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# Very long-chain phenylpropyl and phenylbutyl esters from *Taxus baccata* needle cuticular waxes

Reinhard Jetter*, Adelheid Klinger, Stefanie Schäffer

*Julius-von-Sachs-Institut für Biowissenschaften, Universität Würzburg, Julius-von-Sachs-Platz 3, D-97082 Würzburg, Germany*

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**Abstract**

The cuticular wax of *Taxus baccata* L. needles was found to contain four different classes of long-chain esters that were identified by various chemical transformations with product assignment employing GC–MS. Homologous series of (1) 3-(4′-hydroxyphenyl)-propyl esters of $C_{20}$–$C_{36}$ fatty acids, (2) 4-(4′-hydroxyphenyl)-2-butyl esters of $C_{18}$–$C_{28}$ fatty acids, (3) 3-(3′,4′-dihydroxyphenyl)-propyl esters of $C_{20}$–$C_{32}$ fatty acids, and (4) 4-(3′,4′-dihydroxyphenyl)-2-butyl esters of $C_{18}$–$C_{28}$ fatty acids were identified. The four compound classes amounted to 0.1–3.6 μg/cm$^2$ of needle surface area, corresponding to 0.2–7.6% of the wax mixture, respectively. While both phenylpropyl ester series had a maximum for the homolog containing tetracosanoic acid, in the phenylbutyl esters homologs containing eicosanoic and docosanoic acids predominated.


*Keywords:* *Taxus baccata*; Gymnospermae; Yew; Cuticular wax; Leaves; Phenolics; Fatty acid esters

## 1. Introduction

The cuticle is an extracellular membrane covering all primary aboveground plant organs. It consists of a matrix of cutin (a biopolymer of di- and trihydroxy fatty acids) that is encrusted with 'intracuticular waxes' and covered with 'epicuticular waxes'. Diverse biological functions have been attributed to these waxes: preventing transpirational water loss over the plant surface (Schönherr, 1976); guarding leaf surfaces from accumulation of air-borne particles and spores (Barthlott and Neinhuis, 1997); keeping leaf surfaces dry (Holloway, 1970) and thus preventing the germination of pathogen spores (Kolattukudy, 1980; Deising et al., 1992); and directing the behavior of herbivorous insects that probe the surface for infochemicals (Espelie et al., 1991; Eigenbrode and Espelie, 1995).

The specific physiological and ecological functions of plant cuticles can only be understood based on their characteristic wax composition. On the one hand, saturated, unbranched very-long chain aliphatics have been reported as predominant wax constituents of diverse plant taxa (Baker, 1982). On the other hand, aromatic wax components have been identified in cuticular wax mixtures of only a small number of plant species (Walton, 1990). The occurrence of phenolics near the plant surface is of special interest, as these compounds might serve as protectants because of their light absorbing properties (Vogelmann, 1993; Krauss et al., 1997). Also, the geometry and electronic attributes of the aromatic ring system differ distinctly from those of other wax constituents, and it has been speculated that aromatic compounds might disturb the molecular arrangement of cuticular waxes. Compounds containing both phenolic and long-chain aliphatic moieties could influence the ecophysiological properties of the cuticle (Riederer and Schreiber, 1995).

In the course of ongoing studies on the chemical composition of cuticular lipids of diverse plant taxa, gymnosperm needles were analyzed. Cuticular waxes on *Taxus baccata* (Taxaceae) needles were found to contain various unknown constituents that had MS characteristics similar to phenolic compounds. The structure elucidation of these compounds is a prerequisite for further investigations into the structure and function of *T. baccata* cuticles. Therefore, the objective of the present work was to identify these novel constituents by various chemical transformations and product structure assignment employing GC–MS.

* Corresponding author. Fax: +49-931-888-6235.
*E-mail address:* jetter@botanik.uni-wuerzburg.de (R. Jetter).

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## 2. Results and discussion

The surface extracts from needles of *Taxus baccata* were separated into 14 distinct fractions by TLC on silica gel with $CHCl_3$–EtOH (99:1). Among these, two prominent bands migrating with $R_f$ 0.21 and 0.16 between primary alcohol and fatty acid standards were found to contain uncommon wax constituents and were designated as fractions A and B. According to their GC retention behavior (Table 1) and their MS characteristics, the constituents of these two bands belonged to two pairs of related homologous series $A_1$, $A_2$ and $B_1$, $B_2$, respectively.

In a first experiment, GC–MS data of underivatized fraction A were acquired. Although pairs of compounds could only be partially separated, the base ions $m/z = 134$ and 148 could be assigned to the compound classes $A_1$ and $A_2$, respectively, according to their GC-MS single ion traces. Homologs of class $A_1$ were found to elute shortly after those of $A_2$ (Table 1). A fragment ion at $m/z = 134$, interpreted as a hydroxyphenylpropenyl ion generated by elimination of the acid moiety, had previously been described for 3-(4′-hydroxyphenyl)-propyl esters (Boll et al., 1992; Olsen et al., 1998). All other MS signals reported for these esters were also characteristic of the compounds in class $A_1$, and it was surmised that the homologs in $A_1$ represented fatty acid esters of a hydroxyphenylpropanol.

This structure assignment was corroborated by GC–MS analysis of the corresponding acetate ester and TMSi ether derivatives. Although derivatization improved both the GC separation of individual compounds and the MS information obtainable from them, few reference spectra for the acetates or TMSi ethers of hydroxyphenylpropanol esters were available. The TMSi ether MS of compounds $A_1$ showed a base peak at $m/z = 206$ (Fig. 1a) that had previously been interpreted as an acid elimination product $[TMSiO–Ph–CH_2\text{-}CH=CH_2]^+$ of this compound type (Olsen et al., 1998). These derivatives were additionally characterized by other prominent MS fragment ions, either consisting of the phenolic $[TMSiO–Ph–CH_2]^+$, or the phenylpropyl moiety $[TMSiO–Ph–(CH_2)_3–OH]^+$, $[Me_2SiO–Ph–CH_2–CH=CH_2]^+$, or the entire molecule $[M]^+$, $[M–Me]^+$. Analogous fragments were found for the acetate derivatives of the compounds of the $A_1$ type, including the ions $[M]^+$ and [M-ketene]$^+$, representing the entire ester structure, the acid elimination products [M-acid]$^+$ and [M-acid-ketene]$^+$, as well as the phenylpropyl alcohol $[AcO–Ph–(CH_2)_3–OH]^+$ and its ketene elimination product. Finally, the hydroxybenzyl ion at $m/z = 107$ confirmed the phenolic structure, while two series of fragments $m/z = 55$, 69, 83, etc. and $m/z = 57$, 71, 85, etc. indicated the presence of an alkyl moiety.

