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Effects of *p*-Vinylphenyl Glycosides and Other Related Compounds on the Oviposition Behavior of *Ceratitis capitata*

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Abstract Elaphoside-A [*p*-vinylphenyl (β-D-glucopyranosyl)-(1→3)-β-D-allopyranoside], a Mediterranean fruit fly oviposition deterrent, was previously isolated from an Argentine collection of the fern *Elaphoglossum piloselloides*. In order to establish the structural requirements for the observed oviposition inhibition, we synthesized and characterized 4 known and 21 new aromatic glycosides structurally related to elaphoside-A. Their effects on the oviposition behavior of *Ceratitis capitata* females are discussed.

Keywords Oviposition deterrence · *Ceratitis capitata* · Aromatic glycosides · *Elaphoglossum piloselloides*

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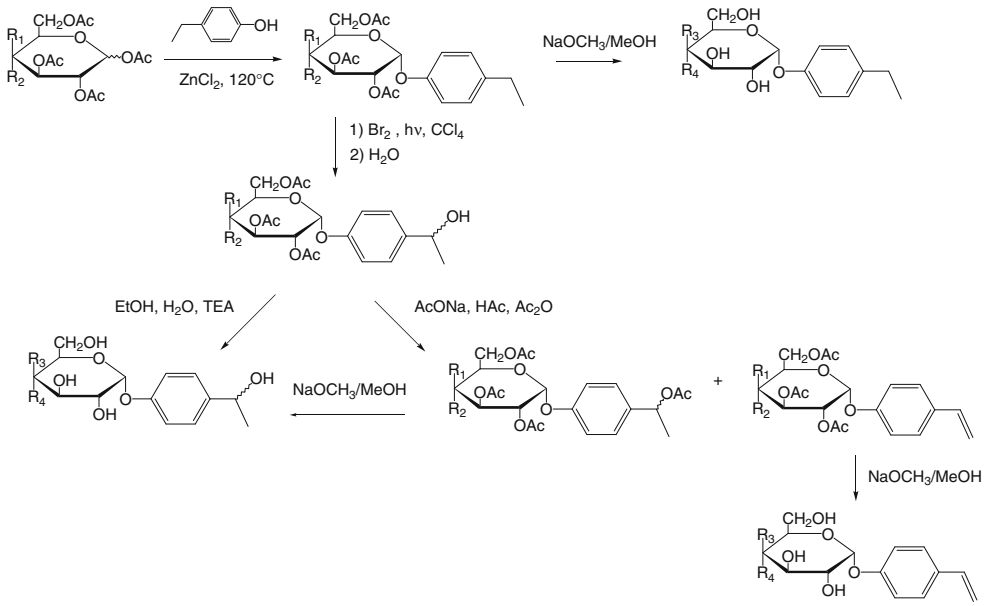
Introduction

The influence of chemical agents on the ovipositional behavior of insects can be used to control pests as well as vector insects. Some natural products display oviposition-deterrent activity against different insects. A chromene from *Blepharispermum subsessile* (Compositae) is an oviposition deterrent for *Phthorimacea operculella* (Kulkarni et al. 1987). Essential oils from medicinal plants have been successfully tested as oviposition deterrents on *Thrips tabaci* (Koschier and Sedy 2003) and the *Anopheles stephensi*, *Aedes aegypti*, and *Culex quinquefasciatus* mosquito species (Prajapati et al. 2005). The ovipositional response of the fruit fly *Anastrepha suspensa* (Loew) to stimulants and deterrents was studied by Szentesi et al. (1979). Factors that affect the oviposition behavior of some tephritid fruit flies include host-plant odor as well as the physical and chemical characteristics of the oviposition substrate, such as size, shape, color, and presence of deterrent chemicals.

The Mediterranean fruit fly *Ceratitis capitata* (Tephritidae) causes important economic damage in the north of Argentina and other countries; therefore, substances that affect their behavior can be used in the development of pest-control agents. Previously, it was reported that elaphoside-A [*p*-vinylphenyl (β-D-glucopyranosyl)-(1→3)-β-D-allopyranoside], a bitter-tasting styrene glycoside isolated from the methanol extract of the fern *Elaphoglossum piloselloides*, partially inhibited the oviposition of *C. capitata* when incorporated into the surface of an artificial fruit at a concentration of 6 μg/cm^2. The number of eggs laid on treated artificial fruit was 48% lower than that oviposited on control (nontreated) fruit at the mentioned dose (Socolsky et al. 2003). In order to determine the structural requirements



Scheme 1 Synthesis of α-ANOMERS. When R_1=OAc, R_2=H, R_3=OH and R_4=H, the scheme is illustrated for α-D-galactopyranosyl derivatives. When R_1=H, R_2=OAc, R_3=H and R_4=OH, α-D-glucopyranosyl derivatives are obtained, and when R_1=H, R_2=*O*-2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl, R_3=H and R_4=*O*-β-D-galactopyranosyl, α-lactose derivatives are obtained

for activity, a synthetic scheme (Scheme 1) was designed by varying the sugar moiety and the alkyl substituent at the *para* position of the aromatic ring to obtain 25 glycosides (**1**–**25**) structurally related to the active natural product (Fig. 1). In addition, four compounds (**26**–**29**) were obtained by chemical modification and degradation of elaphoside-A. Compounds **1**–**10**, **12**–**22**, and **24**–**29** were tested for their capacity to inhibit the oviposition of *C. capitata* in comparison with elaphoside-A and the commercial *p*-vinylanisole (**30**).

Methods and Materials

General Infrared spectra were recorded on a Shimadzu FT/IR-8400S. Optical activities were determined on a JASCO P-1030 polarimeter. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Gemini 200, Varian Unity 300, Bruker 500 or Varian Unity 600, with tetramethylsilane (TMS) as internal standard. Low- and high-resolution mass spectra were measured on a JEOL JMS AX-500 spectrometer. Column chromatography was performed over silica gel (230–400 Mesh, Merck) with hexane-AcOEt or toluene-EtOH gradients as mobile phases. For thin-layer chromatography, silica gel precoated aluminum plates (Kiesel gel 60 F254, Merck) were employed. The visualization of spots was accomplished by spraying the plates with a H_2SO_4 solution followed by heating. High-performance liquid chromatography (HPLC) separations were performed using C8 and C18 Phenomenex columns (*Luna*, 5 μm, 10×250 mm) with pure methanol or methanol–water mixtures as mobile phases.

Insects A colony of *C. capitata* was initiated with pupae obtained from infested oranges from the northwest of Argentina. Adults were fed on an artificial diet made of water and a mixture of sugar and yeast hydrolysate (3:1). They were maintained in a rearing room with a photoperiod 12L:12D, at 24±2°C and 60±10% relative humidity.

Oviposition-Deterrent Activity Artificial fruits (oviposition substrates) were prepared by boiling a mixture of peach juice (500 ml), agar (15 g), and sodium benzoate (one teaspoonful) as preservative (Fig. 2). This agar solution was poured into cylindrical molds, allowed to gel, and sliced. The agar cylinders were then wrapped in plastic wrap Rolopac to avoid dehydration. The surface of the wrapped cylinder was pricked with a needle and treated with an acetone or methanol solution of the sample to be tested. An amount of 15 μg/cm^2 of the test compound was deposited. Control cylinders were impregnated only with the solvent that was then removed in vacuo. Three groups of *C. capitata* adults were selected from the laboratory colony. Each group, consisting of seven male–female pairs, was placed in a small cage and covered with voile (a light, almost transparent cloth made of silk). Two agar cylinders (sample and control) were placed over the voile, and females oviposited on one or the other according to their preference (Fig. 2). After 4 days, eggs were gently rinsed from the agar and counted.

Statistical Analysis Results are reported as mean±SEM. Differences in the mean values were evaluated using the *t* test for all pairwise comparisons. In all statistical analyses, *P* values>0.05 were considered not significant.

