

Glycosidic juvenogens: Derivatives bearing α,β -unsaturated ester functionalities

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Abstract—A series of the protected alkyl glycosides **5a/5b–12a/12b** was synthesized from the parent isomeric alcohols (insect juvenile hormone bioanalogs; juvenoids), 4-[4'-(2''-hydroxycyclohexyl)methylphenoxy]-3-methyl-but-2-enoic acid ethyl ester (**1a/1b–4a/4b**; racemic structures) and (**1a–4a**; enantiopure structures). Cadmium carbonate was used as a promoter of this Koenigs–Knorr reaction, and the products were obtained in 82–92% yields. Deprotection of the carbohydrate functionality of **5a/5b–12a/12b** was carefully performed using ethanolysis in the presence of zinc acetate, due to the presence of another ester functionality in the aglycone part of the molecule of protected alkyl glycosides. Resulting alkyl glycosides **13a/13b–20a/20b** (diastereoisomeric mixtures) and **13a–20a** (enantiopure compounds), biochemically activated hormonogenic compounds (juvenogens), were obtained in 82–93% yields. Finally, chiral HPLC separation of the diastereoisomeric mixtures of alkyl glycosides was applied to get sufficient quantities of the respective enantiomers **13b–20b** of the alkyl glycosides for their structure elucidation and ¹³C chemical shift assignment by ¹H and ¹³C NMR spectroscopy. Partial introductory entomological screening tests of the target alkyl glycosides **13a/13b–20a/20b** were performed on the red firebug (*Pyrrhocoris apterus*). The results of this biological testing clearly demonstrated the time-extended effect of several juvenogens on *P. apterus* due to their biochemical activation, i.e., hydrolysis of the juvenogen molecule, which results in liberation of the biologically active juvenoid in the insect organism.

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1. Introduction

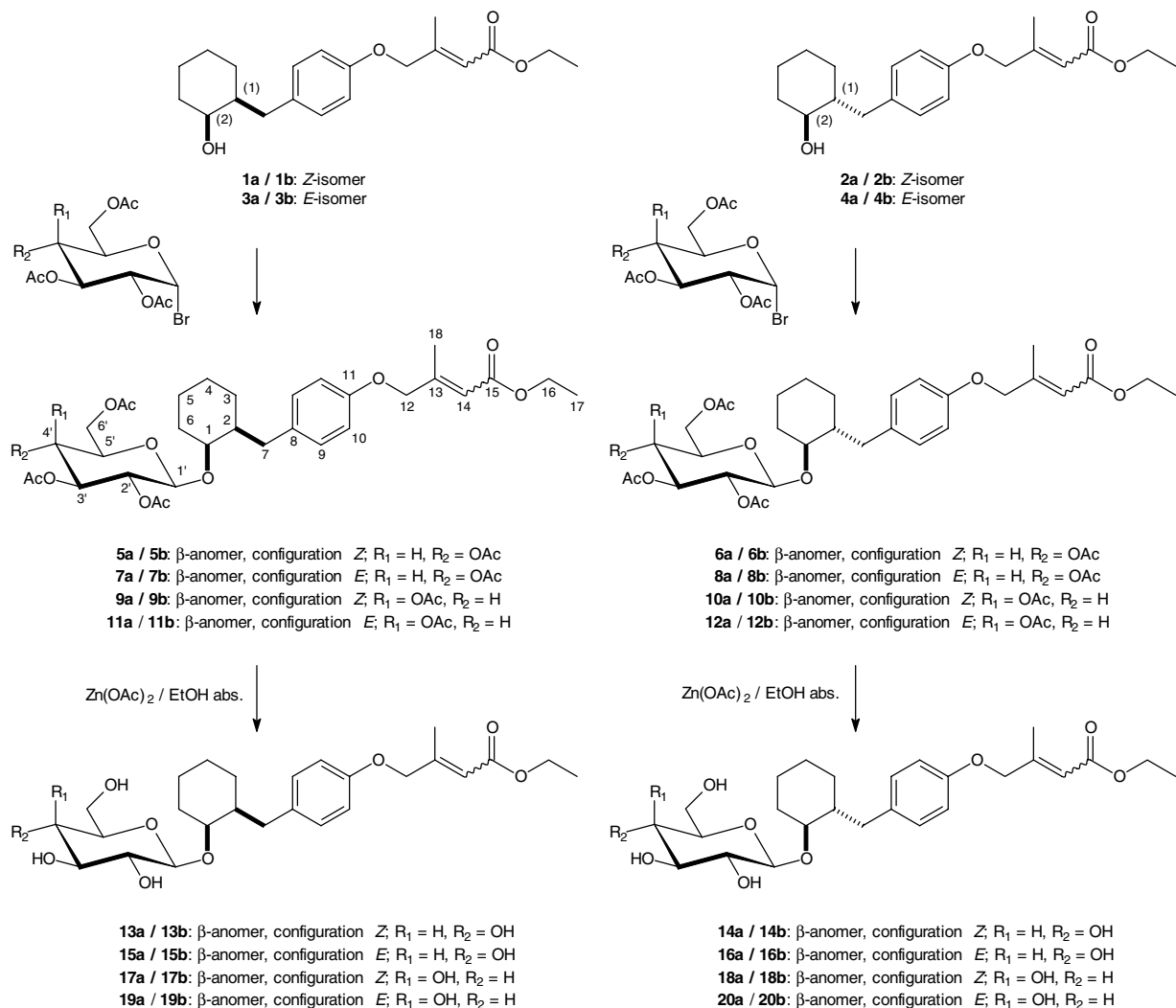
Insect pest management agents have been targets of our projects for many years (for reviews, see^{1,2}). Insect juvenile hormone bioanalogs (JHAs, juvenoids) represent the environmentally most safe agents in insect pest management.^{1–4} These compounds mimic the mode of action of natural insect juvenile hormones (JHs), showing their effect either in morphological and/or gonadotropic level, or in caste differentiation (in social insects, like termites).^{2,4–9}

A series of α,β -unsaturated esters was designed and synthesized for application as juvenoids against insects in

the past years.¹⁰ The compounds displayed high biological activity on a variety of insect pests.¹ One of the most important results achieved was the finding that the respective *Z* and *E* isomers of ethyl 4-[4'-(2'',2''-ethylenedioxcyclohexyl)methylphenoxy]-3-methyl-but-2-enoate, which relates to the juvenoids **1a/1b–4a/4b**, used in this investigation (Scheme 1), displayed similar level of biological activity on aphids (*Acyrtosiphon pisum*).¹¹ This important finding proved for the first time among this series of compounds that important insect pests can be found, on which *E* and *Z* isomers of the selected juvenoid structure display similar (almost equal) level of biological activity. Before this finding was observed, the juvenoids of the 2-(4'-alkoxybenzyl)cyclohexanone series, bearing the α,β -unsaturated ester functionality in the *Z* configuration in the molecule, had always been proven to show very low biological activity on most of insects.¹ The encouraging finding¹¹ focused again our attention to this series of compounds. Considering the potential target insect pests (aphids and bugs, i.e.

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Scheme 1. Reaction pathway. The numbers (1) and (2) placed in the structures **1a/1b–4a/4b** indicate the chiral centers C(1) and C(2) for the assignment of the absolute configuration, and they respect the chemical nomenclature rules. In turn, the numbering of the positions located in the other structure should only be used for indication of the appropriate signals in the 1H and ^{13}C NMR spectra.

herbivorous insect species), one of the possible ways of their treatment by juvenoids is represented by the systemic application of convenient derivatives, e.g. glycosides of parent juvenoid alcohols, which can be more easily ingested by insects and can also be more easily applied to the plants.

The key transformation of the juvenoid molecule consists in a synthesis of β -D-glucopyranoside and β -D-galactopyranoside derivatives of the racemic isomers **1a/1b–4a/4b** and of the enantiopure stereoisomers **1a–4a** of the juvenoid structures selected for the target study; the stereoisomers **1a** and **3a** bear the absolute configuration (1*S*,2*S*), **2a** and **4a** can be described as (1*R*,2*S*). The reason for this transformation was to produce hormonogen substances (juvenogens, biochemically activated juvenoids)¹² displaying higher polarity than the parent alcohol, which is a key feature of the novel molecule, due to its proposed systemic application against herbivorous insect pests (aphids or bugs). The term juvenogen has been used for describing complex hormonogen substances generally capable of liberating

the biologically active compound (the juvenoid) under the effect of biotic (mainly enzyme-mediated) or abiotic (environmental) factors.¹² The practical impact of hormonogen compounds consists in their controlled physico-chemical properties, protection of the parent biologically active molecule for extended time period, and an advanced feature of hormonogen compounds to act as biochemically activated slow-release formulations for biologically active compounds. Therefore, application of juvenogens results in extended period, during which the target insect pest is treated by the biologically active compound. The rate of hydrolysis of juvenogens, which results in liberation of the biologically active juvenoid, is dependent on the juvenogen structure. This anticipation was proven during our pioneer experiments,¹³ for which four of the compounds presented in this study (**13a/13b–16a/16b**), were already synthesized in their diastereoisomeric forms, i.e., their synthesis started from racemic alcohols. However, their detailed synthesis has never been published, and their partial 1H NMR data presented therein¹³ were recorded using an old 60 MHz NMR instrument available that

time. Therefore, when now focusing on the glycosidic derivatives **5a/5b–20a/20b** of the parent racemic juvenoids **1a/1b–4a/4b** and those of enantiopure juvenoids **1a–4a**, for a more detailed study of the juvenogens, and we present completed analytical data (^1H and ^{13}C NMR, IR and mass spectra, and elemental analyses) of the enantiopure compounds **5a–20a** and **5b–20b**. The products **5a/5b–20a/20b** (diastereoisomeric mixtures) have been synthesized and subjected to the partial introductory screening tests on the red firebug (*Pyrhrocoris apterus*).

Recently, we have published a paper on a stereospecific reduction of the respective *E* and *Z* isomers of ethyl 4-[4'-(2''-oxocyclohexyl)methylphenoxy}-3-methyl-but-2-enoate by *Saccharomyces cerevisiae* whole cells, affording the requested enantiomers **1a–4a** of the corresponding alcohols with > 99% enantiomeric purity.¹⁴ The described procedure¹⁴ was used to prepare the compounds **1a–4a** in this study and to use them in the synthesis of the juvenogens **5a–20a**.

The objectives of this investigation were: (a) to synthesize diastereoisomeric and enantiomerically pure target alkyl glycosides; (b) to separate diastereoisomeric mixtures of alkyl glycosides to get all possible enantiomers of the studied alkyl glycosides in their enantiomerically pure states; (c) to perform a detailed structure elucidation and ^{13}C chemical shift assignments of the products **5a–20a** and **5b–20b** by ^1H and ^{13}C NMR spectroscopy; (d) to get basic introductory results on biological activity of the prepared target alkyl glycosides by performing the screening tests on the red firebug (*P. apterus*).

2. Results and discussion

The Koenigs–Knorr synthesis^{15,16} of the intermediate products **5a/5b–12a/12b** was performed using the respective 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl- and 2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranosyl bromide as the activating species of the carbohydrate unit (Scheme 1). The separated racemic isomers **1a/1b–4a/4b** and the enantiopure stereoisomers **1a–4a** of the juvenoid alcohols were used as glycosyl acceptors. Cadmium carbonate was used as optimized promoter of the Koenigs–Knorr synthesis of alkyl glycosides.^{17–19} The carbohydrate units bring new chirality features to the intermediate products **5a/5b–12a/12b**, and, therefore, these acetylated compounds were isolated in the forms of diastereoisomeric mixtures. Subsequently, the final products of this synthesis, the juvenogens **13a/13b–20a/20b**, were also obtained as diastereoisomeric mixtures (Scheme 1). A 1:1 ratio of the respective diastereoisomers **5a/5b–20a/20b** was found in each mixture, which means that there was no detectable preference of either enantiomer of the isomeric racemic alcohols **1a/1b–4a/4b** during the Koenigs–Knorr synthesis. The Koenigs–Knorr synthesis was performed under rigorously anhydrous conditions by careful removal of traces of humidity potentially present or entering the system, by continuous maintaining of the azeotropic conditions in

the system through the whole reaction time; toluene was used as convenient solvent due to its higher safety and higher boiling point in comparison with benzene to assist in maintaining anhydrous conditions during the reaction. The second synthetic step required application of a careful approach to the deprotection of the carbohydrate unit due to the presence of another ester functionality in the aglycone part of the molecule; its presence is necessary for keeping biological activity of the juvenoids **1a/1b–4a/4b** and the juvenogens **13a/13b–20a/20b**. Therefore, removal of the acetate groups from the carbohydrate units was performed by alcoholysis in the presence of zinc acetate.²⁰ The same synthetic procedure was applied for the synthesis of the enantiopure compounds **5a–20a**, which started from the enantiopure alcohols **1a–4a**. These alcohols were obtained by a stereoselective enzymic reduction of the corresponding parent ketones using *Saccharomyces cerevisiae* whole cells.¹⁴

It was found that the Koenigs–Knorr synthesis resulted in higher yields of the intermediate products **9a/9b–12a/12b** (β -D-galactopyranosides), in comparison with **5a/5b–8a/8b** (β -D-glucopyranosides). The deprotection of the compounds **5a/5b–12a/12b** showed no visible preference from any point of view. The same result was obtained when the synthetic procedure started from enantiopure alcohols **1a** to **4a**.