Taken together, these data confirmed that compounds of the $A_1$ type represented fatty acid esters of 3-(4′-hydroxyphenyl)-propanol. Seventeen homologs with acid chain lengths of $C_{20}$–$C_{36}$ were identified. Only 3-(4′-hydroxyphenyl)-propyl tetracosanoate had been described as a constituent of stem and leaf wax of *Piper clarkii*

Table 1
GC retention times (min) of phenolic esters in *Taxus baccata* needle wax under the conditions used and MS data available

| Fatty acid carbon number | Fraction $A_1$ (4′-hydroxyphenyl)-propyl esters | Fraction $A_2$ (4′-hydroxyphenyl)-2-butyl esters | Fraction $B_1$ (3′,4′-dihydroxyphenyl)-propyl esters | Fraction $B_2$ (3′,4′-dihydroxyphenyl)-2-butyl esters |
|---|---|---|---|---|
| 18 | – | 26.1 t | – | 29.0 t |
| 19 | – | – | – | – |
| 20 | 29.8 T A | 29.7 T a u | 32.7 T | 32.5 T A |
| 21 | 31.6 t a | 31.5 T | 34.4 t | 34.2 T A |
| 22 | 33.4 T[a] A U | 33.3 T[a] a u | 36.2 T[a] A[a] | 35.9 T[a] A[a] |
| 23 | 35.1 T A u | 35.0 T | 37.8 T A | 37.5 T A |
| 24 | 36.8 T A U | 36.7 T a u | 39.5 T A | 39.2 T A |
| 25 | 38.5 T A u | 38.4 T | 41.0 T A | 40.7 T A |
| 26 | 40.1 T A U | 40.0 T | 42.6 T A | 42.3 T A |
| 27 | 41.7 T A | – | 44.3 T a | 44.1 t |
| 28 | 43.3 T A | 43.2 t | 45.7 T A | 45.6 t |
| 29 | 44.8 t | – | 47.1 t | – |
| 30 | 46.4 T A | – | 48.5 t | – |
| 31 | 47.9 t | – | 50.0 t | – |
| 32 | 49.3 T A | – | 51.5 t | – |
| 33 | 51.3 t | – | – | – |
| 34 | 53.1 T A | – | – | – |
| 35 | 55.8 t | – | – | – |
| 36 | 58.2 T a | – | – | – |

T, A, U: full mass spectra of the TMSi ether, the acetate or the underivatized compound, respectively, could be acquired. t, a, u: the TMSi ether, the acetate or the underivatized compound was identified by inspection of characteristic fragments.

[a] Cf. Fig. 1.

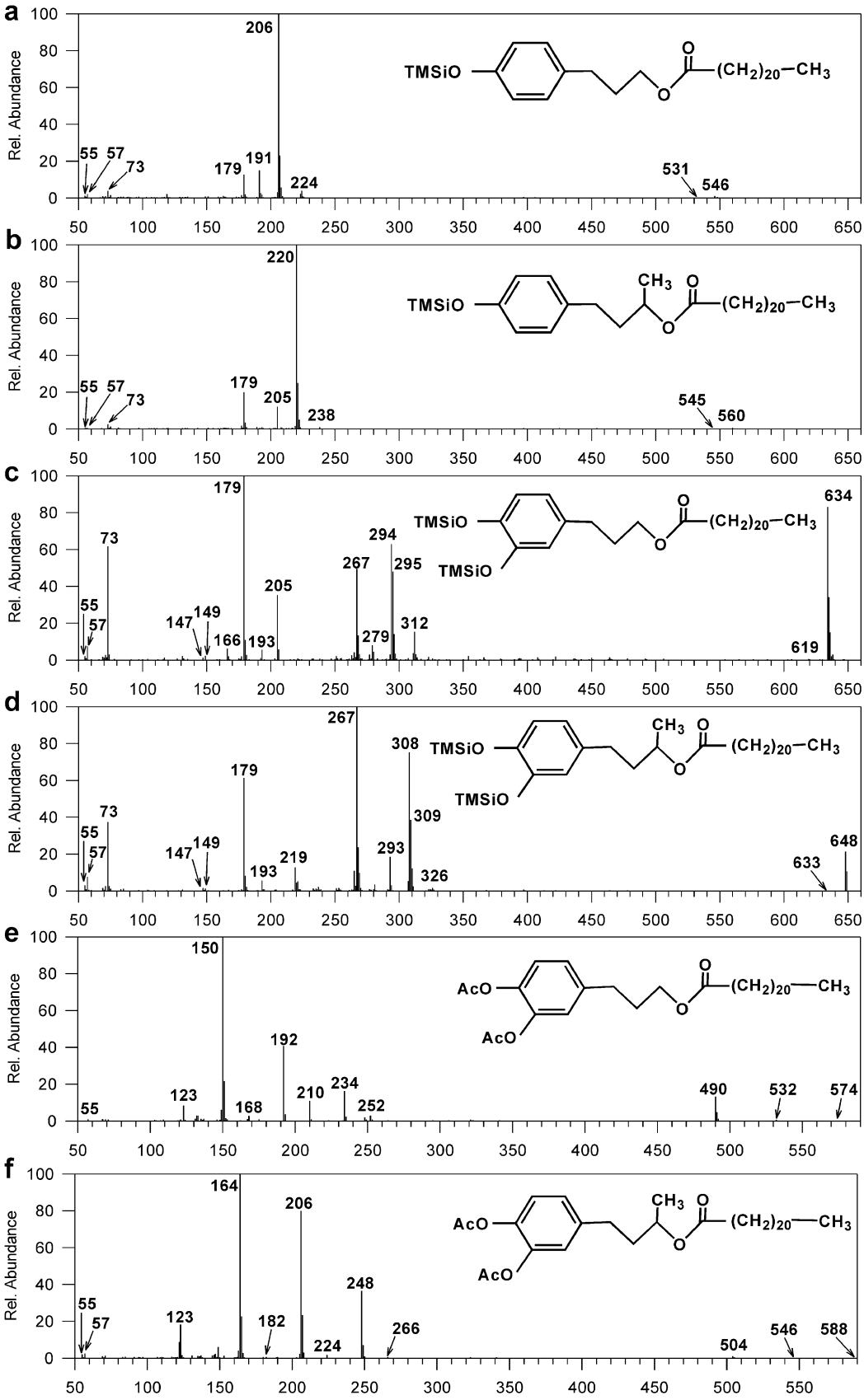


Fig. 1. Mass spectra of phenylalkyl esters from needle wax of *Taxus baccata*. Spectra of (a–d) the TMSi ethers or (e and f) the acetate esters are shown for one representative homolog from each of the classes of esters.