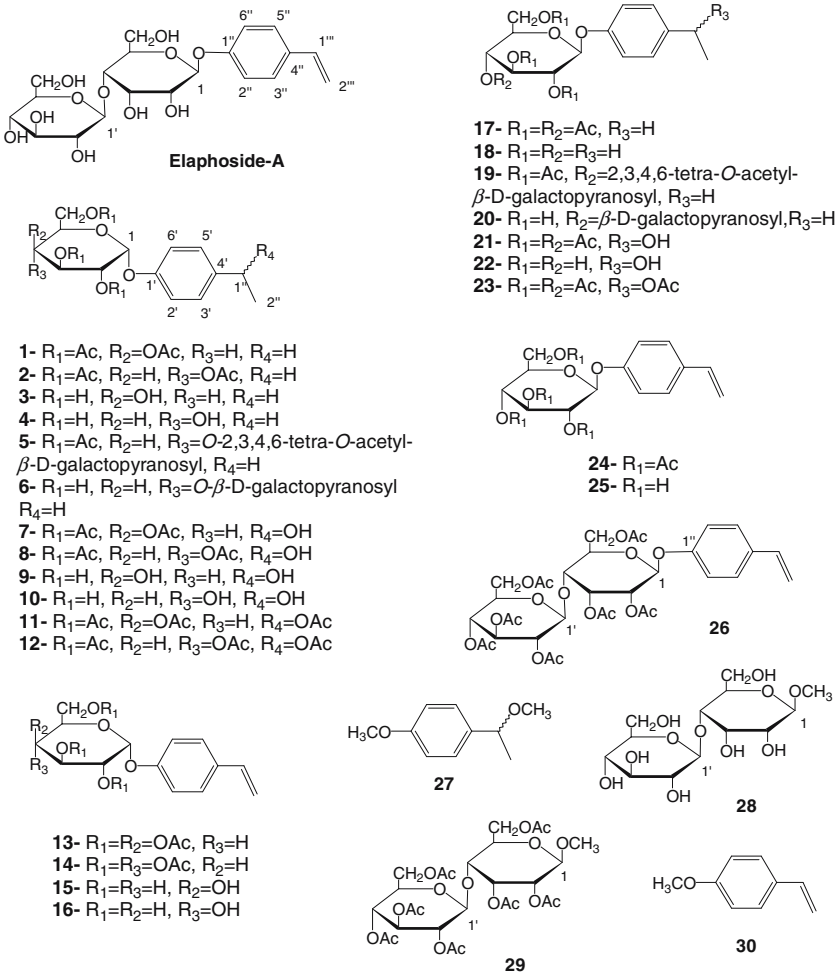


Fig. 1 Chemical structures of the compounds evaluated for oviposition-deterrent activity

Synthesis of Aromatic Glycosides All synthetic compounds were prepared by previously reported methods (Conchie et al. 1957; Clingman 1964; Cannizzaro et al. 1998; Burger et al. 2004). The selected sugars were the monosaccharides D-glucose, D-galactose, and the disaccharide lactose. The synthetic scheme for the α-anomeric compounds is presented in Scheme 1. To obtain the β-anomeric compounds of glucose, *p*-toluenesulfonic acid was used as catalyst for the first reaction step instead of $ZnCl_2$. The β-anomeric glycoside of lactose was obtained by the Paulsen condensation method (Burger et al. 2004).

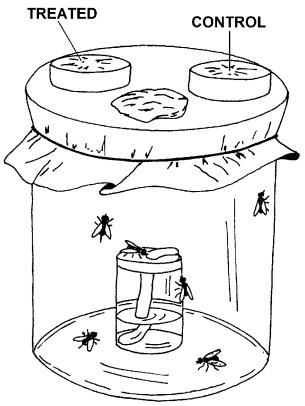


Fig. 2. Experimental setup for oviposition bioassay. Agar cylinders with peach juice were employed as artificial fruits. One of them contains the compound of interest on the surface (*treated*) and the other does not (*control*). They are placed over the cage containing the flies

Aromatic Glycosides Tested in Bioassays The synthetic compounds **1**–**25** (Fig. 1) were purified by reverse-phase HPLC, and their structures were established by spectroscopic methods (1 and 2D NMR, high-resolution mass spectrometry (MS), and infrared (IR)). NMR data are compiled (see Appendix).

Compounds **26**–**29** Compound **26,** *p*-vinylphenyl (2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-β-D-allopyranoside was obtained by acetylation of elaphoside-A (Socolsky et al. 2003). Compounds **27**, *p*-(1-metoxyethyl) anisole obtained as a racemic mixture, and **28,** methyl (β-D-glucopyranosyl)-(1→3)-β-D-allopyranoside, were products of methanolysis of elaphoside-A. Finally, compound **29**, methyl (2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→3)-2,4,6-

tri-*O*-acetyl-β-D-allopyranoside, was obtained by acetylation of the methylated sugar.

Results and Discussion

For all compounds, the ^{1}H NMR spectra showed two doublet signals characteristic of a *para*-disubstituted benzene ring. One of them was located between 7.38 and 7.10 ppm (2H, d, J≈8 Hz), and the other between 7.12 and 6.92 ppm (2H, d, J≈8 Hz). The ethyl group of compounds **1**–**6** and **17**–**20** produced a quartet located between δ 2.60 and 2.47 (2H, q, J≈8 Hz), and a triplet in the 1.21–1.04 ppm range (3H, t, J≈8 Hz). The signals for the 1″-hydroxyethyl substituent of compounds **7**–**10**, **21**, and **22** were located in the δ 4.88–4.75 range (1H, q, J≈6.5 Hz) and 1.48–1.32 (3H, d, J≈6.5 Hz). Regarding the vinyl group of compounds **13**–**16**, **24**, and **25**, three characteristic signals were observed in the proton spectrum at δ 6.66 (1H, dd, J≈18, 11 Hz), 5.65–5.63 (1H, dd, J≈18, 1 Hz), and 5.18–5.10 ppm (1H, dd, J≈11, 1 Hz). Finally, the 1″-acetoxyethyl substituent of compounds **11**, **12**, and **23** showed three signals at δ 5.86 5.83 (1H, q, J=6.5 Hz), δ 2.17–2.04 (3H, s), and δ 1.52–1.51 (3H, d, J=6.5 Hz). The proton NMR spectra of compounds **1**–**25** showed characteristic signals for the sugar moieties glucose, galactose, and lactose. Compounds **7**–**12** and **21**–**23** were obtained as mixtures of C-1″ epimers; therefore, in their ^{1}H and ^{13}C NMR spectra, some signals were duplicated. As the diastereomers' mixtures could not be resolved by high-resolution chromatographic methods, these compounds were tested as a 1:1 mixture of both epimers; therefore, the final concentration of each epimer was 7.5 μg/cm^2.

The previously described synthetic glycosides **1**–**10**, **12**–**22**, **24**, and **25** (Fig. 1) were evaluated in the bioassay (Fig. 2) in order to determine the structural requirements for oviposition-deterrent activity, taking into account that elaphoside-A is a very active compound. Our aim was to investigate how the activity is influenced by hydroxylation of the vinyl group and different sugar residues attached to

Table 1 Effect of aromatic glycosides on the oviposition-behavior of *C. capitata*

Compound	Number of Eggs Laid on the Control Fruit [a]	Number of Eggs Laid on the Treated Fruit [a]	Io=(100T/C)−100
Elaphoside-A	897.3±120.7a	464.7±73.0b	−47.9
1	979.0±51.6a	751.3±41.0b	−23.3
2	1081.7±137.4a	1091.0±123.4a	0.9
3	786.3±98.0a	744.7±89.7a	−5.3
4	1023.3±78.0a	657.3±83.8b	−35.8
5	395.3±47.6a	390.0±55.3a	−1.3
6	530.3±46.6a	356.3±63.7b	−32.8
7	1029.3±109.9a	666.7±47.2b	−35.2
8	1072.7±73.5a	990.3±17.9a	−7.7
9	1159.0±17.6a	894.0±85.1b	−22.9
10	1212.7±80.8a	810.3±83.1b	−33.2
12	1068.0±69.7a	1036.7±64.0a	−2.9
13	1140.3±127.6a	986.0±21.6a	−13.5
14	1090.3±76.6a	1014.3±87.9a	−7.0
15	976.7±23.6a	697.3±23.5b	−28.6
16	991.7±36.9a	687.7±29.3b	−30.6
17	1126.7±67.6a	1136.7±140.3a	0.9
18	353.0±35.8a	319.3±58.4a	−9.5
19	352.3±45.3a	242.0±35.0b	−31.3
20	1135.3±87.1a	1050.7±148.8a	−7.4
21	977.3±7.5a	820.0±52.6b	−16.0
22	697.0±61.6a	752.0±101.5a	7.9
24	1028.7±77.6a	963.0±61.8a	−6.4
25	757.3±52.0a	633.7±45.9b	−16.3
26	505.7±99.6a	458.0±96.7a	−9.4
27	645.3 ±34.4a	369.0±39.9b	−42.8
28	520.7±11.0a	432.0±43.6a	−17.0
29	511.7±29.9a	412.3±20.0b	−10.0
30	571.7±26.4a	312.0±15.1b	−45.4

Numbers represent mean±SEM, n=3. Means within a row followed by the same letter are not significantly different (P>0.05, paired t test)

the styrene moiety and acetylation of the sugars. We also tested the activity of products **26**–**29** obtained by derivatization and degradation of elaphoside-A (Fig. 1). The effects of elaphoside-A and *p*-vinylanisole (**30**) were evaluated under the same experimental conditions for comparison.

