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Resorcinol and *m*-guaiacol alkylated derivatives and
asymmetrical secondary alcohols in the leaves from *Tamarix*
canariensis

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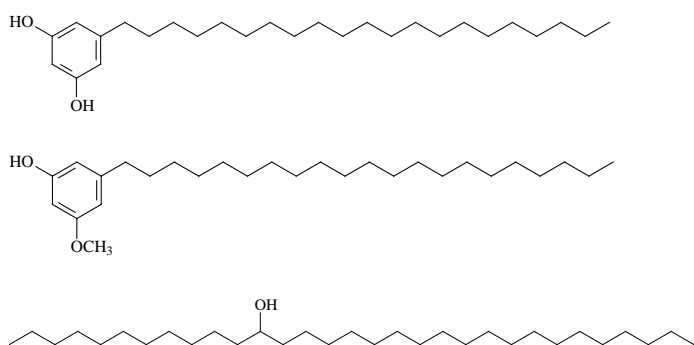
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Graphical abstract



Abstract

In the study of leaves from the halotolerant saltcedar (*Tamarix canariensis* Willd.) we have found a new abundant source of resorcinolic as well as guaiacolic compounds. A homologous series of 5-*n*-alkylresorcinols with long side alkyl chain reported previously in the literature almost exclusively in cereals are described here for the first time in *Tamaricaceae*. These polyketide derived phenolic compounds are characterized by a series ranging from *n*-C₁₅ to *n*-C₂₇ and maximizing at *n*-C₂₁ including non-negligible amounts of the even-numbered homologues. We also have characterized for the first time as natural compounds a homologous series of 5-*n*-alkylguaiacols similarly constituted by an odd-numbered alkyl chain linked to the benzene ring at position 5. They also include a hydroxyl group at carbon 1 of the phenolic nucleus and a methoxy group at position 3. The homologues are in the range of 13-27 carbon atoms (C_{max} at C₂₁). Finally, we firstly report in *Tamaricaceae* eight series of unsymmetrical secondary alcohols ranging from *n*-C₂₅ to *n*-C₃₅ with hentriacontan-12-ol as the major homologue. This saltcedar leaves waxes contained high amounts of alkylresorcinol (17,2 g/kg dw), alkylguaiacol (14,4 g/kg dw) and secondary alcohols (44,4 g/kg dw).

Highlights: -Alkylguaiacols described for the first time as natural products.

-We characterize the mass spectrum of their trimethylsilyl derivatives never shown.

-First report on secondary alcohols and alkylresorcinols in Tamaricaceae.

Keywords: *Tamarix canariensis* Willd.; saltcedar tree; *Tamaricaceae*; Leaf epicuticular waxes; alkylresorcinols; alkylguaiacols; secondary alcohols; total extracts; Gas chromatography-Mass spectrometry (GC/MS); trimethylsilyl (TMS) derivatives.

1. Introduction

The saltcedar tree (canary island tamarisk) (*Tamarix canariensis* Willd.) is a perennial shrub to small tree member belonging to the *Tamaricaceae* family that grows in saline and temporally flooded soils. This macrophanerophyte member of the riparian and halophytic vegetation is native to Northern Europe and temperate, tropical, arid and semi-arid Asia (Eurasia) and the Mediterranean region. It develops pink flowers from March to May in the younger appendages of the plant.

Except available data on phenolic lipids such as flavonoids, tannins and lignans in *Tamarix* genus (Nawwar *et al.*, 1982; Souliman *et al.*, 1991; Parmar *et al.*, 1994; Orabi *et al.*, 2009) no other studies on chemical composition of *T. canariensis* have been reported previously in the literature.

Phenolic compounds with linear alkyl chain attached to a single benzene ring are alkyl phenolics. When the nucleus to which the alkyl side-chain is attached is a dihydroxybenzene three isomers can exist. These structurally related compounds are called catechol, resorcinol and hydroquinone and they include two hydroxyl groups

linked to the aromatic ring in *orto* (1,2), *meta* (1,3) and *para* (1,4) positions, respectively. This group of molecules includes short- and long-chain members of the different isomeric series when they are alkylated with a frequently linear side-chain.

5-*n*-Alkylresorcinols (alkylresorcinols, ARs), also named 1,3-dihydroxy-5-alkylbenzene derivatives or cardols are long-chain dihydric alkylphenols more abundant than the alkylcatechols also called urushiols as natural compounds (**Kozubek and Tyman, 1999**). Both are also more abundant in nature than the alkyl derivatives of hydroquinone (**Tyman, 1979**).

These amphiphilic phenolic compounds are recognized to be associated not only to higher plants but also with many other different organisms from bacteria and fungi to lower and higher plants (**Kozubek and Tyman, 1999**). Despite this heterogeneous origin they has been usually reported in high concentrations mainly in the outer layers of cereal (Gramineae \equiv Poaceae) grains specially in common wheat (*Triticum aestivum* L.), durum wheat (*Triticum durum*), rye (*Secale cereale* L.), triticale (*Triticum* x *Secale*) and barley (*Hordeum vulgare* L.). Minor amounts were isolated in some other higher plants used for food as in mango (*Mangifera indica*) (**Knödler et al., 2009**) and in lower plants like bacteria, mosses and algae, e.g: *Apatococcus constipatus* (**Zarnowski et al., 2000**). (S1) Supplementary material 1 shows as the homologue composition varies with species in which these compounds have been described in the literature and mainly as odd-numbered alkyl side-chain, the members of this class of compounds usually varies from C17 to C25 including minor amounts of unsaturated homologues (alk(en)ylresorcinols) with a chain unsaturation degree of one (mono-) or two (diunsaturated). Several epidemiological studies have associated the consumption of

foods as whole-grain cereals with decrease incidence of degenerative diseases including diabetes, obesity, coronary heart disease and some cancers (**Ross *et al.*, 2001, Chen *et al.*, 2004**).

Figure 1 shows the molecular structure of the AR homologue with a saturated and straight hydrocarbon side-chain length of 21 carbon atoms and a single phenolic ring (5-henicosyl-1,3-benzendiol). Congeners with an odd number of carbon atoms (C_{13} - C_{27}) that constitutes the alkyl side-chain attached to position 5 of the aromatic ring are most of times the major homologues described in higher plants.

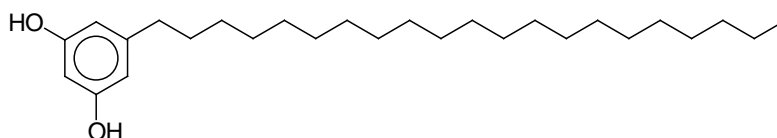


Figure 1. 5-*n*-heneicosylresorcinol (n - $C_{21:0}$) molecular structure

In almost the totality of cases the homologous series ranges from n - $C_{17:0}$ to n - $C_{25:0}$ being the maximum different within each species. Some of these include unsaturated members (alkenylresorcinols) but they are always in lower amounts as compared with the saturated counterparts.

The aim of this study is to describe new natural products and their abundance in *Tamarix* through their chemical description, both qualitative and semiquantitative, of the main lipids extractable from the leave tissues of *T. canariensis* that were not previously described, to the best of our knowledge. As a consequence of the conducted analysis here is presented evidence of a new natural source of phenolic compounds which have been identified as 5-*n*-alkylguaiacols. We also found long-chain secondary alcohols and alkylresorcinols not previously characterized in *Tamaricaceae*.

2. Results and discussion

2.1. General aspects

Although the total extract of the epicuticular waxes from the leaves of this higher plant contained several families of compounds some of them previously described by other authors in members of the genus *Tamarix*, we have focused our attention in the saltcedar composition on the three more abundant classes of chemical compounds: Alkylresorcinols, alkylguaiacols and secondary alcohols, all of them isolated for the first time from the saltcedar. Total contents of these three compounds classes were high, compared to those reported previously in other plant sources.

Little is known about the content of alkyl phenolic derivatives in higher plants others than cereal species. Here in this study we present the results from the total lipid extraction of the leaves from the saltcedar. The TIC chromatogram (Figure 2) showed that the main peaks belonged to two series of novel phenolic compounds and eight homologous series of secondary alcohols.

As Figure 2 shows, alkylphenolic derivatives are the main compounds in the overall chromatogram resulting from the total lipid extract of the leaves of the saltcedar.