(Piperaceae) (Boll et al., 1992). The same ester, together with homologs containing $C_{25}$, $C_{26}$, $C_{32}$ and $C_{34}$ fatty acids, had previously been reported as constituents of needles of *Taxus canadensis*, but the possible localization of these compounds in the cuticular waxes had not been investigated (Olsen et al., 1998).

For compounds of class $A_2$, the MS of the underivatized constituents were found to be indistinguishable from those of class $A_1$, except for the hydroxyphenylalkenyl ion at $m/z = 148$. Additionally, the TMSi derivatives of compounds $A_2$ showed fragmentation patterns that were analogous to those of class $A_1$ (Fig. 1b). Ions interpreted to contain the entire molecule $[M]^+$, $[M–Me]^+$ or the phenylalkyl moiety [M–acid ketene]$^+$, [M-acid]$^+$, [M–Me-acid]$^+$ were shifted by $\Delta m/z = 14$ as compared to $A_1$ types. In contrast, those fragments comprising only the benzylic moiety $[TMSiO–Ph–CH_2]^+$ were identical for both classes. The acetates of compounds $A_2$ also showed all the fragments described for the corresponding hydroxyphenylpropyl esters, but all those ions containing the alkyl side chain of the aromatic alcohol were shifted by 14 mass units. Together with the similarities in the chromatographic behavior of both A series, this information led to the assumption that class $A_2$ compounds comprised esters of a second phenolic alcohol with an additional methyl group in the alkyl side chain. Although the possible hydroxyphenylbutyl alcohol isomers cannot be distinguished using the current spectroscopic information, it seems very plausible that $A_2$-type compounds contained esters of 4-(4′-hydroxyphenyl)-2*R*-butanol (alias (-)-rhododendrol), an alcohol previously identified in the needles of *Taxus baccata* (Das et al., 1993a, b) and *T. brevifolia* (Chu et al., 1994). Accordingly, the two compound classes $A_1$ and $A_2$ were found to represent fatty acid esters of two homologous phenolic diols, 3-(4′-hydroxyphenyl)-propanol and 4-(4′-hydroxyphenyl)-butanol. In the second series, ester homologs containing fatty acids with chain lengths $C_{18}$–$C_{28}$ were identified, all of which represented novel compounds.

In accordance with these findings and with reference data, spectra of class $B_1$-type compounds could be interpreted. Their acetate MS showed two series of ions $[M]^+$, [M–ketene]$^+$, [M–2xketene]$^+$ and [M–acid]$^+$, [M–acid-ketene]$^+$, [M–acid-2xketene]$^+$ (Fig. 1e) that had previously been described for 3-(3′,4′-dihydroxyphenyl)-propyl esters (Bohlmann et al., 1981). A corresponding series of three fragments, not reported before, could be rationalized as the alcohol $[(AcO)_2–Ph–(CH_2)_3–OH]^+$ and its two ketene elimination products. Finally, the dihydroxybenzyl ion $m/z = 123$ confirmed the phenolic structure, while two series of alkyl fragments at $m/z = 55$, 69, 83, etc. and $m/z = 57$, 71, 85, etc. indicated the presence of the fatty acid moiety. The MS of TMSi ethers of compound class $B_1$ showed very prominent ions interpreted as $[M]^+$, $[(TMSiO)_2–Ph–(CH_2)_3–OH]^+$, [M–acid]$^+$, [M–acid–HOTMSi]$^+$, $[(TMSiO)_2–Ph–CH_2]^+$ and $[TMSiO–Ph–CH_2]^+$ (Fig. 1c). Hence, very similar fragmentation patterns were inferred for both derivatives, confirming that the constituents of fraction $B_1$ represented a series of 3-(3′,4′-dihydroxyphenyl)-propanol esters. Thirteen homologs comprising esterified $C_{20}$–$C_{32}$ fatty acids were identified. Only one of these, dihydroxyphenylpropanyl arachidate, had previously been described as a constituent of aerial parts of *Symphyopappus compressus* (Asteraceae) (Bohlmann et al., 1981) and *Phonus arborescens* (Asteraceae) (Barrero et al., 1997).

Compounds in fraction $B_2$ eluted shortly before those of $B_1$ (Table 1) and yielded acetate and TMSi derivatives with MS characteristics very similar to those of $B_1$ (Fig. 1d and f). On one hand, all the small mass signals representing either only the alkyl chain of the fatty acid or the (di-)hydroxybenzyl moiety of the alcohol were identical for both compound classes. On the other hand, those fragments containing the alkyl side chain of the aromatic alcohol, together with their secondary products generated by loss of ketene or HOTMSi units, had masses shifted by $\Delta m/z = +14$ between $B_1$ and $B_2$-types. Consequently, compounds in $B_2$ could be regarded as homologs of the dihydroxyphenylpropanol esters identified in $B_1$, and the additional methyl group had to be located either on the terminal or the central methylene group of the phenylpropyl side chain. An alcohol of this type, 4-(3′,4′-dihydroxyphenyl)-2-butanol, had previously been described as a constituent of *T. baccata* needles (Das et al., 1993a, b). By analogy to the structural assignment for compound class $A_2$, it can be inferred that compounds in class $B_2$ were of the 4-(3′,4′-dihydroxyphenyl)-2-butanol ester series. Ten homologs comprising esterified $C_{18}$–$C_{28}$ fatty acids were identified, all of which represented novel compounds.