Oviposition-Deterrent Activity The results are summarized in Table 1. To facilitate their interpretation, an oviposition index was defined as Io=(100*T*/*C*)−100, where *T* is the number of eggs laid in the treated artificial fruit, and *C* is the number of eggs deposited in the control fruit. This index takes negative values for oviposition deterrents and positive values for oviposition attractants.

As shown (Table 1), the only compounds that inhibit oviposition at a rate close to that of the natural product elaphoside-A are **27** (racemic mixture) and **30**, indicating that the presence of a methoxy group attached to the aromatic ring confers activity to the compound. It is noted that the effect of each enantiomer in mixture **27** could not be assessed since the racemate could not be resolved.

None of the synthetic glycosides was as active as elaphoside-A, although the α-anomeric compounds **4**, **6**, **7**, **10**, and **16**, as well as the β-anomeric peracetylated glycoside of the disaccharide lactose (**19**), were fairly active, with Io<−30. Acetylation of elaphoside-A led to a loss of activity. An Io=−47.9 was determined for elaphoside-A, while nonsignificant effects were displayed by the peracetylated analog **26**. Accordingly, pairwise comparison of effects produced by the peracetylated glycosides **2**, **5**, **8**, **13**, **14**, and **24** (Io, 0.9, −1.3, −7.7, −13.5, −7.0, and −6.4, respectively) with those of the corresponding non-acetylated analogs **4**, **6**, **10**, **15**, **16**, and **25** (Io, −35.8, −32.8, −33.2, −28.6, −30.6, and −16.3, respectively), indicated that acetylation produced decrease or loss of the activity. In contrast, pairwise comparison of the effects produced by the α-anomers of glucose **4**, **10**, and **16** (Io, −35.8, −33.2, and −30.6, respectively) with those of the corresponding β-anomers **18**, **22**, and **25** (Io, −9.5, 7.9, −16.3, respectively) indicates that the former are more deterrent than the latter.

To evaluate the changes in activity when the vinyl group, present in the natural product elaphoside-A, was chemically modified, glycosides carrying the substituents ethyl (**1**–**6**, and **7**–**20**), 1″-hydroxyethyl (**7**–**10**, **21**, and **22**), and 1″-acetoxyethyl (**12**) were evaluated in the bioassay. As shown (Table 1), different effects were observed in each case, and thus, no structure–activity relationships could be derived.

While elaphoside-A (Io=−47.9) and the most active synthetic glycoside, *p*-ethylphenyl α-D-glucopyranoside **4** (Io=−35.8), are bitter-tasting substances, their peracetylated derivatives **26** (Io=−9.4) and **2** (Io=+0.9), respectively, had no apparent taste. Thus, taste may play a role in the election of the oviposition substrate by *C. capitata*.

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Appendix

p-Ethylphenyl 2,3,4,6-Tetra-*O*-Acetyl-α-D-Galactopyranoside (**1**)

High-resolution fast atom bombardment mass spectrum (HR-FAB-MS) *m/z*: 475.1599 $[M + Na]^+$, calculated for $C_{22}H_{28}O_{10}Na$: 475.1580; $[\alpha]_D$ +251.8 ($CHCl_3$, c 1.0 g/dl, 19.4°C); IR ν_{max} [cm^{-1}] (neat), 1,747, 1,608, 1,510, 1,371, 1,217, 1,070; ^1H NMR (500 MHz, $CDCl_3$), δ 6.98 (d, *J*=8.8 Hz, H-2′, H-6′), 7.13 (d, *J*=8.5 Hz, H-3′, H-5′), 2.60 (q, *J*=7.5 Hz, H-1″), 1.21 (t, *J*=7.5 Hz, H-2″), 5.73 (d, *J*=3.6 Hz, H-1), 5.28 (dd, *J*=10.9, 3.7 Hz, H-2), 5.58 (dd, *J*=11.0, 3.4 Hz, H-3), 5.53 (dd, *J*=3.4, 1.1 Hz, H-4), 4.37 (t, *J*=6.6 Hz, H-5), 4.13 (dd, *J*=11.2, 6.3 Hz, H-6a), 4.07 (dd, *J*=11.2, 7.2 Hz, H-6b), 2.16, 2.07, 2.02, 1.94 (s, CH_3C=O); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.4 (C-1′), 116.8 (C-2′, C-6′), 128.9 (C-3′, C-5′), 139.0 (C-4′), 28.1 (C-1″), 15.8 (C-2″), 95.1 (C-1), 67.9 (C-2), 67.6 (C-3), 68.0 (C-4), 67.1 (C-5), 61.5 (C-6), 170.4, 170.3, 170.2, 170.0 (C=O), 20.74, 20.69, 20.64, 20.58 (CH_3C=O).

p-Ethylphenyl 2,3,4,6-Tetra-*O*-Acetyl-α-D-Glucopyranoside (**2**)

High-resolution chemical ionization mass spectrum (HR-CI-MS) *m/z*: 453.1775 $[M + H]^+$, calculated for $C_{22}H_{29}O_{10}$: 453.1761; ^1H NMR (500 MHz, $CDCl_3$): δ 7.00 (d, *J*=8.6 Hz, H-2′, H-6′), 7.13 (d, *J*=8.4 Hz, H-3′, H-5′), 2.60 (q, *J*=7.6 Hz, H-1″), 1.21 (t, *J*=7.6 Hz, H-2″), 5.70 (d, *J*=3.8 Hz, H-1), 5.03 (dd, *J*=10.2, 3.6 Hz, H-2), 5.70 (t, *J*=9.8 Hz, H-3), 5.15 (t, *J*=9.9 Hz, H-4), 4.14 (ddd, *J*=10.3, 4.5, 2.2 Hz, H-5), 4.25 (dd, *J*=12.3, 4.6 Hz, H-6a), 4.06 (dd, *J*=12.3, 2.3 Hz, H-6b), 2.06, 2.05, 2.04, 2.04 (s, CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.1 (C-1′), 116.5 (C-2′, C-6′), 128.8 (C-3′, C-5′), 139.0 (C-4′), 28.0 (C-1″), 15.7 (C-2″), 94.3 (C-1), 70.4 (C-2), 70.1 (C-3), 68.3 (C-4), 67.8 (C-5), 61.6 (C-6), 170.5, 170.1, 169.6 (C=O), 20.66, 20.59, 20.57, 20.54 (CH_3C=O).

p-Ethylphenyl α-D-Galactopyranoside (**3**)