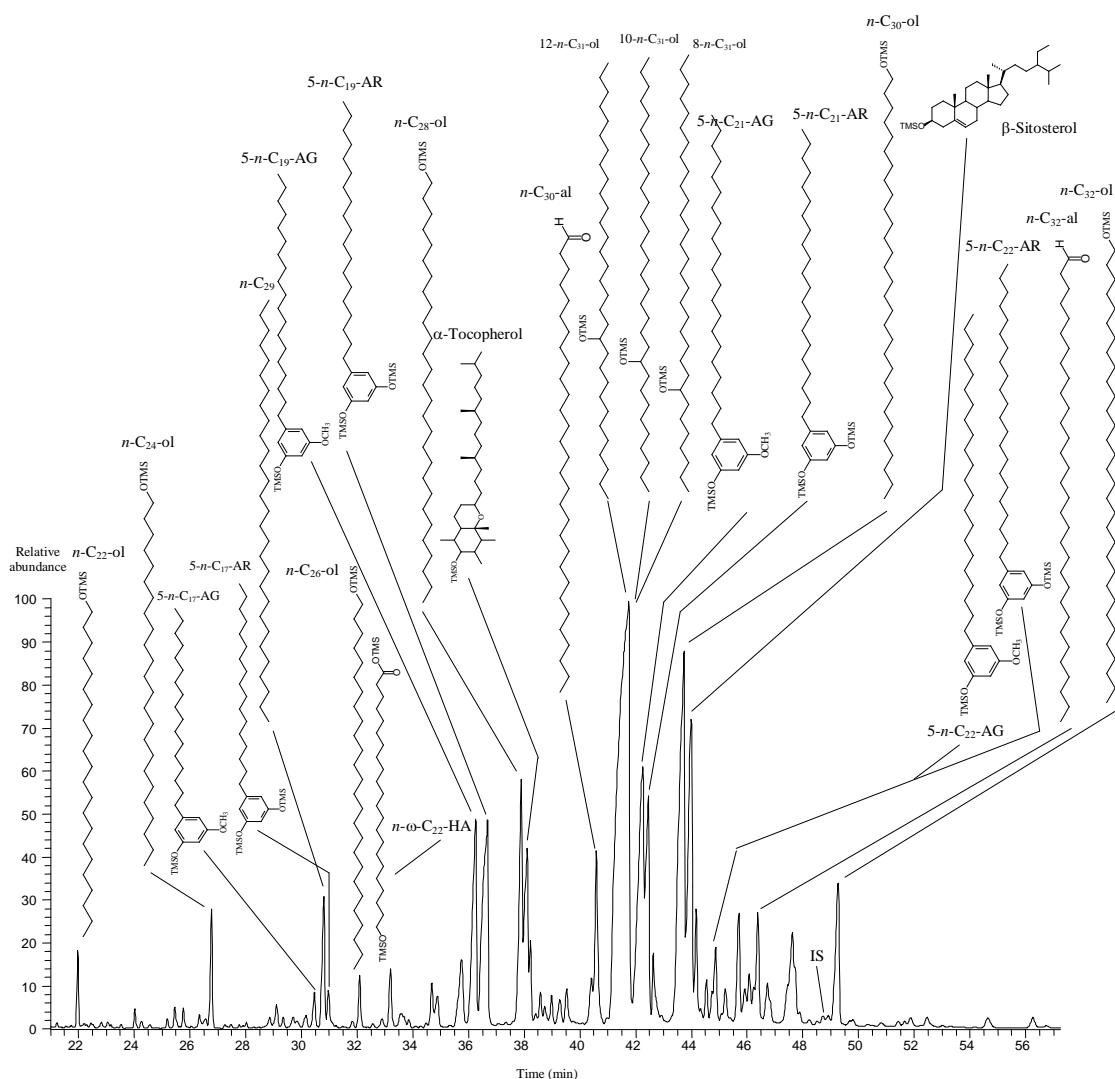


Figure 2. Partial GC-MS Total Ion Current (TIC) from the silylated total extract of the leaves of *Tamarix canariensis*. Compounds were analyzed as TMS derivatives. IS = Internal standard. C_n = *n*-alkyl C number.

Table 1 shows the content of ARs and alkylguaiacols (AGs) homologues as the sum of saturated derivatives with 13-27 carbon atoms in the side chain. The concentration of ARs was higher than reported by other studies excepting that reported by **Landberg *et al.* (2008)** on the intermediate layer of wheat (*Triticum aestivum*) grains (16,000 $\mu\text{g/g}$). Our results show also a homologue distribution very similar to the published results in

other plant species. For example, **Knödler *et al.* (2010)** in a recent study developed in common wheat (*Triticum aestivum*) and durum wheat (*T. durum*) revealed in both cereal species that the homologues C21:0 and C19:0 were the most abundant. These series are nearly always dominated by the saturated homologues. However, **Knödler *et al.* (2009)** showed a profile dominated by two unsaturated homologues (C17:2 and C17:1) in mango (*Mangifera indica*) peel.

Table 1.

Alkylphenolic derivatives composition of cuticular waxes extracted from the leaves of *Tamarix canariensis* including their concentration and relative homologue abundance^{‡, †}

Alkylphenolic derivatives mg·kg ⁻¹ dry weight (%)		
Chain length #	5- <i>n</i> -alkylresorcinols	5- <i>n</i> -alkylguaiacols
13	not detected	1.4 (0.01)
14	7.0 (0.04)	2.8 (0.01)
15	235.1 (1.37)	192.3 (1.3)
16	9.8 (0.06)	7.8 (0.05)
17	1064.0 (6.18)	757.4 (5.2)
18	62.0 (0.36)	46.2 (0.3)
19	6089.0 (35.39)	4034.1 (27.9)
20	593.3 (3.45)	557.5 (3.9)
21	6313.3 (36.69)[‡]	5601.3 (38.8)
22	443.8 (2.58)	683.6 (4.7)
23	2035.2 (11.83)	2296.9 (16.0)
24	69.4 (0.40)	108.8 (0.7)
25	213.1 (1.24)	142.7 (1.0)
26	13.9 (0.08)	6.3 (0.04)
27	57.3 (0.33)	9.6 (0.07)
Total	17,206 (100)	14,449 (100)

[‡]absolute values of individual homologues from each class of aliphatic compound are expressed in mg·kg⁻¹ of dry weight (≡ μg·g⁻¹ dw)

[‡]in bold are indicated the most abundant members of the series and in parenthesis their abundances

[†]Abundance data obtained by peak integration from *m/z* 268 (ARs) and *m/z* 210 (AGs) mass chromatogram

2.2. 5-*n*-Alkylresorcinols (ARs)

A homologous series of ARs with saturated alkyl side chain at position 5 of the benzene ring and varying from *n*-C_{13:0} to *n*-C_{27:0} with an odd over even dominance were identified in the total lipid extract from the leaves of the saltcedar. Total yield of these

phenolic lipids was $17.2 \text{ g}\cdot\text{kg}^{-1}$. The most abundant homologues were henicosylresorcinol ($n\text{-C}_{21}$) ($6.31 \text{ g}/\text{kg}$; 36.7%) and nonadecylresorcinol ($n\text{-C}_{19}$) ($6.09 \text{ g}/\text{kg}$; 35.4%). Despite this predominance of the odd members, the abundance of the even numbered alkyl chain homologues was not negligible.

Figure 3 shows the mass chromatogram corresponding to the base peak at m/z 268 for the derivatized ARs. n -Alkylresorcinols are defined as phenolic lipids with an alkyl chain attached to position 5 of the 1,3-dihydroxybenzene ring.

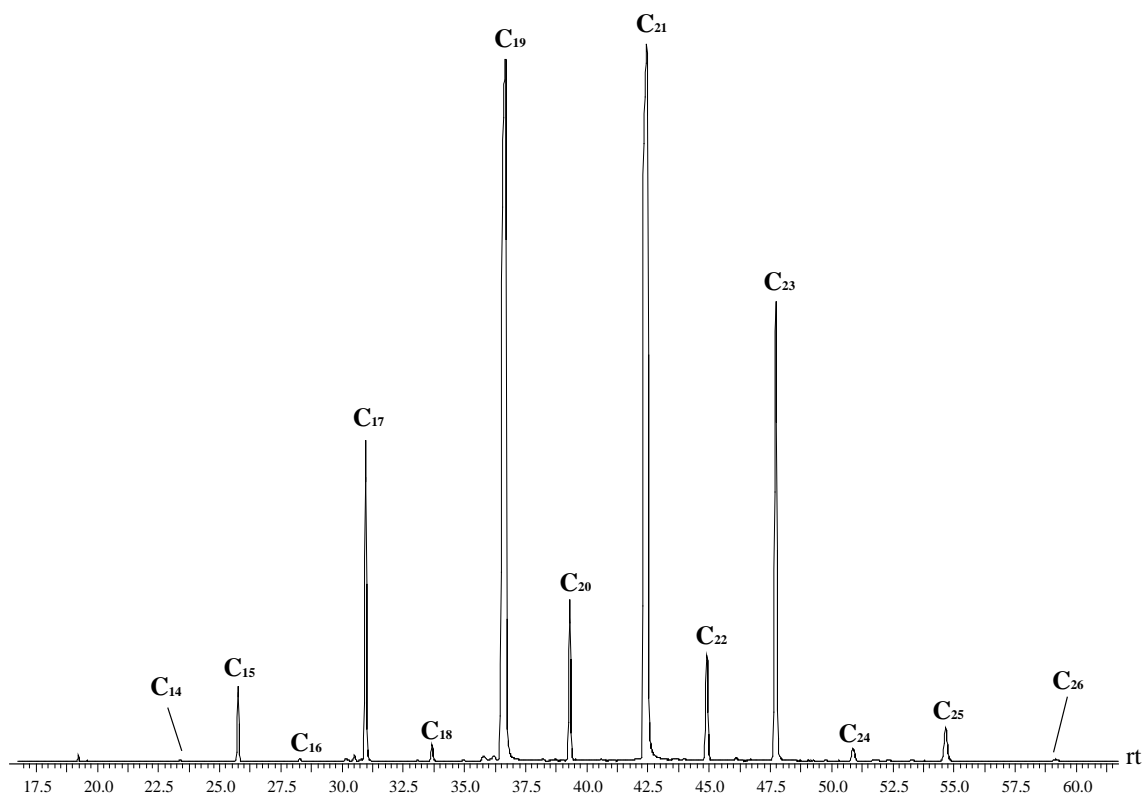


Figure 3. Mass chromatogram of base peak at $m/z = 268$ characteristic of the TMS derivatives of 5- n -alkylresorcinols extracted from leaves of the saltcedar (*Tamarix canariensis*). $C_n = n$ -alkyl C number.

5-*n*-Alkylresorcinols were identified according to its mass spectra. Figure 4 shows the EI mass spectrum of the homologue 5-*n*-nonadecylresorcinol (1,3-dihydroxy-5-*n*-nonadecylbenzene) (*n*-C_{19:0}). The EI fragmentation pattern of the TMS ether derivative of this alkyl phenol is characterized by the following fragment ions previously reported by **Avsejs *et al.* (2002)**. The most prominent ion peak was at *m/z* 268 (base peak) which represents the tropylium ion to which a proton is transferred through a McLafferty rearrangement (**Occolovitz, 1964**). Such cleavage, characteristic of these phenolic compounds, occurs on the side-chain in β position to the benzene ring.

Additional proofs to confirm the *n*-alkyl position at C-5 are giving by comparison of 124/123 ratio between *n*-alkylcatechols and *n*-alkylresorcinols. ARs (cardols) have been shown by other authors to give a base peak at *m/e* 124 ($[(\text{HO})_2\text{C}_6\text{H}_3\text{CH}_3 = \text{C}_7\text{H}_8\text{O}_2]^+$) (**Occolovitz, 1964; Briggs, 1974; Madrigal *et al.*, 1977**). Whereas urushiols (alkylcatechols, ACs) give a base peak at *m/z* 123 which corresponds to the ion $[(\text{HO})_2\text{C}_6\text{H}_3\text{CH}_2]^+$ (**Nakano *et al.*, 1970**). The same occurs when these compounds are derivatized with BSTFA. The base peak of these ARs TMS derivatives was at *m/z* 268 $[(\text{TMSO})_2\text{C}_6\text{H}_3\text{CH}_3]^+$ according to **Madrigal *et al.* (1977)** but that of the ACs was at *m/z* 267 $[(\text{TMSO})_2\text{C}_6\text{H}_3\text{CH}_2]^+$ (**Billets *et al.*, 1976**).

Since these basic works, more recently other investigators (**Niimura and Miyakoshi, 2003**) are showing that the ratio between the relative intensity (%) of both ions *m/z* 124/123 was different in both cases. The value of this ratio is > 1 for the ARs and the opposite is true for the ACs. Table 2 shows the published values of these ratios in the literature.

