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

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ABSTRACT

We have discovered that leaves from the halotolerant plant saltcedar (*Tamarix canariensis* [Willd.]) are a source of resorcinols and guaiacols. Specifically, the waxes of the saltcedar leaves contained high amounts of 5-*n*-alkylresorcinols (ARs; 17 g/kg dry weight), 5-*n*-alkyl-*m*-guaiacols (AGs; 14 g/kg dw) and secondary alcohols (44 g/kg dw). Herein we provide the report of 5-*n*-alkylresorcinols with long side-alkyl chains as natural compounds in Tamaricaceae. These compounds are homologous to ones previously reported almost exclusively in cereals. The ARs span the formulas n-C_{14} to n-C_{27}, the most abundant of which is n-C_{21}. Although the odd-C-numbered compounds dominate, there are non-negligible amounts of the even-numbered homologs. We also provide, the first-ever report of 11 homologs of 5-*n*-alkyl-*m*-guaiacols (AGs) as natural compounds from the sample plant, which we characterized as the corresponding trimethylsilyl (TMS)-ether derivatives. The AGs contain a hydroxyl group at carbon 1 of the phenolic nucleus, a methoxy group at position 3, and a (predominantly odd-C-numbered) linear alkyl chain linked to the benzene ring at position 5. They span the formulas n-C_{13} to n-C_{27}, the most abundant of which is n-C_{21}. Finally, we also isolated from saltcedar a series of eight asymmetric secondary alcohols, whose formulas range from n-C_{25} to n-C_{35} and whose major homolog is *n*-hentriacontan-12-ol.

1. Introduction

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

Only a handful of studies on the chemical composition of *T. canariensis* have been published, and these deal with phenolic lipids such as flavonoids, tannins and lignans in the *Tamarix* genus (Nawwar et al., 1982; Souliman et al., 1991; Parmar et al., 1994; Orabi et al., 2009). Recognizing this paucity, we sought to characterize the lipid composition of saltcedar leaves.

Phenols comprising a linear alkyl chain attached to a single benzene ring are known as 5-*n*-alkylphenols. Compounds in which the alkyl side-chain is attached to a dihydroxybenzene can exist in three isomer classes: *catechols*, *resorcinols* or *hydroquinones*, in which there are two hydroxyl groups linked to the aromatic ring at the *ortho* (1,2), *meta* (1,3) or *para* (1,4) positions, respectively. 5-*n*-Alkylresorcinols (ARs; also known as *1,3-dihydroxy-5-alkylbenzenes*, or *cardols*) are long-chain dihydric alkylphenols that are more abundant in nature than are alkylcatechols (which, as natural compounds, are known as *urushiols*) (Kozubek and Tyman, 1999). Both of these compound families are more abundant in nature than are the alkyl derivatives of hydroquinone (Tyman, 1979).

5-*n*-Alkylresorcinols have been associated with higher plants, lower plants, bacteria and fungi (Kozubek and Tyman, 1999). Despite their heterogeneous origin, they have been reported in high concentrations mainly in the outer layers of cereal (Gramineae ≡ - Poaceae) grains, especially 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 of these compounds have been isolated in other higher food plants, such as mango (*Mangifera indica*) (Knödler et al., 2009), and in lower

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organisms, such as mosses or algae (*e.g. Apatococcus constipates*) (Zarnowski et al., 2000). (S1) Supplementary Figure 1 shows the diverse composition of homologs in species that have been reported to contain these odd-numbered alkyl-substituted phenols. This chemical class primarily encompasses compounds of formula C_{17} to C_{25} and includes minor amounts of unsaturated homologs (alk[en]ylresorcinols) whose chain unsaturation degree is one (monounsaturated) or two (diunsaturated). Several epidemiological studies have associated the consumption of foods such as whole-grain cereals with lower incidence of degenerative diseases, including diabetes, obesity, coronary heart disease and certain cancers (Ross et al., 2001; Chen et al., 2004).

Fig. 1 shows the molecular structure of the AR homolog 5-henicosyl-1,3-benzendiol, which comprises a single phenolic ring with a straight, saturated, 21-C hydrocarbon side. In higher plants the most widely described congeners are those whose side-chain varies between C_{14} to C_{27} and is attached to position 5 of the phenol ring.

Nearly all of these reported ARs have a formula ranging from *n*-$C_{17:0}$ to *n*-$C_{25:0}$, although the most abundant structure varies by species. Some of these include unsaturated members (alkenylresorcinols), although in relatively low proportions relative to their saturated counterparts.

Little is known about the content of alkyl phenols in higher plants other than cereals. In the study reported here, we sought to address this lack of knowledge by studying *T. canariensis*. Herein we provide the first-ever report of a series of natural phenols and other compounds isolated from *T. canariensis via* total lipid extraction of its leaves. We qualitatively and semi-quantitatively analyzed the most abundant of these compounds, which we ultimately identified as 5-*n*-alkyl-*m*-guaiacols (AGs). We also found 5-*n*-alkylresorcinols and long-chain secondary alcohols that have not previously been reported in Tamaricaceae.

2. Results and discussion

2.1. General aspects

Although the total extract of the epicuticular waxes from the leaves of *T. canariensis* contained several families of compounds, some of which had previously been described in members of the genus *Tamarix* by other authors, we focused on the three most abundant chemical classes: ARs, AGs and *secondary alcohols*. The total amounts of compounds from these three classes were relatively high compared to those previously reported in other *Tamarix* plants. We attributed the main peaks in the Total Ion Current (TIC) chromatogram (Fig. 2) to two series of previously unreported phenols and eight homologous series of secondary alcohols.