High-resolution electron impact mass spectrum (HR-EI-MS) *m/z*: 284.1258 $[M]^+$, calculated for $C_{14}H_{20}O_6$: 284.1260; $[\alpha]_D$ +222.5 (MeOH, c 1.0 g/dl, 20.3°C); IR ν_{max} [cm^{-1}] (neat), 3,366, 1,609, 1,511, 1,228, 1,080, 1,032; ^{1}H NMR (500 MHz, MeOH-d_4): δ 6.97 (d, *J*=8.9 Hz, H-2′, H-6′), 7.11 (d, *J*=8.9 Hz, H-3′, H-5′), 2.58 (q, *J*=7.6 Hz, H-1″), 1.19 (t, *J*=7.6 Hz, H-2″), 5.43 (d, *J*=3.2 Hz, H-1), 3.96–3.91 (overlapping signals, H-2, H-3, H-5), 3.98 (dd, *J*=2.8, 1.1 Hz, H-4), 3.71 (dd, *J*=11.4, 5.7 Hz, H-6a), 3.67 (dd, *J*=11.4, 6.6 Hz, H-6b); ^{13}C NMR (50 MHz, MeOH-d_4): δ 156.9 (C-1′), 118.4 (C-2′, C-6′), 129.6 (C-3′, C-5′), 139.5 (C-4′), 29.1 (C-1″), 16.4 (C-2″), 100.0 (C-1), 70.1 (C-2)[1], 71.4 (C-3)[1], 70.8 (C-4), 73.0 (C-5), 62.5 (C-6).

p-Ethylphenyl α-D-Glucopyranoside (**4**)

HR-FAB-MS *m/z*: 307.1174 $[M + Na]^+$, calculated for $C_{14}H_{20}O_6Na$: 307.1158; ^{1}H NMR (500 MHz, D_2O): δ 6.98 (d, *J*=8.7 Hz, H-2′, H-6′), 7.13 (d, *J*=8.7 Hz, H-3′, H-5′), 2.47 (q, *J*=7.5 Hz, H-1″), 1.04 (t, *J*=7.5 Hz, H-2″), 5.46 (d, *J*=3.6 Hz, H-1), 3.58 (dd, *J*=9.8, 3.6 Hz, H-2), 3.78 (t, *J*=9.4 Hz, H-3), 3.38 (t, *J*=9.6 Hz, H-4), 3.65 (ddd, *J*=9.7, 4.7, 2.5 Hz, H-5), 3.63–3.60 (overlapping signals, H-6a, H-6b); ^{13}C NMR (125 MHz, D_2O): δ 154.8 (C-1′), 118.2 (C-2′, C-6′), 129.9 (C-3′, C-5′), 140.5 (C-4′), 28.2 (C-1″), 16.0 (C-2″), 98.2 (C-1), 71.9 (C-2), 73.8 (C-3), 70.2 (C-4), 73.2 (C-5), 61.1 (C-6).

p-Ethylphenyl 2,3,6,2′,3′,4′,6′-Hepta-*O*-Acetyl-α-Lactoside (**5**)

HR-EI-MS *m/z*: 740.2523 $[M]^+$, calculated for $C_{34}H_{44}O_{18}$: 740.2527; $[\alpha]_D$ +83.3 ($CHCl_3$, c 1.0 g/dl, 20.1°C); IR ν_{max} [cm^{-1}] (neat), 1,747, 1,510, 1,369, 1,217, 1,047; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.00 (d, *J*=8.5 Hz, H-2″, H-6″), 7.12 (d, *J*=8.5 Hz, H-3″, H-5″), 2.60 (q, *J*=7.6 Hz, H-1‴), 1.21 (t, *J*=7.6 Hz, H-2‴), 5.60 (d, *J*=3.6 Hz, H-1), 4.95 (dd, *J*=10.3, 3.7 Hz, H-2), 5.69 (dd, *J*=10.2, 9.6 Hz, H-3), 3.84 (t, *J*=9.7 Hz, H-4), 4.05 (ddd, *J*=10.1, 4.6, 1.9 Hz, H-5), 4.42 (dd, *J*=12.0, 1.9 Hz, H-6a), 4.14 (dd, *J*=12.1, 4.8 Hz, H-6b), 4.50 (d, *J*=7.9 Hz, H-1′), 5.12 (dd, *J*=10.3, 7.9 Hz, H-2′), 4.96 (dd, *J*=10.4, 3.5 Hz, H-3′), 5.36 (dd, *J*=3.6, 1.1 Hz, H-4′), 3.89 (td, *J*=7.3, 1.1 Hz, H-5′), 4.16 (dd, *J*=11.2, 6.4 Hz, H-6′a), 4.09 (dd, *J*=11.2, 7.3 Hz, H-6′b), 2.17, 2.09, 2.08, 2.05, 2.04, 2.02, 1.96 (s, C*H*$_3$C=O); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.2 (C-1″), 116.5 (C-2″, C-6″), 128.8 (C-3″, C-5″), 138.9 (C-4″), 28.0 (C-1‴), 15.8 (C-2‴), 94.3 (C-1), 70.68 (C-2), 69.8 (C-3), 76.2 (C-4), 68.7 (C-5), 61.7 (C-6), 101.0 (C-1′), 69.1 (C-2′), 71.0 (C-3′), 66.6 (C-4′), 70.73 (C-5′), 60.9 (C-6′) 170.32, 170.30, 170.1, 170.0, 169.7, 169.6, 169.1 (C=O), 20.8, 20.7, 20.62, 20.58, 20.57, 20.4 (*C*H$_3$C=O).

p-Ethylphenyl α-Lactoside (**6**)

HR-EI-MS *m/z*: 446.1790 $[M]^+$, calculated for $C_{20}H_{30}O_{11}$: 446.1788; $[\alpha]_D$ +126.3 (MeOH, c 1.0 g/dl, 20.0°C); IR ν_{max} [cm^{-1}] (neat), 3,387, 1,610, 1,510, 1,373, 1,227, 1,070, 1,020; ^{1}H NMR (600 MHz, MeOH-d_4): δ 7.05 (d, *J*=8.7 Hz, H-2″, H-6″), 7.11 (d, *J*=8.8 Hz, H-3″, H-5″), 2.58 (q, *J*=7.6 Hz, H-1‴), 1.19 (t, *J*=7.6 Hz, H-2‴), 5.42 (d, *J*=3.7 Hz, H-1), 3.62 (dd, *J*=9.8, 3.7 Hz, H-2), 3.98 (dd, *J*= 9.7, 8.8 Hz, H-3), 3.67 (dd, *J*=9.9, 8.7 Hz, H-4), 3.79 (t, *J*=3.3 Hz, H-5), 3.87 (dd, *J*=12.2, 3.6 Hz, H-6a), 3.74 (dd, *J*=12.3, 3.5 Hz, H-6b), 4.38 (d, *J*=7.7 Hz, H-1′), 3.56 (dd, *J*=9.7, 7.7 Hz, H-2′), 3.49 (dd, *J*=9.8, 3.3 Hz, H-3′), 3.82 (dd, *J*=3.3, 0.7 Hz, H-4′), 3.60 (ddd, *J*=7.5, 4.7, 0.9 Hz, H-5′), 3.80 (dd, *J*=11.4, 7.5 Hz, H-6′a), 3.71 (dd, *J*=11.5, 4.6 Hz, H-6′b); ^{13}C NMR (150 MHz, MeOH-d_4): δ 156.6 (C-1″), 118.1 (C-2″, C-6″), 129.7 (C-3″, C-5″), 139.6 (C-4″), 29.1 (C-1‴), 16.5 (C-2‴), 99.2 (C-1), 73.1 (C-2), 73.4 (C-3), 80.6 (C-4), 77.2 (C-5), 62.6 (C-6), 105.2 (C-1′), 72.7 (C-2′)[1], 74.9 (C-3′), 70.4 (C-4′), 72.6 (C-5′)[1], 61.6 (C-6′).

p-(1″-Hydroxyethyl)-Phenyl 2,3,4,6-Tetra-*O*-Acetyl-α-D-Galactopyranoside (Mixture of Epimers **7**)