To further verify the structure of the four classes of phenolic esters, one homolog of each series was synthesized by transesterification of methyl docosanoate with respective alcohols. Only 3-(4′-hydroxyphenyl)-propanol being commercially available, the other three alcohols were generated by reduction of the corresponding phenylbutanones and phenylpropanoic acid and characterized using their acetate and TMSi ether MS (Kraus and Spiteller, 1997). The resulting compounds, after transformation into TMSi derivatives, exactly matched the GC retention behavior and MS characteristics of one representative of the compound classes $A_1$, $A_2$, $B_1$ and $B_2$, respectively. Consequently, both the postulated alcohol structures and the fatty acid chain length assignment for all four homologous series of phenolic esters in *T. baccata* wax were unambiguously confirmed.

The homolog pattern of the esterified fatty acids was further investigated after cleavage of the original esters.

Treatment with $LiAlH_4$ yielded series of unbranched $C_{20}$–$C_{30}$ and $C_{20}$–$C_{36}$ alcohols for fractions A and B, respectively. A corresponding series of fatty acid methyl esters, with identical homolog patterns, was released by $BF_3$/MeOH treatment. Hence, the original ester structure and the exclusive presence of unbranched, saturated very long-chain fatty acids were confirmed. Beside the acid moieties of the original esters, the alcohols could also be detected, by both reductive cleavage and transesterification, which yielded two pairs of alcohols from fractions A and B, respectively. All four alcohol products were further characterized by GC co-injection experiments as well as MS comparisons with synthetic standards. Both their TMSi ethers and their acetates proved to be identical with corresponding derivatives of synthetic 3-(4′-hydroxyphenyl)-propanol, 3-(3′,4′-dihydroxyphenyl)-propanol, 4-(4′-hydroxyphenyl)-2-butanol and 4-(3′,4′-dihydroxyphenyl)-2-butanol, respectively. The alcohol moieties of the *T. baccata* wax esters were hence unambiguously identified, ruling out all isomeric alternatives and confirming the ester structures inferred above.

All four homologous series of phenolic esters identified in the respective TLC fractions of *T. baccata* needle wax could also be detected in the whole wax mixture. These compounds amounted to surface coverages of 0.1–3.6 μg/cm$^2$, representing 0.2–7.6% of the total wax mixture (Table 2). In all four classes, those homologs containing fatty acids with even carbon numbers were dominant. It is noteworthy that both phenylpropyl ester series had a maximum for the homolog containing tetracosanoic acid, while in the phenylbutyl ester homologs eicosanoic and docosanoic acids predominated (Table 2). This finding could either imply that two different pools of fatty acid precursors are used for the esterification of the phenylpropyl and the phenylbutyl alcohols or that two acyl transferases differing both in alcohol and in fatty acid chain length specificities are involved.

Other very long-chain derivatives of phenolics, most of them containing a propenyl side chain, had been identified previously from various plant species. In many cases, a phenyl propenoic acid had been found esterified with typical wax alcohols, e. g. *p*-coumarates in *Rosa rugosa* (Hashidoko et al., 1992). The localization of these highly lipophilic compounds within the plant had rarely been investigated, except for the long-chain caffeates and ferulates of poplar bud exudates (Greenaway and Whatley, 1991), and *p*-coumaryl alcohol esters in the stem bark of *Buddleja globosa* (Houghton, 1989). Interestingly, all these phenolic esters combine the aliphatic and aromatic moieties known as

Table 2
Composition of the phenolic ester fractions from *Taxus baccata* needle wax. Leaf coverages (μg/cm$^2$) of the compound classes were assessed in the original wax mixture by adding respective GC–FID peak areas. Relative amounts (%) of the individual homologs were quantified by GC-MS using characteristic fragments (*m*/*z*) of respective TLC fractions.

| Fatty acid carbon number | Fraction $A_1$ (4′-hydroxyphenyl)-propyl esters | Fraction $A_2$ (4′-hydroxyphenyl)-2-butyl esters | Fraction $B_1$ (3′,4′-dihydroxyphenyl)-propyl esters | Fraction $B_2$ (3′,4′-dihydroxyphenyl)-2-butyl esters |
|---|---|---|---|---|
| | Characteristic fragment | | | |
| | 206 | 220 | 294 | 308 |
| 18 | – | tr[a] | – | tr |
| 19 | – | – | – | – |
| 20 | 2.9 | 32.7 | 9.1 | 36.5 |
| 21 | 0.4 | 1.6 | 0.6 | 1.6 |
| 22 | 20.8 | 39.8 | 14.7 | 35.2 |
| 23 | 2.6 | 1.4 | 1.5 | 1.4 |
| 24 | 51.0 | 22.1 | 49.3 | 23.3 |
| 25 | 2.7 | 0.6 | 2.8 | 0.5 |
| 26 | 13.4 | 1.7 | 17.2 | 1.4 |
| 27 | 0.5 | – | 0.8 | tr |
| 28 | 2.6 | tr | 3.1 | 0.1 |
| 29 | tr | – | tr | – |
| 30 | 0.9 | – | 0.6 | – |
| 31 | tr | – | tr | – |
| 32 | 1.0 | – | 0.3 | – |
| 33 | tr | – | – | – |
| 34 | 0.9 | – | – | – |
| 35 | tr | – | – | – |
| 36 | 0.2 | – | – | – |
| Total coverage | 1.5 | 0.1 | 3.6 | 3.5 |

[a] tr: 0.01–0.1% detectable.

building blocks of the polymer suberin. The geometry of mixed ester molecules could indicate that covalent links exist between the aliphatic and aromatic domains of suberin.

## 3. Experimental

### 3.1. Plant waxes and sample preparation

Plants were grown in the Botanical Garden of the University of Würzburg. Four batches of twigs carrying ca. 500 current-year needles (fresh weight 25 g) were harvested in early summer and immediately immersed twice for 30 s in $CHCl_3$ at room temp, yielding ca. 12 mg of crude extract. For absolute quantification of phenylalkyl esters within the whole wax mixture, a defined amount of tetracosane was added as internal standard. The resulting solns of cuticular waxes were dried, filtered and the solvent removed under reduced pressure. Extracted needle surface areas were calculated by multiplying average needle numbers per twig, the number of twigs and the average (projected) needle surface area. The latter was assessed by multiplication of average needle lengths and widths.

