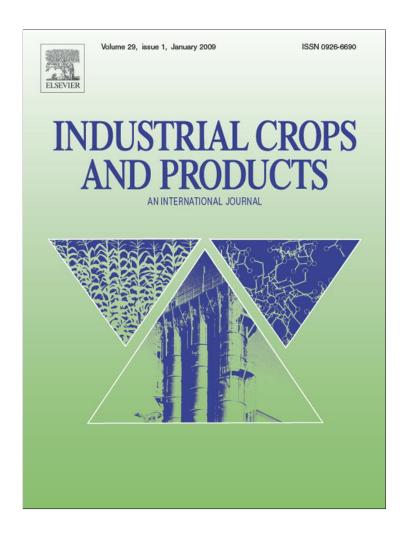
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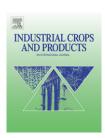
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Quercus suber and Betula pendula outer barks as renewable sources of oleochemicals: A comparative study*

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ABSTRACT

A comparative study on the chemical composition of oak cork (Quercus suber L.) and corresponding industrial residues and birch (Betula pendula L.) outer bark is reported. Cork oak samples have lower extractives contents (6–9%) and higher contents of carbohydrates and lignin (23–27 and 33–38%, respectively) than those found for birch outer bark (40, 6 and 9%, respectively); suberin contents accounted for around 30% of cork, 11% of industrial cork powder and 45% of birch outer bark. Analysis of the suberin monomeric composition revealed that C18 and C22 ω -hydroxyfatty acids (including mid-chain epoxyand dihydroxy-derivatives), followed by α , ω -dicarboxylic acids, are the main components in both suberins, with 9,10-epoxy-18-hydroxyoctadecanoic, 18-hydroxyoctadec-9-enoic, 9,10,18-trihydroxyoctadecanoic and octadec-9-enoic acids as the major components. The differences in the relative amounts of these acids in the suberin samples and the impact on the potential exploitation of the different industrial by-products are discussed.

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1. Introduction

The foreseeable gradual depletion of fossil resources and the need for sustainable development of world's industrial production systems are driving both the scientific community and industry to look for alternative and renewable resources for production of energy, materials and chemical commodities. Biomass emerges in this context as the logical raw material for the sustainable production of chemicals. In fact, from the estimated 1.7×10^{11} ton of biomass produced annually by pho-

tosynthesis, only 6×10^9 ton are used, and only 3% of this in non-food applications (Kamm and Kamm, 2004; Kamm et al., 2006). The production of chemicals from biomass in this new venture will be carried out in the so-called biorefineries, which will transform multiple biomass feedstocks, to produce a portfolio of products, including fuels, energy, chemicals and materials (Kamm and Kamm, 2004; Kamm et al., 2006). Among these biorefineries of the future, the lignocellulosic feedstock (LCF) biorefineries, will probably be the most successful, on the one hand, because of the availability of feedstocks (both ded-

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icated crops, and agro-food wastes, or even paper wastes) at competitive prices and, on the other hand, because they do not compete with the supply of food (Fernando et al., 2006). The implementation of the biorefinery concepts in already existing agroforest-based activities and the concomitant need to upgrade the by-products generated in the processing of agricultural and forest products, represent a short-term response to this goal (Kamm et al., 2006). In this context, the processing of oak cork, and pulping of birch are well established industrial activities that generate considerable amounts of cork and outer bark residues, which for the time being are under-exploited and could have considerable value as sources of oleochemicals.

The outer bark of *Quercus suber* is commonly known as cork (hereafter designated as such). Cork production and its processing industry (mainly for the production of cork stoppers and thermal and/or acoustic insulation materials) exist mainly in the Mediterranean region (Silva et al., 2005). In Portugal, about 185,000 ton/year of cork are produced, representing more than 50% of the world production (APCOR, 2008). This industry generates substantial amounts of the so-called "cork powder", representing about~40,000 ton/year in Portugal (Gil, 1988), that is not suitable for current industrial uses. This byproduct is currently burned to produce energy.

