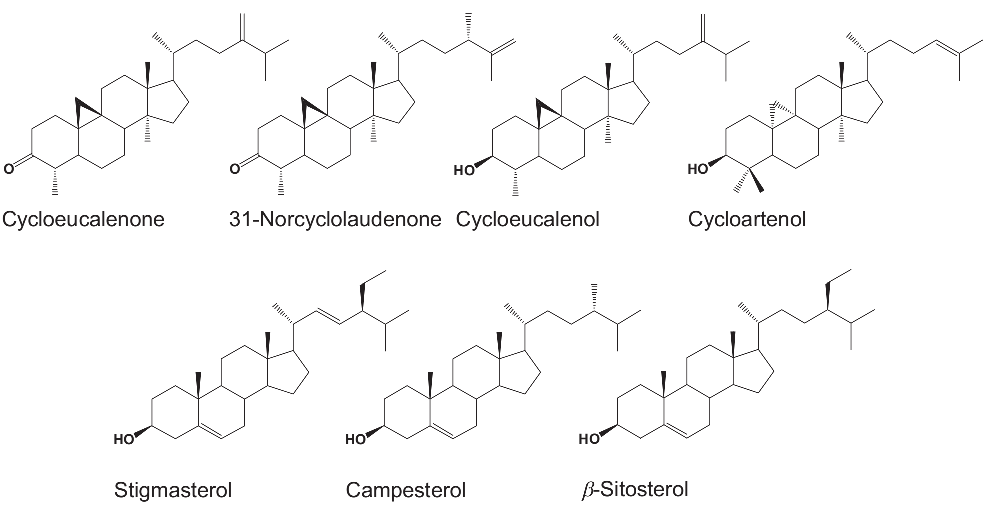

Fig. 3. Structures of the sterols identified in the cultivars studied.

Table 1
Compounds identified in the dichloromethane extracts of unripe peel from banana cultivars expressed in mg kg^{-1} of dry material.

rt (min)	Compound	'Chinese Cavendish'	'Giant Cavendish'	'Dwarf Red'	'Grand Nain'	'Eilon'	'Gruesa'	'Silver'	'Ricasa'	'Williams'	'Zelig'
	Fatty acids	1207	2174	1528	1382	1723	1013	2064	1669	639	2116
	Saturated	760	780	1057	506	599	550	1017	591	351	1146
9.3	Octanoic acid	6	2	21	6	2	3	27	4	3	5
11.5	Dodecanoic acid	3	3	22	6	3	5	11	6	3	4
16.4	Tetradecanoic acid	7	6	22	7	9	9	13	13	5	9
18.6	Pentadecanoic acid	14	15	11	10	13	9	14	15	7	20
20.7	Hexadecanoic acid	533	588	582	373	446	328	752	418	244	803
22.8	Heptadecanoic acid	24	16	11	18	15	22	14	17	9	30
24.7	Octadecanoic acid	55	61	51	32	42	42	67	44	26	80
26.6	Nonadecanoic acid	10	4	7	7	3	11	11	8	5	12
28.4	Eicosanoic acid	22	30	23	0	28	55	20	26	20	89
31.8	Heneicosanoic acid	11	8	33	15	6	11	18	10	2	11
33.4	Docosanoic acid	8	5	11	4	3	8	6	5	2	9
35.0	Tricosanoic acid	21	17	102	8	13	14	25	10	10	32
36.5	Tetracosanoic acid	6	4	7	2	2	5	5	2	3	10
38.0	Pentacosanoic acid	12	10	124	5	6	11	13	5	5	14
39.4	Hexacosanoic acid	4	3	5	0	0	3	1	0	0	4
43.4	Triacontanoic acid	24	8	25	13	8	14	20	8	7	14
	Unsaturated	430	1383	430	860	1118	442	1024	1065	281	959
20.2	Hexadec-9-enoic acid	6	9	14	8	9	7	8	17	3	9
23.9	Octadeca-9,12-dienoic acid	185	518	160	357	427	165	443	441	104	408
24.0	Octadeca-9,12,15-trienoic acid	202	762	177	439	631	220	486	542	155	491
24.2	Octadec-9-enoic acid	37	94	79	56	51	48	87	65	19	51
	Diacids	13	9	36	14	6	13	22	11	6	7
15.4	Nonadioic acid	10	8	35	11	6	7	22	10	4	7
16.6	Decanedioic acid	3	1	1	3	0	6	0	1	2	0
	ω-Hydroxy acids	4	2	5	2	0	8	1	2	1	4
37.3	22-Hydroxydocosanoic acid	4	2	5	2	0	8	1	2	1	4
	Long chain aliphatic alcohols	107	20	220	86	16	114	44	65	62	91
19.0	Hexadecan-1-ol	23	1	10	35	4	17	4	12	14	22
22.4	(Z)-octadec-9-en-1-ol	48	2	4	14	2	43	4	5	32	40
23.1	Octadecan-1-ol	16	1	1	22	2	20	4	34	9	13
30.4	Docosan-1-ol	3	2	22	3	1	8	6	2	1	1
33.7	Tetracosan-1-ol	5	3	130	4	2	8	11	4	1	4
39.6	Octacosan-1-ol	12	11	53	8	5	18	15	8	5	11
	Aromatic compounds	8	3	14	15	6	7	7	8	2	5
21.6	Trans ferulic acid	8	3	14	15	6	7	7	8	2	5
	Sterols	3238	2775	12,378	2535	2461	3149	6488	4025	1591	2854
40.4	Campesterol	166	155	741	111	139	206	133	167	110	181
41.0	Stigmasterol	328	272	206	211	250	373	198	304	194	334
41.3	31-Norcyclolaudenone	338	372	1357	371	351	474	1975	336	199	409
41.5	Cycloeucalenone	1835	1484	9453	1397	1331	1473	3713	2569	806	1376
41.8	β-Sitosterol	506	451	535	413	378	554	435	601	269	506
42.3	Cycloeucalenol	31	20	86	32	5	32	34	23	7	26
42.4	Cycloartenol	34	21	0	0	7	37	0	25	6	22
	Tocopherols	31	63	30	14	64	73	20	59	27	63
39.1	α-Tocopherol	31	63	30	14	64	73	20	59	27	63