Because the synthetic procedure afforded the diastereoisomeric compounds **5a/5b–20a/20b** and the enantiopure compounds **5a–20a** directly, enough material was also available for the detailed structure assignment by ^1H and ^{13}C NMR spectroscopy. In fact, the ^1H and ^{13}C NMR spectra of the enantiomers **5b–20b** were extracted from the respective spectra of the diastereoisomeric mixtures **5a/5b–20a/20b** by using the spectra of the pure enantiomers **5a–20a** to identify signals belonging to the enantiomers **5b–20b**. Employing a chiral HPLC separation technique on a cyclodextrin-based chiral Nucleodex- β -OH column, we succeeded to separate the diastereoisomeric mixtures **13a/13b–20a/20b**, and got small quantities of **13b–20b** to record their NMR spectra. No separation of the enantiomers of the protected compounds **5a/5b–12a/12b** was observed under the applied isocratic chromatographic conditions; methanol/water (9:1) was used as mobile phase. The NMR experiments employed in this study though enabled finally unambiguous structure assignment of all alkyl β -D-glucopyranosides prepared (**5a–20b**). The NMR data were determined on the basis of both, 1D and 2D NMR experiments. The critical analysis of the 1D ^1H NMR and $^1\text{H},^1\text{H}$ PFG COSY spectra^{21–23} of pure enantiomers **5a–20b** allowed extracting the ^1H chemical shifts and coupling constants. However, positions of the ^1H signals of the cyclohexane moiety could be extracted neither directly from the 1D NMR spectra nor from the $^1\text{H},^1\text{H}$ PFG COSY spectra, and it was necessary to estimate these values from the $^1\text{H},^{13}\text{C}$ PFG HSQC spectra^{24,25} using the knowledge of the ^{13}C NMR chemical shifts from the model compounds with similar structure.²⁶ The 2D $^1\text{H},^{13}\text{C}$ PFG HSQC spectra were used for unambiguous assignment of the ^{13}C NMR chemical shifts of the remaining carbon atoms. The ^1H NMR

data of the protected and unprotected alkyl glycosides **5a–20b** are summarized in the Experimental section, while their ^{13}C NMR data are collected in Tables 1–4.

The alkyl glycosides **13a/13b–20a/20b** have been subjected to biological screening tests against the red firebug (*P. apterus*), employing a drinking assay (Table 5). The ID-50 value generally indicates the amount of a biologically active compound to be used for obtaining a 50% inhibition of metamorphosis. The ID-50 value (Table 5) represents the value calculated for each compound from five experiments running simultaneously with different concentrations of the tested compound. It clearly follows from the screening tests that a majority of juvenogens (**13a/13b**, **15a/15b**, and **17a/17b**) derived from the parent alcohols **1a/1b** and **3a/3b** displayed higher activity than these parent alcohols. However, when using the juvenogens **14a/14b**, **16a/16b**, **18a/18b**, and **20a/20b** derived from the parent alcohols **2a/2b** and **4a/4b**, the results are not so convincing. The juvenogen (i.e., an alkyl glycoside) is metabolized by β -glycosidases present in the insect organism, due to which process the biologically active aglycone (the juvenoid) is liberated in the insect body.^{12,13} It has not been proved yet, if both, the juvenogens and the juvenoids, can be transported to the target site in the insect body. However, it has already been proven that application of different juvenogen structures can extend the mode of action of the parent juvenoid.^{7,8,12,13}

3. Conclusion

Following the specified objectives of this investigation, several partial results were achieved and evaluated: (a) a series of new juvenogens, insect hormonogenic compounds (**13a–20b**), was prepared using the Koenigs–Knorr synthesis of alkyl glycosides, followed by a careful deprotection by alcoholysis of the acetyl groups in the presence of zinc acetate. These substances were synthesized either in the form of diastereoisomeric compounds or in the form of enantiopure stereoisomers; (b) small quantities of the target diastereoisomeric compounds were separated from their diastereoisomeric mixtures using chiral HPLC technique to get all possible stereoisomers as enantiopure chemical species; (c) the target compounds **13a–20b**, as well as their protected precursors **5a–12b**, were subjected to a detailed structure elucidation, which enabled unambiguous structure assignment of the products **5a–20b**; (d) several compounds of this series were subjected to the introductory screening tests on *P. apterus*, and the results showed that the juvenogens **13a/13b** and **17a/17b** displayed higher activity than the parent alcohol **1a/1b**, and the juvenogen **15a/15b** was more active than its parent alcohol **3a/3b**, which result clearly demonstrates the extended effect of juvenogens, biochemically activated hormonogenic compounds, in comparison with their parent juvenoid alcohols.

Table 1. The ^{13}C NMR data of the protected alkyl glucosides **5a/5b–8a/8b** (measured in CDCl_3 at 303 K)

Carbon atom No.	Compound							
	5a^a	5b^a	6a^b	6b^b	7a^c	7b^c	8a^d	8b^d
1	79.98 (d)	74.99 (d)	85.58 (d)	81.07 (d)	80.01 (d)	74.70 (d)	85.59 (d)	80.93 (d)
2	43.80 (d)	43.87 (d)	45.11 (t)	44.33 (t)	43.75 (d)	43.86 (d)	45.13 (d)	44.34 (d)
3	26.65 (t)	26.72 (t)	29.74 (t)	29.67 (t)	26.67 (t)	26.82 (t)	29.78 (t)	29.72 (t)
4	25.34 (t)	25.05 (t)	24.77 (t)	24.45 (t)	25.36 (t)	25.05 (t)	24.76 (t)	24.77 (t)
5	20.71 (t)	20.68 (t)	24.91 (t)	24.88 (t)	20.40 (t)	20.23 (t)	24.92 (t)	24.90 (t)
6	31.92 (t)	28.86 (t)	33.71 (t)	31.25 (t)	29.69 (t)	28.80 (t)	33.71 (t)	31.25 (t)
7	37.28 (t)	37.19 (t)	37.33 (t)	37.33 (t)	37.26 (t)	37.11 (t)	37.35 (t)	37.32 (t)
8	133.31 (s)	133.80 (s)	132.74 (s)	133.25 (s)	133.78 (s)	134.19 (s)	133.22 (s)	133.70 (s)
9	129.90 (d)	130.34 (d)	130.13 (d)	130.43 (d)	129.94 (d)	130.39 (d)	130.17 (d)	130.48 (d)
10	114.47 (d)	114.07 (d)	114.36 (d)	114.15 (d)	114.71 (d)	114.28 (d)	114.58 (d)	114.35 (d)
11	156.67 (s)	156.83 (s)	156.83 (s)	156.68 (s)	156.37 (s)	156.54 (s)	156.52 (s)	156.38 (s)
12	67.30 (t)	67.24 (t)	67.28 (t)	67.26 (t)	71.61 (t)	71.61 (t)	71.70 (t)	71.64 (t)
13	156.37 (s)	156.23 (s)	156.39 (s)	156.24 (s)	153.05 (s)	152.85 (s)	153.05 (s)	152.90 (s)
14	117.44 (d)	117.36 (d)	117.43 (d)	117.37 (d)	115.79 (d)	115.70 (d)	115.76 (d)	115.70 (d)
15	165.94 (s)	165.91 (s)	165.93 (s)	165.93 (s)	166.58 (s)	166.52 (s)	166.57 (s)	166.54 (s)
16	59.99 (t)	59.94 (t)	59.97 (t)	59.90 (t)	59.83 (t)	59.78 (t)	59.82 (t)	59.78 (t)
17	14.28 (q)	14.28 (q)	14.28 (q)	14.28 (q)	14.29 (q)	14.29 (q)	14.28 (q)	14.28 (q)
18	21.35 (q)	21.34 (q)	21.33 (q)	21.32 (q)	15.68 (q)	15.68 (q)	15.68 (q)	15.68 (q)
1'	101.76 (d)	98.24 (d)	102.04 (d)	98.56 (d)	101.77 (d)	98.17 (d)	102.02 (d)	98.50 (d)
2'	71.67 (d)	71.78 (d)	71.83 (d)	71.71 (d)	71.76 (d)	71.84 (d)	71.83 (d)	71.81 (d)
3'	73.10 (d)	73.13 (d)	73.08 (d)	73.13 (d)	73.10 (d)	73.13 (d)	73.07 (d)	73.11 (d)
4'	68.64 (d)	68.94 (d)	68.80 (d)	68.82 (d)	68.72 (d)	68.97 (d)	68.79 (d)	68.82 (d)
5'	71.53 (d)	71.59 (d)	71.63 (d)	71.63 (d)	71.52 (d)	71.76 (d)	71.61 (d)	71.12 (d)
6'	62.28 (t)	62.01 (t)	62.30 (t)	62.12 (t)	62.30 (t)	62.12 (t)	62.30 (t)	62.12 (t)

Signals of the protecting acetate functionalities on the monosaccharide part of the molecules: ^a 20.48 (q), 20.61 (q), 20.65 (q), 20.70 (q), 20.71 (q), 20.74 (q), 20.74 (q), 20.84 (q), 169.21 (s), 169.22 (s), 169.44 (s), 169.45 (s), 170.33 (s), 170.37 (s), 170.59 (s), 170.71 (s); ^b 20.59 (q), 20.60 (q), 20.69 (q), 20.71 (q), 20.73 (q), 20.78 (q), 20.78 (q), 20.78 (q), 169.26 (s), 169.29 (s), 169.41 (s), 169.41 (s), 170.33 (s), 170.36 (s), 170.60 (s), 170.65 (s); ^c 20.53 (q), 20.59 (q), 20.63 (q), 20.67 (q), 20.70 (q), 20.72 (q), 20.77 (q), 20.84 (q), 169.17 (s), 169.21 (s), 169.41 (s), 169.43 (s), 170.34 (s), 170.55 (s), 170.55 (s), 170.71 (s); ^d 20.51 (q), 20.53 (q), 20.53 (q), 20.59 (q), 20.67 (q), 20.67 (q), 20.69 (q), 20.70 (q), 169.25 (s), 169.29 (s), 169.40 (s), 169.41 (s), 170.33 (s), 170.35 (s), 170.59 (s), 170.64 (s).

Table 2. The ^{13}C NMR data of the protected alkyl galactosides **9a/9b–12a/12b** (measured in CDCl_3 at 303 K)

Carbon atom No.	Compound							
	9a^a	9b^a	10a^b	10b^b	11a^c	11b^c	12a^d	12b^d
1	80.14 (d)	75.45 (d)	85.81 (d)	81.38 (d)	80.09 (d)	75.11 (d)	85.84 (d)	81.30 (d)
2	43.75 (d)	43.79 (d)	45.09 (t)	44.27 (t)	43.65 (d)	43.74 (d)	45.14 (d)	44.31 (d)
3	26.58 (t)	26.65 (t)	29.76 (t)	29.57 (t)	26.57 (t)	26.70 (t)	29.79 (t)	29.64 (t)
4	25.28 (t)	24.80 (t)	24.76 (t)	24.43 (t)	25.27 (t)	24.90 (t)	24.78 (t)	24.45 (t)
5	20.89 (t)	21.03 (t)	24.92 (t)	24.81 (t)	20.40 (t)	20.86 (t)	24.95 (t)	24.85 (t)
6	31.92 (t)	28.94 (t)	33.80 (t)	31.31 (t)	31.88 (t)	28.85 (t)	33.83 (t)	31.32 (t)
7	37.27 (t)	37.04 (t)	37.32 (t)	37.37 (t)	37.22 (t)	37.19 (t)	37.35 (t)	37.40 (t)
8	133.34 (s)	133.87 (s)	132.73 (s)	133.28 (s)	133.75 (s)	134.20 (s)	133.24 (s)	133.79 (s)
9	129.91 (d)	130.32 (d)	130.15 (d)	130.38 (d)	129.92 (d)	130.35 (d)	130.21 (d)	130.46 (d)
10	114.44 (d)	114.09 (d)	114.28 (d)	114.10 (d)	114.63 (d)	114.25 (d)	114.53 (d)	114.34 (d)
11	156.62 (s)	156.81 (s)	156.76 (s)	156.59 (s)	156.27 (s)	156.45 (s)	156.47 (s)	156.31 (s)
12	67.19 (t)	67.29 (t)	67.08 (t)	67.08 (t)	71.65 (t)	71.72 (t)	71.73 (t)	71.75 (t)
13	156.48 (s)	156.32 (s)	156.48 (s)	156.34 (s)	153.12 (s)	152.90 (s)	153.11 (s)	153.00 (s)
14	117.41 (d)	117.33 (d)	117.36 (d)	117.32 (d)	115.66 (d)	115.54 (d)	115.67 (d)	115.61 (d)
15	165.96 (s)	165.95 (s)	165.94 (s)	165.94 (s)	166.57 (s)	166.53 (s)	166.60 (s)	166.58 (s)
16	60.91 (t)	59.97 (t)	59.98 (t)	59.96 (t)	59.83 (t)	59.79 (t)	59.86 (t)	59.83 (t)
17	14.30 (q)	14.30 (q)	14.28 (q)	14.28 (q)	14.27 (q)	14.27 (q)	14.30 (q)	14.30 (q)
18	21.39 (q)	21.37 (q)	21.35 (q)	21.35 (q)	15.68 (q)	15.68 (q)	15.71 (q)	15.71 (q)
1'	102.32 (d)	98.93 (d)	102.55 (d)	99.28 (d)	102.30 (d)	98.82 (d)	102.55 (d)	99.27 (d)
2'	69.17 (d)	69.31 (d)	69.21 (d)	69.27 (d)	69.12 (d)	69.28 (d)	69.22 (d)	69.30 (d)
3'	71.16 (d)	71.17 (d)	71.15 (d)	71.15 (d)	71.11 (d)	71.13 (d)	71.16 (d)	71.16 (d)
4'	67.17 (d)	67.19 (d)	67.23 (d)	67.20 (d)	67.11 (d)	67.14 (d)	67.10 (d)	67.10 (d)
5'	70.44 (d)	70.48 (d)	70.41 (d)	70.48 (d)	70.42 (d)	70.42 (d)	70.43 (d)	70.51 (d)
6'	61.39 (t)	61.39 (t)	61.25 (t)	61.36 (t)	61.35 (t)	61.33 (t)	61.25 (t)	61.37 (t)

Signals of the protecting acetate functionalities on the monosaccharide part of the molecules: ^a 20.59 (q), 20.59 (q), 20.65 (q), 20.67 (q), 20.71 (q), 20.76 (q), 20.76 (q), 20.78 (q), 169.38 (s), 169.38 (s), 169.91 (s), 169.99 (s), 170.26 (s), 170.44 (s), 170.45 (s), 170.53 (s); ^b 20.57 (q), 20.60 (q), 20.63 (q), 20.65 (q), 20.67 (q), 20.72 (q), 20.73 (q), 20.86 (q), 169.97 (s), 170.23 (s), 170.27 (s), 170.37 (s), 170.41 (s), 170.42 (s), 170.43 (s), 170.50 (s); ^c 20.40 (q), 20.56 (q), 20.62 (q), 20.63 (q), 20.67 (q), 20.73 (q), 20.75 (q), 21.00 (q), 169.38 (s), 169.87 (s), 169.96 (s), 170.22 (s), 170.26 (s), 170.40 (s), 170.42 (s), 170.49 (s); ^d 20.56 (q), 20.65 (q), 20.67 (q), 20.69 (q), 20.74 (q), 20.75 (q), 20.85 (q), 20.88 (q), 169.40 (s), 169.46 (s), 170.24 (s), 170.26 (s), 170.37 (s), 170.39 (s), 170.43 (s), 170.48 (s).