Birch (Betula pendula) is an important species for pulp production in the Nordic countries. Birch logs contain about 3.4% outer bark (Jensen, 1948). Thus, a birch kraft pulp mill, with an annual pulp production of 400,000 ton/year generates about 28,000 ton of outer bark (Ekman, 1983), which is, at the present, burnt in the biomass boilers of kraft pulp mills for energy production. Based on birch kraft pulp production figures, the total potential of birch outer bark in Finland can be estimated to be 200,000 ton/year (Paper and wood insights, 2006). These two bark by-products bear in common the fact that their main constituent is suberin. Suberin is an aromatic-aliphatic crosslinked polyester. It is widespread in the plant kingdom, where it plays a key role as a protective barrier between the plant and the surrounding environment. It is found mainly in the cell walls of normal and wounded external tissues of aerial and/or subterranean parts of many plants, mainly in the outer bark of higher plants and in tuber periderms (Bernards, 2002). However, only the two species considered in the present paper produce suberin-rich biomass residues in amounts that can justify their exploitation as renewable sources of chemicals.

Suberin is of interest mainly because it constitutes an abundant source of ω -hydroxyfatty acids, α, ω -dicarboxylic acids and homologous mid-chain dihydroxy or epoxy derivatives (Gandini et al., 2006) that, apart from these sources, are not abundant in nature. In fact, hydroxyfatty acids can only additionally be found in exploitable amounts in the seed oils of Ricinus communis (castor oil) and Lesquerella spp., as well as in the extra-cellular aliphatic polyester covering most of the aerial surfaces of plants, known as cutin (Christie, 2008).

The most interesting applications for suberin components that are being investigated involves their use in the synthesis of polymeric materials (Gandini et al., 2006), notably polyols through oxypropylation (Evtiouguina et al., 2000, 2002), polyurethanes synthesis, either from the oxypropylated material (Evtiouguina et al., 2001) or from depolymerized suberin mixtures (Cordeiro et al., 1997, 1999), and finally polyesters,

either from depolymerized suberin mixtures (Sousa et al., 2007) or from isolated monomers (Olsson et al., 2007).

The efficient isolation and exploitation of the suberin fractions of cork powder or birch outer bark requires a detailed knowledge of the chemical composition of each substrate, and of the suberin depolymerization mixtures in particular. Cork is mainly composed of lignin (\sim 25%), polysaccharides (\sim 20%), suberin (\sim 40%), extractives (\sim 15%) and minor amounts of inorganic salts (\sim 1%). These figures are, however, much variable, being influenced by the geographical origin and quality of the tree, and/or even the different parts of the tree from which the cork is harvested (Pereira, 1988; Conde et al., 1998, 1999). Birch outer bark has a high content of extractives, varying between 20 and 45%. The suberin content, if calculated on extractive-free outer bark, is fairly constant with an average of about 50% by weight (Ekman, 1983). Suberin is easily depolymerized under alkaline hydrolysis/alcoholysis conditions; the chemical composition of the ensuing suberin depolymerization mixtures (as well as its relationship with the structure of the native biopolymer) has been the object of a large number of publications which have been extensively reviewed in recent years (Bernards, 2002; Gandini et al., 2006). Although these depolymerization mixtures are mainly composed of ωhydroxyfatty acids, α,ω -dicarboxylic acids and homologous mid-chain dihydroxy or epoxy derivatives, the relative abundance of these components is, on one hand, dependent on the nature of the biomass source, as mentioned above and, on the other hand, on the depolymerization and extraction conditions (Bernards, 2002; Gandini et al., 2006).