fruits of tropical plants, including bananas (del Río and Gutiérrez, 2006; Oliveira et al., 2006) and in plants in general.

Long chain fatty acids account for 639–2174 mg kg^{-1} of dry peels for 'Williams' and 'Giant Cavendish', respectively (Table 1 and Fig. 2). The identified components ranged from octanoic to triacontanoic acids, including four unsaturated structures (C16 and C18), two diacids (nonadioic and decanedioic acids) and an ω-hydroxy fatty acid (Table 1). The presence of ω-hydroxy fatty acids in banana peels has been previously reported in other *Musa* varieties (del Río and Gutiérrez, 2006; Oliveira et al., 2006). Hexadecanoic acid is the most abundant saturated fatty acid, with the highest content observed in the cultivar 'Zelig' (803 mg kg^{-1} of dry peel) and the lower in the 'Williams' (244 mg kg−1 of dry peel). Regarding the unsaturated fatty acids, they found to be very abundant, especially in 'Giant Cavendish', 'Eilon', 'Ricasa' and 'Silver' banana peels, with 1383, 1118, 1065 and 1024 mg kg^{-1} of dry material, respectively; highlighting the content of octadeca-9,12,15-trienoic (linolenic) acid (762 mg kg^{-1} of dry peel) in the 'Giant Cavendish'. Diacids and ω-hydroxy acids were identified in minor amounts. In addition, a considerable number of odd numbered chain fatty acids, ranging from pentadecanoic acid to pentacosanoic acid, were also identified. Tricosanoic and pentacosanoic acids, in particular, were found among the major components in the 'Dwarf Red' peel, with 102 and 124 mg kg^{-1} of dry material, respectively. These compounds are frequently found in other plants belonging to the *Musaceae* family (del Río and Gutiérrez, 2006), and we have previously reported their presence in different morphological parts and fruits of 'Dwarf Cavendish', with values ranging from trace quantities for the nonanoic acid (in petioles/midrib, leaf blades, floral stalks, leaf sheaths and rachis) to 244 mg kg^{-1} of dry leaf blades