### 3.2. Qualitative analyses

Substance classes were separated by TLC (sandwich technique, silica gel, mobile phase $CHCl_3$–EtOH (99:1), and localized by staining with primuline and UV-light). Bands were immediately removed from the plates, eluted with $CHCl_3$, and filtered. Finally, the solvent was removed in a stream of $N_2$ and samples were stored in the dark at 4°. Two bands, designated as fractions A ($R_f$ 0.21) and B ($R_f$ 0.16), contained unknown compounds and were subjected to detailed qualitative analyses. To this end, either the underivatized constituents or their derivatization products were analyzed using GC (30 m DB-1 WCOT i.d. 320 μm, on-column-injection at 50 °C, oven 2 min at 50 °C, 40 °C $min^{-1}$ to 200 °C, 2 min at 200 °C, 3 °C $min^{-1}$ to 320 °C, 30 min at 320 °C and He carrier gas inlet pressures 1 min at 5 kPa, 4 kPa $min^{-1}$ to 18 kPa, 0,6 kPa $min^{-1}$ to 40 kPa, 37 min at 40 kPa) with MS detection (70 eV, $m/z$ 50–650).

Constituents of fractions A and B were derivatized in four alternative reactions: (1) compounds containing free hydroxyl groups were transformed into TMSi ethers by reaction with bis-(*N,N*-trimethylsilyl)-trifluoroacetamide in pyridine for 30 min at 70 °C; (2) hydroxyl groups were acetylated by adding pyridine and $Ac_2O$ to the dried fraction, heating the mixture to 70 °C for 5 min, keeping it at RT overnight and then removing the solvent in a stream of $N_2$; (3) for qualitative analysis of the alcohols and fatty acids in esters of fractions A and B, transesterification with $BF_3$/MeOH (60 min at 70 °C) was performed and the reaction products were isolated by addition of $H_2O$ and extraction with $Et_2O$; (4) alternatively, esters were reductively cleaved by addition to excess of $LiAlH_4$ in refluxing THF over 48 h. The mixt. of LiAl-alcoholate complexes was hydrolyzed with 10% $H_2SO_4$, with the alcohols being obtained by extraction of the soln with $Et_2O$. The corresponding compounds of interest were purified by TLC ($SiO_2$, $CHCl_3$-EtOH 99:1) and were transformed into the corresponding TMSi ethers.

### 3.3. Quantitative analyses

For quantitative analysis of the entire wax mixture, compounds containing hydroxyl groups were transformed to TMSi derivatives (as above). Surface coverages of individual compounds were then determined by GC-FID (as above, with $H_2$ carrier gas inlet pressures 41 min at 50 kPa, 10 kPa $min^{-1}$ to 150 kPa, 30 min at 150 kPa). Needle surface coverages of individual constituents were calculated as mean values of four independent analyses; values for the separate analyses differed between 9% and 24% for 3-(4′-hydroxyphenyl)-propyl esters and 3-(3′,4′-dihydroxyphenyl)-propyl esters, respectively. Values for compound classes were calculated by summing those of all identified homologs.

Homolog patterns were assessed using the TMSi ether derivatives of compounds in fractions A and B. Single ion chromatograms were reconstructed for four distinguishable compound classes $A_1$, $A_2$, $B_1$ and $B_2$ using corresponding fragments $[TMSiO–Ph–CH_2–CH=CH_2]^+$, $[TMSiO–Ph–CH_2–CH=CH–CH_3]^+$, $[(TMSiO)_2–Ph–CH_2–CH=CH_2]^+$ and $[(TMSiO)_2–Ph–CH_2–CH=CH–CH_3]^+$, respectively, generated by acid elimination from the esters. Relative abundances of individual homologs were calculated by integration of these single ion traces.

### 3.4. Synthesis of selected phenylalkyl esters

Very-long-chain fatty acid methyl esters were transesterified with phenylalkyl alcohols by modification of a procedure for selective monoacetylation of diols (Breton, 1997). Unless stated otherwise, chemicals were purchased from Sigma-Aldrich, Deisenhofen, FRG. Commercial 3-(4′-hydroxyphenyl)-propanol was used without further purification. 3-(3′,4′-Dihydroxyphenyl)-propanol and 4-(4′-hydroxyphenyl)-2-butanol were generated from the corresponding acid and ketone, respectively, using $LiAlH_4$ as described above. 4-(3′-Methoxy-4′-hydroxyphenyl)-2-butanone (0.5 mmol, Pfaltz and Bauer, Waterbury, CT, USA) was demethylated using 1 M $BBr_3$ (5.0 mmol) in THF (−78 °C, 1h), the reaction mixture was allowed to warm to room temp and extracted with $Et_2O$/water. The organic phase was dried over $Na_2SO_4$, concentrated under $N_2$, and purified by TLC ($SiO_2$, $CHCl_3$–EtOH 99:1). The resulting 4-

(3′,4′-dihydroxyphenyl)-2-butanone was isolated and reduced to the corresponding alcohol with $LiAlH_4$ as described above. GC–MS of the TMSi and acetate derivatives served to identify the intermediate and final reaction products. In four parallel reactions, the phenylalkyl alcohols (ca. 100 μmol) and methyl docosanoate (5 mmol) were dissolved in 1.5 ml of hexane and added to heterogenous silica gel-supported $NaHSO_4$ catalyst. The mixture was heated to 70 °C for 1 h, left at RT overnight, filtered and concentrated under a stream of $N_2$.

### 3.5. Mass spectral data of selected compounds

GC–EIMS (70 eV) *m/z* (rel. int.). *Underivatized phenylalkyl esters: 3-(4′-hydroxyphenyl)-propyl docosanoate* $[M]^+$ 474 (0.1), $[HO–Ph–(CH_2)_3–OH]^+$ 152 (1), $[HO–Ph–CH_2–CH=CH_2]^+$ 134 (100), $[HO–Ph–CH_2]^+$ 107 (14), 85 (1), 83 (2), 71 (1), 69 (0.4), 57 (0.5), 55 (2). *3-(4′-Hydroxyphenyl)-propyl tetracosanoate* $[M]^+$ 502 (0.1), $[HO–Ph–(CH_2)_3–OH]^+$ 152 (2), $[HO–Ph–CH_2–CH=CH_2]^+$ 134 (100), $[HO–Ph–CH_2]^+$ 107 (9), 85 (0.1), 83 (0.2), 71 (1), 69 (0.4), 57 (2), 55 (1). *4-(4′-Hydroxyphenyl)-2-butyl docosanoate* $[M]^+$ 488 (0.1), $[HO–Ph–(CH_2)_2–CHOH–CH_3]^+$ 166 (1), $[HO–Ph–CH_2–CH=CH–CH_3]^+$ 148 (100), $[HO–Ph–CH_2]^+$ 107 (8). *4-(4′-Hydroxyphenyl)-2-butyl tetracosanoate* $[M]^+$ 516 (0.1), $[HO–Ph–(CH_2)_2–CHOH–CH_3]^+$ 166 (1), $[HO–Ph–CH_2–CH=CH–CH_3]^+$ 148 (100), $[HO–Ph–CH_2]^+$ 107 (5).