Within the scope of an European research project aiming to develop new concepts for the upgrading of pulp and cork mill waste streams to value-added chemicals, one of the main goals is the valorization of industrial cork powder (ICP) and birch outer bark, particularly through the use of suberin components as a renewable source of monomers for the synthesis of polymeric materials. In this context, a detailed knowledge of the chemical composition of the two bark by-products is required, particularly in what concerns the depolymerized suberin mixtures. The present paper reports the results of the overall characterization of birch outer bark, cork and industrial cork powder and the detailed characterization of depolymerized suberin obtained by mild alkaline hydrolysis or alkaline methanolysis. The suberin depolymerization products are in this paper designated as "dep-suberin". Mild alkaline hydrolysis conditions yield dep-suberin components as free acids, and preserves epoxide-containing structures (Ekman and Eckerman, 1985). Alkaline methanolysis yields dep-suberin components as methyl esters and the epoxy-containing structures are largely converted to the corresponding methoxyhydrin structures (Gandini et al., 2006).

2. Experimental

2.1. Samples

Quercus suber L. cork (QsC) planks, "Amadia" grade, were sampled in the south part of Portugal (Herdade da Moinhola, Amorim Florestal mill, Portugal, March 2005). The ICP was sampled in the Corticeira Amorim mill (Portugal, February

2005). Cork was ground in a Retsch SK hammer mill, sieved, and the 40–60 mesh fraction was used for further analyses. ICP was sieved to 40–60 mesh and used as such.

Betula pendula outer bark samples (BoB) were collected from the debarking line at a birch kraft pulp mill in Finland (Metsä-Botnia, Kaskinen). The industrial bark was ground in a laboratory mill to pass a 6-mm screen, followed by separation in water into floating outer bark and sedimented inner bark. The outer bark was air dried and sieved to 40–60 mesh. Ash contents were quantified following TAPPI T 221 om-93.

2.2. Isolation of extractives

BoB extractives were fully removed by Soxhlet extraction with ethanol during 20 h, whereas QsC and ICP were sequentially Soxhlet-extracted with dichloromethane, methanol and water during 10 h for each solvent. The extracts were dried to constant weight and quantified gravimetrically.

All preparative procedures described from this point onwards were carried out in duplicate.

2.3. Suberin depolymerization

Extractive-free samples were submitted to two different depolymerization procedures: (i) alkaline hydrolysis (for all samples) and (ii) alkaline methanolysis (for QsC and ICP).

- (i) Alkaline hydrolysis. Alkaline hydrolysis was carried out with a solution of 0.5 M KOH in ethanol/water (9:1, v/v) at 70 °C for 1.5 h (Ekman and Eckerman, 1985). The mixture of hydrolyzed suberin monomers was cooled to room temperature and acidified with dilute sulfuric acid to about pH 3–3.5, and extracted three times with methyl t-butyl ether (MTBE). The solvent was then removed in a rotary evaporator and the residue weighed.
- (ii) Alkaline methanolysis. Cork samples (QsC, ICP) were refluxed with a dried methanol solution of 0.6 M NaOCH₃ during 4h, followed by solid residue filtration, and 1h reflux with methanol (Lopes et al., 2000). The combined liquid fractions were mixed, acidified to about pH 3-3.5 with diluted H₂SO₄, and then extracted three times with dichloromethane. The solvent was then removed in a rotary evaporator and the residue weighed.

2.4. Klason lignin

Acid-insoluble (Klason) lignin of the solid residue (obtained after suberin extraction) was quantified as described elsewhere (Browning, 1967).

2.5. Analysis of carbohydrates

Neutral monosaccharides were released from the solid residue (obtained after suberin extraction) by treatment with 72% $\rm H_2SO_4$ at 25 °C, followed by hydrolysis with 1 M $\rm H_2SO_4$ at 100 °C (Saemen hydrolysis) as described elsewhere (Coimbra et al., 1996) and quantified as alditol acetate derivatives by GC (Selvendran et al., 1979).