Table 3. The ^{13}C NMR data of the alkyl glucosides **13a/13b–16a/16b** (measured in CD_3OD at 303 K)

Carbon atom No.	Compound							
	13a	13b	14a	14b	15a	15b	16a	16b
1	80.52 (d)	76.57 (d)	85.34 (d)	80.77 (d)	80.53 (d)	76.50 (d)	85.90 (d)	81.18 (d)
2	45.21 (d)	45.58 (d)	46.85 (d)	46.18 (d)	45.21 (d)	45.59 (d)	47.43 (d)	46.69 (d)
3	28.32 (t)	28.25 (t)	30.89 (t)	31.10 (t)	28.31 (t)	28.28 (t)	31.40 (t)	31.59 (t)
4	26.10 (t)	26.60 (t)	25.89 (t)	25.68 (t)	25.46 (t)	26.61 (t)	26.43 (t)	26.20 (t)
5	23.31 (t)	22.33 (t)	26.17 (t)	26.33 (t)	24.53 (t)	24.24 (t)	26.71 (t)	26.86 (t)
6	33.24 (t)	30.13 (t)	35.15 (t)	32.22 (t)	33.23 (t)	30.58 (t)	35.73 (t)	32.74 (t)
7	37.40 (t)	38.37 (t)	38.50 (t)	38.58 (t)	37.45 (t)	38.42 (t)	39.00 (t)	39.05 (t)
8	135.94 (s)	136.10 (s)	134.99 (s)	135.19 (s)	136.22 (s)	136.37 (s)	135.73 (s)	135.91 (s)
9	131.82 (d)	131.92 (d)	131.37 (d)	131.45 (d)	131.84 (d)	131.96 (d)	131.90 (d)	132.00 (d)
10	115.73 (d)	115.64 (d)	115.24 (d)	115.20 (d)	115.97 (d)	115.87 (d)	115.92 (d)	115.87 (d)
11	158.56 (s)	158.53 (s)	157.79 (s)	157.77 (s)	158.25 (s)	158.20 (s)	158.25 (s)	158.21 (s)
12	68.62 (t)	68.62 (t)	68.18 (t)	68.18 (t)	73.03 (t)	73.01 (t)	73.02 (t)	73.02 (t)
13	158.44 (s)	158.40 (s)	158.11 (s)	158.06 (s)	155.98 (s)	155.94 (s)	155.96 (s)	155.94 (s)
14	118.92 (d)	118.90 (d)	118.47 (d)	118.47 (d)	116.51 (d)	116.49 (d)	116.52 (d)	116.50 (d)
15	167.95 (s)	167.93 (s)	167.46 (s)	167.46 (s)	168.62 (s)	168.60 (s)	168.61 (s)	168.61 (s)
16	61.61 (t)	61.61 (t)	61.11 (t)	61.11 (t)	61.41 (t)	61.41 (t)	61.41 (t)	61.41 (t)
17	15.11 (q)	15.09 (q)	14.57 (q)	14.57 (q)	15.09 (q)	15.09 (q)	15.08 (q)	15.08 (q)
18	21.93 (q)	21.92 (q)	21.41 (q)	21.40 (q)	16.25 (q)	16.25 (q)	16.25 (q)	16.25 (q)
1'	105.65 (d)	102.23 (d)	105.65 (d)	101.35 (d)	105.65 (d)	102.22 (d)	106.21 (d)	101.81 (d)
2'	76.08 (d)	75.77 (d)	75.65 (d)	75.21 (d)	76.08 (d)	75.77 (d)	76.14 (d)	75.68 (d)
3'	78.83 (d)	78.83 (d)	78.31 (d)	78.28 (d)	78.83 (d)	78.83 (d)	78.76 (d)	78.75 (d)
4'	72.28 (d)	72.37 (d)	71.77 (d)	71.98 (d)	72.28 (d)	72.37 (d)	72.21 (d)	72.42 (d)
5'	78.22 (d)	78.29 (d)	77.78 (d)	77.90 (d)	78.22 (d)	78.29 (d)	78.29 (d)	78.42 (d)
6'	63.35 (t)	63.46 (t)	62.88 (t)	63.07 (t)	63.35 (t)	63.46 (t)	63.32 (t)	63.52 (t)

Table 4. The ^{13}C NMR data of the alkyl galactosides **17a/17b–20a/20b** (measured in CD_3OD at 303 K)

Carbon atom No.	Compound							
	17a	17b	18a	18b	19a	19b	20a	20b
1	80.52 (d)	76.63 (d)	85.83 (d)	81.25 (d)	80.54 (d)	76.90 (d)	85.83 (d)	81.24 (d)
2	45.30 (d)	45.67 (d)	47.45 (d)	46.71 (d)	45.29 (d)	45.68 (d)	47.44 (d)	46.71 (d)
3	28.33 (t)	28.29 (t)	31.41 (t)	31.60 (t)	28.31 (t)	28.30 (t)	31.41 (t)	31.61 (t)
4	26.13 (t)	26.57 (t)	26.44 (t)	26.22 (t)	26.10 (t)	26.58 (t)	26.44 (t)	26.22 (t)
5	23.28 (t)	22.35 (t)	26.71 (t)	26.86 (t)	23.27 (t)	22.31 (t)	26.72 (t)	26.87 (t)
6	33.26 (t)	30.17 (t)	35.76 (t)	32.78 (t)	33.26 (t)	30.17 (t)	35.77 (t)	32.80 (t)
7	37.46 (t)	38.26 (t)	39.03 (t)	39.03 (t)	37.48 (t)	38.26 (t)	39.04 (t)	39.04 (t)
8	135.99 (s)	136.14 (s)	135.50 (s)	135.64 (s)	136.27 (s)	136.42 (s)	135.78 (s)	135.91 (s)
9	131.83 (d)	131.93 (d)	131.88 (d)	131.98 (d)	131.84 (d)	131.97 (d)	131.90 (d)	132.01 (d)
10	115.72 (d)	115.62 (d)	115.67 (d)	115.62 (d)	116.00 (d)	115.85 (d)	115.91 (d)	115.85 (d)
11	158.55 (s)	158.50 (s)	158.56 (s)	158.52 (s)	158.23 (s)	158.18 (s)	158.24 (s)	158.20 (s)
12	68.62 (t)	68.62 (t)	68.62 (t)	68.62 (t)	73.00 (t)	73.00 (t)	73.03 (t)	73.03 (t)
13	158.44 (s)	158.41 (s)	158.41 (s)	158.40 (s)	155.98 (s)	155.95 (s)	155.97 (s)	155.95 (s)
14	118.92 (d)	118.90 (d)	118.92 (d)	118.91 (d)	116.51 (d)	116.48 (d)	116.51 (d)	116.50 (d)
15	167.95 (s)	167.93 (s)	167.94 (s)	167.94 (s)	168.63 (s)	168.61 (s)	168.63 (s)	168.61 (s)
16	61.62 (t)	61.62 (t)	61.61 (t)	61.61 (t)	61.41 (t)	61.41 (t)	61.41 (t)	61.41 (t)
17	15.08 (q)	15.08 (q)	15.08 (q)	15.08 (q)	15.08 (q)	15.08 (q)	15.08 (q)	15.08 (q)
18	21.93 (q)	21.92 (q)	21.93 (q)	21.92 (q)	16.25 (q)	16.25 (q)	16.25 (q)	16.25 (q)
1'	106.31 (d)	102.96 (d)	106.84 (d)	102.53 (d)	106.31 (d)	102.96 (d)	106.83 (d)	102.53 (d)
2'	73.53 (d)	73.24 (d)	73.57 (d)	73.13 (d)	73.53 (d)	73.23 (d)	73.58 (d)	73.13 (d)
3'	75.70 (d)	75.74 (d)	75.66 (d)	75.64 (d)	75.70 (d)	75.73 (d)	75.66 (d)	75.64 (d)
4'	70.75 (d)	70.75 (d)	70.75 (d)	70.81 (d)	70.78 (d)	70.74 (d)	70.75 (d)	70.83 (d)
5'	76.86 (d)	76.89 (d)	76.92 (d)	77.01 (d)	76.86 (d)	76.90 (d)	76.93 (d)	77.02 (d)
6'	62.79 (t)	62.83 (t)	62.88 (t)	62.91 (t)	62.83 (t)	62.86 (t)	62.88 (t)	62.95 (t)

Table 5. Juvenilizing effect of selected compounds on the red firebug (*P. apterus*)

Compound	ID-50 (drinking assay) [$\mu\text{g}\cdot\text{ind}^{-1}$]	Compound	ID-50 (drinking assay) [$\mu\text{g}\cdot\text{ind}^{-1}$]
1a/1b	18.0	2a/2b	inactive
13a/13b	1.1	14a/14b	inactive
17a/17b	2.3	18a/18b	3.0
3a/3b	0.05	4a/4b	0.32
15a/15b	0.0021	16a/16b	1.3
19a/19b	0.11	20a/20b	1.9

4. Experimental

4.1. General

The ^1H NMR and the ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 spectrometer (in a FT mode) at 500.1 and 125.8 MHz, respectively, in CDCl_3 or in CD_3OD at 303 K. For standardization, in the ^1H NMR either internal signal of tetramethylsilane ($\delta 0.0$) or a proton trace signal ($\delta 3.31$ for CHD_2OD) was used, and in the ^{13}C NMR spectra solvent signals for both CDCl_3 ($\delta 77.00$) and CD_3OD ($\delta 49.50$) were used. 2D NMR experiments were measured using following characteristic parameters: ^1H , ^1H PFG COSY–spectral width 9 ppm in both f_1 , f_2 dimensions, delay 1 s, data matrix for processing 2048×2048 data points; ^1H , ^{13}C PFG HSQC – spectral width 9 ppm in f_2 and 160 ppm in f_1 , delay 1 s, data matrix for processing 2048×2048 data points (lists of all acquisition and processing parameters are available from D. Šaman on request). IR spectra were recorded either in a solution (CCl_4) or using a KBr technique on a Bruker IFS 88 instrument. MS

(FAB) were recorded on a VG analytical 70 - 250 SE mass spectrometer, ZAB-EQ (BEQQ configuration) at 70 eV. Preparative column chromatography was performed on a silica gel type 60 (particle size 0.04–0.063 mm; Fluka, Switzerland). TLC was performed on aluminum sheets precoated with silica gel 60 (Merck, Germany). Analytical HPLC was carried out on a TSP (Thermoseparation Products, USA) instrument equipped with a ConstaMetric 4100 Bio pump and a SpectroMonitor 5000 UV DAD. The purity of the products was checked using a Sepharon SGX C-18 reverse phase column (250×4 mm, particle size 5 μm ; Watrex, Czech Republic) and/or on a chiral Nucleodex β -OH column (150×4 mm; Macherey–Nagel, Germany) using methanol / water (4:1, v/v) as mobile phase at 0.5 mL min^{-1} (Sepharon SGX C-18 RP column) or at 0.3 mL min^{-1} (Nucleodex β -OH column). The eluate was monitored at 220, 254, and 275 nm and UV spectra were run from 200 to 300 nm. Optical rotations were measured on an Autopol IV polarimeter (Rudolph Research Analytical, USA). Elemental analyses were performed on a Perkin Elmer 2400, series II CHNS/O analyzer (USA).