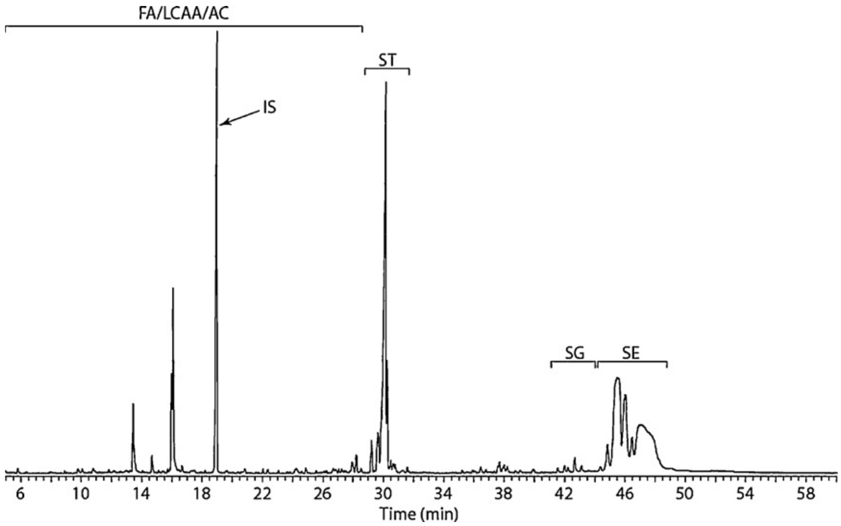

Fig. 4. GC–MS chromatogram of the derivatized dichloromethane extract from the unripe banana peel of the hybrid 'Williams', obtained by a DB-1 15 m column. FA, fatty acids; LCAA, long-chain aliphatic alcohols; AC, aromatic compounds; ST, sterols; SG, steryl glucosides; SE, steryl esters; IS, internal standard.

for the pentacosanoic acid (Oliveira et al., 2006, 2008). These compounds are also quite common in other plants belonging to the *Poaceae* family (Coelho et al., 2007; Villaverde et al., 2009) or in the straw of different cereals (Sun and Sun, 2001; Xiao et al., 2001).

α-Tocopherol, the most biologically active form of vitamin E, was the only tocopherol detected in the studied banana peels, accounting for 14–73 mg kg^{-1} of dry material (Table 1). The low content of tocopherols in these peel extracts is certainly associated with their low maturation state as previously reported for 'Dwarf Cavendish' where during the ripening process a significant increase in the tocopherols content can be observed which could attain up to 750 mg kg^{-1} of dry material (Oliveira et al., 2008). The same behavior was detected in other fruits (Moco et al., 2007).

Long-chain aliphatic alcohols (Table 1 and Fig. 2) represent between 16 and 220 mg kg^{-1} of dry peel. Only tetracosan-1-ol was identified in significant amounts (130 mg kg^{-1} of dry peel) in 'Dwarf Red'. 'Dwarf Cavendish' showed higher contents for this family (503 mg of compound/kg), with triacontan-1-ol as the most abundant compound with 156 mg kg^{-1} of dry peel (Oliveira et al., 2008).

In order to verify the presence of the esterified structures already reported for unripe, mature and defective banana fruits from 'Dwarf Cavendish' (Oliveira et al., 2005, 2008), the lipophilic extracts of all banana peels were also analyzed by GC–MS with a short length (15 m) column, using chromatographic conditions that enable the elution and detection of such low-volatile lipophilic compounds (Freire et al., 2002b): steryl glucosides, namely campesteryl 3β-D-glucopyranose, stigmasteryl 3β-D-glucopyranoside and sitosteryl 3β-D-glucopyranoside at rt 42.0, 42.2 and 42.7, were only detected in small amounts, and broad peaks corresponding to mixtures of steryl esters were found to be considerably abundant (Fig. 4).

4. Conclusion

From the chemical composition described above, the unripe peels residues and particularly those from 'Dwarf Red', followed by 'Silver' and 'Ricasa' are abundant sources of phytosterols.

Considering that the sterol family has a wide variety of nutraceutical applications, such as reducing the cholesterol absorption and its blood levels (Quílez et al., 2003) and that those residues are generated in large quantities in the tropical regions where *Musa* species are cultivated level, the exploitation of these abundant components could be a relevant contribution to their valorization.

However, environmental regulations will require for their industrial exploitation the choice of more environmentally friendly extraction systems, such as supercritical CO_2 extraction, which is seen as a good alternative for this type of compounds (Reverchon and De Marco, 2006) and is being considered in another study which will also address the selective isolation of the steryl esters fraction mentioned above. Finally, under these conditions the remaining residues could still be exploited for other applications, including energy conversion.

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