Table 2. Values of the m/z 124/123 ratio of the alkylresorcinols (ARs) and alkylcatechols (ACs) compounds calculated from the MS published by several authors in the last decades.

Alkylresorcinols (ARs) (cardols)		Alkylcatechols (ACs) (urushiols)	Reference
Ratio m/z 124/123	Ratio m/z 268/267 [†]	Ratio m/z 124/123	
3.1 (>1) (<i>n</i> -C ₁₅)	-	-	Athukorala <i>et al.</i> , 2010
-	6.7 (>1) (<i>n</i> -C ₁₇)	-	Ross <i>et al.</i> , 2004
1.5 (>1) (<i>n</i> -C ₁₅)	-	0.9 (<1) (<i>n</i> -C ₁₅)	Niimura and Miyakoshi, 2003
-	4.0 (>1) (<i>n</i> -C ₁₉)	-	Linko <i>et al.</i> , 2002
-	50.0 (>1) (<i>n</i> -C ₁₉)	-	Avsejs <i>et al.</i> , 2002
2.9 (>1) (<i>n</i> -C ₁₉)	-	-	Seitz, 1992
-	2.0 (>1) (<i>n</i> -C ₂₁)	-	This study

[†]in the EIMS of the trimethylsilylated mixture of compounds

Other ions also present are at m/z 73 ($[(\text{CH}_3)_3\text{Si}]^+$), m/z 520 due to the molecular peak, and also m/z 281 related to m/z 137 plus 2 additional trimethylsilyl groups ($[\text{C}_8\text{H}_9\text{O}_2]^+$ according to **Briggs, 1974**). Finally, the fragment m/z 310 is probably related to (m/z 166 ($[\text{C}_{10}\text{H}_{14}\text{O}_2]^+$ according to the same study) and 2 additional trimethylsilyl groups. Both fragments 281 and 310 are characteristics in the mass spectrum of TMS derivatives of 5-*n*-alkylresorcinols (Figure 4).

In our case, the analysis of the EIMS of the compound showed a 268/267 ion ratio close to that reported on the literature (**Zarnowski *et al.*, 2000 and references therein**) for a meta position 1,3- for the two hydroxyl groups in the aromatic ring.

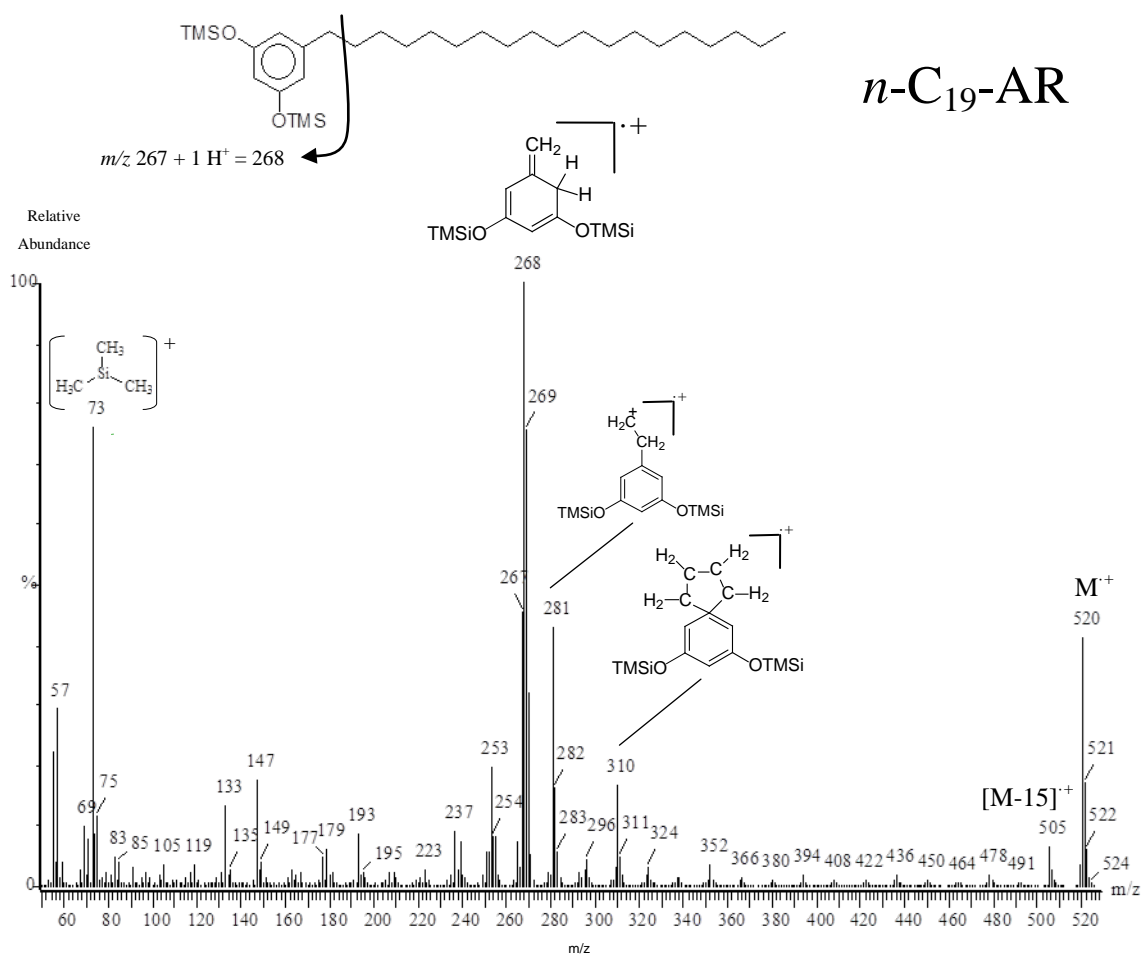


Figure 4. Electron impact (EI) mass spectrum of (1,3-dihydroxy-5-*n*-nonadecylbenzene) as bis-trimethylsilyl ether contained in the leaves of the saltcedar (*Tamarix canariensis*) and representative of the respective homologous series of resorcinol linked to an aliphatic and saturated side chain. The structure for this homolog is also shown.

2.3. 5-*n*-Alkylguaiacols (AGs)

While 5-*n*-alkylresorcinols have been previously described many times in the last decades, to the best of our knowledge we describe here for the first time as natural products a series of AGs.

GC/MS analysis of the total lipid extract of the leaves from the saltcedar revealed the presence of a homologous series of compounds (Figure 5) ranging from n -C_{13:0} to n -C_{27:0} with an odd over even dominance. Total yield of these phenolic lipids was 14,4 g·kg⁻¹. The most abundant homologues were heneicosylguaiacol (n -C₂₁) (5,60 g/kg; 38.8%) and nonadecylresorcinol (n -C₁₉) (4,03 g/kg; 27.9%). So the AG profile of the homologues was similar to that of the AR above discussed and this could indicate a similar metabolic synthesis and the same structural role when they are incorporated to the leaf waxy scaffold. Total alkylguaiacol content and individual amount of each homologue in the leaves of this tamarisk are given in Table 2.

The electron impact fragmentation of all these congeners was characterized by EI mass spectra (shown in Fig. 6) with one prominent fragment ion at m/z 210 which is consistent with long-chain alkyl derivatives of 1-hydroxy-3-methoxy-5-alkylbenzene which are related to guaiacol skeleton.

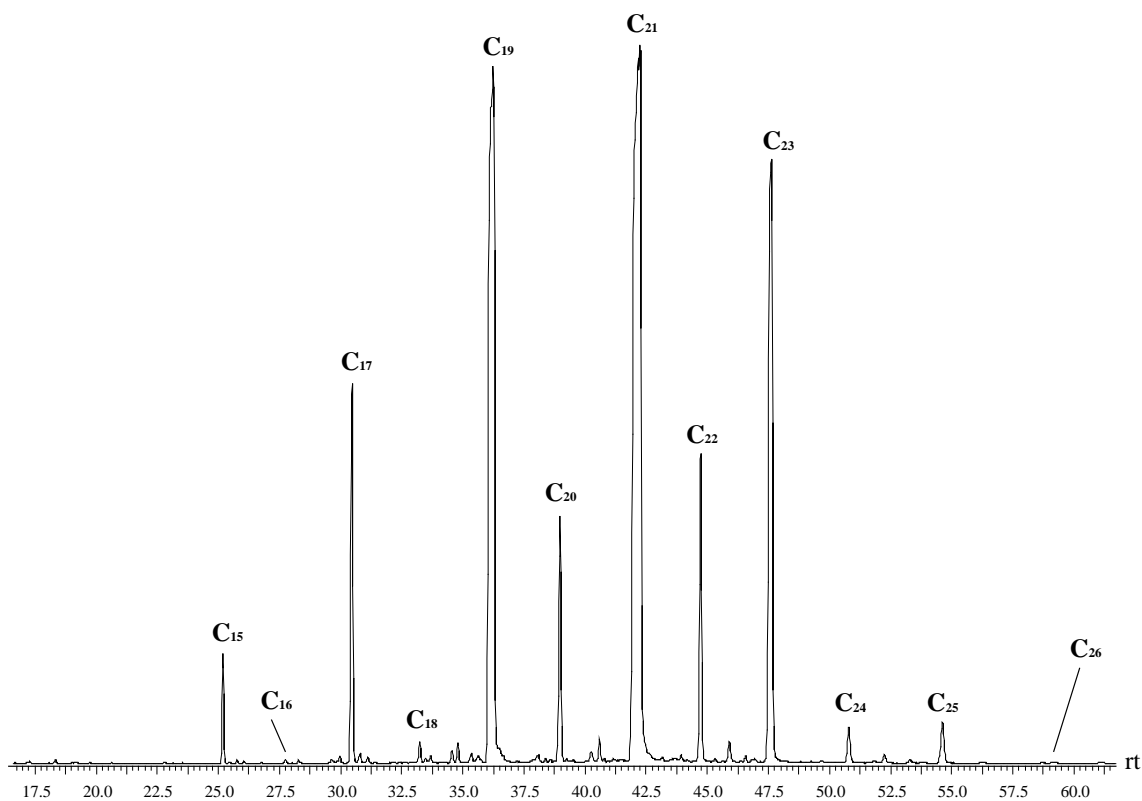


Figure 5. Mass chromatogram of m/z 210 of the total lipid extract (as TMSi ethers) of the leaves of *Tamarix canariensis*. $C_n = n$ -alkyl C number

Methoxy and hydroxyl groups of short chain members of alkylguaiacols which are related to coniferyl alcohol have been scarcely identified in natural samples and always as 1-hydroxy-2-methoxy-4-alkylbenzene derivatives (between phenolics: vanillic acid, *cis* and *trans*-ferulic acid, *p*-coumaric acid, 4-acetylguaiacol) (Effendi *et al.*, 2008; Hosoya *et al.*, 2008), however long chain members have not been described to the best of our knowledge.