HR-FAB-MS *m/z*: 491.1509 $[M + Na]^+$, calculated for $C_{22}H_{28}O_{11}Na$: 491.1529; IR ν_{max} [cm^{-1}] (neat), 3,481, 1,745, 1,608, 1,510, 1,371, 1,217, 1,066; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.04 (d, *J*=8.6 Hz, H-2′, H-6′), 7.32 (d, *J*=8.6 Hz, H-3′, H-5′), 4.87 (q, *J*=6.4 Hz, H-1″), 1.48/1.47 (d, *J*=6.5 Hz, H-2″)[2], 5.76 (d, *J*=3.2 Hz, H-1), 5.28 (dd, *J*=10.9, 3.6 Hz, H-2), 5.58 (dd, *J*=10.9, 3.4 Hz, H-3), 5.53 (dd, *J*=3.4, 1.0 Hz, H-4), 4.35 (t, *J*=6.6 Hz, H-5), 4.12 (dd, *J*=11.3, 6.3 Hz, H-6a), 4.07 (dd, *J*=11.3, 6.6 Hz, H-6b)/4.07 (dd, *J*=11.2, 6.6 Hz, H-6b)[2], 2.17, 2.08, 2.03, 1.95 (s, C*H*$_3$CO); ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.6 (C-1′), 116.7 (C-2′, C-6′), 126.7 (C-3′, C-5′), 140.5 (C-4′), 69.8/69.7 (C-1″)[2], 25.18/25.16 (C-2″)[2], 95.0 (C-1), 67.78 (C-2), 67.5 (C-3), 67.83 (C-4), 67.1 (C-5), 61.4 (C-6), 170.4, 170.3, 170.2, 170.0 (C=O), 20.7, 20.63, 20.59, 20.55 (*C*H$_3$C=O).

p-(1″-Hydroxyethyl)-Phenyl 2,3,4,6-Tetra-*O*-Acetyl-α-D-Glucopyranoside (Mixture of Epimers **8**)

HR-FAB-MS *m/z*: 491.1509 $[M + Na]^+$, calculated for $C_{22}H_{28}O_{11}Na$: 491.1529; IR ν_{max} [cm^{-1}] (neat), 3,500, 1,751, 1,608, 1,508, 1,369, 1,219, 1,043; ^{1}H NMR

[1] Interchangeable signals.

[2] Duplicated signals due to the presence of the two C-1 epimers.

(500 MHz, $CDCl_3$): δ 7.07 (d, J=8.6 Hz, H-2′, H-6′), 7.32 (d, J=8.6 Hz, H-3′, H-5′), 4.88 (q, J=6.4 Hz, H-1″), 1.48/1.48 (d, J=6.5 Hz, H-2″)[3], 5.73 (d, J=3.8 Hz, H-1)/5.73 (d, J=4.0 Hz, H-1)[3], 5.04 (dd, J=10.2, 3.7 Hz, H-2), 5.71 (t, J=9.9 Hz, H-3), 5.16 (dd, J=10.2, 9.5 Hz, H-4), 4.12 (ddd, J=10.3, 4.4, 2.2 Hz, H-5), 4.25 (dd, J=12.3, 4.5 Hz, H-6a), 4.05/4.04 (dd, J=12.3, 1.9 Hz, H-6b)[3], 2.06, 2.05, 2.04, 2.04 (s, CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.3 (C-1′), 116.5 (C-2′, C-6′), 126.7 (C-3′, C-5′), 140.6 (C-4′), 69.7/69.6 (C-1″)[3], 25.2 (C-2″), 94.3 (C-1), 70.4 (C-2), 70.0 (C-3), 68.2 (C-4), 67.9 (C-5), 61.5 (C-6), 170.5, 170.14, 170.12, 169.6 (C=O), 20.7, 20.61, 20.57, 20.55 (*C*H_3C=O).

p-(1″-Hydroxyethyl)-Phenyl α-D-Galactopyranoside (Mixture of Epimers **9**)

HR-EI-MS *m/z*: 300.1210 $[M]^+$, calculated for $C_{14}H_{20}O_7$: 300.1209; ^{1}H NMR (500 MHz, MeOH-d_4): δ 7.12 (d, J=8.5 Hz, H-2′, H-6′), 7.28 (d, J=8.5 Hz, H-3′, H-5′), 4.77 (q, J=6.5 Hz, H-1″), 1.40 (d, J=6.5 Hz, H-2″), 5.47 (d, J=3.0 Hz, H-1)/5.47 (d, J=2.5 Hz, H-1)[3], 3.96–3.93 (overlapping signals, H-2, H-3), 3.97 (dd, J=2.5, 1.3 Hz, H-4), 3.92 (t, J=6.3 Hz, H-5), 3.69 (dd, J=11.3, 5.7 Hz, H-6a), 3.66/3.66 (dd, J=11.4, 6.7 Hz, H-6b)[3]; ^{13}C NMR (125 MHz, MeOH-d_4): δ 157.9 (C-1′), 118.2 (C-2′, C-6′), 127.6 (C-3′, C-5′), 141.5 (C-4′), 70.44/70.40 (C-1″)[3], 25.5 (C-2″), 99.8 (C-1), 70.0 (C-2)[4], 71.4 (C-3)[4], 70.8 (C-4), 73.0 (C-5), 62.4 (C-6).

p-(1″-Hydroxyethyl)-Phenyl α-D-Glucopyranoside (Mixture of Epimers **10**)

HR-EI-MS *m/z*: 300.1212 $[M]^+$, calculated for $C_{14}H_{20}O_7$: 300.1209; ^{1}H NMR (500 MHz, MeOH-d_4): δ 7.12 (d, J=8.5 Hz, H-2′, H-6′), 7.28 (d, J=8.6 Hz, H-3′, H-5′), 4.77 (q, J=6.4 Hz, H-1″), 1.40 (d, J=6.5 Hz, H-2″), 5.46 (d, J=3.6 Hz, H-1), 3.56 (dd, J=9.7, 3.7 Hz, H-2), 3.85 (t, J=9.3 Hz, H-3), 3.43 (t, J=9.3 Hz, H-4), 3.65 (ddd, J=9.6, 4.6, 2.5 Hz, H-5), 3.72 (dd, J=11.7, 2.1 Hz, H-6a), 3.68 (dd, J=11.8, 4.6 Hz, H-6b); ^{13}C NMR (125 MHz, MeOH-d_4): δ 157.7 (C-1′), 118.0 (C-2′, C-6′), 127.7 (C-3′, C-5′), 141.5 (C-4′), 70.41/70.37 (C-1″)[3], 25.5 (C-2″), 99.4 (C-1), 73.3 (C-2), 74.9 (C-3), 71.5 (C-4), 74.3 (C-5), 62.3 (C-6).

p-(1″-Acetoxyethyl)-Phenyl 2,3,4,6-Tetra-*O*-Acetyl-α-D-Galactopyranoside (Mixture of Epimers **11**)

HR-CI-MS *m/z*: 510.1757 $[M]^+$, calculated for $C_{24}H_{30}O_{12}$: 510.1737; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.04 (d, J=8.5 Hz, H-2′, H-6′)/7.03 (d, J=8.7 Hz, H-2′, H-6′)[3], 7.30 (d, J=8.5 Hz, H-3′, H-5′), 5.84/5.84 (q, J=6.5 Hz, H-1″)[3], 1.52/1.51 (d, J=6.5 Hz, H-2″)[3], 5.77/5.76 (d, J=3.6 Hz, H-1)[3], 5.28 (dd, J=10.9, 3.7 Hz, H-2)/5.27 (dd, J=11.0, 3.6 Hz, H-2)[3], 5.57 (dd, J=10.9, 3.5 Hz, H-3), 5.52 (d, J=3.4 Hz, H-4), 4.33 (t, J=6.8 Hz, H-5), 4.12 (dd, J=11.2, 6.5 Hz, H-6a), 4.07 (dd, J=11.2, 6.9 Hz, H-6b), 2.17, 2.06, 2.05, 2.05, 2.03 (s, CH_3CO); ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.8 (C-1′), 116.6 (C-2′, C-6′), 127.6 (C-3′, C-5′), 136.3 (C-4′), 71.74/71.69 (C-1″)[3], 22.0 (C-2″), 94.7 (C-1), 67.7 (C-2), 67.4 (C-3), 67.8 (C-4), 67.1 (C-5), 61.3 (C-6), 170.3, 170.2, 170.1, 170.0 (C=O), 21.3, 20.59, 20.55, 20.47 (*C*H_3C=O).

p-(1″-Acetoxyethyl)-Phenyl 2,3,4,6-Tetra-*O*-Acetyl-α-D-Glucopyranoside (Mixture of Epimers **12**)