4.2. Ethyl 4-{4'-[2''-(2''',3''',4''',6''')-tetra-O-acetyl- β -D-glucopyranosyloxy]cyclohexyl]methylphenoxy}-3-methylbut-2-enoate (**5a/5b–8a/8b**) and ethyl 4-{4'-[2''-(2''',3''',4''',6''')-tetra-O-acetyl- β -D-galactopyranosyloxy]cyclohexyl]methylphenoxy}-3-methylbut-2-enoate (**9a/9b–12a/12b**)

The respective isomers of the alcohol (**1–4**; 200 mg; 0.6 mmol) were dissolved in toluene (45 mL), and cadmium carbonate (335 mg; 2.0 mmol) was added. A part of toluene (7–10 mL) was distilled off under the azeotropic conditions to remove traces of water from

the system. A solution of 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl bromide or 2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranosyl bromide (800 mg; 2.0 mmol) in toluene (2 mL) was added during 5 min to the reaction mixture, which was stirred and heated under azeotropic condition for additional 16 h. A mixture of inorganic salts was removed by filtration, and the solvent was evaporated from the filtrate, affording a dry residue. Column chromatography on silica gel yielded the pure products in the respective yields: **5a/5b**: 46%; **6a/6b**: 34%; **7a/7b**: 32%; **8a/8b**: 33%; **9a/9b**: 92%; **10a/10b**: 91%; **11a/11b**: 49%; **12a/12b**: 35%.

Compound **5a/5b**: $^1\text{H NMR}$ (CDCl_3): **5a**: 1.17–1.46 (m, 6H, H-3, H-4a, H-5, H-6a), 1.29 (t, $J = 7.1$, 3H, H-17), 1.55–1.69 (m, 3H, H-2, H-4b, H-6b), 2.01 (dt, $J = 0.7$, 0.7, 1.5, 3H, H-18), 2.40 (dd, $J = 7.7$, 13.6, 1H, H-7a), 2.52 (dd, $J = 6.9$, 13.6, 1H, H-7b), 3.65 (ddd, $J = 2.7$, 4.6, 9.8, 1H, H-5'), 3.65 (dt, $J = 2.3$, 2.3, 4.4, 1H, H-1), 4.10 (dd, $J = 2.7$, 11.8, 1H, H-6'a), 4.17 (q, $J = 7.1$, 2H, H-16), 4.21 (dd, $J = 4.6$, 11.8, 1H, H-6'b), 4.55 (d, $J = 7.9$, 1H, H-1'), 5.10 (dd, $J = 7.9$, 9.7, 1H, H-2'), 5.14 (t, $J = 9.6$, 1H, H-4'), 5.18 (dq, $J = 0.7$, 0.7, 1.7, 2H, H-12), 5.22 (t, $J = 9.5$, 1H, H-3'), 5.83 (m, $J = 1.5$, 1H, H-14), 6.86 (m, 2H, H-10), 7.04 (m, 2H, H-9); signals ($\text{CH}_3\text{CO-}$): 2.02 (s, 3H), 2.04 (s, 3H), 2.07 (s, 3H), 2.08 (s, 3H); **5b**: 1.17–1.46 (m, 6H, H-3, H-4a, H-5, H-6a), 1.30 (t, $J = 7.1$, 3H, H-17), 1.55–1.69 (m, 3H, H-2, H-4b, H-6b), 2.01 (dt, $J = 0.7$, 0.7, 1.5, 3H, H-18), 2.52 (dd, $J = 6.9$, 13.6, 1H, H-7a), 2.70 (dd, $J = 7.5$, 13.6, 1H, H-7b), 3.65 (ddd, $J = 2.7$, 4.6, 9.8, 1H, H-5'), 3.81 (dt, $J = 2.3$, 2.3, 4.4, 1H, H-1), 4.15 (dd, $J = 2.7$, 11.8, 1H, H-6'a), 4.18 (q, $J = 7.1$, 2H, H-16), 4.29 (dd, $J = 4.6$, 11.8, 1H, H-6'b), 4.55 (d, $J = 7.9$, 1H, H-1'), 5.06 (t, $J = 9.6$, 1H, H-4'), 5.08 (dd, $J = 7.9$, 9.7, 1H, H-2'), 5.15 (dq, $J = 0.7$, 0.7, 1.7, 2H, H-12), 5.23 (t, $J = 9.5$, 1H, H-3'), 5.81 (m, $J = 1.5$, 1H, H-14), 6.83 (m, 2H, H-10), 7.11 (m, 2H, H-9); signals ($\text{CH}_3\text{CO-}$): 2.02 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H), 2.06 (s, 3H). IR (CCl_4): 3029 (w), 1760 (s), 1753 (s), 1715 (m), 1648 (w), 1612 (w), 1511 (m), 1340 (w), 1246 (s), 1221 (s), 1151 (s), 1097 (m), 1039 (s), 898 (w). MS: $m/z = 663$ (1; $[\text{M}+\text{H}]^+$), 331 (30), 315 (8), 289 (4), 271 (13), 233 (9), 217 (7), 169 (100), 127 (93), 109 (85). For $\text{C}_{34}\text{H}_{46}\text{O}_{13}$ (662.74) calculated C, 61.62; H, 7.00. Found: C, 61.78; H, 6.92.

Compound **6a/6b**: $^1\text{H NMR}$ (CDCl_3): **6a**: 0.86 (m, 1H, H-3a), 1.06 (m, 1H, H-5a), 1.19 (m, 1H, H-6a), 1.20 (m, 1H, H-4a), 1.29 (t, $J = 7.1$, 3H, H-17), 1.54 (m, 1H, H-5b), 1.59 (m, 1H, H-2), 1.64 (m, 1H, H-3b), 1.71 (m, 1H, H-4b), 1.98 (m, 1H, H-6b), 2.02 (dt, $J = 0.8$, 0.8, 1.5, 3H, H-18), 2.10 (dd, $J = 8.8$, 13.7, 1H, H-7a), 3.07 (dd, $J = 3.5$, 13.7, 1H, H-7b), 3.20 (dt, $J = 4.2$, 9.5, 9.5, 1H, H-1), 3.70 (ddd, $J = 2.7$, 4.9, 10.0, 1H, H-5'), 4.13 (dd, $J = 2.7$, 12.1, 1H, H-6'a), 4.17 (q, $J = 7.1$, 2H, H-16), 4.25 (dd, $J = 4.9$, 12.1, 1H, H-6'b), 4.63 (d, $J = 7.7$, 1H, H-1'), 5.07 (dd, $J = 9.4$, 10.0, 1H, H-4'), 5.07 (dd, $J = 7.7$, 9.7, 1H, H-2'), 5.16 (dq, $J = 0.8$, 0.8, 0.8, 1.6, 2H, H-12), 5.22 (t, $J = 9.5$, 1H, H-3'), 5.81 (m, $J = 1.5$, 1H, H-14), 6.83 (m, 2H, H-10), 7.00 (m, 2H, H-9); signals ($\text{CH}_3\text{CO-}$): 1.95 (s, 3H), 2.00 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), **6b**: 0.86

(m, 1H, H-3a), 1.06 (m, 1H, H-5a), 1.20 (m, 1H, H-4a), 1.29 (t, $J = 7.1$, 3H, H-17), 1.40 (m, 1H, H-6a), 1.54 (m, 1H, H-5b), 1.59 (m, 1H, H-2), 1.64 (m, 1H, H-3b), 1.71 (m, 1H, H-4b), 2.02 (dt, $J = 0.8$, 0.8, 1.5, 3H, H-18), 2.12 (m, 1H, H-6b), 2.17 (dd, $J = 9.0$, 13.6, 1H, H-7a), 3.13 (dd, $J = 3.5$, 13.6, 1H, H-7b), 3.32 (dt, $J = 4.3$, 9.5, 9.5, 1H, H-1), 3.67 (ddd, $J = 2.7$, 4.9, 10.0, 1H, H-5'), 4.16 (dd, $J = 2.7$, 12.1, 1H, H-6'a), 4.17 (q, $J = 7.1$, 2H, H-16), 4.26 (dd, $J = 4.9$, 12.1, 1H, H-6'b), 4.61 (d, $J = 7.8$, 1H, H-1'), 5.01 (dd, $J = 7.8$, 9.7, 1H, H-2'), 5.10 (dd, $J = 9.4$, 10.0, 1H, H-4'), 5.16 (dq, $J = 0.8$, 0.8, 0.8, 1.6, 2H, H-12), 5.22 (t, $J = 9.5$, 1H, H-3'), 5.81 (m, $J = 1.5$, 1H, H-14), 6.82 (m, 2H, H-10), 7.06 (m, 2H, H-9); signals ($\text{CH}_3\text{CO-}$): 2.01 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.07 (s, 3H). IR (CCl_4): 3030 (w), 1761 (s), 1753 (s), 1716 (m), 1649 (w), 1612 (w), 1511 (m), 1340 (w), 1246 (s), 1220 (s), 1151 (s), 1098 (m), 1039 (s), 906 (w), 880 (w). MS: $m/z = 663$ (1; $[\text{M}+\text{H}]^+$), 369 (5), 331 (30), 233 (6), 187 (8), 169 (81), 139 (10), 127 (100), 109 (68), 99 (65). For $\text{C}_{34}\text{H}_{46}\text{O}_{13}$ (662.74) calculated C, 61.62; H, 7.00. Found: C, 61.69; H, 6.46.

Compound **7a/7b**: $^1\text{H NMR}$ (CDCl_3): **7a**: 1.16–1.46 (m, 4H, H-3, H-5), 1.21–1.25 (m, 1H, H-4a), 1.29 (t, $J = 7.1$, 3H, H-17), 1.29–1.36 (m, 1H, H-6a), 1.62–1.65 (m, 1H, H-4b), 1.63 (m, 1H, H-2), 1.87 (m, 1H, H-6b), 2.20 (dt, $J = 0.6$, 0.6, 1.5, 3H, H-18), 2.41 (dd, $J = 6.2$, 13.7, 1H, H-7a), 2.53 (dd, $J = 6.9$, 13.5, 1H, H-7b), 3.65 (dt, $J = 2.3$, 2.3, 4.5, 1H, H-1), 3.84 (ddd, $J = 2.3$, 4.6, 10.0, 1H, H-5'), 4.13 (dd, $J = 2.3$, 12.1, 1H, H-6'a), 4.18 (q, $J = 7.1$, 2H, H-16), 4.26 (dd, $J = 4.6$, 12.1, 1H, H-6'b), 4.48 (dq, $J = 0.5$, 0.5, 1.5, 2H, H-12), 4.55 (d, $J = 7.9$, 1H, H-1'), 5.11 (dd, $J = 7.9$, 9.4, 1H, H-2'), 5.15 (t, $J = 9.8$, 1H, H-4'), 5.22 (t, $J = 9.5$, 1H, H-3'), 6.07 (m, $J = 1.6$, 1H, H-14), 6.83 (m, 2H, H-10), 7.05 (m, 2H, H-9); signals ($\text{CH}_3\text{CO-}$): 2.01 (s, 3H), 2.05 (s, 3H), 2.07 (s, 3H), 2.07 (s, 3H); **7b**: 1.16–1.46 (m, 4H, H-3, H-5), 1.21–1.25 (m, 1H, H-4a), 1.29 (t, $J = 7.1$, 3H, H-17), 1.29–1.36 (m, 1H, H-6a), 1.62–1.65 (m, 1H, H-4b), 1.63 (m, 1H, H-2), 1.87 (m, 1H, H-6b), 2.19 (dt, $J = 0.6$, 0.6, 1.5, 3H, H-18), 2.39 (dd, $J = 7.1$, 13.5, 1H, H-7a), 2.71 (dd, $J = 7.8$, 13.7, 1H, H-7b), 3.65 (ddd, $J = 2.6$, 5.7, 10.2, 1H, H-5'), 3.80 (dt, $J = 2.3$, 2.3, 4.3, 1H, H-1), 4.10 (dd, $J = 2.6$, 12.0, 1H, H-6'a), 4.17 (q, $J = 7.1$, 2H, H-16), 4.20 (dd, $J = 5.7$, 12.0, 1H, H-6'b), 4.45 (dq, $J = 0.5$, 0.5, 1.5, 2H, H-12), 4.54 (d, $J = 7.9$, 1H, H-1'), 5.06 (dd, $J = 9.4$, 10.2, 1H, H-4'), 5.10 (dd, $J = 7.9$, 9.4, 1H, H-2'), 5.23 (t, $J = 9.5$, 1H, H-3'), 6.05 (m, $J = 1.5$, 1H, H-14), 6.77 (m, 2H, H-10), 7.12 (m, 2H, H-9); signals ($\text{CH}_3\text{CO-}$): 2.02 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H), 2.06 (s, 3H). IR (CCl_4): 3030 (w), 1761 (s), 1753 (s), 1720 (m), 1665 (w), 1612 (w), 1511 (m), 1327 (w), 1247 (s), 1224 (s), 1149 (s), 1097 (s), 1040 (s), 897 (w), 849 (w). MS: $m/z = 663$ (2; $[\text{M}+\text{H}]^+$), 408 (1), 331 (49), 233 (19), 188 (10), 169 (100), 139 (13), 109 (77). For $\text{C}_{34}\text{H}_{46}\text{O}_{13}$ (662.74) calculated C, 61.62; H, 7.00. Found: C, 61.60; H, 6.89.