Identification of 5-*n*-alkylguaiacol silylated components was deduced from the base peak at m/z 210 which corresponds to molecules with a guaiacolic hydroxyl group derivatized with TMS and their corresponding molecular ion peak. The homologues range from n -C_{13:0} to n -C_{27:0} maximizing at n -C₂₁.

Interestingly the series includes prominent odd-numbered alkyl chain members as occurred with the ARs. The content and relative composition of the dominant homologues in ARs and AGs series was very similar. Table 3 includes the composition of this novel series of silylated long-chain guaiacolic lipids with the retention times and diagnostic ions referred to the chromatogram showed in Figure 5. Total yield of these polar lipids was very abundant (14.4 g·kg⁻¹).

In almost all works reported in the last decades related with resorcinolic 1,3-derivatives of alkyl phenols the alkyl and also the alkenyl side chain is meta to at least one phenolic hydroxyl group (Occolowitz, 1964). The proposed fragmentation mechanism under

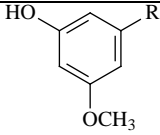
electron impact of these compounds has a main cleavage of this molecule containing an alkyl substituted aromatic ring by breakage in the β position to the benzene ring generating a benzylic carbocation (m/z 209) which may further rearrange to the tropylium ion (m/z 210) in a close pathway as ARs previously discussed.

(S2) Supplementary material 2 shows the mass spectra of each of the main alkylguaiacol homologues (n -C₁₅, n -C₁₆, n -C₁₇, n -C₁₈, n -C₁₉, n -C₂₀, n -C₂₁, n -C₂₂, n -C₂₃, n -C₂₄ and n -C₂₅). Figure 6 illustrates separately from the others the EI mass fragmentation of the second member most abundant of this series of phenolic alkylguaiacol derivatives (5- n -nonadecylguaiacol) bearing a C₁₉ n -alkyl chain as its TMS ether in order to interpret the main fragments. The analysis of this MS reveals similarities with that of the AR counterpart (n -C_{19,0}) (Figure 4). Alkylguaiacols are phenolic compounds characterized by possessing one hydroxyl group at position 1 and a methoxy group at position 3 of the benzene ring. Structure of these compounds substituted with a long alkyl chain at the position 5 of the aromatic ring as ARs was deduced. Proceeding as in the case of the 5- n -alkylresorcinols, inspection of the EIMS of the member of this serie (retention time: 38.9 min) in the total ion chromatogram (TIC) showed a 209/210-abundance ion ratio of 22%. For identification of spectra the data were compared with those of ARs published by **Occolowitz (1964)** and others which are detailed in the following MS main ions description (> 5% relative intensity normalized to the base ion). This confirmatory analysis of the presence of substituted guaiacols was done on the homologue which corresponded to a molecule with an alkyl side-chain of 19 carbon atom and characterized by the following other fragment ions appearing in a quantitative order of higher to lower abundance: m/z 210 (base peak) which corresponds similarly to observed in the ARs mass spectra, to the McLafferty

rearrangement and this ion occurs together with another at m/z 209 which is also prominent due to the dihydroxytropylium ion formed by direct β -cleavage (**Deszcz and Kozubek, 2000; Ross et al., 2001**), m/z 73 ($[(CH_3)_3Si]^+$), m/z 223 which represents the result of a γ -cleavage with respect to the benzene ring. Finally, fragment ions m/z 195, m/z 210, m/z 223, m/z 252, m/z 447 and m/z 462 ($[M]^+$) result from subtracting 58 Dalton $(CH_3)_2Si$ to those of the corresponding 5-*n*-nonadecylresorcinol (Figure 4) providing unambiguous evidence on their molecular structure according to their alkyl chain length. Fragments m/z 121 and 135 are characteristic of guaiacols according to **TTTT et al. (1999)**. The structural information for all AGs homologues described in this study is shown in Table 3.

Table 3

Gas chromatographic – mass spectrometry structural characteristics of 5-*n*-alkylguaiacols as their TMS-ethers derivatives identified in the leaves from *Tamarix canariensis*.

Compound		DB-5		main fragments m/z [‡]
		retention time (min)	$[M]^+$	
1-Hydroxy-3-methoxy-5- <i>n</i> -tridecylguaiacol (<i>n</i> -C _{13:0})		20,6	378(-)	210(-), 73(-), 223(-), 195(-), 252(-)
1-Hydroxy-3-methoxy-5- <i>n</i> -tetradecylguaiacol (<i>n</i> -C _{14:0})		22,8	392(-)	210(-), 73(-), 223(-), 195(-), 252(-)
1-Hydroxy-3-methoxy-5- <i>n</i> -pentadecylguaiacol (<i>n</i> -C _{15:0})		25,2	406(10)	210(100), 73(22), 223(14), 195(6), 252(4)
1-Hydroxy-3-methoxy-5- <i>n</i> -hexadecylguaiacol (<i>n</i> -C _{16:0})		27,7	420(-)	210(-), 73(-), 223(-), 195(-), 252(-)
1-Hydroxy-3-methoxy-5- <i>n</i> -heptadecylguaiacol (<i>n</i> -C _{17:0})		30,5	434(10)	210(100), 73(18), 223(14), 195(8), 252(6)
1-Hydroxy-3-methoxy-5- <i>n</i> -octadecylguaiacol (<i>n</i> -C _{18:0})		33,2	448(-)	210(-), 73(-), 223(-), 195(-), 252(-)
1-Hydroxy-3-methoxy-5- <i>n</i> -nonadecylguaiacol (<i>n</i> -C _{19:0})		36,2	462(32)	210(100), 73(48), 223(14), 195(8), 252(5)
1-Hydroxy-3-methoxy-5- <i>n</i> -eicosylguaiacol (<i>n</i> -C _{20:0})		39,0	476(10)	210(100), 73(35), 223(41), 195(20), 252(15)
1-Hydroxy-3-methoxy-5-<i>n</i>-henicosylguaiacol (<i>n</i>-C_{21:0})[†]		42,2	490(56)	210(100), 73(70), 223(68), 195(34), 252(28)
1-Hydroxy-3-methoxy-5- <i>n</i> -docosylguaiacol (<i>n</i> -C _{22:0})		44,7	504(10)	210(100), 73(22), 223(12), 195(7), 252(4)
1-Hydroxy-3-methoxy-5- <i>n</i> -tricosylguaiacol (<i>n</i> -C _{23:0})		47,6	518(14)	210(100), 73(29), 223(20), 195(12), 252(8)
1-Hydroxy-3-methoxy-5- <i>n</i> -tetracosylguaiacol (<i>n</i> -C _{24:0})		50,8	532(10)	210(100), 73(35), 223(15), 195(8), 252(6)
1-Hydroxy-3-methoxy-5- <i>n</i> -pentacosylguaiacol (<i>n</i> -C _{25:0})		54,6	546(10)	210(100), 73(-), 223(66), 195(8), 252(8)
1-Hydroxy-3-methoxy-5- <i>n</i> -hexacosylguaiacol (<i>n</i> -C _{26:0})		59,2	560(-)	210(-), 73(-), 223(-), 195(-), 252(-)
1-Hydroxy-3-methoxy-5- <i>n</i> -heptacosylguaiacol (<i>n</i> -C _{27:0})		64,7	574(-)	210(-), 73(-), 223(-), 195(-), 252(-)

[†]In bold is indicated the homologue most abundant of this series of guaiacolic lipids

[‡]Ions are ordered following the relative intensity to the base peak (100)

(-) intensity not calculated due to their low abundance

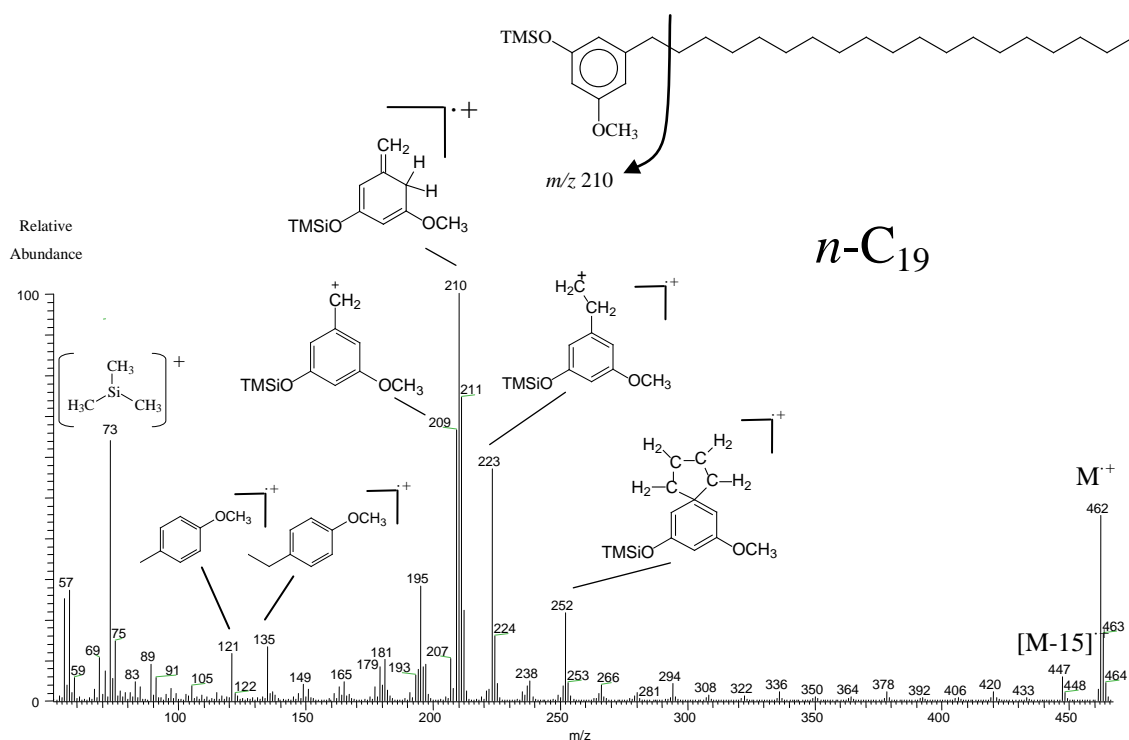


Figure 6. Electron impact (EI) mass spectrum of the major 5-*n*-alkylguaiacol (1-hydroxy-3-methoxy-5-*n*-nonadecylguaiacol \equiv 5-*n*-nonadecylguaiacol) (*n*-C₁₉) present in the leaves of the saltcedar (*Tamarix canariensis*). The structure for that compound is also shown.