*TMSi ethers of phenylalkyl esters*: *3-(4′-hydroxyphenyl)-propyl docosanoate* $[M]^+$ 546 (1), $[M–Me]^+$ 531 (0.1), $[TMSiO–Ph–(CH_2)_3–OH]^+$ 224 (4), $[TMSiO–Ph–CH_2–CH=CH_2]^+$ 206 (100), $[Me_2SiO–Ph–CH_2–CH=CH_2]^+$ 191 (15), $[TMSiO–Ph–CH_2]^+$ 179 (13), 85 (0.5), 83 (0.5), 73 (4), 71 (1), 69 (1), 57 (2), 55 (1). *3-(4′-Hydroxyphenyl)-propyl tetracosanoate* $[M]^+$ 574 (1), $[M-Me]^+$ 559 (0.2), $[TMSiO–Ph–(CH_2)_3–OH]^+$ 224 (4), $[TMSiO–Ph–CH_2–CH=CH_2]^+$ 206 (100), $[Me_2SiO–Ph–CH_2–CH=CH_2]^+$ 191 (16), $[TMSiO–Ph–CH_2]^+$ 179 (15), 85 (1), 83 (1), 73 (4), 71 (1), 69 (1), 57 (2), 55 (1). *4-(4′-Hydroxyphenyl)-2-butyl docosanoate* $[M]^+$ 560 (0.2), $[M-Me]^+$ 545 (0.1), $[TMSiO–Ph–(CH_2)_2–CHOH–CH_3]^+$ 238 (1), $[TMSiO–Ph–CH_2–CH=CH–CH_3]^+$ 220 (100), $[Me_2SiO–Ph–CH_2–CH=CH–CH_3]^+$ 205 (12), $[TMSiO–Ph–CH_2]^+$ 179 (20), 85 (0.2), 83 (0.3), 73 (2), 57 (0.3), 55 (0.2). *4-(4′-Hydroxyphenyl)-2-butyl tetracosanoate* $[M]^+$ 588 (1), $[M-Me]^+$ 573 (0.2), $[TMSiO–Ph–(CH_2)_2–CHOH–CH_3]^+$ 238 (2), $[TMSiO–Ph–CH_2–CH=CH–CH_3]^+$ 220 (100), $[Me_2SiO–Ph–CH_2–CH=CH–CH_3]^+$ 205 (8), $[TMSiO–Ph–CH_2]^+$ 179 (14), 85 (0.2), 83 (0.2), 73 (1), 57 (0.2), 55 (0.1). *3-(3′,4′-Dihydroxyphenyl)-propyl docosanoate* $[M]^+$ 634 (83), $[M-Me]^+$ 619 (0.4), $[(TMSiO)_2–Ph–(CH_2)_3–OH]^+$ 312 (15), 295 (48), $[(TMSiO)_2–Ph–CH_2–CH=CH_2]^+$ 294 (63), $[Me_2SiO–Ph–CH_2–CH=CH_2]^+$ 279 (8), $[(TMSiO)_2–Ph–CH_2]^+$ 267 (50), $[TMSiO–Ph–CH_2–CH=CH_2]^+$ 205 (5), 193 (5), $[TMSiO–Ph–CH_2]^+$ 179 (100), 166 (6), 149 (2), 147 (1), 85 (0.1), 83 (0.1), 73 (61), 71 (3), 69 (2), 57 (7), 55 (2). *3-(3′,4′-Dihydroxyphenyl)-propyl tetracosanoate* $[M]^+$ not detectable, $[M-Me]^+$ 647 (1), $[(TMSiO)_2–Ph–(CH_2)_3–OH]^+$ 312 (15), 295 (70), $[(TMSiO)_2–Ph–CH_2–CH=CH_2]^+$ 294 (70), $[Me_2SiO–Ph–CH_2–CH=CH_2]^+$ 279 (7), $[(TMSiO)_2–Ph–CH_2]^+$ 267 (26), $[TMSiO–Ph–CH_2–CH=CH_2]^+$ 205 (42), 193 (5), $[TMSiO–Ph–CH_2]^+$ 179 (100), 166 (5), 149 (2), 147 (2), 85 (2), 83 (4), 73 (70), 71 (6), 69 (2), 57 (17), 55 (4). *4-(3′,4′-Dihydroxyphenyl)-2-butyl docosanoate* $[M]^+$ 648 (21), $[M-Me]^+$ 633 (0.1), $[(TMSiO)_2–Ph–(CH_2)_2–CHOH–CH_3]^+$ 326 (1), 309 (38), $[(TMSiO)_2–Ph–CH_2–CH=CH–CH_3]^+$ 308 (75), $[Me_2SiO–Ph–CH_2–CH=CH–CH_3]^+$ 293 (18), $[(TMSiO)_2–Ph–CH_2]^+$ 267 (100), $[TMSiO–Ph–CH_2–CH=CH–CH_3]^+$ 219 (13), 193 (5), $[TMSiO–Ph–CH_2]^+$ 179 (61), 149 (1), 147 (1), 85 (1), 83 (1), 73 (37), 71 (2), 69 (1), 57 (7), 55 (3). *4-(3′,4′-Dihydroxyphenyl)-2-butyl tetracosanoate* $[M]^+$ not detectable, $[M–Me]^+$ not detectable, $[(TMSiO)_2–Ph–(CH_2)_2–CHOH–CH_3]^+$ 326 (1), 309 (35), $[(TMSiO)_2–Ph–CH_2–CH=CH–CH_3]^+$ 308 (65), $[Me_2SiO–Ph–CH_2–CH=CH–CH_3]^+$ 293 (17), $[(TMSiO)_2–Ph–CH_2]^+$ 267 (100), $[TMSiO–Ph–CH_2–CH=CH–CH_3]^+$ 219 (12), 193 (6), $[TMSiO–Ph–CH_2]^+$ 179 (54), 149 (1), 147 (2), 85 (2), 83 (1), 73 (30), 71 (4), 69 (2), 57 (7), 55 (3).

