C-Glycoside Synthesis *via* Glycal Alkylation by Olefinic Derivatives[1,2]

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Treatment of peracetylated glycals with olefins in the presence of Lewis acids gave 2,3-unsaturated *C*-glycosides in good to excellent yields. The reaction was completely regioselective and showed a high degree of stereoselectivity leading mostly to the α-isomer. Generally the addition gave the *C*-glycoside with an unsaturated aglycone. However, with methylenecyclobutane and 1,1 disubstituted linear olefins halogeno derivatives were recovered. The reaction was also performed with acetylated 2-hydroxy glycals. In these conditions keto unsaturated α-*C*-glycosides were isolated.

C-Glycosides[3] have attracted considerable attention recently[4–10] due to their biological properties and their potency as building blocks for the preparation of polycyclic, naturally occurring molecules. Most of the 2,3-unsaturated *C*-glycoside syntheses involve the use of Carbon Ferrier[11] reactions in the formation of the C–C bond. Addition of trimethylsiloxy ethers,[12] enol acetates,[13] malonate derivatives,[8e] and allylsilane[14] to glycals have been reported.

In spite of their synthetic versatility the limited accessibility to these reagents has severely restricted the use of these methods for organic synthesis. As part of a programme directed toward the study of 2- and 4-oxo unsaturated *C*-glycosides in order to investigate their chemical and biological properties as well as their use as building blocks for the preparation of naturally occurring biomolecules, we have been interested in developing a mild, stereospecific, and straightforward route to synthesize unsaturated *C*-glycosides with a polyfunctional aglycone. Alkenes which are known to react with electrophilic derivatives in the presence of Lewis acids[15] constituted a source of readily available material. We have reported[1] a new method for synthesizing *C*-glycosides from peracetylated glycals using olefins[16] in the presence of Lewis acids. Herein we report on the full scope of this reaction with some important improvements concerning the stereoselectivity as well as the chemoselectivity of the reaction. In addition we have extended our process to the condensation of olefins with 2-hydroxy glycals and we have prepared 2*H*-pyranones in good yield. This direct access to 2-oxo *C*-glycosides avoids the deprotection of enol esters which requires multistep reactions[17] or processes not always compatible with the stability of the glycosides.[18]

Results and Discussion

Initial investigations were directed toward 1,1-disubstituted olefins (Table 1). Thus treatment of the triacetyl derivative of D-glucal, (**1**),[19] with methylenecyclohexane (**5**) in dichloromethane at room temperature for 3 minutes in the presence of $SnBr_4$ led to exclusive alkylation at C-1′† to afford, after flash chromatography,[20] the *C*-glycoside (**6**) in 94% yield. The structural assignment was based on ^1H NMR data. In particular, observation of three olefinic resonances at δ_H 5.5, 5.76, and 5.93 assigned respectively to 2-H, 3′-H, and 2′-H from the 2D NOESY spectrum indicated the regioselective addition of compound (**5**) at C-1′ with the formation of an olefinic aglycone. The coupled ^{13}C NMR spectrum confirmed the assigned structure, with three olefinic doublets at δ_C 123.38 (C-3′), 124.30 (C-2), and 133.64 (C-2′) and a quaternary signal at δ_C 134.03 (C-1).

To determine the influence of the sugar in this reaction the 6-deoxy glycal (**2**) and 2-hydroxy glycal derivatives (**3**) and (**4**) were examined. Alkylation of diacetyl-L-rhamnal (**2**) with compound (**5**) produced a cyclohexenyl *C*-glycoside but with a lower stereoselectivity affording a mixture of α and β anomers (**7a**) and (**7b**) in a 85:15 ratio with an overall yield of 90%.

Methylenecyclohexane (**5**) reacted at room temperature with peracetylated 2-hydroxyglucal (**3**) to yield the *C*-glycoside (**8**). Analysis by ^1H and ^{13}C NMR spectroscopy indicated that the product obtained arose from the attack of the olefin at C-1, followed by enol ester cleavage and finally enone formation by β-elimination. The conjugated double bond of compound (**8**) was identified by olefinic resonances at δ_H 6.32 (3′-H) and 6.86 (4′-H) and δ_C 127.28 (C-3) and 145.10 (C-4), and the carbonyl signal at δ_C 195.91. Condensation between compound (**5**) and the L-hydroxy glycal derivative (**4**) at 0 °C in the presence of boron trifluoride–diethyl ether led to the cyclohexenyl 2′-oxo *C*-glycoside (**9**).