The same residues were also submitted to acid methanolysis with 2 M HCl in anhydrous methanol. After 5 h at 100 $^{\circ}\text{C},$

the samples were neutralised with pyridine, and sorbitol was added as internal standard. The sample was transferred to a new flask, dried and converted into TMS as reported elsewhere (Sundberg et al., 1996).

2.6. Chromatographic analysis

Dep-suberins were converted to TMS derivatives according to a known procedure (Ekman, 1983). Derivatized cork dep-suberin samples were analyzed by GC–MS using a Trace GC 2000 gas chromatograph, connected to a mass selective detector Finnigan Trace MS, and previously described chromatographic conditions (Lopes et al., 2000). For quantitative analysis, GC–MS was calibrated with pure reference compounds representative of the major classes of components present in cork, relative to the *n*-tetracosane, the internal standard used. Identification of chromatographic peaks is based on the equipments spectral library (Wiley–Nist), and also on comparison with previously published data (Cordeiro et al., 1998; Ekman, 1983; Ekman and Eckerman, 1985; Lopes et al., 2000; and references therein).

Derivatized birch outer bark dep-suberin samples were analysed on a Hewlett Packard model 5973 GC/MSD system following previously described chromatographic conditions (Ekman and Eckerman, 1985) and identified as referred to above, while quantitative analyses were performed on a PerkinElmer Autosystem XL GC.

The monosaccharide alditol acetates were analyzed by GC using a Varian 3350 GC, following previously described chromatographic conditions (Pinto et al., 2005). Monosaccharides from acid methanolysis were analysed by GC as described elsewhere (Sundberg et al., 1996).

All quantitative analysis were performed at least in triplicate and accepted when the variability between analyses was lower than 5%. Quantitative results presented are the average of the triplicate analysis of the duplicate samples.

3. Results and discussion

3.1. Overall chemical composition

The overall composition of the studied samples is shown in Table 1. The yields of dep-suberin obtained by hydrolysis of BoB and QsC (45 and 29%, respectively) are within the ranges reported in the literature (Gandini et al., 2006). How-

Table 1 – Group composition (wt.%) of Betula pendula outer bark (BoB), Quercus suber cork (QsC) and industrial cork powder (ICP)

Component	ВоВ	QsC	ICP
Extractives	40	9	6
Ash	1	4	6
Klason lignin	9	33	38
Carbohydrates	6	23	27
Dep-suberin			
Alkaline hydrolysis	45	29	11
Alkaline methanolysis	-	33	11

ever, for QsC, the reported value is at the lower limit of the mentioned ranges. ICP yielded considerably lower amounts of dep-suberin (11%) when compared to the native cork (QsC).

The three samples also gave considerably different yields for the other components: while BoB had a high content of extractives (40%) and low contents of other macromolecular components (9% of Klason lignin and 6% of polysaccharides), QsC and ICP had lower contents of extractives (9 and 6%, respectively) and higher amounts of Klason lignin (33 and 38%, respectively) and carbohydrates (23 and 27%, respectively). The Klason lignin content of QsC was high when compared to published results for natural cork (Pereira, 1988; Marques et al., 1994).

The extractives content of QsC are within the typical values found for mature ("Amadia" grade) cork (Pereira, 1988; Lopes et al., 2000). The major components of the dichloromethane and methanol extracts of QsC and ICP were triterpenoid components (10.3 and 17.1 g/kg, respectively), with cerine and friedeline as the major components in QsC and betulinic acid in ICP extracts, as recently reported in detail (Sousa et al., 2006). The ethanol extract of BoB was also mainly composed of triterpenoids, with betulinol representing about 80% of the total.

The total carbohydrates as monomeric sugars were obtained by acid hydrolysis. The sugars of non-cellulosic carbohydrates were obtained by acid methanolysis. From these results, the cellulose content was calculated as the total amount of glucose by acid hydrolysis with subtraction of glucose from acid methanolysis (Table 2). The non-cellulosic carbohydrates, most probably originating mainly from hemicelluloses, were calculated as the total sum of sugars from acid methanolysis.