HR-CI-MS *m/z*: 510.1708 $[M]^+$, calculated for $C_{24}H_{30}O_{12}$: 510.1737; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07/7.06 (d, J=8.8 Hz, H-2′, H-6′)[3], 7.30 (d, J=8.8 Hz, H-3′, H-5′), 5.84/5.83 (q, J=6.5 Hz, H-1″)[3], 1.51 (d, J=6.7 Hz, H-2″), 5.73/5.72 (d, J=3.7 Hz, H-1)[3], 5.04 (dd, J=10.3, 3.6 Hz, H-2)/5.03 (dd, J=10.2, 3.7 Hz, H-2)[3], 5.70 (t, J=9.9 Hz, H-3), 5.16 (dd, J=10.1, 9.4 Hz, H-4)/5.15 (dd, J=10.2, 9.5 Hz, H-4)[3], 4.10 (ddd, J=10.2, 4.3, 2.1 Hz, H-5), 4.25/4.24 (dd, J=12.3, 4.3 Hz, H-6a)[3], 4.05 (dd, J=12.4, 2.0 Hz, H-6b), 2.17, 2.06, 2.04 (s, CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.7/155.6 (C-1′)[3], 116.5 (C-2′, C-6′), 127.6 (C-3′, C-5′), 136.39/136.37 (C-4′)[3], 71.8/71.7 (C-1″)[3], 22.04/22.02 (C-2″)[3], 94.20/94.15 (C-1)[3], 70.4 (C-2), 70.0 (C-3), 68.3 (C-4), 68.0 (C-5), 61.5 (C-6), 170.5, 170.2, 170.11, 170.08, 169.5 (C=O), 21.3, 20.65, 20.58, 20.55 (*C*H_3C=O).

p-Vinylphenyl 2,3,4,6-Tetra-*O*-Acetyl-α-D-Galactopyranoside (**13**)

HR-EI-MS *m/z*: 450.1522 $[M]^+$, calculated for $C_{22}H_{26}O_{10}$: 450.1526; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02 (d, J=8.7 Hz, H-2′, H-6′), 7.35 (d, J=8.7 Hz, H-3′, H-5′), 6.66 (dd, J=17.8, 10.9 Hz, H-1″), 5.65 (dd, J=17.6, 0.7 Hz, H-2″*trans*), 5.18 (dd, J=10.9, 0.5 Hz, H-2″*cis*), 5.78 (d, J=3.7 Hz, H-1), 5.29 (dd, J=10.7, 3.7 Hz, H-2), 5.58 (dd, J=10.8, 3.3 Hz, H-3), 5.53 (dd, J=3.3, 1.0 Hz, H-4), 4.34 (td, J=7.0, 0.9 Hz, H-5), 4.12 (dd, J=11.3, 6.3 Hz, H-6a), 4.06 (dd, J=11.3, 7.1 Hz, H-6b), 2.17, 2.08, 2.03, 1.94 (s, CH_3C=O); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9 (C-1′), 116.8 (C-2′, C-6′), 127.4 (C-3′, C-5′), 132.7 (C-4′), 135.9 (C-1″), 112.9 (C-2″), 94.8 (C-1), 67.8 (C-2), 67.5 (C-3), 67.9 (C-4), 67.2 (C-5), 61.4 (C-6), 170.4, 170.3, 170.2, 170.0 (C=O), 20.7, 20.65, 20.61, 20.5 (*C*H_3C=O).

p-Vinylphenyl 2,3,4,6-Tetra-*O*-Acetyl-α-D-Glucopyranoside (**14**)

HR-EI-MS *m/z*: 450.1534 $[M]^+$, calculated for $C_{22}H_{26}O_{10}$: 450.1526; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.05 (d, J=

[3] See footnote 2.
[4] See footnote 1.

8.7 Hz, H-2′, H-6′), 7.36 (d, *J*=8.7 Hz, H-3′, H-5′), 6.66 (dd, *J*=17.5, 10.9 Hz, H-1″), 5.65 (dd, *J*=17.5, 0.7 Hz, H-2″*trans*), 5.19 (dd, *J*=10.8, 0.7 Hz, H-2″*cis*), 5.74 (d, *J*= 3.7 Hz, H-1), 5.04 (dd, *J*=10.3, 3.6 Hz, H-2), 5.70 (t, *J*= 9.9 Hz, H-3), 5.16 (t, *J*=9.4 Hz, H-4), 4.11 (ddd, *J*= 10.3, 4.4, 2.2 Hz, H-5), 4.25 (dd, *J*=12.3, 4.6 Hz, H-6a), 4.05 (dd, *J*=12.3, 2.3 Hz, H-6b), 2.06, 2.05, 2.04, 2.04 (s, CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.7 (C-1′), 116.6 (C-2′, C-6′), 127.4 (C-3′, C-5′), 132.7 (C-4′), 135.8 (C-1″), 112.9 (C-2″), 94.2 (C-1), 70.4 (C-2), 70.0 (C-3), 68.3 (C-4), 68.0 (C-5), 61.6 (C-6), 170.5, 170.1, 169.6 (C=O), 20.7, 20.62, 20.60, 20.57 (*C*H_3C=O).

p-Vinylphenyl α-D-Galactopyranoside (**15**)

HR-EI-MS *m/z*: 282.1097 $[M]^+$, calculated for $C_{14}H_{18}O_6$: 282.1103; $[\alpha]_D$ +275.8 (MeOH, c 1.0 g/dl, 20.1°C); IR ν_{max} [cm^{-1}] (neat), 3,389, 1,629, 1,605, 1,508, 1,234, 1,082, 1,033; ^{1}H NMR (500 MHz, MeOH-d_4): δ 7.12 (d, *J*=8.8 Hz, H-2′, H-6′), 7.35 (d, *J*=8.8 Hz, H-3′, H-5′), 6.66 (dd, *J*=17.7, 11.0 Hz, H-1″), 5.63 (dd, *J*=17.5, 0.9 Hz, H-2″*trans*), 5.10 (dd, *J*=11.0, 0.9 Hz, H-2″*cis*), 5.49 (d, *J*=2.2 Hz, H-1), 3.89–3.84 (overlapping signals, H-2, H-3), 3.97 (dd, *J*=1.8, 1.1 Hz, H-4), 3.91 (t, *J*=6.3 Hz, H-5), 3.70 (dd, *J*=11.4, 5.6 Hz, H-6a), 3.66 (dd, *J*=11.4, 6.6 Hz, H-6b); ^{13}C NMR (125MHz, MeOH-d_4): δ 158.5 (C-1′), 118.3 (C-2′, C-6′), 128.3 (C-3′, C-5′), 133.4 (C-4′), 137.5 (C-1″), 112.4 (C-2″), 99.7 (C-1), 70.0 (C-2)[5], 71.4 (C-3)[5], 70.8 (C-4), 73.1 (C-5), 62.4 (C-6).

p-Vinylphenyl α-D-Glucopyranoside (**16**)

HR-EI-MS *m/z*: 282.1102 $[M]^+$, calculated for $C_{14}H_{18}O_6$: 282.1103; ^{1}H NMR (500 MHz, MeOH-d_4): δ 7.11 (d, *J*= 8.8 Hz, H-2′, H-6′), 7.35 (d, *J*=8.5 Hz, H-3′, H-5′), 6.66 (dd, *J*=17.7, 11.0 Hz, H-1″), 5.64 (dd, *J*=17.7, 0.8 Hz, H-2″*trans*), 5.11 (dd, *J*=11.0, 0.7 Hz, H-2″*cis*), 5.47 (d, *J*= 3.6 Hz, H-1), 3.56 (dd, *J*=9.7, 3.7 Hz, H-2), 3.84 (t, *J*= 9.3 Hz, H-3), 3.42 (t, *J*=9.4 Hz, H-4), 3.64 (ddd, *J*=9.8, 4.7, 2.5 Hz, H-5), 3.73 (dd, *J*=11.9, 2.5 Hz, H-6a), 3.68 (dd, *J*=11.9, 4.7 Hz, H-6b); ^{13}C NMR (50 MHz, MeOH-d_4): δ 158.3 (C-1′), 118.1 (C-2′, C-6′), 128.3 (C-3′, C-5′), 133.4 (C-4′), 137.5 (C-1″), 112.4 (C-2″), 99.2 (C-1), 73.3 (C-2), 74.9 (C-3), 71.5 (C-4), 74.4 (C-5), 62.3 (C-6).