Alkylation of glycal (**1**) performed with the bulky t-butylmethylenecyclohexane (**10**) exhibited identical selectivity. Reaction performed in the presence of $EtAlCl_2$ produced the *C*-glycoside with an unsaturated aglycone as a 98:2 mixture of α and β anomers[1] (91% overall yield). However, $SnBr_4$ catalysis afforded only the α-*C*-glycoside (**11**) (92%). Condensation between compound (**10**) and diacetyl-L-rhamnal (**2**) gave a mixture of the anomers (**12a**) and (**12b**) (α/β 88:12) in 93% yield.

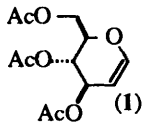
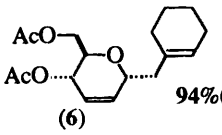
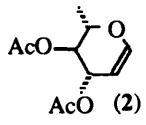
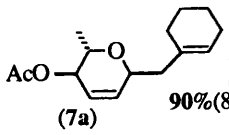
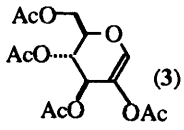
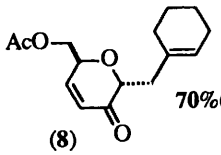
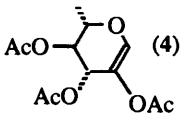
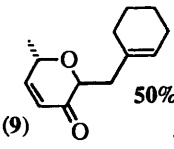
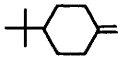
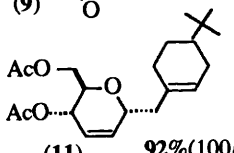
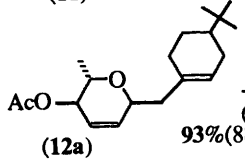
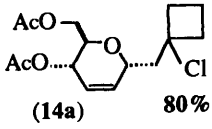
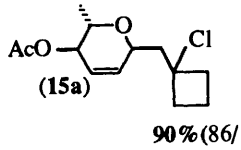
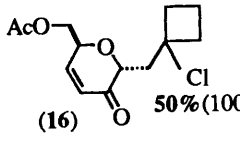
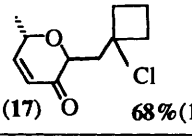
To probe the influence of ring size on the chemoselectivity of the reaction, alkylations with methylenecyclobutane (**13**) were examined. Condensation of compound (**13**) with triacetyl-D-glucal (**1**) in the presence of $EtAlCl_2$ at −20 °C produced a 91:9 mixture of α and β *C*-glycosides (**14a**) and (**14b**) in 80% overall yield. The ^1H NMR spectra closely resembled those of compound (**6**) but revealed only two olefinic resonances: (**14a**) δ_H 5.75 (m), (**14b**) δ_H 5.8 (m). The presence of a chlorocyclobutyl group was indicated by the ^{13}C spectra with a characteristic quaternary signal at δ_C 69.8, and was confirmed by elemental analysis.

Reaction of compound (**13**) with glycals (**2**), (**3**), and (**4**) produced only chlorocyclobutylmethyl *C*-glycosides. 2′-Hydroxy glycals afforded only α-anomers in 50–68% yield. In contrast, treatment of diacetyl-L-rhamnal (**2**) with compound (**13**) in the presence of diethylaluminium chloride afforded a 86:14 ratio of α and β *C*-glycosides (**15a**) and (**15b**) (90% overall yield). This result clearly indicates the loss of stereoselectivity induced by 6-deoxyglycals.

Our success in alkylation with cyclic alkenes prompted further exploration and our attention focused on 1,1-disubstituted polyfunctional olefins. Results of glycal condensation with

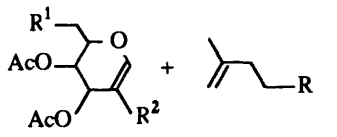
† For consistency, the numbering system used throughout this paper is that of *N*-glycosides (anomeric carbon at the 1′ position).

Table 1. Reaction of 1,1-disubstituted olefins with glycals.