*Acetates of phenylalkyl esters*: *3-(4′-hydroxyphenyl)-propyl docosanoate* $[M]^+$ 544 (0.1), [M-ketene]$^+$ 502 (0.1), $[AcO–Ph–(CH_2)_3–OH]^+$ 194 (1), $[AcO–Ph–CH_2–CH=CH_2]^+$ 176 (28), $[HO–Ph–(CH_2)_3–OH]^+$ 152 (2), $[HO–Ph–CH_2–CH=CH_2]^+$ 134 (100), $[HO–Ph–CH_2]^+$ 107 (7), 85 (0.2), 83 (0.1), 71 (0.5), 69 (0.1), 57 (1), 55 (0.3). *3-(4′-Hydroxyphenyl)-propyl tetracosanoate* $[M]^+$ 572 (0.1), [M-ketene]$^+$ 530 (0.1), $[AcO–Ph–(CH_2)_3–OH]^+$ 194 (1), $[AcO–Ph–CH_2–CH=CH_2]^+$ 176 (37), $[HO–Ph–(CH_2)_3–OH]^+$ 152 (1), $[HO–Ph–CH_2–CH=CH_2]^+$ 134 (100), $[HO–Ph–CH_2]^+$ 107 (7), 85 (0.4), 83 (1), 71 (1), 69 (0.4), 57 (1), 55 (1). *4-(4′-Hydroxyphenyl)-2-butyl docosanoate* $[M]^+$ 558 (0.1), [M-ketene]$^+$ 516 (0.2), $[AcO–Ph–(CH_2)_2–CHOH–CH_3]^+$ 208 (0.3), $[AcO–Ph–CH_2–CH=CH–CH_3]^+$ 190 (13), $[HO–Ph–(CH_2)_2–CHOH–CH_3]^+$ 166 (1), $[HO–Ph–CH_2–CH=CH–CH_3]^+$ 148 (100), $[HO–Ph–CH_2]^+$ 107 (5), 85 (0.2), 83 (0.1), 71 (0.3), 69 (0.2), 57 (0.3), 55 (0.2). *4-(4′-Hydroxyphenyl)-2-butyl tetracosanoate* $[M]^+$ 586 (0.1), [M–ketene]$^+$ 544 (0.1), $[AcO–Ph–(CH_2)_2–CHOH-CH_3]^+$ 208 (0.3), $[AcO–Ph–CH_2–CH=CH–CH_3]^+$ 190 (13), $[HO–Ph–(CH_2)_2–CHOH–CH_3]^+$ 166 (1), $[HO–Ph–CH_2–CH=CH–CH_3]^+$ 148 (100), $[HO–Ph–CH_2]^+$ 107 (4), 85 (0.4), 83 (1), 71 (1), 69 (0.4), 57 (1), 55 (1). *3-(3′,4′-Dihydroxyphenyl)-propyl docosanoate* $[M]^+$ 574 (0.1), [M–ketene]$^+$ 532 (0.3), [M–2xketene]$^+$ 490 (13), $[(AcO)_2–Ph–(CH_2)_3–OH]^+$ 252 (3), $[(AcO)_2–Ph–CH_2–CH=CH_2]^+$ 234 (16), $[(AcO)(HO)–Ph–(CH_2)_3–OH]^+$

210 (11), [(AcO)(HO)–Ph–$CH_2$–CH = $CH_2$]$^+$ 192 (40), [(HO)$_2$–Ph–($CH_2$)$_3$–OH]$^+$ 168 (2), [(HO)$_2$–Ph–$CH_2$–CH = $CH_2$]$^+$ 150 (100), [(HO)$_2$–Ph–$CH_2$]$^+$ 123 (8), 85 (0.2), 83 (0.1), 71 (0.5), 69 (0.6), 57 (0.6), 55 (0.1). *3-(3′,4′-Dihydroxyphenyl)-propyl tetracosanoate* [M]$^+$ 602 (0.1), [M–ketene]$^+$ 560 (0.2), [M–2xketene]$^+$ 518 (16), [(AcO)$_2$–Ph–($CH_2$)$_3$–OH]$^+$ 252 (3), [(AcO)$_2$–Ph–$CH_2$–CH = $CH_2$]$^+$ 234 (24), [(AcO)(HO)–Ph–($CH_2$)$_3$–OH]$^+$ 210 (14), [(AcO)(HO)–Ph–$CH_2$–CH = $CH_2$]$^+$ 192 (48), [(HO)$_2$–Ph–($CH_2$)$_3$–OH]$^+$ 168 (4), [(HO)$_2$–Ph–$CH_2$–CH = $CH_2$]$^+$ 150 (100), [(HO)$_2$–Ph–$CH_2$]$^+$ 123 (9), 85 (1), 83 (1), 71 (1), 69 (1), 57 (2), 55 (1). *4-(3′,4′-Dihydroxyphenyl)-2-butyl docosanoate* [M]$^+$ 588 (0.1), [M–ketene]$^+$ 546 (0.1), [M–2xketene]$^+$ 504 (1), [(AcO)$_2$–Ph–($CH_2$)$_2$–CHOH–$CH_3$]$^+$ 266 (0.5), [(AcO)$_2$–Ph–$CH_2$–CH = CH–$CH_3$]$^+$ 248 (36), [(AcO)(HO)–Ph–($CH_2$)$_2$–CHOH–$CH_3$]$^+$ 224 (2), [(AcO)(HO)–Ph–$CH_2$–CH = CH–$CH_3$]$^+$ 206 (80), [(HO)$_2$–Ph–($CH_2$)$_2$–CHOH–$CH_3$]$^+$ 182 (1), [(HO)$_2$–Ph–$CH_2$–CH = CH–$CH_3$]$^+$ 164 (100), [(HO)$_2$–Ph–$CH_2$]$^+$ 123 (18), 85 (1), 83 (1), 71 (1), 69 (1), 57 (2), 55 (2). *4-(3′,4′-Dihydroxyphenyl)-2-butyl tetracosanoate* [M]$^+$ 616 (0.1), [M–ketene]$^+$ 574 (0.1), [M–2xketene]$^+$ 532 (1), [(AcO)$_2$–Ph–($CH_2$)$_2$–CHOH–$CH_3$]$^+$ 266 (1), [(AcO)$_2$–Ph–$CH_2$–CH = CH–$CH_3$]$^+$ 248 (47), [(AcO)(HO)–Ph–($CH_2$)$_2$–CHOH–$CH_3$]$^+$ 224 (2), [(AcO)(HO)–Ph–$CH_2$–CH = CH–$CH_3$]$^+$ 206 (89), [(HO)$_2$–Ph–($CH_2$)$_2$–CHOH–$CH_3$]$^+$ 182 (1), [(HO)$_2$–Ph–$CH_2$–CH = CH–$CH_3$]$^+$ 164 (100), [(HO)$_2$–Ph–$CH_2$]$^+$ 123 (17), 85 (1), 83 (0.1), 71 (1), 69 (1), 57 (2), 55 (1).