2.4. Asymmetrical *n*-secondary alcohols

The extract of the leaves of the saltcedar is dominated by a secondary alkanol in the middle-right region of the TIC chromatogram (Fig. 1). Analysis of this abundant peak through its MS includes two prominent ions at m/z 257 (as the base peak) and m/z 369. These allowed us to identify it as the *n*-hentriacontan-12-ol (12-*n*-C₃₁-ol). Having recognized all the members of this series of 12-fatty alcohols the others, namely 14-, 13-, 11-, 10-, 9-, 8- and 7-hydroxyl fatty alcohols were also easily determined. So we present here for the first time in *Tamarix* genus to the best of our knowledge some of these homologous series of asymmetrical secondary alcohols. Table 4 resumes the

reports on secondary alcohols isolated from members of the Tamaricaceae family conducted by several authors during the last decades and shows that they are apparently scarcely represented in this family. For example, **Andhiwal and Kishore, 1984**, identified almost exclusively the hentriacontan-12-ol homologue in *Tamarix gallica*. Different asymmetrical *n*-secondary alcohols cited in the literature of the Tamaricaceae family are described in Table 4.

Table 4. Secondary alcohols previously identified in other studies on Tamaricaceae family

Species	Homologues detected	Reference
<i>Myricaria paniculata</i> - stems	12- <i>n</i> -C ₃₁ -ol	Li <i>et al.</i> , 2005
<i>Psorospermum androsaemifolium</i> - leaves	12- <i>n</i> -C ₃₁ -ol	Poumale <i>et al.</i> , 2008
<i>Tamarix dioica</i>	7- <i>n</i> -C ₃₁ -ol	Agrawal <i>et al.</i> , 1991
<i>Tamarix gallica</i> – Aerial parts	10- <i>n</i> -C ₂₉ -ol, 12- <i>n</i> -C ₂₉ -ol, 12- <i>n</i> -C ₃₁ -ol (97%), 12- <i>n</i> -C ₃₃ -ol, 14- <i>n</i> -C ₃₃ -ol	Andhiwal and Kishore, 1984
<i>Tamarix hampeana</i> - flowers	19- <i>n</i> -C ₄₆ -ol	Aykaç and Akgül, 2010

For diagnostic purposes Figure 7 shows how the relative position of the hydroxyl group over the aliphatic chain of these compounds allows the unambiguous identification of the homologue of each series (from 7- to 14-) due to the formation of two very distinctive ions. For example, the branched alcohol at the C-12 position resulting from *n*-hentriacontane paraffin as their trimethylsilylated derivative show the following two prominent fragments due to the α -cleavage, m/z 257, which is the diagnostic ion for all members of the 12- series and m/z 369. Corresponding to the other α -cleavage.

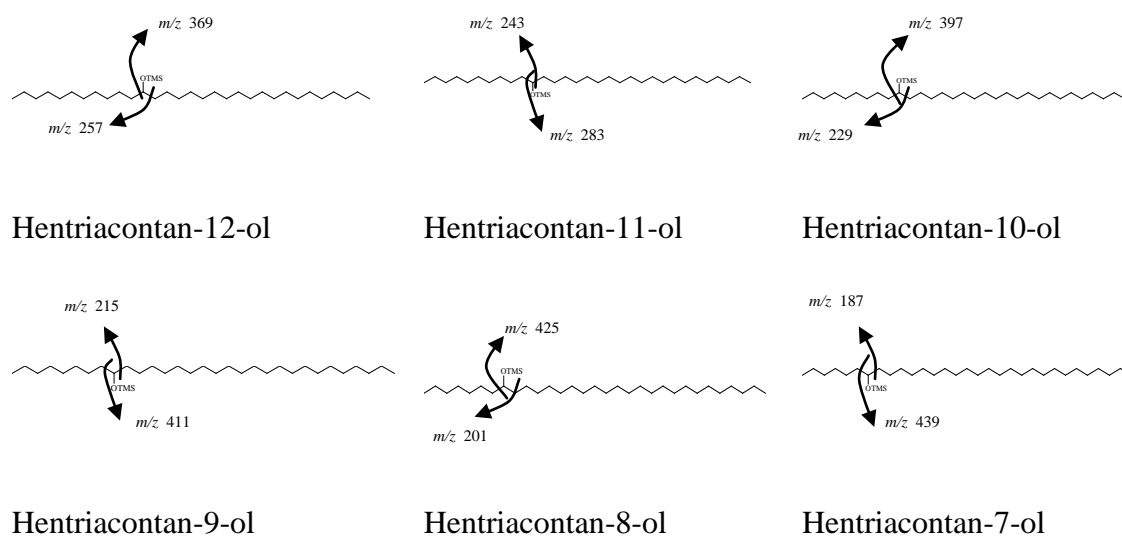


Figure 7. Main fragments observed in the mass spectra of the asymmetrical secondary alcohols identified in the leaves of the saltcedar with the hydroxyl group located in the 12-, 11-, 10-, 9-, 8- and 7- positions when the homologues are derived of the hentriacontan-*X*-ol where *X* represents the carbon atom which supports the functional group.

Figure 8 shows the concentration of the 53 homologues expressed as mg·kg⁻¹ of dry weight of these series of *n*-secondary alcohols identified in our study evidencing that the *n*-C₃₃ member was the most abundant among the 14- and 13-*n*-fatty alcohols, *n*-C₃₁ member was the most abundant among the 12- 11- 9- and 8-*n*-fatty alcohols while the *n*-C₂₉ was clearly the major in the 10- and 7- series. The most abundant isomer homologue was hentriacontan-12-ol.

Finally, the *n*-alkanes (*n*-C₁₉ – *n*-C₃₂) of the leaves of this plant maximized together with several of these fatty alcohols at odd carbon numbered homologues (C-29 and C-31). These could suggest that they are synthesized by a different pathway from those homologues such as the *n*-alkanols (*n*-C₇ – *n*-C₃₃) ($C_{max} = n-C_{30}$) and *n*-alkanoic acids (*n*-C₆ – *n*-C₃₃) ($C_{max} = n-C_{16}$ and *n*-C₃₀).

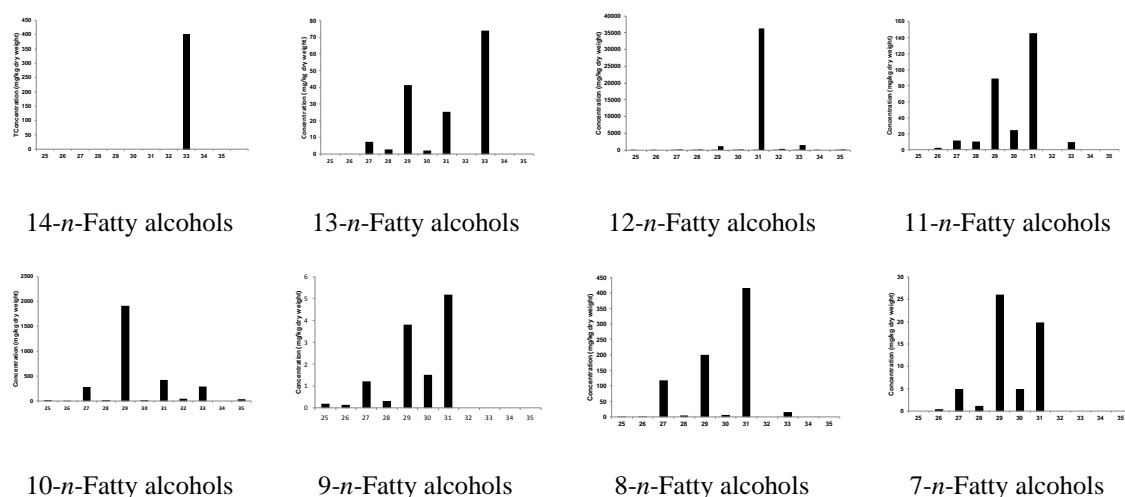


Figure 8. Homologue series of all 53 secondary alcohols (14-, 13-, 12-, 11-, 10-, 9-, 8- and 7-) identified in the leaves of the saltcedar (*Tamarix canariensis*).

Below (Figure 9) is presented the mass spectrum of the hentriacontan-12-ol as its trimethylsilylated derivative. The fragmentation was dominated as was indicated before by two prominent ions in the middle of the MS resulting from the α -cleavage to the TMSi group and both fragments enable to locate the position of the OH group of the original alcohol as was indicated in a previous study on the secondary alcohols from several plants (**Holloway *et al.*, 1976**). So, in this *n*-C₃₁ homologue TMSi ether derivative mass spectrum, ion *m/z* 257, that is also the base ionic peak, corresponding to a fragment [C₁₂H₂₄OSi(CH₃)₃]⁺ derived from the shorter chain end resulting from α -cleavage, was slightly stronger (and the base peak) than the second α -fragment *m/z* 369 [C₂₀H₄₀OSi(CH₃)₃]⁺ from the longer chain end. This silylated derivative was further characterized by the molecular ion *m/z* 524 which shows very low abundance, the M-15 fragment *m/z* 509 due to the loss of a methyl group and the expected silylated fragments derived from fatty alcohols *m/z* 75 (*ca* 75% rel. intensity) > 103 (*ca* 69% rel. intensity) altogether with the trimethylsilyl (TMS) fragment ion (*m/z* = 73) (*ca* 79% rel. intensity) which was the most abundant of these ions in the lower end of the MS.