Compound **8a/8b**: $^1\text{H NMR}$ (CDCl_3): **8a**: 0.87 (m, 1H, H-3a), 1.07 (m, 1H, H-5a), 1.18 (m, 1H, H-6a), 1.20 (m, 1H, H-4a), 1.29 (t, $J = 7.1$, 3H, H-17), 1.53 (m,

1H, H-5b), 1.55 (m, 1H, H-2), 1.62 (m, 1H, H-3b), 1.72 (m, 1H, H-4b), 2.00 (m, 1H, H-6b), 2.00–2.23 (m, 1H, H-7a), 2.19 (dt, $J = 0.6, 0.6, 1.5$, 3H, H-18), 3.07 (dd, $J = 3.1, 13.5$, 1H, H-7b), 3.20 (dt, $J = 4.1, 9.5, 9.5$, 1H, H-1), 3.71 (ddd, $J = 2.6, 5.3, 10.0$, 1H, H-5'), 4.13 (dd, $J = 2.6, 12.1$, 1H, H-6'a), 4.18 (q, $J = 7.1, 2H, H-16$), 4.29 (dd, $J = 4.7, 12.1$, 1H, H-6'b), 4.47 (bd, $J = 1.5, 1H, H-14$), 4.63 (d, $J = 8.0, 1H, H-1'$), 5.07 (dd, $J = 8.0, 9.5, 1H, H-2'$), 5.11 (t, $J = 9.8, 1H, H-4'$), 5.22 (t, $J = 9.5, 1H, H-3'$), 6.06 (m, $J = 1.5, 2H, H-12$), 6.80 (m, 2H, H-10), 7.01 (m, 2H, H-9); signals (CH_3CO-): 2.01 (s, 3H), 2.03 (s, 3H), 2.09 (s, 3H), 2.11 (s, 3H); **8b**: 0.87 (m, 1H, H-3a), 1.07 (m, 1H, H-5a), 1.18 (m, 1H, H-6a), 1.20 (m, 1H, H-4a), 1.29 (t, $J = 7.1, 3H, H-17$), 1.53 (m, 1H, H-5b), 1.55 (m, 1H, H-2), 1.62 (m, 1H, H-3b), 1.72 (m, 1H, H-4b), 2.00 (m, 1H, H-6b), 2.00–2.23 (m, 1H, H-7a), 2.19 (dt, $J = 0.6, 0.6, 1.5, 3H, H-18$), 3.13 (dd, $J = 3.7, 13.7, 1H, H-7b$), 3.32 (dt, $J = 4.0, 9.5, 9.5, 1H, H-1$), 3.68 (ddd, $J = 2.8, 4.7, 10.0, 1H, H-5'$), 4.12 (dd, $J = 2.8, 12.5, 1H, H-6'a$), 4.18 (q, $J = 7.1, 2H, H-16$), 4.26 (dd, $J = 5.3, 12.5, 1H, H-6'b$), 4.47 (m, 1H, H-14), 4.62 (d, $J = 8.0, 1H, H-1'$), 5.01 (dd, $J = 8.0, 9.5, 1H, H-2'$), 5.09 (t, $J = 9.8, 1H, H-4'$), 5.25 (t, $J = 9.5, 1H, H-3'$), 6.06 (m, $J = 1.5, 2H, H-12$), 6.80 (m, 2H, H-10), 7.08 (m, 2H, H-9); signals (CH_3CO-): 2.04 (s, 3H), 2.07 (s, 3H), 2.11 (s, 3H), 2.16 (s, 3H). IR (CCl_4): 3031 (w), 1762 (s), 1753 (s), 1720 (m), 1665 (w), 1612 (w), 1511 (m), 1327 (w), 1248 (s), 1224 (s), 1149 (m), 1099 (s), 1040 (s), 907 (w), 880 (w). MS: $m/z = 663$ (1; $[M+H]^+$), 408 (1), 353 (2), 331 (38), 271 (6), 233 (8), 169 (100), 139 (11), 109 (75). For $C_{34}H_{46}O_{13}$ (662.74) calculated C, 61.62; H, 7.00. Found: C, 61.58; H 7.01.

Compound **9a/9b**: 1H NMR ($CDCl_3$): **9a**: 0.90 (m, 1H, H-3a), 1.17 (m, 1H, H-5a), 1.20 (m, 1H, H-4a), 1.29 (t, $J = 7.1, 3H, H-17$), 1.36 (m, 1H, H-6a), 1.50 (m, 1H, H-5b), 1.62 (m, 1H, H-3b), 1.63 (m, 1H, H-2), 1.65 (m, 1H, H-4b), 1.83 (m, 1H, H-6b), 2.00 (dt, $J = 0.7, 0.7, 1.5, 3H, H-18$), 2.39 (dd, $J = 8.0, 13.6, 1H, H-7a$), 2.53 (dd, $J = 6.6, 13.6, 1H, H-7b$), 3.66 (dt, $J = 2.4, 2.4, 4.8, 1H, H-1$), 3.85 (dt, $J = 1.2, 6.6, 6.6, 1H, H-5'$), 4.08 (dd, $J = 6.4, 11.3, 1H, H-6'a$), 4.16 (dd, $J = 6.7, 11.3, 1H, H-6'b$), 4.17 (q, $J = 7.1, 2H, H-16$), 4.51 (d, $J = 8.0, 1H, H-1'$), 5.03 (dd, $J = 3.5, 10.5, 1H, H-3'$), 5.16 (dq, $J = 0.7, 0.7, 0.7, 1.5, 2H, H-12$), 5.26 (dd, $J = 7.9, 10.5, 1H, H-2'$), 5.39 (dd, $J = 1.2, 3.5, 1H, H-4'$), 5.80 (m, $J = 1.5, 1H, H-14$), 6.86 (m, 2H, H-10), 7.05 (m, 2H, H-9); signals (CH_3CO-): 2.03 (s, 3H), 2.05 (s, 3H), 2.06 (s, 3H), 2.08 (s, 3H); **9b**: 0.90 (m, 1H, H-3a), 1.17 (m, 1H, H-5a), 1.20 (m, 1H, H-4a), 1.29 (t, $J = 7.1, 3H, H-17$), 1.36 (m, 1H, H-6a), 1.50 (m, 1H, H-5b), 1.62 (m, 1H, H-3b), 1.63 (m, 1H, H-2), 1.65 (m, 1H, H-4b), 1.83 (m, 1H, H-6b), 2.02 (dt, $J = 0.7, 0.7, 1.5, 3H, H-18$), 2.43 (dd, $J = 7.2, 13.8, 1H, H-7a$), 2.73 (dd, $J = 7.1, 13.8, 1H, H-7b$), 3.81 (dt, $J = 2.4, 2.4, 4.8, 1H, H-1$), 3.87 (dt, $J = 1.3, 6.5, 6.5, 1H, H-5'$), 4.16 (d, $J = 6.5, 2H, H-6'$), 4.17 (q, $J = 7.1, 2H, H-16$), 4.50 (d, $J = 7.9, 1H, H-1'$), 5.04 (dd, $J = 3.5, 10.5, 1H, H-3'$), 5.17 (dq, $J = 0.7, 0.7, 0.7, 1.5, 2H, H-12$), 5.30 (dd, $J = 8.0, 10.5, 1H, H-2'$), 5.40 (dd, $J = 1.3, 3.5, 1H, H-4'$), 5.81 (m, $J = 1.5, 1H, H-14$), 6.82 (m, 2H, H-10), 7.11 (m, 2H, H-9); signals

(CH_3CO-): 2.05 (s, 3H), 2.10 (s, 3H), 2.12 (s, 3H), 2.14 (s, 3H). IR (CCl_4): 2982 (w), 1716 (m), 1650 (w), 1612 (w), 1511 (m), 1369 (s), 1340 (w), 1245 (s), 1050 (s), 1221 (s), 1152 (s), 1099 (m), 1080 (s). MS: $m/z = 685$ (1; $[M+Na]^+$), 662 (1; $[M]^+$), 331 (16), 269 (6), 188 (6), 169 (29), 127 (100), 99 (89). For $C_{34}H_{46}O_{13}$ (662.74) calculated C, 61.62; H, 7.00. Found: C, 61.70; H 6.92.

Compound **10a/10b**: 1H NMR ($CDCl_3$): **10a**: 0.88 (m, 1H, H-3a), 1.05 (m, 1H, H-5a), 1.18 (m, 1H, H-6a), 1.20 (m, 1H, H-4a), 1.29 (t, $J = 7.1, 3H, H-17$), 1.54 (m, 1H, H-5b), 1.57 (m, 1H, H-2), 1.63 (m, 1H, H-3b), 1.71 (m, 1H, H-4b), 1.95 (m, 1H, H-6b), 2.00–2.18 (m, 1H, H-7a), 2.01 (dt, $J = 0.6, 0.6, 1.5, 3H, H-18$), 3.08 (dd, $J = 3.2, 13.2, 1H, H-7b$), 3.22 (dt, $J = 4.3, 9.6, 9.6, 1H, H-1$), 3.92 (dt, $J = 1.2, 5.9, 6.5, 1H, H-5'$), 4.10 (dd, $J = 5.9, 11.2, 1H, H-6'a$), 4.17 (q, $J = 7.1, 2H, H-16$), 4.23 (dd, $J = 6.5, 11.2, 1H, H-6'b$), 4.60 (d, $J = 7.9, 1H, H-1'$), 5.04 (dd, $J = 3.4, 10.5, 1H, H-3'$), 5.17 (bd, $J = 1.5, 2H, H-12$), 5.31 (dd, $J = 7.9, 10.5, 1H, H-2'$), 5.39 (dd, $J = 1.2, 3.4, 1H, H-4'$), 5.82 (m, $J = 1.5, 1H, H-14$), 6.84 (m, 2H, H-10), 7.05 (m, 2H, H-9); signals (CH_3CO-): 1.99 (s, 3H), 2.04 (s, 3H), 2.06 (s, 3H), 2.09 (s, 3H); **10b**: 0.88 (m, 1H, H-3a), 1.05 (m, 1H, H-5a), 1.18 (m, 1H, H-6a), 1.20 (m, 1H, H-4a), 1.29 (t, $J = 7.1, 3H, H-17$), 1.54 (m, 1H, H-5b), 1.57 (m, 1H, H-2), 1.63 (m, 1H, H-3b), 1.71 (m, 1H, H-4b), 1.95 (m, 1H, H-6b), 2.00–2.18 (m, 1H, H-7a), 2.02 (dt, $J = 0.6, 0.6, 1.5, 3H, H-18$), 3.20 (dd, $J = 3.6, 13.5, 1H, H-7b$), 3.32 (dt, $J = 4.2, 9.5, 9.5, 1H, H-1$), 3.89 (dt, $J = 1.2, 6.4, 6.4, 1H, H-5'$), 4.11 (dd, $J = 6.2, 11.1, 1H, H-6'a$), 4.17 (q, $J = 7.1, 2H, H-16$), 4.19 (dd, $J = 6.5, 11.1, 1H, H-6'b$), 4.55 (d, $J = 7.9, 1H, H-1'$), 5.04 (dd, $J = 3.4, 10.5, 1H, H-3'$), 5.17 (bd, $J = 1.5, 2H, H-12$), 5.20 (dd, $J = 7.9, 10.5, 1H, H-2'$), 5.39 (dd, $J = 1.2, 3.4, 1H, H-4'$), 5.81 (m, $J = 1.5, 1H, H-14$), 6.83 (m, 2H, H-10), 7.06 (m, 2H, H-9); signals (CH_3CO-): 2.03 (s, 3H), 2.05 (s, 3H), 2.12 (s, 3H), 2.14 (s, 3H). IR (CCl_4): 2982 (w), 1757 (s), 1716 (m), 1649 (w), 1612 (w), 1511 (m), 1370 (s), 1340 (w), 1247 (s), 1220 (s), 1172 (s), 1098 (m), 1051 (s), 911 (w), 879 (w), 602 (w). MS: $m/z = 685$ (2; $[M+Na]^+$), 662 (1; $[M]^+$), 331 (18), 269 (6), 233 (3), 188 (6), 169 (18), 127 (100), 99 (81). For $C_{34}H_{46}O_{13}$ (662.74) calculated C, 61.62; H, 7.00. Found: C, 61.43; H, 7.05.