*TMSi ethers of ester cleavage products*: *3-(4′-hydroxyphenyl)-propanol* [M]$^+$ 296 (7), [M–Me]$^+$ 281 (11), [TMSiO–Ph–$CH_2$–CH = $CH_2$]$^+$ 206 (100), [$Me_2$SiO–Ph–$CH_2$–CH = $CH_2$]$^+$ 191 (70), [TMSiO–Ph–$CH_2$]$^+$ 179 (15), 133 (6), 103 (1), 89 (11), 73 (21). *4-(4′-Hydroxyphenyl)-2-butanol* [M]$^+$ 310 (3), [M–Me]$^+$ 295 (4), [TMSiO–Ph–$CH_2$–CH = CH–$CH_3$]$^+$ 220 (100), [$Me_2$SiO–Ph–$CH_2$–CH = CH–$CH_3$]$^+$ 205 (77), [TMSiO–Ph–$CH_2$]$^+$ 179 (12), 147 (3), 103 (13), 89 (2), 73 (30). *3-(3′,4′-Dihydroxyphenyl)-propanol* [M]$^+$ 384 (64), [M–Me]$^+$ 369 (5), [M–2xMe]$^+$ 354 (33), [(TMSiO)$_2$–Ph–$CH_2$–CH = $CH_2$]$^+$ 294 (27), [(TMSiO)$_2$–Ph–$CH_3$]$^+$ 268 (28), [(TMSiO)$_2$–Ph–$CH_2$]$^+$ 267 (27), 232 (12), 220 (18), 217 (15), [TMSiO–Ph–$CH_2$–CH = $CH_2$]$^+$ 205 (100), [TMSiO–Ph–$CH_2$]$^+$ 179 (71), 149 (29), 73, (52). *4-(3′,4′-Dihydroxyphenyl)-2-butanol* [M]$^+$ 398 (70), [M-Me]$^+$ 383 (11), [(TMSiO)$_2$–Ph–$CH_2$–CH = CH-$CH_3$]$^+$ 308 (90), [($Me_2$SiO)(TMSiO)–Ph–$CH_2$–CH = CH–$CH_3$]$^+$ 293 (34), [(TMSiO)$_2$–Ph–$CH_3$]$^+$ 268 (100), [(TMSiO)$_2$–Ph–$CH_2$]$^+$ 267 (27), 251 (7), [TMSiO–Ph–$CH_2$–CH = $CH_2$]$^+$ 219 (19), [TMSiO–Ph–$CH_2$]$^+$ 179 (54), 73, (88).

*Acetates of ester cleavage products*: *3-(4′-hydroxyphenyl)-propanol* [M]$^+$ 236 (2), [M–ketene]$^+$ 194 (15), [M–HOAc]$^+$ 176 (13), [HO–Ph–$CH_2$–CH = $CH_2$]$^+$ 134 (100), 133 (54), 121 (6) [HO–Ph–$CH_2$]$^+$ 107 (41), [Ph–$CH_2$]$^+$ 91 (9), 77 (13), 65 (4), 55 (2). *4-(4′-Hydroxyphenyl)-2-butanol* [M]$^+$ 250 (0.3), [M-ketene]$^+$ 208 (3), [M–HOAc]$^+$ 190 (18), [HO–Ph–$CH_2$–CH = CH–$CH_3$]$^+$ 148 (100), 133 (93), 121 (6) [HO–Ph–$CH_2$]$^+$ 107 (35), [Ph–$CH_2$]$^+$ 91 (7), 77 (8), 65 (0.4), 55 (2). *3-(3′,4′-Dihydroxyphenyl)-propanol* [M]$^+$ 294 (3), [M–ketene]$^+$ 252 (19), [M–HOAc]$^+$ 234 (5), [(AcO)(HO)–Ph–($CH_2$)$_3$–OH]$^+$ 210 (97), [(AcO)(HO)–Ph–$CH_2$–CH = $CH_2$]$^+$ 192 (4), [(HO)$_2$–Ph–$CH_2$–CH = $CH_2$]$^+$ 150 (100), 149 (11), 137 (6), [(HO)–Ph–$CH_2$–CH = $CH_2$]$^+$ 132 (14), 131 (7), [(HO)$_2$–Ph–$CH_2$]$^+$ 123 (23), 122 (10), [HO–Ph–$CH_2$]$^+$ 107 (3), [Ph–$CH_2$]$^+$ 91 (9), 77 (9), 65 (3), 55 (3).*4–(3′,4′-Dihydroxyphenyl)-2-butanol* [M]$^+$ 308 (0.4), [M–ketene]$^+$ 266 (5), [M–HOAc]$^+$ 248 (18), [(AcO)(HO)–Ph–($CH_2$)$_2$–CHOH–$CH_3$]$^+$ 224 (61), [(AcO)(HO)–Ph–$CH_2$–CH = CH–$CH_3$]$^+$ 206 (16), [(HO)$_2$–Ph–$CH_2$–CH = CH–$CH_3$]$^+$ 164 (100), 149 (26), [(HO)–Ph–$CH_2$–CH = CH–$CH_3$]$^+$ 146 (5), 137 (6), 131 (9), [(HO)$_2$–Ph–$CH_2$]$^+$ 123 (29), 122 (31), [HO–Ph–$CH_2$]$^+$ 107 (4), [Ph–$CH_2$]$^+$ 91 (9), 77 (6), 65 (4), 55 (3).

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