p-Ethylphenyl 2,3,4,6-Tetra-*O*-Acetyl-β-D-Glucopyranoside[6] (**17**)

HR-EI-MS *m/z*: 452.1654 $[M]^+$, calculated for $C_{22}H_{28}O_{10}$: 452.1682; $[\alpha]_D$ −22.2 ($CHCl_3$, c 1.0 g/dl, 20.7°C); IR ν_{max} [cm^{-1}] (neat), 1,751, 1,608, 1,510, 1,367, 1,221, 1,047; ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.92 (d, *J*=8.7 Hz, H-2′, H-6′), 7.12 (d, *J*=8.7 Hz, H-3′, H-5′), 2.60 (q, *J*=7.6 Hz, H-1″), 1.21 (t, *J*=7.6 Hz, H-2″), 5.05 (d, *J*=7.6 Hz, H-1), 5.26 (dd, *J*=9.2, 7.5 Hz, H-2), 5.29 (t, *J*=9.2 Hz, H-3), 5.17 (t, *J*= 9.5 Hz, H-4), 3.85 (ddd, *J*=10.0, 5.3, 2.5 Hz, H-5), 4.29 (dd, *J*=12.3, 5.3 Hz, H-6a), 4.17 (dd, *J*=12.3, 2.4 Hz, H-6b), 2.08, 2.06, 2.05, 2.04 (s, CH_3C=O); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.9 (C-1′), 116.9 (C-2′, C-6′), 128.7 (C-3′, C-5′), 139.2 (C-4′), 28.0 (C-1″), 15.7 (C-2″), 99.3 (C-1), 71.1 (C-2), 72.7 (C-3), 68.2 (C-4), 71.8 (C-5), 61.9 (C-6), 170.5, 170.2, 169.3, 169.2 (C=O), 20.61, 20.55, 20.53, 20.50 (*C*H_3C=O).

p-Ethylphenyl β-D-Glucopyranoside (**18**)

HR-FAB-MS *m/z*: 307.1156 $[M + Na]^+$, calculated for $C_{14}H_{20}O_6Na$: 307.1158; $[\alpha]_D$ −65.4 (MeOH, c 1.0 g/dl, 19.9°C); IR ν_{max} [cm^{-1}] (neat), 3,335, 1,611, 1,511, 1,233, 1,070; ^{1}H NMR (500 MHz, D_2O): δ 6.96 (d, *J*=8.5 Hz, H-2′, H-6′), 7.14 (d, *J*=8.5 Hz, H-3′, H-5′), 2.49 (q, *J*=7.6 Hz, H-1″), 1.06 (t, *J*=7.5 Hz, H-2″), 4.96 (d, *J*=7.6 Hz, H-1), 3.43 (dd, *J*=9.4, 7.6 Hz, H-2), 3.48 (t, *J*=9.1 Hz, H-3), 3.36 (t, *J*=9.3 Hz, H-4), 3.48 (ddd, *J*=9.9, 5.7, 2.0 Hz, H-5), 3.80 (dd, *J*=12.3, 1.8 Hz, H-6a), 3.62 (dd, *J*=12.4, 5.7 Hz, H-6b); ^{13}C NMR (50 MHz, MeOH-d_4): δ 157.1 (C-1′), 117.7 (C-2′, C-6′), 129.6 (C-3′, C-5′), 139.4 (C-4′), 29.0 (C-1″), 16.4 (C-2″), 102.5 (C-1), 74.8 (C-2), 77.9 (C-3)[5], 71.3 (C-4), 78.0 (C-5)[5], 62.4 (C-6).

p-Ethylphenyl 2,3,6,2′,3′,4′,6′-Hepta-*O*-Acetyl-β-Lactoside (**19**)

HR-FAB-MS *m/z*: 763.2396 $[M + Na]^+$, calculated for $C_{34}H_{44}O_{18}Na$: 763.2425; $[\alpha]_D$ −22.4 ($CHCl_3$, c 1.0 g/dl, 22.4°C); IR ν_{max} [cm^{-1}] (neat), 3,028, 1,751, 1,608, 1,508, 1,369, 1,219, 1,057; ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.89 (d, *J*=8.6 Hz, H-2″, H-6″), 7.10 (d, *J*=8.7 Hz, H-3″, H-5″), 2.60 (q, *J*=7.6 Hz, H-1‴), 1.20 (t, *J*=7.6 Hz, H-2‴), 5.01 (d, *J*=7.8 Hz, H-1), 5.16 (dd, *J*=9.3, 7.8 Hz, H-2), 5.27 (t, *J*=9.1 Hz, H-3), 3.89 (t, *J*=9.4 Hz, H-4), 3.77 (ddd, *J*=9.9, 5.8, 2.2 Hz, H-5), 4.50 (dd, *J*=12.3, 2.6 Hz, H-6a), 4.15 (dd, *J*=12.0, 5.6 Hz, H-6b), 4.51 (d, *J*=8.0 Hz, H-1′), 5.13 (dd, *J*=10.4, 7.9 Hz, H-2′), 4.97 (dd, *J*=10.4, 3.5 Hz, H-3′), 5.36 (dd, *J*=3.4, 1.0 Hz, H-4′), 3.90 (t, *J*=7.1 Hz, H-5′), 4.13 (dd, *J*=11.0, 6.8 Hz, H-6′a), 4.10 (dd, *J*=11.2, 7.3 Hz, H-6′b), 2.16, 2.09, 2.08, 2.07, 2.06, 1.97 (s, CH_3C=O); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.8 (C-1″), 116.8 (C-2″, C-6″), 128.7 (C-3″, C-5″), 139.2 (C-4″), 28.0 (C-1‴), 15.7 (C-2‴), 99.0 (C-1), 71.5 (C-2), 72.8 (C-3), 76.2 (C-4), 72.7 (C-5), 62.0 (C-6), 101.0 (C-1′), 69.0 (C-2′), 70.9 (C-3′), 66.6 (C-4′), 70.7 (C-5′), 60.8 (C-6′) 170.41, 170.38, 170.3, 170.2,

[5] See footnote 1.

[6] Known compound (Helferich and Höfmann, 1952; Ojika et al. 1984).

170.1, 169.6, 169.0 (C= O), 20.9, 20.8, 20.67, 20.65, 20.62, 20.59, 20.50 (CH_3C=O).

p-Ethylphenyl β-Lactoside (**20**)

^{1}H NMR (300 MHz, pyridin-d_5): δ 7.26 (d, *J*=8.7 Hz, H-2″, H-6″), 7.43 (d, *J*=8.7 Hz, H-3″, H-5″), 2.64 (q, *J*= 6.8 Hz, H-1‴), 1.26 (t, *J*=6.8 Hz, H-2‴), 5.73 (d, *J*= 7.5 Hz, H-1), 4.81–4.20 (overlapping signals H-2, H-3, H-4, H-6a, H-6b, H-2′, H-3′, H-4′, H-5′, H-6′a, H-6′b), 4.24 (ddd, *J*=9.3, 6.3, 2.7 Hz, H-5), 5.31 (d, *J*=8.1 Hz, H-1′); ^{13}C NMR (75 MHz, pyridin-d_5): δ 156.7 (C-1″), 117.1 (C-2″, C-6″), 129.2 (C-3″, C-5″), 138.0 (C-4″), 28.3 (C-1‴), 16.2 (C-2‴), 102.0 (C-1), 74.6 (C-2), 76.8 (C-3), 81.8 (C-4), 76.8 (C-5), 61.9 (C-6), 105.9 (C-1′), 70.2 (C-2′), 72.6 (C-3′), 77.4 (C-4′), 75.3 (C-5′), 62.1 (C-6′).

p-(1″-Hydroxyethyl)-Phenyl 2,3,4,6-Tetra-*O*-Acetyl-β-D-Glucopyranoside[7] (Mixture of Epimers **21**)