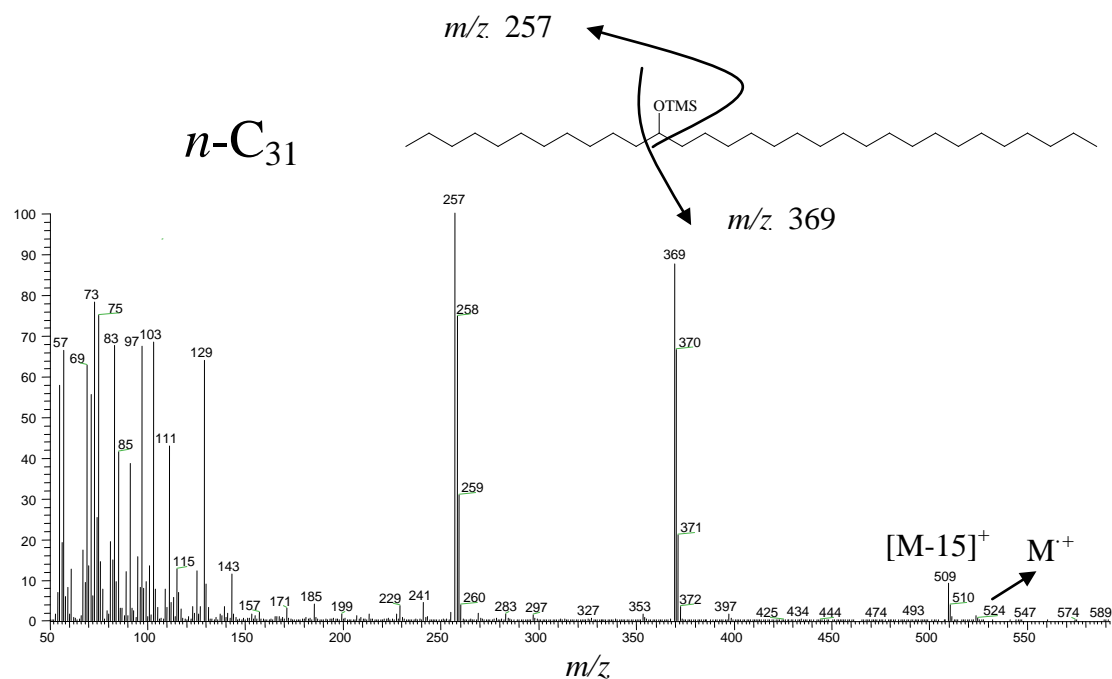


Figure 9. Electron impact (EI) mass spectrum *n*-hentriacontan-12-ol identified in the leaves of the saltcedar (*Tamarix canariensis*) and representative of the respective homologous series of asymmetrical *n*-secondary alcohols. The structure for that compound is also shown.

3. Conclusions

The qualitative composition and semiquantitative content of three groups of natural compounds investigated in the saltcedar (*Tamarix canariensis* Willd.) revealed that could be an important source of naturally occurring non-isoprenoid polyketide-derived phenols both 5-*n*-alkylresorcinols and 5-*n*-alkylguaiacols.

Here in this study, it has been detected: i. Two homologous series of phenolic lipids, namely 1,3-dihydroxy-5-alkylbenzenes (alkylresorcinols, ARs) and 1-hydroxy-3-methoxy-5-*n*-alkylguaiacol (alkylguaiacols, AGs) had very similar pattern and characterized by substituent alkyl chains of length C₁₃ to C₂₇ and including the even-

numbered members were found to be present in the total lipid extract of the leaves from the saltcedar though the odd carbon number homologues dominated.

A homologous series of 5-*n*-alkylguaiacols described for the first time as natural compounds is reported here with a mass spectrometric and gas chromatographic behavior similar to that of ARs. Although odd-numbered hydrocarbon side chain homologues of the ARs and AGs were more abundant members of the series; however, even numbers of carbon atoms were also present. Finally, 53 compounds comprising eight homologous series of secondary alcohols (14-, 13-, 12-, 11-, 10-, 9-, 8- and 7-) centered at the *n*-C₃₁ homologue were also described in *Tamarix* for the first time.

4. Materials and methods

4.1. Sampling site

Branches from the saltcedar (*Tamarix canariensis*) were collected near the Font Salada (46,19° N; 4,8° E; 332 m) in the county of Bages (Barcelona, Catalonia) close to an hypersaline well in the Salat creek near where this tributary of the Gavarresa stream finishes. Samples were transported to the laboratory and further analyzed. A voucher specimen (BCN 106840) was deposited at the Herbarium of the Faculty of Pharmacy, Universitat de Barcelona.

4.2. Analytical procedures

4.2.1. GC/MS preanalytical conditions: sample treatment, extraction, derivatization

Fresh leaves were air-dried at room temperature and crushed and homogenized in a glass mortar using a glass pestle using 25g of previously cleaned sea sand. All inert materials and tools were previously cleaned and rinsed with solvents before use. Ground

samples were introduced in cellulose thimbles and extracted in a Soxhlet apparatus during 24 h using a mixture of the organic solvents pentane / dichloromethane (DCM) (7:3, v/v). In our investigation the extraction of 7,1 g of milled leaves was performed in darkness conditions to avoid photo-oxidation processes of the compounds. 300 μL (0,06 mg) of internal standard (Friedeline; Aldrich) ($200 \text{ mg}\cdot\text{L}^{-1}$) were added to the extract which was subsequently rotoevaporated to approximately 0,5 mL and further concentrated under a nitrogen (N_2) stream. The extract of the sample was derivatized prior to performing the GC/MS analysis. Silylation of hydroxyl and carboxyl groups to get TMSi-ethers and esters respectively was achieved by addition of 300 μL N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA; Merck) and heating at 70°C for 1h prior GC-MS analysis.

4.2.2. GC/MS analysis

One microlitre of derivatized sample was injected (275°C) in a Fisons Instruments Gas Chromatograph equipment in splitless mode coupled to a mass detector (GC 8000/MD 800). Separation was performed on a DB-5ms column (30-m long by 0,32 mm i.d. fused silica capillary column coated with a 0,25 μm low-polarity liquid phase film thickness of 5% methylpolysiloxane, J&W Scientific Folsom, California). The mass scanning in total ion count (TIC) was acquired in the range of 50-650 daltons over 1s. The oven temperature was programmed as follows: starting at 40°C for 1 minute, and up to 230°C at a rate of $20^\circ\text{C min}^{-1}$, then from 230°C to 300°C at 2°C min^{-1} with a 20 min holding time. Helium was used as the mobile carrier gas with a flow rate of 1,0 $\text{mL}\cdot\text{min}^{-1}$. The inlet and transfer line temperatures were set at 300 and 310°C respectively. The ion source temperature was 250°C and ionization was in electronic impact mode (70 eV). Ion source and interface temperatures were 200 and 300°C respectively.

4.3. Identification of the compounds

Compounds were identified by chromatographic and spectroscopic means. In this study ARs compounds were identified by comparing their characteristics mass fragmentation patterns and retention times with those reported in literature (**Avsejs *et al.*, 2002; Ross *et al.*, 2004**). The identification of the new 5-*n*-alkylguaiacols (AGs) homologues was deduced similarly with the ARs from the molecular ion and the base peak m/z 210.

4.4. Quantification

The relative compositions and total amounts of the homologues were estimated from the integrated area of the peaks in the TIC using the MassLab software package.

The semiquantitative results were obtained by using the single internal standard, in our case friedeline.

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Supplementary data

Resorcinol and *m*-guaiacol alkylated derivatives and asymmetrical secondary alcohols in the leaves from *Tamarix canariensis*

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S1. 5-*n*-alk(en)ylresorcinols (saturated and unsaturated) homologues, total amounts (µg/g) (in parenthesis) and plant tissues where they accumulates reported in literature.

S1

5-*n*-Alk(en)ylresorcinols (saturated and unsaturated) homologues, total amounts (µg/g dry weight) (in parenthesis) and plant tissues where they accumulates reported in literature.