The cork samples contained considerable amounts of cellulose, whereas BoB contained a very small amount (Table 2). The same is also true for non-cellulosic carbohydrates. The non-cellulosic carbohydrates of BoB were dominated by arabinose, followed by xylose and several other sugars in smaller amounts (Table 3). The high amount of arabinose indicates the presence of arabinans as predominant hemicelluloses. This topic needs further research since there are no reports in the literature about birch outer bark hemicelluloses composition and structure.

Xylose was the dominating non-cellulosic sugar in both cork samples, indicating the presence of xylans, as previously suggested (Asensio, 1987a,b). This is supported also by the presence of 4-O-methyl glucuronic acid units. However, the complex composition of the neutral and acidic non-cellulosic carbohydrates indicates also the existence of other types of hemicelluloses in cork. This topic in now under investigation.

Table 2 – Cellulose and non-cellulosic carbohydrates, in wt.% of whole samples Component **ICP** BoB OsC 1.8 12.1 11.4 Non-cellulosic carbohydrates

Total carbohydrates

4.2

6.0

11.2

23.3

15.6

27.0

Table 3 - Monosaccharide composition of non-cellulosic carbohydrates (by acid methanolysis and GC), % of pre-extracted samples, with % composition in parenthesis

Component	ВоВ	QsC	ICP
Arabinose	2.7 (46)	2.0 (16)	1.9 (12)
Xylose	0.9 (15)	5.3 (43)	8.6 (52)
4-O-Methyl glucuronic acid	0.1 (2)	0.6 (5)	1.0 (6)
Rhamnose	0.2 (3)	0.5 (4)	0.7 (4)
Galacturonic acid	0.7 (12)	1.6 (13)	1.2 (7)
Galactose	0.8 (14)	1.1 (9)	1.9 (12)
Glucose	0.3 (5)	0.7 (6)	0.8 (5)
Mannose	0.2 (3)	0.4 (3)	0.4 (2)
Total	5.9 (100)	12.2 (100)	16.5 (100)

The predominance of extractives and the low abundance of lignin and carbohydrates in BoB, when compared to QsC and ICP, is an important aspect in by-products processing to obtain dep-suberin fractions. After extractives removal, BoB residues will be considerably enriched in suberin and, upon alkaline hydrolysis/alcoholysis, the ensuing mixtures will be particularly enriched in suberin monomeric units; whereas in the case of QsC and particularly in ICP, the alkaline hydrolysis/alcoholysis mixtures may be more contaminated with lignin and polysaccharides residues.

There are considerable differences in the chemical composition of QsC and ICP. ICP has a higher content of lignin, with smaller amounts of suberin, which is certainly related with the enrichement of ICP in the inner and outer surface fractions of cork planks, rejected during cork stopper manufacture. Particularly the outer surface (the major fraction of ICP) should be more lignified than the "bulk", and certainly enriched in complex mixtures of photodegraded extractives, polysaccharides, lignin and suberin, due to environmental exposure. Finally, the fact that only about 90% of the mass of ICP was accounted for should also be related to the particular nature of this fraction and the remaining 10% should be water-soluble polar organic compounds released during the alkaline hydrolysis.

3.2. Dep-suberin chemical composition

The chemical composition of dep-suberin fractions from BoB, OsC and ICP obtained under different depolymerization conditions is shown in Table 4. The GC-MS analyses of dep-suberin samples from alkaline hydrolysis show that, for all substrates, only part of the dep-suberin isolated by solvent extraction (Table 2) corresponds to suberin monomeric components (60, 37 and 36%, respectively, for BoB, QsC and IcP), although, in the case of QsC and ICP a small percentage (less than 6%) of other suberin related components, not shown in Table 4, were also detected. The high percentage of undetected components means that a non-volatile fraction, not detectable by GC-MS, is present in these dep-suberin extracts; this observation is in agreement with previously reported results for Quercus suber cork (Lopes et al., 2000; Gandini et al., 2006). A tentative explanation is that this fraction should be composed by suberan-type high molecular-mass aliphatic moieties, nondetectable by GC-MS (Tegelaar et al., 1995).