HR-CI-MS *m/z*: 469.1716 $[M + H]^+$, calculated for $C_{22}H_{29}O_{11}$: 469.1710; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.97 (d, *J*=8.6 Hz, H-2′, H-6′), 7.31 (d, *J*=8.6 Hz, H-3′, H-5′), 4.88 (q, *J*=5.8 Hz, H-1″), 1.48 (d, *J*=6.5 Hz, H-2″), 5.07 (d, *J*=7.6 Hz, H-1)/5.07 (d, *J*=7.4 Hz, H-1)[8], 5.27 (t, *J* =9.1 Hz, H-2), 5.30 (t, *J*=9.0 Hz, H-3), 5.17 (t, *J*=9.4 Hz, H-4), 3.86 (ddd, *J*=9.9, 5.3, 2.3 Hz, H-5), 4.29 (dd, *J*=12.3, 5.2 Hz, H-6a), 4.17 (dd, *J*=12.3, 2.2 Hz, H-6b)/4.17 (dd, *J*= 12.2, 2.2 Hz, H-6b)[8], 2.08, 2.06, 2.05, 2.04 (s, CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.2 (C-1′), 117.06/117.04 (C-2′, C-6′)[8], 126.7 (C-3′, C-5′), 140.9 (C-4′), 69.9/69.8 (C-1″)[8], 25.23/25.22 (C-2″)[8], 99.2 (C-1), 71.2 (C-2), 72.7 (C-3), 68.3 (C-4), 72.1 (C-5), 62.0 (C-6), 170.5, 170.2, 169.4, 169.3 (C=O), 20.7, 20.64, 20.63, 20.60 (CH_3C=O).

p-(1″-Hydroxyethyl)-Phenyl β-D-Glucopyranoside (Mixture of Epimers **22**)

HR-EI-MS *m/z*: 300.1198 $[M]^+$, calculated for $C_{14}H_{20}O_7$: 300.1209; IR ν_{max} [cm^{-1}] (neat), 3,367, 1,610, 1,510, 1,230, 1,068; ^{1}H NMR (500 MHz, D_2O): δ 7.00 (d, *J*=8.8 Hz, H-2′, H-6′), 7.26 (d, *J*=8.8 Hz, H-3′, H-5′), 4.75 (q, *J*=6.5 Hz, H-1″), 1.32 (d, *J*=6.5 Hz, H-2″), 4.98 (d, *J*=7.5 Hz, H-1), 3.43 (dd, *J*=8.9, 7.5 Hz, H-2), 3.48 (t, *J*=8.9 Hz, H-3), 3.36 (dd, *J*=9.8, 8.9 Hz, H-4), 3.48 (ddd, *J*=9.8, 5.5, 2.4 Hz, H-5), 3.79 (dd, *J*=12.4, 2.1 Hz, H-6a), 3.62 (dd, *J*=12.4, 5.7 Hz, H-6b); ^{13}C NMR (125 MHz, D_2O): δ 156.7 (C-1′), 117.5 (C-2′, C-6′), 128.0 (C-3′, C-5′), 140.6 (C-4′), 70.10/70.06 (C-1″)[8], 24.3 (C-2″), 101.1 (C-1), 73.8 (C-2), 76.9 (C-3), 70.3 (C-4), 76.4 (C-5), 61.4 (C-6).

[7] See footnote 6.

[8] See footnote 2.

p-(1″-Acetoxyethyl)-Phenyl 2,3,4,6-Tetra-*O*-Acetyl-β-D-Glucopyranoside (Mixture of Epimers **23**)

HR-EI-MS *m/z*: 510.1736 $[M]^+$, calculated for $C_{24}H_{30}O_{12}$: 510.1737; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.99 (d, *J*= 8.7 Hz, H-2′, H-6′), 7.31 (d, *J*=8.6 Hz, H-3′, H-5′), 5.86 (q, *J*=6.5 Hz, H-1″), 1.51 (d, *J*=6.5 Hz, H-2″), 5.08/5.07 (d, *J*= 7.6 Hz, H-1)[8], 5.29 (dd, *J*=9.3, 7.5 Hz, H-2), 5.32 (t, *J*= 9.1 Hz, H-3), 5.19 (t, *J*=9.5 Hz, H-4), 3.87 (ddd, *J*=10.0, 5.3, 2.5 Hz, H-5), 4.31 (dd, *J*=12.3, 5.3 Hz, H-6a), 4.18/4.17 (dd, *J*=12.3, 2.3 Hz, H-6b)[8], 2.08/2.08[8], 2.06, 2.05, 2.05, 2.04 (s, CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.4 (C-1′), 116.9 (C-2′, C-6′), 127.57/127.55 (C-3′, C-5′)[8], 136.7 (C-4′), 71.8 (C-1″), 22.1/22.0 (C-2″)[8], 99.0 (C-1), 71.1 (C-2), 72.7 (C-3), 68.3 (C-4), 72.0 (C-5), 61.9 (C-6), 170.6, 170.3, 170.2, 169.4, 169.3 (C=O), 21.3, 20.7, 20.62, 20.60, 20.58 (CH_3C=O).

p-Vinylphenyl 2,3,4,6-Tetra-*O*-Acetyl-β-D-Glucopyranoside[7] (**24**)

HR-EI-MS *m/z*: 450.1518 $[M]^+$, calculated for $C_{22}H_{26}O_{10}$: 450.1526; $[\alpha]_D$ −20.8 ($CHCl_3$, c 1.0 g/dl, 21.2°C); IR ν_{max} [cm^{-1}] (neat), 3,022, 1,755, 1,630, 1,606, 1,508, 1,367, 1,221, 1,047; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.95 (d, *J*=8.7 Hz, H-2′, H-6′), 7.34 (d, *J*= 8.7 Hz, H-3′, H-5′), 6.66 (dd, *J*=17.8, 10.9 Hz, H-1″), 5.65 (dd, *J*=17.5, 0.7 Hz, H-2″*trans*), 5.19 (dd, *J*=10.9, 0.7 Hz, H-2″*cis*), 5.08 (d, *J*=7.5 Hz, H-1), 5.27 (dd, *J*= 9.1, 7.5 Hz, H-2), 5.30 (t, *J*=9.0 Hz, H-3), 5.17 (t, *J*= 9.5 Hz, H-4), 3.86 (ddd, *J*=10.0, 5.2, 2.5 Hz, H-5), 4.29 (dd, *J*=12.3, 5.5 Hz, H-6a), 4.17 (dd, *J*=12.3, 2.5 Hz, H-6b), 2.08, 2.06, 2.05, 2.04 (s, CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.4 (C-1′), 117.0 (C-2′, C-6′), 127.3 (C-3′, C-5′), 133.0 (C-4′), 135.8 (C-1″), 113.0 (C-2″), 99.1 (C-1), 71.1 (C-2), 72.7 (C-3), 68.3 (C-4), 72.0 (C-5), 61.9 (C-6), 170.5, 170.2, 169.3, 169.2 (C=O), 20.63, 20.58, 20.56, 20.54 (CH_3C=O).

p-Vinylphenyl β-D-Glucopyranoside[7] (**25**)

HR-EI-MS *m/z*: 282.1097 $[M]^+$, calculated for $C_{14}H_{18}O_6$: 282.1103; $[\alpha]_D$ −81.5 (MeOH, c 1.0 g/dl, 21.0°C); IR ν_{max} [cm^{-1}] (neat), 3,318, 1,627, 1,606, 1,509, 1,245, 1,076, 1,046; ^{1}H NMR (600 MHz, MeOH-d_4): δ 7.04 (d, *J*= 8.5 Hz, H-2′, H-6′), 7.38 (d, *J*=8.5 Hz, H-3′, H-5′), 6.66 (dd, *J*=17.6, 10.9 Hz, H-1″), 5.64 (dd, *J*=17.3, 0.9 Hz, H-2″*trans*), 5.11 (dd, *J*=11.0, 0.9 Hz, H-2″*cis*), 4.90 (d, *J*= 7.6 Hz, H-1), 3.46–3.36 (overlapping signals, H-2, H-3, H-4, H-5), 3.89 (dd, *J*=12.1, 2.0 Hz, H-6a), 3.68 (dd, *J*=12.1, 5.6 Hz, H-6b); ^{13}C NMR (150 MHz, MeOH-d_4): δ 158.8 (C-1′), 117.7 (C-2′, C-6′), 128.3 (C-3′, C-5′), 133.5 (C-4′), 137.5 (C-1″), 112.4 (C-2″), 102.2 (C-1), 74.9 (C-2), 78.2 (C-3), 71.4 (C-4), 78.0 (C-5), 62.5 (C-6).

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