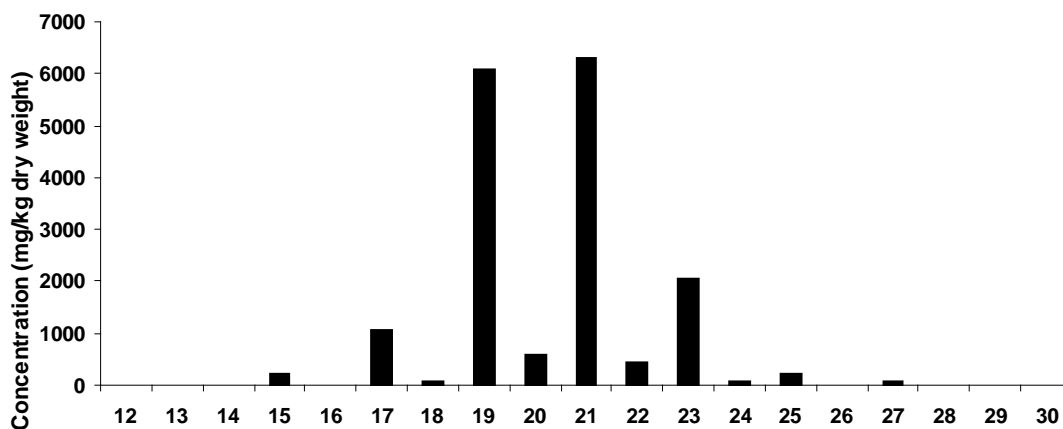
Origin, source, plant tissue, concentration (µg/g), homologue composition and name of the constituents	Reference
<i>Apatococcus constipatus</i> (Green microalga): <i>n</i> -C _{15:0} [†] , <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} [†] , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; (0,2-5,7)	Zarnowski <i>et al.</i> , 2000
<i>Avena sativa</i> (Oat): whole grain crisp bread, <i>n</i> -C _{17:0} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; (40)	Landberg <i>et al.</i> , 2008
<i>Azotobacter chroococcum</i> (Bacterium): <i>n</i> -C _{15:0} , <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} .	Zarnowski <i>et al.</i> , 2004b
<i>Eriophorum angustifolium</i> (Common cottongrass): <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i>-C_{25:0} , <i>n</i> -C _{27:0} ; (139).	Avsejs <i>et al.</i> , 2002
<i>Eriophorum vaginatum</i> (Tussock cottongrass): <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} , <i>n</i> -C _{27:0} , 240.	Avsejs <i>et al.</i> , 2002
<i>Ginkgo biloba</i> (Ginkgo): <i>n</i> -C _{15:1} , <i>n</i> -C _{15:0} , <i>n</i> -C _{17:1} , <i>n</i>-C_{17:2} , <i>n</i> -C _{17:0} , fruit pulp (34-454) and leaves (27-87)	Zarnowska <i>et al.</i> , 2000
<i>Hordeum vulgare</i> (Barley): grains: <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i>-C_{25:0} .	Hengtrakul <i>et al.</i> , 1991
<i>Hordeum vulgare</i> (Barley): <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i> -C _{19:1} , <i>n</i>-C_{21:0} , <i>n</i> -C _{21:1} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; (41-210).	Zarnowski <i>et al.</i> , 2002
<i>Hordeum vulgare</i> (Barley): <i>n</i> -C _{15:0} , <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i>-C_{25:0} ; (42-51).	Ross <i>et al.</i> , 2003
<i>Hordeum vulgare</i> (Barley): whole grains, <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i>-C_{25:0} ; (90-100).	Landberg <i>et al.</i> , 2009
<i>Hordeum vulgare</i> (Barley): whole grains (285-296), ground grains (261-280)	Sampietro <i>et al.</i> , 2009
<i>Hordeum vulgare</i> (Barley): (32-103).	Shewry <i>et al.</i> , 2013
<i>Labisia pumila</i> : Leaves, 1-O-methyl-6-acetoxy-5-(pentadec-10Z-enyl)resorcinol, 1-O-methyl-6-acetoxy-5-pentadecylresorcinol, 5-(pentadec-10Z-enyl)resorcinol, 5-(pentadecyl)resorcinol.	Al-Mekhlafi <i>et al.</i> , 2012
<i>Mangifera indica</i> (mango): peels, 5-(11'Z-heptadecenyl)-resorcinol and 5-(8'Z,11'Z-heptadecadienyl)-resorcinol.	Knödler <i>et al.</i> , 2008
<i>Mangifera indica</i> (mango): <i>n</i> -C _{15:0} , <i>n</i> -C _{15:1} , <i>n</i> -C _{17:0} , <i>n</i>-C_{17:1} , <i>n</i> -C _{17:2} , <i>n</i> -C _{17:3} , <i>n</i> -C _{19:1} , <i>n</i> -C _{19:2} ; peels (79-1850) and pulp (5-187).	Knödler <i>et al.</i> , 2009
<i>Oryza sativa</i> (Rice): sedes, <i>n</i> -C _{13:0} , <i>n</i> -C _{15:0} , 5-(8'Z-heptadecenyl)-resorcinol(<i>n</i> -C _{17:1}), <i>n</i> -C _{17:0} , 50.	Suzuki <i>et al.</i> , 1996
<i>Panicum miliaceum</i> (Proso millet): grains: <i>n</i> -C _{15:0} , <i>n</i> -C _{17:1} , <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:1} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} .	Hengtrakul <i>et al.</i> , 1991
<i>Pisum sativum</i> (Pea): <i>n</i> -C _{13:0} , <i>n</i> -C _{15:0} , <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} , <i>n</i> -C _{27:0} , whole seeds (0.02-0.33), pericarps (0.45-26.5) and cotyledons (0.06-0.72).	Zarnowski and Kozubek, 1999
<i>Rhynchospora alba</i> (white beak-sedge): <i>n</i> -C _{21:0} , <i>n</i>-C_{23:0} , <i>n</i> -C _{25:0} ; (46).	Avsejs <i>et al.</i> , 2002
<i>Secale cereale</i> (Rye): bran; <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{21:1} , <i>n</i> -C _{23:0} , <i>n</i> -C _{23:1}	Mullin and Collins, 1991
<i>Secale cereale</i> (Rye): grains: <i>n</i> -C _{15:0} , <i>n</i> -C _{17:1} , <i>n</i> -C _{19:2} , <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} , <i>n</i> -C _{20:2} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:1} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} .	Hengtrakul <i>et al.</i> , 1991
<i>Secale cereale</i> (Rye): whole grain, <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} ; (1130-1240).	Mullin <i>et al.</i> , 1992
<i>Secale cereale</i> (Rye): kernels from developing seedlings, <i>n</i> -C _{17:0} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; (2-8).	Deszcz and Kozubek, 2000
<i>Secale cereale</i> (Rye): <i>n</i> -C _{17:0} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; 549 – 1.022; kernel of whole grains (626-698) and flour (639-677)	Ross <i>et al.</i> , 2001
<i>Secale cereale</i> (Rye): <i>n</i> -C _{15:0} , <i>n</i> -C _{17:0} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; (720-761).	Ross <i>et al.</i> , 2003
<i>Secale cereale</i> (Rye): bran oil, <i>n</i> -C _{17:0} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; (5- <i>n</i> -(2'-keto-14'-(Z)-heneicosenyl)resorcinol, 5- <i>n</i> -(2'-ketoheneicosyl)resorcinol), (38000).	Iwatsuki <i>et al.</i> , 2003
<i>Secale cereale</i> (Rye): whole grain flour; (726)	Chen <i>et al.</i> , 2004
<i>Secale cereale</i> (Rye): <i>n</i>-C_{17:0} , <i>n</i> -C _{19:1} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; whole grain flour (927), whole grain organic flour (1008), rye bran (4108) and whole grain rye bread (524)	Mattila <i>et al.</i> , 2005
<i>Secale cereale</i> (Rye): commercial raw rolled rye flakes: <i>n</i> -C _{15:0} , <i>n</i> -C _{17:0} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} , <i>n</i> -C _{27:0} , <i>n</i> -C _{29:0} .	Francisco <i>et al.</i> , 2005a
<i>Secale cereale</i> (Rye): bran: <i>n</i> -C _{15:0} , <i>n</i> -C _{17:0} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} , <i>n</i> -C _{27:0} , <i>n</i> -C _{29:0} .	Francisco <i>et al.</i> , 2005b
<i>Secale cereale</i> (Rye): grains, <i>n</i> -C _{17:0} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; whole grain intact and milled (833 and 643); bran and aleurone milled (2.921 and 1.230).	Landberg <i>et al.</i> , 2007
<i>Secale cereale</i> (Rye): whole-grain crisp bread, <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; (690)	Linko-Parvinen <i>et al.</i> , 2007
<i>Secale cereale</i> (Rye): seedlings, controls, <i>n</i> -C _{15:0} , <i>n</i> -C _{17:1} , <i>n</i>-C_{17:0} , <i>n</i> -C _{19:1} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:1} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:1} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; (2-8).	Magnucka <i>et al.</i> , 2007
<i>Secale cereale</i> (Rye): whole grains (952-1096), ground grains (950-1017), whole bran (2144-2246), whole flour (1163-1284)	Gajda <i>et al.</i> , 2008
<i>Secale cereale</i> (Rye): <i>n</i>-C_{17:0} , <i>n</i> -C _{19:1} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; bran (outermost), shorts, C flour and B (innermost) flour; (1966, 772, 34 and 26); wholemeal grain flour; (1430).	Heiniö <i>et al.</i> , 2008
<i>Secale cereale</i> (Rye): wax cuticle of leaves: <i>n</i> -C _{13:0} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:0} , <i>n</i>-C_{23:0} , <i>n</i> -C _{25:0} , <i>n</i> -C _{27:0} .	Ji and Jetter, 2008
<i>Secale cereale</i> (Rye): whole grain crisp bread, <i>n</i> -C _{17:0} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; (776).	Landberg <i>et al.</i> , 2008
<i>Secale cereale</i> (Rye): <i>n</i> -C _{15:0} , <i>n</i> -C _{17:1} , <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:1} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:1} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:1} , <i>n</i> -C _{25:0} ; outer parts, kernels, of grains (1343-1427).	Landberg <i>et al.</i> , 2009
<i>Secale cereale</i> (Rye): <i>n</i> -C _{17:0} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} , wholegrain flour (972), refined flour (90), bran (2753).	Andersson <i>et al.</i> , 2010
<i>Secale cereale</i> (Rye), (797-1231).	Shewry <i>et al.</i> , 2013
<i>Trichophorum cespitosum</i> : <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i>-C_{25:0} , <i>n</i> -C _{27:0} ; (177)	Avsejs <i>et al.</i> , 2002
<i>xTriticosecale</i> (Triticale): grains: <i>n</i> -C _{15:0} , <i>n</i> -C _{17:1} , <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:1} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} .	Hengtrakul <i>et al.</i> , 1991
<i>xTriticosecale</i> (Triticale): <i>n</i> -C _{17:0} , <i>n</i>-C_{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; (439-647).	Ross <i>et al.</i> , 2003
<i>xTriticosecale</i> (Triticale): <i>n</i> -C _{15:0} , <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i> -C _{19:1} , <i>n</i>-C_{21:0} , <i>n</i> -C _{21:1} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; (360-700).	Athukorala <i>et al.</i> , 2010
<i>Triticum aestivum</i> (Soft wheat): bran, <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} , <i>n</i> -C _{27:0} .	Mullin and Collins, 1991
<i>Triticum aestivum</i> (Soft wheat): grains: <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:1} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} .	Hengtrakul <i>et al.</i> , 1991
<i>Triticum aestivum</i> (Common wheat): bran, <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; (2.010-2.700).	Mullin <i>et al.</i> , 1992

(Continued)