Table 4 – Main dep-suberin monomers of ICP, BoB and QsC isolated by alkaline hydrolysis and methanolysis identified l
GC-MS expressed in mg compound/g of dry starting material or mg compound/g of extracted suberin (in parenthesis)

	Hydrolysis		Methanolysis		
	BoBa	QsC ^a	ICP ^a		ICP
Hexadecanedioic acid	1 (2)	3 (10)	1 (9)	Tr	tr
Octadecanedioic acid	2 (2)	1 (3)	tr	Tr	tr
Octadec-9-enedioic acid	13 (29)	8 (28)	3 (27)	Tr	tr
Eicosanedioic acid	4 (9)	1 (3)	tr	Tr	tr
Docosanedioic acid	16 (36)	3 (10)	1 (9)	1 (3)	tr
Alkanedioic acids	36 (80)	16 (55)	5 (45)	1 (3)	0
16-Hydroxyhexadecanoic acid	1 (2)	2 (7)	1 (9)	1 (3)	1 (9)
Dihydroxyhexadecanoic acid	9 (20)	tr	tr	Tr	Tr
18-Hydroxyoctadec-9-enoic acid	39 (87)	23 (79)	8 (73)	6 (18)	4 (36)
20-Hydroxyeicosanoic acid	9 (20)	4 (14)	1 (9)	1 (3)	1 (9)
20-Hydroxyeicos-10-enoic acid	5 (11)	3 (10)	1 (9)	1 (3)	Tr
22-Hydroxydocosanoic acid	42 (93)	23 (79)	7 (64)	23 (70)	8 (73)
24-Hydroxytetracosanoic acid	1 (2)	4 (14)	2 (18)	3 (9)	2 (18)
Hydroxyalkanoic acids	106 (236)	58 (200)	20 (182)	35 (106)	16 (145)
9,10-Epoxy-18-hydroxyoctadecanoic acid	99 (220)	14 (48)	4 (36)	-	_
9,10-Epoxyoctadecanedioic acid	tr	10 (34)	2 (18)	-	-
9,10,18-Trihydroxyoctadecanoic acid	29 (64)	5 (17)	3 (27)	3 (9)	2 (18)
9,18-Dihydroxy-10-methoxyoctadecanoic acid	-	-	-	5 (15)	2 (18)
9,10-Dihydroxyoctadecanedioic acid	tr	5 (17)	2 (18)	-	-
Epoxy derivatives	128 (284)	34 (117)	14 (127)	8 (24)	4 (36)
Total	270 (600)	108 (372)	39 (355)	44 (133)	20 (182)

The major groups of components found in the dep-suberin fractions (Table 4) are alkanedioic and ω -hydroxyalkanoic acids and the corresponding epoxy-derivatives (typical chromatograms of both dep-suberin samples are shown in Fig. 1, while the structures of the most abundant identified compounds are shown in Fig. 2). In the case of cork, dep-suberin contained smaller amounts of fatty acids and alcohols (less than 2% in both subtrates), and ferulic acid (less than 4%)

were also detected, in accordance with previously reported results (Gandini et al., 2006). The relative abundance of individual components is largely different between birch and cork samples. For BoB, the most abundant component is 9,10-epoxy-18-hydroxyoctadecanoic acid (99 mg/g), which accounts for about 37% of the identified components, followed by 22-hydroxydocosanoic (42 mg/g), 18-hydroxyoctadec-9-enoic (39 mg/g) and 9,10,18-trihydroxyoctadecanoic acid

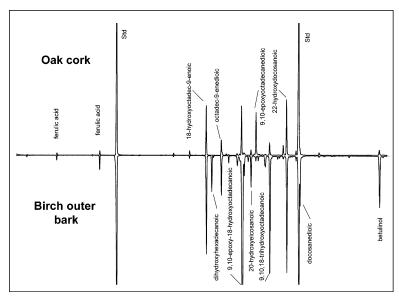


Fig. 1 – Comparison of depolymerized cork and birch outer bark suberin acid composition by GC-MS.