Compound **11a/11b**: 1H NMR ($CDCl_3$): **11a**: 0.90 (m, 1H, H-3a), 1.18 (m, 1H, H-5a), 1.20 (m, 1H, H-4a), 1.29 (t, $J = 7.1, 3H, H-17$), 1.37 (m, 1H, H-6a), 1.44 (m, 1H, H-5b), 1.61 (m, 1H, H-3b), 1.63 (m, 1H, H-2), 1.66 (m, 1H, H-4b), 1.83 (m, 1H, H-6b), 2.20 (bd, $J = 1.5, 3H, H-18$), 2.40 (dd, $J = 8.0, 13.7, 1H, H-7a$), 2.54 (dd, $J = 6.7, 13.7, 1H, H-7b$), 3.66 (dt, $J = 2.4, 2.4, 4.8, 1H, H-1$), 3.85 (dt, $J = 1.2, 6.7, 6.7, 1H, H-5'$), 4.08 (dd, $J = 6.8, 11.2, 1H, H-6'a$), 4.16 (dd, $J = 6.6, 11.2, 1H, H-6'b$), 4.17 (q, $J = 7.1, 2H, H-16$), 4.48 (dq, $J = 0.6, 0.6, 0.6, 1.5, 2H, H-12$), 4.51 (d, $J = 8.0, 1H, H-1'$), 5.04 (dd, $J = 3.4, 10.5, 1H, H-3'$), 5.26 (dd, $J = 7.9, 10.5, 1H, H-2'$), 5.38 (dd, $J = 1.2, 3.4, 1H, H-4'$), 6.06 (m, $J = 1.5, 1H, H-14$), 6.83 (m,

2H, H-10), 7.06 (m, 2H, H-9); signals (CH_3CO -): 2.05 (s, 3H), 2.06 (s, 3H), 2.09 (s, 3H), 2.12 (s, 3H); **11b**: 0.90 (m, 1H, H-3a), 1.18 (m, 1H, H-5a), 1.20 (m, 1H, H-4a), 1.29 (t, $J = 7.1$, 3H, H-17), 1.37 (m, 1H, H-6a), 1.44 (m, 1H, H-5b), 1.61 (m, 1H, H-3b), 1.63 (m, 1H, H-2), 1.66 (m, 1H, H-4b), 1.83 (m, 1H, H-6b), 2.20 (bd, $J = 1.5$, 3H, H-18), 2.44 (dd, $J = 7.0$, 13.8, 1H, H-7a), 2.74 (dd, $J = 7.4$, 13.8, 1H, H-7b), 3.81 (dt, $J = 2.3$, 2.3, 4.6, 1H, H-1), 3.87 (dt, $J = 1.3$, 6.7, 6.7, 1H, H-5'), 4.17 (dd, $J = 6.8$, 11.0, 1H, H-6'a), 4.17 (q, $J = 7.1$, 2H, H-16), 4.19 (dd, $J = 6.6$, 11.0, 1H, H-6'b), 4.47 (dq, $J = 0.6$, 0.6, 0.6, 1.5, 2H, H-12), 4.50 (d, $J = 7.9$, 1H, H-1'), 5.05 (dd, $J = 3.4$, 10.5, 1H, H-3'), 5.30 (dd, $J = 8.0$, 10.5, 1H, H-2'), 5.40 (dd, $J = 1.3$, 3.4, 1H, H-4'), 6.06 (m, $J = 1.5$, 1H, H-14), 6.80 (m, 2H, H-10), 7.12 (m, 2H, H-9); signals (CH_3CO -): 2.08 (s, 3H), 2.14 (s, 3H), 2.18 (s, 3H), 2.20 (s, 3H). IR (CCl_4): 1758 (s), 1720 (m), 1665 (w), 1612 (w), 1511 (m), 1369 (s), 1328 (w), 1250 (s), 1046 (s), 1222 (s), 1172 (s), 1149 (s), 1098 (m), 989 (w), 849 (w). MS: $m/z = 685$ (3; $[\text{M}+\text{Na}]^+$), 662 (2; $[\text{M}]^+$), 331 (49), 269 (6), 233 (46), 188 (16), 169 (51), 127 (44), 99 (100). For $\text{C}_{34}\text{H}_{46}\text{O}_{13}$ (662.74) calculated C, 61.62; H, 7.00. Found: C, 62.01; H, 6.73.

Compound **12a/12b**: ^1H NMR (CDCl_3): **12a**: 0.87 (m, 1H, H-3a), 1.05 (m, 1H, H-5a), 1.18 (m, 1H, H-6a), 1.20 (m, 1H, H-4a), 1.29 (t, $J = 7.1$, 3H, H-17), 1.55 (m, 1H, H-5b), 1.57 (m, 1H, H-2), 1.63 (m, 1H, H-3b), 1.72 (m, 1H, H-4b), 1.93 (m, 1H, H-6b), 2.00–2.17 (m, 1H, H-7a), 2.20 (bt, $J = 1.5$, 3H, H-18), 3.08 (dd, $J = 3.2$, 13.5, 1H, H-7b), 3.22 (dt, $J = 4.3$, 9.6, 9.6, 1H, H-1), 3.92 (ddd, $J = 1.3$, 5.9, 6.2, 1H, H-5'), 4.10 (dd, $J = 6.2$, 11.3, 1H, H-6'a), 4.17 (q, $J = 7.1$, 2H, H-16), 4.22 (dd, $J = 6.2$, 11.3, 1H, H-6'b), 4.48 (dq, $J = 0.6$, 0.6, 0.6, 1.5, 2H, H-12), 4.60 (d, $J = 8.0$, 1H, H-1'), 5.04 (dd, $J = 3.1$, 10.5, 1H, H-3'), 5.31 (dd, $J = 8.0$, 10.5, 1H, H-2'), 5.39 (dd, $J = 1.4$, 3.1, 1H, H-4'), 6.07 (m, $J = 1.5$, 1H, H-14), 6.81 (m, 2H, H-10), 7.02 (m, 2H, H-9); signals (CH_3CO -): 1.96 (s, 3H), 1.98 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H); **12b**: 0.87 (m, 1H, H-3a), 1.05 (m, 1H, H-5a), 1.18 (m, 1H, H-6a), 1.20 (m, 1H, H-4a), 1.29 (t, $J = 7.1$, 3H, H-17), 1.55 (m, 1H, H-5b), 1.57 (m, 1H, H-2), 1.63 (m, 1H, H-3b), 1.72 (m, 1H, H-4b), 1.93 (m, 1H, H-6b), 2.00–2.17 (m, 1H, H-7a), 2.20 (bt, $J = 1.5$, 3H, H-18), 3.20 (dd, $J = 3.6$, 13.2, 1H, H-7b), 3.32 (dt, $J = 4.2$, 9.7, 9.7, 1H, H-1), 3.88 (dt, $J = 1.3$, 6.2, 6.2, 1H, H-5'), 4.11 (dd, $J = 5.9$, 11.1, 1H, H-6'a), 4.17 (q, $J = 7.1$, 2H, H-16), 4.19 (dd, $J = 6.2$, 11.1, 1H, H-6'b), 4.47 (dq, $J = 0.6$, 0.6, 0.6, 1.5, 2H, H-12), 4.55 (d, $J = 7.9$, 1H, H-1'), 5.04 (dd, $J = 3.1$, 10.5, 1H, H-3'), 5.20 (dd, $J = 7.9$, 10.5, 1H, H-2'), 5.39 (dd, $J = 1.4$, 3.1, 1H, H-4'), 6.06 (m, $J = 1.5$, 1H, H-14), 6.80 (m, 2H, H-10), 7.09 (m, 2H, H-9); signals (CH_3CO -): 1.99 (s, 3H), 2.00 (s, 3H), 2.04 (s, 3H), 2.06 (s, 3H). IR (CCl_4): 1757 (s), 1721 (m), 1665 (w), 1612 (w), 1511 (m), 1369 (s), 1328 (w), 1249 (s), 1048 (s), 1222 (s), 1150 (s), 1098 (m), 912 (w), 879 (w), 602 (w). MS: $m/z = 685$ (1; $[\text{M}+\text{Na}]^+$), 662 (1; $[\text{M}]^+$), 331 (70), 269 (8), 233 (51), 188 (24), 169 (81), 127 (63), 99 (100). For $\text{C}_{34}\text{H}_{46}\text{O}_{13}$ (662.74) calculated C, 61.62; H, 7.00. Found: C, 60.99; H 6.87.

4.3. Ethyl 4-{4'-[2''-(β -D-glucopyranosyloxy)cyclohexyl]methylphenoxy}-3-methyl-but-2-enoate (**13a/13b**) and ethyl 4-{4'-[2''-(β -D-galactopyranosyloxy)cyclohexyl-methyl]phenoxy}-3-methyl-but-2-enoate (**17a/17b**–**20a/20b**)

Zinc acetate dihydrate (62 mg; 0.282 mmol) was added to a solution of **5a/5a**–**12a/12b** (186 mg; 0.282 mmol) in absolute ethanol (15 mL), and the reaction mixture was heated at the solvent boiling point for 32 h. When completed, the solvent was evaporated under reduced pressure and the residue was applied on the top of a column for chromatographic purification, affording the products in the respective yields: **13a/13b**: 83%; **14a/14b**: 71%; **15a/15b**: 67%; **16a/16b**: 62%; **17a/17b**: 61%; **18a/18b**: 74%; **19a/19b**: 93%; **20a/20b**: 64%.

Compound **13a/13b**: ^1H NMR (CD_3OD): **13a**: 1.28 (t, $J = 7.1$, 3H, H-17), 1.29 (m, 1H, H-4a), 1.33 (m, 1H, H-3a), 1.37 (m, 1H, H-5a), 1.39 (m, 1H, H-6a), 1.52 (m, 1H, H-3b), 1.66 (m, 1H, H-4b), 1.74 (m, 1H, H-5b), 1.75 (m, 1H, H-2), 2.00 (dt, $J = 0.8$, 0.8, 1.5, 3H, H-18), 2.03 (m, 1H, H-6b), 2.52 (dd, $J = 8.4$, 13.6, 1H, H-7a), 2.85 (dd, $J = 6.6$, 13.6, 1H, H-7b), 3.20 (ddd, $J = 2.4$, 5.7, 9.7, 1H, H-5'), 3.27 (dd, $J = 7.9$, 9.2, 1H, H-2'), 3.32 (t, $J = 9.5$, 1H, H-4'), 3.37 (t, $J = 9.4$, 1H, H-3'), 3.65 (dd, $J = 5.7$, 11.8, 1H, H-6'a), 3.73 (dt, $J = 2.4$, 2.4, 4.8, 1H, H-1), 3.82 (dd, $J = 2.4$, 11.8, 1H, H-6'b), 4.16 (q, $J = 7.1$, 2H, H-16), 4.32 (d, $J = 7.8$, 1H, H-1'), 5.14 (dq, $J = 0.8$, 0.8, 0.8, 1.5, 2H, H-12), 5.85 (m, $J = 1.5$, 1H, H-14), 6.81 (m, 2H, H-10), 7.15 (m, 2H, H-9); **13b**: 1.28 (t, $J = 7.1$, 3H, H-17), 1.29 (m, 1H, H-4a), 1.32 (m, 1H, H-6a), 1.33 (m, 1H, H-3a), 1.33 (m, 1H, H-5a), 1.52 (m, 1H, H-3b), 1.66 (m, 1H, H-4b), 1.67 (m, 1H, H-2), 1.77 (m, 1H, H-5b), 1.96 (m, 1H, H-6b), 2.00 (dt, $J = 0.8$, 0.8, 1.5, 3H, H-18), 2.42 (dd, $J = 7.9$, 13.7, 1H, H-7a), 2.81 (dd, $J = 6.5$, 13.7, 1H, H-7b), 3.25 (ddd, $J = 2.4$, 5.6, 9.6, 1H, H-5'), 3.25 (dd, $J = 7.8$, 9.3, 1H, H-2'), 3.27 (t, $J = 9.7$, 1H, H-4'), 3.35 (dd, $J = 9.3$, 9.7, 1H, H-3'), 3.72 (dd, $J = 5.6$, 11.6, 1H, H-6'a), 3.89 (dd, $J = 2.4$, 11.6, 1H, H-6'b), 3.92 (dt, $J = 2.5$, 2.5, 4.6, 1H, H-1), 4.16 (q, $J = 7.1$, 2H, H-16), 4.34 (d, $J = 7.9$, 1H, H-1'), 5.14 (dq, $J = 0.8$, 0.8, 0.8, 1.5, 2H, H-12), 5.85 (m, $J = 1.5$, 1H, H-14), 6.81 (m, 2H, H-10), 7.15 (m, 2H, H-9). **13a/13b**: IR (KBr): 3607 (w), 3534 (m), 1712 (s), 1664 (m), 1511 (s), 1329 (m), 1232 (s), 1177 (m), 1152 (s), 1093 (s), 1074 (s), 1030 (s), 1014 (s), 894 (w), 843 (w). MS: $m/z = 517$ (14; $[\text{M}+\text{Na}]^+$), 494 (4; $[\text{M}]^+$), 391 (1), 333 (5), 315 (3), 233 (1), 149 (19), 127 (100), 105 (5), 99 (97), 79 (22), 57 (27). For $\text{C}_{26}\text{H}_{38}\text{O}_9$ (494.59) calculated C, 63.14; H, 7.74. Found: C, 63.20; H, 7.69. **13a/13b**: $[\alpha]_{\text{D}}^{20} -13.2$ (c 0.25, CH_3OH). **13a**: $[\alpha]_{\text{D}}^{20} +14.0$ (c 0.19, CH_3OH). **13b**: $[\alpha]_{\text{D}}^{20} -36.2$ (c 0.17, CH_3OH).