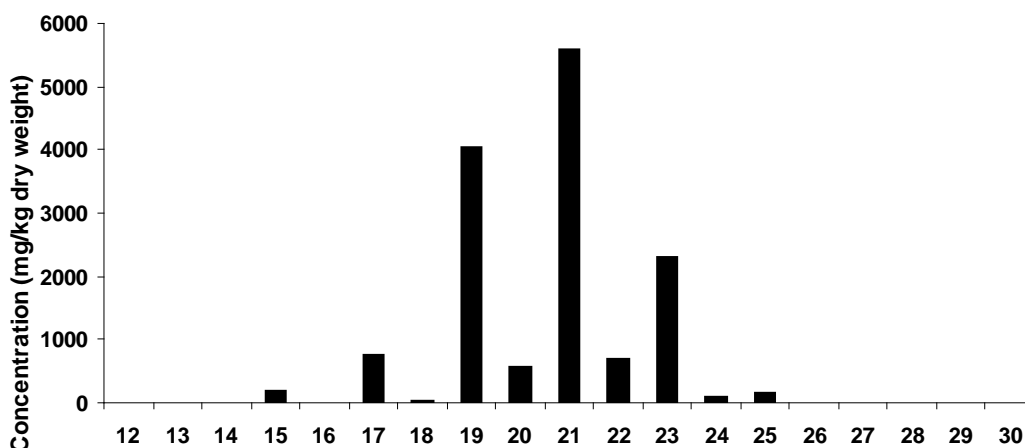
Origin, source, plant tissue, concentration ($\mu\text{g/g}$), Homologue composition [†] and name of the constituents	Reference
<i>Triticum aestivum</i> (Soft wheat): <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} . (489-1,429).	Ross <i>et al.</i> , 2003
<i>Triticum aestivum</i> (Soft wheat): bran oil, <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} . (5- <i>n</i> -(14'- <i>Z</i>)-nonadecenyl)resorcinol, 5- <i>n</i> -(2'-keto-14'- <i>Z</i> -heneicosenyl)resorcinol, 5- <i>n</i> -(2'-keto-heneicosyl)resorcinol). (19100).	Iwatsuki <i>et al.</i> , 2003
<i>Triticum aestivum</i> (soft winter & spring wheat): grains, <i>n</i> -C _{15:0} , <i>n</i> -C _{17:1} , <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:1} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} . (212-240).	Zarnowski <i>et al.</i> , 2004
<i>Triticum aestivum</i> (Common spring wheat): grains, <i>n</i> -C _{19:1} (x2), <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} (x3), <i>n</i> -C _{19:0} , <i>n</i> -C _{21:1} (x2), <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} . (19-302).	Zarnowski and Suzuki, 2004
<i>Triticum aestivum</i> (Soft wheat): spring and winter varieties (227 – 639): <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} and cereal ingredients: whole grain wheat, rye and barley – rye bran and flour – wheat bran (412/726/8 – 2.758/99 – 2.211): <i>n</i> -C _{17:0} , <i>n</i>-C_{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i>-C_{25:0}	Chen <i>et al.</i> , 2004
<i>Triticum aestivum</i> (Soft wheat): crisp bread, <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} . (308)	Linko-Parvinen <i>et al.</i> , 2007
<i>Triticum sp.</i> (Soft wheat): grains, <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; whole grain wheat intact and milled (576 and 528); wheat bran and aleurone milled (2.923 and 1.024).	Landberg <i>et al.</i> , 2007
<i>Triticum aestivum</i> (Soft wheat): <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} , winter wheat grain (220-652) and spring wheat grain (254-537).	Andersson <i>et al.</i> , 2008
<i>Triticum aestivum</i> (Soft wheat): whole-grain flour, <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; 47; whole grain pasta, <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} , 194; refined grain crisp bread, <i>n</i> -C _{17:0} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} , 31; refined grain soft bread, <i>n</i> -C _{17:0} , <i>n</i>-C_{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} , 37; refined grain flour, <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; 25; refined grain pasta, <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; 8.	Landberg <i>et al.</i> , 2008
<i>Triticum aestivum</i> (Common spring wheat): <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:1} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:1} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; outer parts, kernels, of grains (500-655).	Landberg <i>et al.</i> , 2009
<i>Triticum aestivum</i> (Winter wheat): <i>n</i> -C _{17:1} , <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:1} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:1} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:1} , <i>n</i> -C _{25:0} ; outer parts, kernels, of grains (494-536).	Landberg <i>et al.</i> , 2009
<i>Triticum aestivum</i> (Soft wheat): whole grains (740-758), ground grains (725-740).	Sampietro <i>et al.</i> , 2009
<i>Triticum aestivum</i> (Soft wheat): <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} , wholegrain flour (490-710), refined flour (36), bran (3625), wholegrain spelt wheat flour (650) refined spelt wheat flour (80).	Andersson <i>et al.</i> , 2010
<i>Triticum sp.</i> (Soft wheat): bran, <i>n</i> -C _{15:0} , <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:1} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} . (680).	Athukorala <i>et al.</i> , 2010
<i>Triticum aestivum</i> (Soft wheat): whole wheat grains (763-971), ground wheat grains (658-748), whole wheat bran (2759-3186), whole wheat flour (243-269).	Gajda <i>et al.</i> , 2008
<i>Triticum sp.</i> (Soft wheat): bran, <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:1} , <i>n</i> -C _{23:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} . (2672-3645).	Liu <i>et al.</i> , 2012
<i>Triticum aestivum</i> (Soft wheat): bran, <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} . (1365).	Holt <i>et al.</i> , 2012
<i>Triticum aestivum</i> (Soft wheat): bread whole grain, (241-677).	Shewry <i>et al.</i> , 2013
<i>Triticum aestivum</i> subsp. <i>spelta</i> (Spelt), (490-741).	Shewry <i>et al.</i> , 2013
<i>Triticum</i> spp. (Wheat): <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; whole-wheat flour (759), white flour (47), organic white flour (44) and bran (3225).	Mattila <i>et al.</i> , 2005
<i>Triticum dicoccum</i> , (531-714).	Shewry <i>et al.</i> , 2013
<i>Triticum durum</i> (Hard wheat): grains: <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:1} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} .	Hengtrakul <i>et al.</i> , 1991
<i>Triticum durum</i> (Hard wheat): grains, <i>n</i> -C _{15:0} , <i>n</i> -C _{17:0} , <i>n</i> -C _{19:1} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:1} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} ; (185-238).	Zarnowski <i>et al.</i> , 2004a
<i>Triticum durum</i> (Hard wheat): <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} , kernels (251-618) and pasta products (215-270).	Landberg <i>et al.</i> , 2006
<i>Triticum durum</i> (Hard wheat): <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} . (194-531).	Andersson <i>et al.</i> , 2008
<i>Triticum durum</i> (Hard wheat): outer parts, kernels, of grains, <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i>-C_{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} . (370-452).	Landberg <i>et al.</i> , 2009
<i>Triticum durum</i> (Hard wheat): (194-531)	Shewry <i>et al.</i> , 2013
<i>Triticum monococcum</i> (Einkorn): (540-654).	Shewry <i>et al.</i> , 2013
<i>Triticum spelta</i> (Spelt wheat): <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} . (490-741).	Andersson <i>et al.</i> , 2008
<i>Triticum spelta</i> (Einkorn wheat): <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} . (545-654).	Andersson <i>et al.</i> , 2008
<i>Triticum spelta</i> (Emmer wheat): <i>n</i> -C _{17:0} , <i>n</i> -C _{19:0} , <i>n</i> -C _{21:0} , <i>n</i> -C _{23:0} , <i>n</i> -C _{25:0} . (531-714).	Andersson <i>et al.</i> , 2008
<i>Zea mays</i> (Maize): whole grains (10-13) and ground grains (10-12).	Sampietro <i>et al.</i> , 2009

[†]in bold is indicated the most abundant homologue, when data is available[‡]₀ denotes carbon numbered and number of insaturations of *n*-alkyl substituent

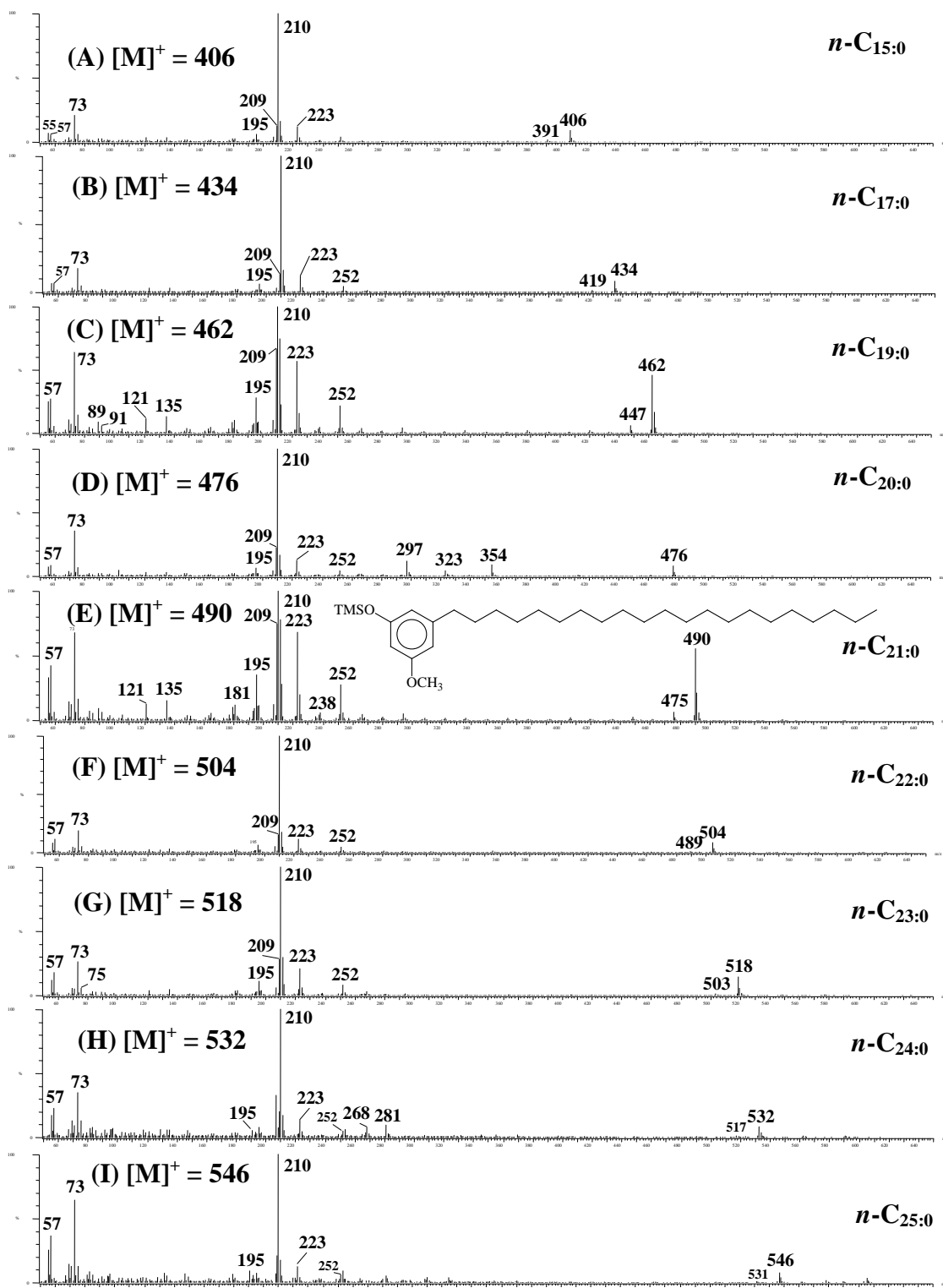
S2. Histogram of 5-*n*-alkylresorcinols contained in the leaves of the saltcedar (*Tamarix canariensis*). Numbers in abscissas refer to the chain length.



S3. Histogram of 5-*n*-alkylguaiacols contained in the leaves of the saltcedar (*Tamarix canariensis*).....S3



S4. EI mass spectra and structural information for 5-*n*-alkyl-*m*-guaiacols extracted from the leaves of *T. canariensis* including the following even- and odd-numbered hydrocarbon side chains homologues: *n*-C_{15:0} (A), *n*-C_{17:0} (B), *n*-C_{19:0} (C), *n*-C_{20:0} (D), *n*-C_{21:0} (E), *n*-C_{22:0} (F), *n*-C_{23:0} (G), *n*-C_{24:0} (H) and *n*-C_{25:0} (I) represented by the molecular ion peaks at 406, 434, 462, 476, 490, 504, 518 and 532 *m/z*, respectively. Structure for the *n*-C_{21:0}, the most abundant homologue, is also shown.



To date the study of the fragmentation of compounds with the base peak at m/z 210 has not been made because the natural occurrence of these compounds has also not been documented in the literature. Because this is the first report of these alkyl benzene derivatives in plants of the family Tamaricaceae.

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