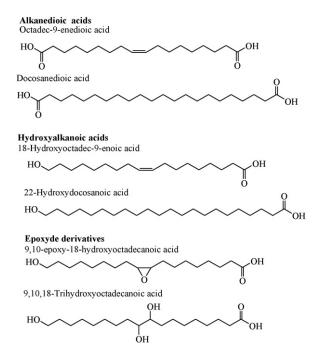


Fig. 2 – Structures of the most abundant components identified in dep-suberin samples.

(29 mg/g), with this last component resulting from the cleavage of the corresponding epoxide. The most abundant alkanedioic acids found in BoB are docosanedioic and octadec-9-enedioic acids (16 and 13 mg/kg, respectively). The major components detected in dep-suberin of QsC and ICP were 22-hydroxydocosanoic (23 and 8 mg/g, respectively) and 18-hydroxyoctadec-9-enoic acids (23 and 7 mg/g, respectively), followed by 9,10-epoxy-18-hydroxyoctadecanoic acid (14 and 4 mg/g, respectively) and 9,10-epoxyoctadecanedioic acid (10 and 2 mg/g, respectively). The low abundance of epoxy derivatives in both QsC and ICP hydrolysis dep-suberin samples is a key difference to BoB, and confirms the low abundance of this type of structures in cork suberin.

Analysis of the QsC and ICP dep-suberins obtained by alkaline methanolysis showed a considerable decrease in the total amount of components detected when compared to the alkaline hydrolysis data. Although the amounts of 22hydroxydocosanoic acid detected (23 and 8 mg/g for QsC and ICP, respectively) are similar to those obtained by alkaline hydrolysis, much lower amounts of 18-hydroxyoctadec-9enoic acids (6 and 4 mg/g, respectively) and the absence of epoxide-containing compounds is observed; cleavage products, namely 9,18-dihydroxy-10-methoxyoctadecanoic acid, were detected in small amounts (Table 4). Considering the decrease in the amounts of compounds detected by GC-MS in dep-suberin obtained by alkaline methanolysis, the above referred increase in the corresponding extraction yield means that a higher amount of non-volatile components was isolated under these conditions. However, taking into account that, under methanolysis conditions, 22-hydroxydocosanoic acid was clearly dominant and was obtained in the same amounts as from hydrolysis, the former can be a good approach for further processing of dep-suberin when the isolation of the pure compound is required.

4. Conclusions

The high content of extractives and low contents of polysaccharides and lignin of birch outer bark enable the isolation of less contaminated dep-suberin, compared to the one obtained under similar conditions from cork or cork byproducts, resulting in higher amounts of suberin monomeric units. Furthermore, the high content of 9,10-epoxy-18hydroxyoctadecanoic acid in BoB dep-suberin, might justify further processing of depolymerization mixtures in order to isolate the pure compound for more valuable applications such as polyester synthesis (Olsson et al., 2007). In the case of cork, the yields of dep-suberin isolation and the amounts of compounds are smaller than for birch, and there is not a dominant component (excepting for 22-hydroxydocosanoic acid in methanolysis dep-suberin) that could justify further working up of the extract to isolate it in a pure state. In this case, the exploitation of dep-suberin will certainly pass through the direct processing of the entire mixture, possibly after a purification step to separate suberin monomers from the undetected fraction.

The even lower amounts of monomers detected in the dep-suberin obtained by methanolysis suggests that this depolymerization pathway is of interest only if the monomers are required in methyl ester form (e.g., for polyester synthesis through transesterification), or for the isolation of 22-hydroxydocosanoic acid, the dominant component detected in this fraction.

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