Compound **14a/14b**: ^1H NMR (CD_3OD): **14a**: 0.91 (m, 1H, H-3a), 1.07 (m, 1H, H-5a), 1.23 (m, 1H, H-6a), 1.25 (m, 1H, H-4a), 1.28 (t, $J = 7.1$, 3H, H-17), 1.60 (m, 1H, H-5b), 1.61 (m, 1H, H-2), 1.63 (m, 1H, H-3b), 1.73 (m, 1H, H-4b), 2.01 (dt, $J = 0.7$, 0.7, 1.4, 3H, H-18), 2.13 (m, 1H, H-6b), 2.16 (dd, $J = 9.9$, 13.4, 1H, H-7a), 3.23–3.40 (m, 5H, H-1, H-7b, H-3', H-4', H-5'), 3.24 (dd, $J = 7.9$, 9.0, 1H, H-2'), 3.68 (dd, $J = 5.3$,

11.8, 1H, H-6'a), 3.85 (dd, $J = 2.3$, 11.8, 1H, H-6'b), 4.17 (q, $J = 7.1$, 2H, H-16), 4.40 (d, $J = 7.9$, 1H, H-1'), 5.14 (m, 2H, H-12), 5.84 (m, 1H, H-14), 6.81 (m, 2H, H-10), 7.10 (m, 2H, H-9); **14b**: 0.91 (m, 1H, H-3a), 1.07 (m, 1H, H-5a), 1.23 (m, 1H, H-6a), 1.25 (m, 1H, H-4a), 1.28 (t, $J = 7.1$, 3H, H-17), 1.60 (m, 1H, H-5b), 1.61 (m, 1H, H-2), 1.63 (m, 1H, H-3b), 1.73 (m, 1H, H-4b), 2.01 (dt, $J = 0.7$, 0.7, 1.4, 3H, H-18), 2.13 (m, 1H, H-6b), 2.23 (dd, $J = 9.4$, 13.8, 1H, H-7a), 3.23–3.40 (m, 4H, H-7b, H-3', H-4', H-5'), 3.22 (dd, $J = 7.9$, 9.0, 1H, H-2'), 3.49 (m, w = 12.0, 1H, H-1), 3.70 (dd, $J = 5.6$, 11.8, 1H, H-6'a), 3.89 (dd, $J = 2.3$, 11.8, 1H, H-6'b), 4.17 (q, $J = 7.1$, 2H, H-16), 4.41 (d, $J = 7.9$, 1H, H-1'), 5.14 (m, 2H, H-12), 5.84 (m, 1H, H-14), 6.82 (m, 2H, H-10), 7.09 (m, 2H, H-9). **14a/14b**: IR (KBr): 3597 (w), 3418 (m), 1706 (s), 1647 (m), 1612 (w), 1511 (s), 1341 (m), 1230 (s), 1177 (m), 1154 (s), 1095 (m), 1074 (s), 1038 (s), 1020 (s), 912 (w), 879 (w). MS: $m/z = 517$ (12; $[M+Na]^+$), 494 (3; $[M]^+$), 391 (9), 333 (2), 315 (1), 269 (2), 233 (2), 219 (1), 167 (13), 149 (86), 127 (51), 105 (10), 99 (44), 79 (40), 57 (100). For $C_{26}H_{38}O_9$ (494.59) calculated C, 63.14; H, 7.74. Found: C, 63.52; H, 7.58. **14a/14b**: $[\alpha]_D^{20} +12.3$ (c 0.21, CH_3OH). **14a**: $[\alpha]_D^{20} +40.0$ (c 0.16, CH_3OH). **14b**: $[\alpha]_D^{20} -63.1$ (c 0.14, CH_3OH).

Compound **15a/15b**: 1H NMR (CD_3OD): **15a**: 1.25 (m, 1H, H-4a), 1.27 (t, $J = 7.1$, 3H, H-17), 1.32 (m, 1H, H-3a), 1.41 (m, 1H, H-5a), 1.45 (m, 1H, H-6a), 1.52 (m, 1H, H-3b), 1.67 (m, 1H, H-4b), 1.72 (m, 1H, H-5b), 1.75 (m, 1H, H-2), 2.05 (m, 1H, H-6b), 2.17 (bd, $J = 1.5$, 3H, H-18), 2.53 (dd, $J = 8.5$, 13.6, 1H, H-7a), 2.85 (dd, $J = 6.5$, 13.6, 1H, H-7b), 3.20 (ddd, $J = 2.4$, 5.6, 9.6, 1H, H-5'), 3.26 (dd, $J = 7.9$, 9.2, 1H, H-2'), 3.33 (t, $J = 9.5$, 1H, H-4'), 3.38 (t, $J = 9.3$, 1H, H-3'), 3.65 (dd, $J = 5.6$, 11.8, 1H, H-6'a), 3.73 (dt, $J = 2.5$, 2.5, 4.6, 1H, H-1), 3.82 (dd, $J = 2.4$, 11.8, 1H, H-6'b), 4.15 (q, $J = 7.1$, 2H, H-16), 4.34 (d, $J = 7.9$, 1H, H-1'), 4.53 (bd, $J = 1.5$, 2H, H-12), 6.01 (m, $J = 1.5$, 1H, H-14), 6.83 (m, 2H, H-10), 7.17 (m, 2H, H-9); **15b**: 1.25 (m, 1H, H-4a), 1.27 (t, $J = 7.1$, 3H, H-17), 1.32 (m, 1H, H-3a), 1.33 (m, 1H, H-6a), 1.37 (m, 1H, H-5a), 1.52 (m, 1H, H-3b), 1.67 (m, 1H, H-4b), 1.69 (m, 1H, H-2), 1.75 (m, 1H, H-5b), 1.97 (m, 1H, H-6b), 2.17 (bd, $J = 1.5$, 3H, H-18), 2.43 (dd, $J = 7.8$, 13.7, 1H, H-7a), 2.82 (dd, $J = 6.7$, 13.7, 1H, H-7b), 3.25 (dd, $J = 7.9$, 9.3, 1H, H-2'), 3.26 (ddd, $J = 2.5$, 5.6, 9.6, 1H, H-5'), 3.27 (t, $J = 9.7$, 1H, H-4'), 3.36 (dd, $J = 9.3$, 9.7, 1H, H-3'), 3.72 (dd, $J = 5.6$, 11.6, 1H, H-6'a), 3.89 (dd, $J = 2.5$, 11.6, 1H, H-6'b), 3.92 (dt, $J = 2.6$, 2.6, 4.6, 1H, H-1), 4.15 (q, $J = 7.1$, 2H, H-16), 4.33 (d, $J = 7.9$, 1H, H-1'), 4.53 (bd, $J = 1.5$, 2H, H-12), 6.01 (m, $J = 1.5$, 1H, H-14), 6.84 (m, 2H, H-10), 7.16 (m, 2H, H-9). **15a/15b**: IR (KBr): 3594 (w), 3417 (m), 1705 (s), 1647 (w), 1611 (w), 1511 (s), 1340 (m), 1231 (s), 1177 (m), 1154 (s), 1093 (m), 1074 (s), 1037 (s), 1018 (s), 894 (w), 846 (w). MS: $m/z = 517$ (7; $[M+Na]^+$), 495 (1; $[M+H]^+$), 391 (2), 191 (6), 149 (29), 127 (6), 105 (8), 79 (22), 57 (100). For $C_{26}H_{38}O_9$ (494.59) calculated C, 63.14; H, 7.74. Found: C, 63.02; H, 7.45. **15a/15b**: $[\alpha]_D^{20} -11.0$ (c 0.27, CH_3OH). **15a**: $[\alpha]_D^{20} +5.7$ (c 0.17, CH_3OH). **15b**: $[\alpha]_D^{20} -27.2$ (c 0.16, CH_3OH).

Compound **16a/16b**: 1H NMR (CD_3OD): **16a**: 0.91 (m, 1H, H-3a), 1.07 (m, 1H, H-5a), 1.16 (m, 1H, H-6a), 1.27 (m, 1H, H-4a), 1.28 (t, $J = 7.1$, 3H, H-17), 1.58 (m, 1H, H-5b), 1.59 (m, 2H, H-2, H-3b), 1.73 (m, 1H, H-4b), 2.14 (m, 1H, H-6b), 2.15 (dd, $J = 10.0$, 13.5, 1H, H-7a), 2.17 (bd, $J = 1.4$, 3H, H-18), 3.20–3.41 (m, 4H, H-7b, H-3', H-4', H-5'), 3.24 (dd, $J = 7.8$, 9.0, 1H, H-2'), 3.24 (dt, $J = 4.2$, 9.8, 9.8, 1H, H-1), 3.68 (dd, $J = 5.2$, 11.8, 1H, H-6'a), 3.85 (dd, $J = 2.2$, 11.8, 1H, H-6'b), 4.15 (q, $J = 7.1$, 2H, H-16), 4.41 (d, $J = 7.8$, 1H, H-1'), 4.48 (bd, $J = 1.4$, 2H, H-12), 6.01 (m, $J = 1.4$, 1H, H-14), 6.83 (m, 2H, H-10), 7.11 (m, 2H, H-9); **16b**: 0.91 (m, 1H, H-3a), 1.07 (m, 1H, H-5a), 1.16 (m, 1H, H-6a), 1.27 (m, 1H, H-4a), 1.28 (t, $J = 7.1$, 3H, H-17), 1.58 (m, 1H, H-5b), 1.59 (m, 2H, H-2, H-3b), 1.73 (m, 1H, H-4b), 2.14 (m, 1H, H-6b), 2.17 (bd, $J = 1.4$, 3H, H-18), 2.24 (dd, $J = 9.3$, 13.6, 1H, H-7a), 3.20–3.41 (m, 3H, H-3', H-4', H-5'), 3.22 (dd, $J = 7.8$, 9.0, 1H, H-2'), 3.40 (dd, $J = 3.7$, 13.6, 1H, H-7b), 3.50 (dt, $J = 4.2$, 10.0, 10.0, 1H, H-1), 3.70 (dd, $J = 5.7$, 11.7, 1H, H-6'a), 3.90 (dd, $J = 2.3$, 11.7, 1H, H-6'b), 4.15 (q, $J = 7.1$, 2H, H-16), 4.40 (d, $J = 7.8$, 1H, H-1'), 4.48 (bd, $J = 1.4$, 2H, H-12), 6.01 (m, $J = 1.4$, 1H, H-14), 6.84 (m, 2H, H-10), 7.10 (m, 2H, H-9). **16a/16b**: IR (KBr): 3593 (w), 3416 (m), 1712 (s), 1664 (m), 1611 (w), 1511 (s), 1328 (m), 1232 (s), 1177 (m), 1152 (s), 1095 (s), 1075 (s), 1040 (s), 1021 (s), 913 (w), 879 (w). MS: $m/z = 517$ (3; $[M+Na]^+$), 495 (1; $[M+H]^+$), 459 (5), 413 (2), 391 (6), 333 (1), 315 (2), 306 (1), 233 (8), 167 (14), 149 (100), 127 (6), 99 (16), 71 (29), 57 (86). For $C_{26}H_{38}O_9$ (494.59) calculated C, 63.14; H, 7.74. Found: C, 63.09; H, 7.55. **16a/16b**: $[\alpha]_D^{20} -17.5$ (c 0.28, CH_3OH). **16a**: $[\alpha]_D^{20} -5.0$ (c 0.18, CH_3OH). **16b**: $[\alpha]_D^{20} -30.5$ (c 0.15, CH_3OH).

Compound **17a/17b**: 1H NMR (CD_3OD): **17a**: 1.28 (t, $J = 7.1$, 3H, H-17), 1.29 (m, 1H, H-4a), 1.34 (m, 1H, H-3a), 1.36 (m, 1H, H-5a), 1.39 (m, 1H, H-6a), 1.52 (m, 1H, H-3b), 1.64 (m, 1H, H-4b), 1.73 (m, 1H, H-5b), 1.75 (m, 1H, H-2), 2.00 (bd, $J = 1.3$, 3H, H-18), 2.03 (m, 1H, H-6b), 2.52 (dd, $J = 8.4$, 13.7, 1H, H-7a), 2.85 (dd, $J = 6.5$, 13.7, 1H, H-7b), 3.44 (dt, $J = 1.1$, 6.2, 6.2, 1H, H-5'), 3.49 (dd, $J = 3.5$, 9.7, 1H, H-3'), 3.60 (dd, $J = 7.8$, 9.7, 1H, H-2'), 3.69 (dd, $J = 6.4$, 11.2, 1H, H-6'a), 3.72 (dd, $J = 6.1$, 11.2, 1H, H-6'b), 3.74 (dt, $J = 2.4$, 2.4, 4.8, 1H, H-1), 3.84 (dd, $J = 1.1$, 3.4, 1H, H-4'), 4.16 (q, $J = 7.1$, 2H, H-16), 4.28 (d, $J = 7.7$, 1H, H-1'), 5.14 (dq, $J = 0.6$, 0.6, 0.6, 1.7, 2H, H-12), 5.85 (m, $J = 1.4$, 1H, H-14), 6.80 (m, 2H, H-10), 7.15 (m, 2H, H-9); **17b**: 1.28 (t, $J = 7.1$, 3H, H-17), 1.29 (m, 1H, H-4a), 1.32 (m, 1H, H-6a), 1.34 (m, 2H, H-3a, H-5a), 1.52 (m, 1H, H-3b), 1.64 (m, 1H, H-4b), 1.69 (m, 1H, H-2), 1.77 (m, 1H, H-5b), 1.96 (m, 1H, H-6b), 2.00 (bd, $J = 1.3$, 3H, H-18), 2.42 (dd, $J = 7.8$, 13.6, 1H, H-7a), 2.81 (dd, $J = 6.6$, 13.6, 1H, H-7b), 3.48 (dt, $J = 1.1$, 6.2, 6.2, 1H, H-5'), 3.48 (dd, $J = 3.4$, 9.7, 1H, H-3'), 3.57 (dd, $J = 7.7$, 9.7, 1H, H-2'), 3.75 (dd, $J = 6.1$, 11.0, 1H, H-6'a), 3.79 (dd, $J = 6.3$, 11.0, 1H, H-6'b), 3.88 (dt, $J = 1.1$, 3.5, 1H, H-4'), 3.91 (dt, $J = 2.5$, 2.5, 4.5, 1H, H-1), 4.16 (q, $J = 7.1$, 2H, H-16), 4.30 (d, $J = 7.8$, 1H, H-1'), 5.14 (dq, $J = 0.6$, 0.6, 0.6, 1.7, 2H, H-12), 5.84 (m, $J = 1.4$, 1H, H-14), 6.79 (m, 2H, H-10), 7.14 (m, 2H, H-9).

17a/17b: IR (KBr): 3585 (w), 3433 (m), 1705 (s), 1648 (w), 1611 (w), 1511 (s), 1340 (m), 1238 (s), 1177 (s), 1154 (s), 1098 (m), 1074 (s), 1062 (s), 1038 (s), 898 (w), 840 (w). MS: $m/z = 495$ (2; $[M+H]^+$), 333 (2), 269 (4), 221 (3), 187 (3), 149 (4), 127 (48), 99 (100). For $C_{26}H_{38}O_9$ (494.59) calculated C, 63.14; H, 7.74. Found: C, 63.23; H, 7.68. **17a/17b:** $[\alpha]_D^{20} - 10.1$ (c 0.25, CH₃OH). **17a:** $[\alpha]_D^{20} + 17.0$ (c 0.15, CH₃OH). **17b:** $[\alpha]_D^{20} - 36.1$ (c 0.17, CH₃OH).