Table 1 shows the content of AR and AG homologs as the sum of saturated derivatives having a side chain that contains 13 to 27 carbon atoms. The concentration of ARs (17.2 g/kg dw) was higher than that reported in other studies, except for that reported by Landberg et al. (2008) for the intermediate layer of wheat (*Triticum aestivum*) grains (16.0 g/kg dw). The homolog distribution that we found is very similar to that reported for ARs in other plant species. For example, in a recent study of common wheat (*T. aestivum*) and durum wheat (*T. durum*), Knödler et al. (2010) reported that the most abundant homologs were C21:0 and C19:0. These series are nearly always dominated by saturated homologs. However, in a previous study on mango (*Mangifera indica*) peel, Knödler et al. (2009) reported that the two unsaturated homologs C17:2 and C17:1 was dominant.

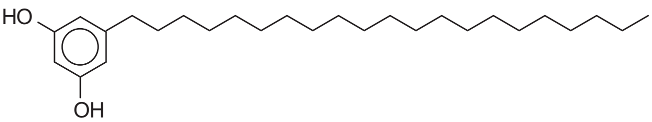

Fig. 1. 5-*n*-Heneicosylresorcinol (*n*-$C_{21:0}$) molecular structure.

2.2. 5-n-Alkylresorcinols (ARs)

We identified a homologous series of ARs, in which position 5 of the 1,3-dihydroxybenzene ring features a saturated alkyl side chain containing *n*-$C_{14:0}$ to *n*-$C_{27:0}$, whereby odd C-numbers dominate. The total yield of these ARs was 17.2 g/kg dw. The most abundant homologs were *n*-henicosylresorcinol (*n*-C_{21}) (6.3 g/kg dw; 37%) and nonadecylresorcinol (*n*-C_{19}) (6.1 g/kg dw; 35%). However, despite the predominance of odd C-numbered compounds, the even C-numbered compounds were not negligible in amount.

Fig. 3 shows the mass chromatogram corresponding to the base peak at *m/z* 268 for all derivatized ARs. The ARs were identified according to their mass spectra. Fig. 4 shows the EI mass spectrum of the homolog 5-*n*-nonadecylresorcinol (1,3-dihydroxy-5-*n*-nonadecylbenzene) (*n*-$C_{19:0}$). The EI fragmentation pattern of the TMS ether derivative of this alkylphenol is characterized by fragment ions previously reported by Avsejs et al. (2002). These include the base peak at *m/z* 268, which corresponds to a tropylium ion to which a proton is transferred through a McLafferty rearrangement (Occolowitz, 1964). Such cleavage, characteristic of these phenolic compounds, occurs on the side-chain beta to the benzene ring.

We found additional evidence corroborating the *n*-alkyl position (C-5) of the compounds that we discovered, by comparing the proportion (in terms of *m/z*) of *n*-ARs to *n*-alkylcatechols (ACs). This was based on literature reports that ARs give a base peak at $m/z = 124$ ($[(HO)_2C_6H_3CH_3 = C_7H_8O_2]^+$; Occolowitz, 1964; Briggs, 1974; Madrigal et al., 1977), whereas ACs give a base peak at $m/z = 123$ ($[(HO)_2C_6H_3CH_2]^+$); Nakano et al., 1970). A similar trend has been described for the corresponding TMS-derivatives of these compounds: TMS derivatives of ARs give a base peak at $m/z = 268$ ($[(TMSO)_2C_6H_3CH_3]^+$; Madrigal et al., 1977), whereas TMS derivatives of ACs give a base peak at $m/z = 267$ ($[(TMSO)_2C_6H_3CH_2]^+$; Billets et al., 1976). However, Niimura and Miyakoshi (2003) recently reported that ARs and ACs exhibit different ratios for the relative intensity (%) of $m/z = 124$ to that of $m/z = 123$: for ARs the value is >1, whereas for ACs the value is <1. The published data on *m/z* values for these compounds are summarized in Table 2. Other ions commonly found in the spectra of these compounds include $m/z = 73$ ($[(CH_3)_3Si]^+$); $m/z = 520$ (molecular peak); $m/z = 281$ (which corresponds to *m/z* 137 plus two additional trimethylsilyl groups $[[C_8H_9O_2]^+]$; Briggs, 1974); and $m/z = 310$ (probably related to $m/z = 166$ ($[C_{10}H_{14}O_2]^+$; Briggs, 1974) plus 2 additional trimethylsilyl groups. Interestingly, in our study, we found $m/z = 281$ and $m/z = 310$ in the mass spectra of the TMS-5-*n*-ARs (see Fig. 4). Analysis of the EI-MS spectra of the compounds showed an ion ratio ($m/z = 268$ to $m/z = 267$) close to that reported for *meta*-1,3-dibsubstituted phenols (Zarnowski et al., 2000 and references therein).

2.3. 5-n-Alkyl-m-guaiacols (AGs)

Naturally occurring ARs have been described extensively over the past few decades. 5-*n*-Alkyl-*m*-guaiacols were first characterized as natural products by Brown, 1992, using EI mass spectra; the same compounds were later characterized further by Kozubek and Tyman (1999). In our study of saltcedar leaves, we identified eleven homologs that, to the best of our knowledge, have never previously been reported. GC/MS analysis of the total lipid extract from the leaves revealed a homologous series of compounds