Compound **18a/18b:** ¹H NMR (CD₃OD): **18a:** 0.90 (m, 1H, H-3a), 1.08 (m, 1H, H-5a), 1.21 (m, 1H, H-6a), 1.28 (t, $J = 7.1$, 3H, H-17), 1.25 (m, 1H, H-4a), 1.57 (m, 2H, H-2, H-5b), 1.61 (m, 1H, H-3b), 1.72 (m, 1H, H-4b), 2.00 (dt, $J = 0.7$, 0.7, 1.6, 3H, H-18), 2.14 (m, 1H, H-6b), 2.14 (dd, $J = 9.9$, 13.7, 1H, H-7a), 3.31 (dt, $J = 4.2$, 9.5, 9.5, 1H, H-1), 3.40 (dd, $J = 3.4$, 13.4, 1H, H-7b), 3.47 (dd, $J = 3.4$, 9.8, 1H, H-3'), 3.50 (dt, $J = 1.2$, 6.3, 6.3, 1H, H-5'), 3.57 (dd, $J = 7.7$, 9.8, 1H, H-2'), 3.72 (dd, $J = 6.3$, 11.1, 1H, H-6'a), 3.75 (dd, $J = 6.1$, 11.1, 1H, H-6'b), 3.85 (dd, $J = 1.2$, 3.4, 1H, H-4'), 4.16 (q, $J = 7.1$, 2H, H-16), 4.37 (d, $J = 7.5$, 1H, H-1'), 5.14 (dq, $J = 0.7$, 0.7, 1.6, 2H, H-12), 5.85 (m, $J = 1.6$, 1H, H-14), 6.80 (m, 2H, H-10), 7.09 (m, 2H, H-9); **18b:** 0.90 (m, 1H, H-3a), 1.08 (m, 1H, H-5a), 1.21 (m, 1H, H-6a), 1.28 (t, $J = 7.1$, 3H, H-17), 1.25 (m, 1H, H-4a), 1.57 (m, 2H, H-2, H-5b), 1.61 (m, 1H, H-3b), 1.72 (m, 1H, H-4b), 2.00 (dt, $J = 0.7$, 0.7, 1.6, 3H, H-18), 2.14 (m, 1H, H-6b), 2.21 (dd, $J = 9.4$, 13.4, 1H, H-7a), 3.24 (dd, $J = 3.6$, 13.7, 1H, H-7b), 3.49 (dd, $J = 3.4$, 9.7, 1H, H-3'), 3.49 (dt, $J = 4.3$, 9.6, 9.6, 1H, H-1), 3.50 (dt, $J = 1.2$, 6.2, 6.2, 1H, H-5'), 3.55 (dd, $J = 7.5$, 9.7, 1H, H-2'), 3.76 (d, $J = 6.3$, 2H, H-6'), 3.86 (dd, $J = 1.2$, 3.4, 1H, H-4'), 4.16 (q, $J = 7.1$, 2H, H-16), 4.36 (d, $J = 7.7$, 1H, H-1'), 5.14 (dq, $J = 0.7$, 0.7, 0.7, 1.6, 2H, H-12), 5.85 (m, $J = 1.6$, 1H, H-14), 6.81 (m, 2H, H-10), 7.08 (m, 2H, H-9). **18a/18b:** IR (KBr): 3590 (w), 3425 (m), 1705 (s), 1648 (m), 1611 (w), 1511 (s), 1340 (m), 1229 (s), 1177 (m), 1154 (s), 1073 (s), 1060 (s), 1048 (m), 1038 (s), 910 (w), 879 (w). MS: $m/z = 495$ (1; $[M+H]^+$), 333 (5), 315 (2), 269 (3), 233 (6), 187 (3), 149 (6), 127 (87), 113 (10), 99 (100), 73 (13). For $C_{26}H_{38}O_9$ (494.59) calculated C, 63.14; H, 7.74. Found: C, 63.27; H, 7.52. **18a/18b:** $[\alpha]_D^{20} - 10.4$ (c 0.20, CH₃OH). **18a:** $[\alpha]_D^{20} + 42.0$ (c 0.16, CH₃OH). **18b:** $[\alpha]_D^{20} - 63.0$ (c 0.19, CH₃OH).

Compound **19a/19b:** ¹H NMR (CD₃OD): **19a:** 1.25 (m, 1H, H-4a), 1.27 (t, $J = 7.1$, 3H, H-17), 1.33 (m, 1H, H-3a), 1.36 (m, 1H, H-5a), 1.39 (m, 1H, H-6a), 1.51 (m, 1H, H-3b), 1.65 (m, 1H, H-4b), 1.74 (m, 1H, H-5b), 1.75 (m, 1H, H-2), 2.03 (m, 1H, H-6b), 2.17 (bd, $J = 1.4$, 3H, H-18), 2.53 (dd, $J = 8.4$, 13.6, 1H, H-7a), 2.86 (dd, $J = 6.5$, 13.6, 1H, H-7b), 3.44 (dt, $J = 1.2$, 6.2, 6.2, 1H, H-5'), 3.49 (dd, $J = 3.4$, 9.7, 1H, H-3'), 3.60 (dd, $J = 7.7$, 9.7, 1H, H-2'), 3.69 (dd, $J = 6.3$, 11.2, 1H, H-6'a), 3.72 (dd, $J = 6.1$, 11.2, 1H, H-6'b), 3.74 (dt, $J = 2.4$, 2.4, 4.9, 1H, H-1), 3.84 (dd, $J = 1.2$, 3.4, 1H, H-4'), 4.15 (q, $J = 7.1$, 2H, H-16), 4.28 (d, $J = 7.8$, 1H, H-1'), 4.53 (bd, $J = 1.4$, 2H, H-12), 6.01 (m, $J = 1.4$, 1H, H-14), 6.83 (m, 2H, H-10), 7.16 (m, 2H, H-9); **19b:** 1.25 (m, 1H, H-4a), 1.27 (t, $J = 7.1$, 3H, H-17), 1.28 (m, 1H, H-6a), 1.33 (m, 1H, H-3a),

1.34 (m, 1H, H-5a), 1.51 (m, 1H, H-3b), 1.65 (m, 1H, H-4b), 1.69 (m, 1H, H-2), 1.77 (m, 1H, H-5b), 1.96 (m, 1H, H-6b), 2.17 (bd, $J = 1.4$, 3H, H-18), 2.43 (dd, $J = 7.8$, 13.7, 1H, H-7a), 2.82 (dd, $J = 6.6$, 13.7, 1H, H-7b), 3.48 (dt, $J = 1.2$, 6.2, 6.2, 1H, H-5'), 3.48 (dd, $J = 3.4$, 9.7, 1H, H-3'), 3.58 (dd, $J = 7.8$, 9.7, 1H, H-2'), 3.76 (dd, $J = 6.2$, 11.0, 1H, H-6'a), 3.80 (dd, $J = 6.2$, 11.0, 1H, H-6'b), 3.88 (dt, $J = 1.2$, 3.4, 1H, H-4'), 3.91 (dt, $J = 2.5$, 2.5, 4.8, 1H, H-1), 4.15 (q, $J = 7.1$, 2H, H-16), 4.30 (d, $J = 7.7$, 1H, H-1'), 4.53 (bd, $J = 1.4$, 2H, H-12), 6.01 (m, $J = 1.4$, 1H, H-14), 6.82 (m, 2H, H-10), 7.17 (m, 2H, H-9). **19a/19b:** IR (KBr): 3584 (w), 3433 (m), 1710 (s), 1664 (m), 1611 (w), 1511 (s), 1329 (m), 1231 (s), 1152 (s), 1099 (m), 1075 (s), 1061 (s), 1042 (s), 898 (w), 844 (w). MS: $m/z = 495$ (1; $[M+H]^+$), 333 (3), 315 (8), 233 (22), 187 (5), 149 (14), 127 (29), 99 (100), 73 (21). For $C_{26}H_{38}O_9$ (494.59) calculated C, 63.14; H, 7.74. Found: C, 63.12; H, 7.52. **19a/19b:** $[\alpha]_D^{20} - 9.9$ (c 0.22, CH₃OH). **19a:** $[\alpha]_D^{20} + 7.1$ (c 0.15, CH₃OH). **19b:** $[\alpha]_D^{20} - 26.0$ (c 0.14, CH₃OH).

Compound **20a/20b:** ¹H NMR (CD₃OD): **20a:** 0.92 (m, 1H, H-3a), 1.08 (m, 1H, H-5a), 1.26 (m, 1H, H-4a), 1.27 (t, $J = 7.1$, 3H, H-17), 1.28 (m, 1H, H-6a), 1.56 (m, 1H, H-5b), 1.60 (m, 1H, H-2), 1.62 (m, 1H, H-3b), 1.70 (m, 1H, H-4b), 2.18 (bd, $J = 1.5$, 3H, H-18), 2.22 (m, 1H, H-6b), 2.22 (dd, $J = 9.6$, 13.4, 1H, H-7a), 3.32 (dt, $J = 4.5$, 9.5, 9.5, 1H, H-1), 3.41 (dd, $J = 3.4$, 13.4, 1H, H-7b), 3.47 (dd, $J = 3.4$, 9.7, 1H, H-3'), 3.50 (dt, $J = 1.2$, 6.2, 6.2, 1H, H-5'), 3.57 (dd, $J = 7.6$, 9.7, 1H, H-2'), 3.86 (dd, $J = 1.2$, 3.4, 1H, H-4'), 3.72 (dd, $J = 6.4$, 11.3, 1H, H-6'a), 3.75 (dd, $J = 6.1$, 11.3, 1H, H-6'b), 4.15 (q, $J = 7.1$, 2H, H-16), 4.37 (d, $J = 7.6$, 1H, H-1'), 4.53 (bd, $J = 1.5$, 2H, H-12), 6.03 (m, $J = 1.5$, 1H, H-14), 6.87 (m, 2H, H-10), 7.11 (m, 2H, H-9); **20b:** 0.92 (m, 1H, H-3a), 1.08 (m, 1H, H-5a), 1.26 (m, 1H, H-4a), 1.27 (t, $J = 7.1$, 3H, H-17), 1.36 (m, 1H, H-6a), 1.54 (m, 1H, H-2), 1.56 (m, 1H, H-5b), 1.62 (m, 1H, H-3b), 1.70 (m, 1H, H-4b), 2.14 (m, 1H, H-6b), 2.14 (dd, $J = 10.1$, 13.7, 1H, H-7a), 2.17 (bd, $J = 1.5$, 3H, H-18), 3.24 (dd, $J = 3.6$, 13.7, 1H, H-7b), 3.48 (dt, $J = 4.4$, 9.6, 9.6, 1H, H-1), 3.49 (dd, $J = 3.4$, 9.7, 1H, H-3'), 3.50 (dt, $J = 1.2$, 6.2, 6.2, 1H, H-5'), 3.55 (dd, $J = 7.7$, 9.7, 1H, H-2'), 3.77 (d, $J = 6.2$, 2H, H-6'), 3.85 (dd, $J = 1.2$, 3.4, 1H, H-4'), 4.15 (q, $J = 7.1$, 2H, H-16), 4.36 (d, $J = 7.7$, 1H, H-1'), 4.53 (bd, $J = 1.5$, 2H, H-12), 6.01 (m, $J = 1.5$, 1H, H-14), 6.88 (m, 2H, H-10), 7.10 (m, 2H, H-9). **20a/20b:** IR (KBr): 3591 (w), 3425 (m), 1712 (s), 1664 (w), 1611 (w), 1511 (s), 1329 (m), 1231 (s), 1177 (m), 1153 (s), 1098 (m), 1074 (s), 1040 (s), 1002 (m), 880 (w). MS: $m/z = 495$ (3; $[M+H]^+$), 391 (3), 333 (10), 315 (10), 233 (40), 187 (13), 149 (71), 127 (35), 99 (100), 73 (33). For $C_{26}H_{38}O_9$ (494.59) calculated C, 63.14; H, 7.74. Found: C, 63.07; H, 7.80. **20a/20b:** $[\alpha]_D^{20} - 13.9$ (c 0.24, CH₃OH). **20a/20b:** $[\alpha]_D^{20} - 1.0$ (c 0.18, CH₃OH). **20a/20b:** $[\alpha]_D^{20} - 25.8$ (c 0.14, CH₃OH).

4.4. Methodology of the screening tests on *Pyrrhocoris apterus*

The red firebug (*P. apterus*) is a well-known experimental model,²⁷ kept in breeding chambers on linden seeds

at a constant rearing temperature (27 °C) using a photoperiod set up for the constant long day (18 h light/6 h dark). For the per-oral application, drinking assay¹³ was used. Each compound was diluted into four concentrations (0.01, 0.1, 1 and 10 µg in 22 µL of the tested solution per individual), and offered to the insects during their last larval instar. The dilution rate was based on the knowledge that water consumption for the last larval instar of this species is approximately 22 µL for one individual in the first day after ecdysis.²⁸ Glass vials containing the test solutions were plugged with pieces of cotton and offered to 30 specimens in a Petri dish. In summary, 150 specimens (for the reference experiment and for the experiments with four above-given concentrations of the tested compounds) were used for one tested compound. The results of the biological screening tests are summarized in Table 5.

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