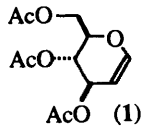
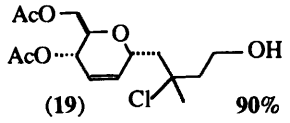
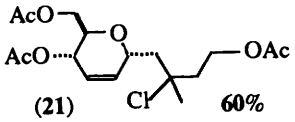
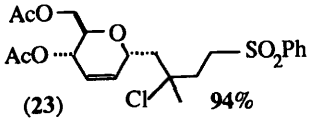
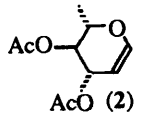
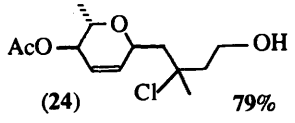
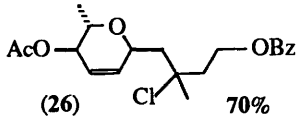
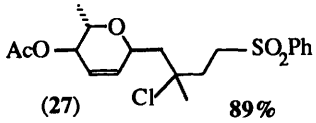
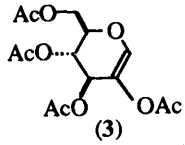
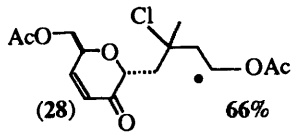
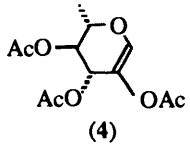
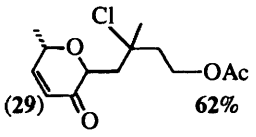
Glycal	Olefin	Lewis acid	Procedure (T/°C, time chromatography)	C-Glycoside [yield/% (α/β)]
 (1)	 (5)	$SnBr_4$	A room temp., 5 min hexane–AcOEt (8:2)	 (6) 94%(100/0)
 (2)	(5)	BF_3·Et_2O	A −25 °C, 10 min hexane–AcOEt (98:2)	 (7a) + (7b) 90%(85/15)
 (3)	(5)	$SnBr_4$	B room temp., 30 min pentane–Et_2O (6:4)	 (8) 70%(100/0)
 (4)	(5)	BF_3·Et_2O	C 0 °C, 45 min hexane–AcOEt (96:4)	 (9) 50%(100/0)
(1)	 (10)	$SnBr_4$	A room temp., 5 min pentane–Et_2O (4:1)	 (11) 92%(100/0)
(2)	(10)	$EtAlCl_2$	A −20 °C, 5 min pentane–Et_2O (19:1)	 (12a) + (12b) 93%(88/12)
(1)	 (13)	$EtAlCl_2$	A −20 °C, 5 min pentane–Et_2O (5:1)	 (14a) + (14b) 80%(91/9)
(2)	(13)	$EtAlCl_2$	A −20 °C, 5 min pentane–Et_2O (5:1)	 (15a) + (15b) 90%(86/14)
(3)	(13)	$EtAlCl_2$	B −20 °C to room temp., 1 h hexane–AcOEt (85:15)	 (16) 50%(100/0)
(4)	(13)	$EtAlCl_2$	B −20 °C to room temp., 1 h hexane–AcOEt (9:5)	 (17) 68%(100/0)

2-methylbut-1-ene derivatives compiled in Table 2 outline the formation of chlorinated C-glycosides and confirmed the high selectivity of the reaction. Variation of the substituent has a marked effect upon condensation. Thus alkylation of glycals (**1**) and (**2**) with the alcohol (**18**) or the sulphone (**22**) produced the corresponding C-glycosides with excellent yields. In contrast, protection of the alcohol with an ester group decreased the reactivity. However, synthesis of polyfunctional 2′-oxo C-glycosides was only possible with the acetate (**20**). With glycal (**2**), improved chemoselectivity and stereocontrol was observed

Table 2. Reaction of 1,1-disubstituted polyfunctional olefins with glycals.



R^1 = H or AcO
R^2 = H or AcO

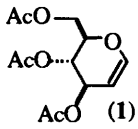
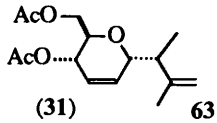
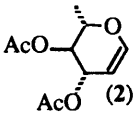
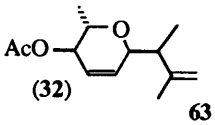
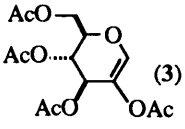
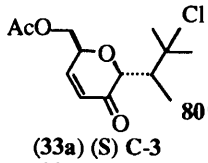
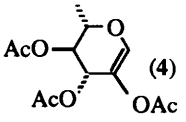
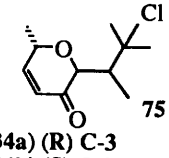
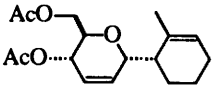
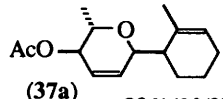
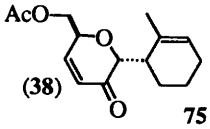
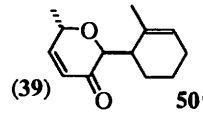
Glycal	Olefin	Lewis acid	Procedure (T/°C, time, chromatography)	C-Glycoside (yield/%)
 (1)	R = OH (**18**)	$SnCl_4$	A 0 °C, 5 min hexane–AcOEt (6:1)	 (**19**) 90%
(1)	R = OAc (**20**)	$SnCl_4$	A 25 °C, 5 min pentane–Et_2O (3:1)	 (**21**) 60%
(1)	R = SO_2Ph (**22**)	$SnCl_4$	A −20 °C, 5 min hexane–AcOEt (3:1)	 (**23**) 94%
 (2)	R = OH (**18**)	$TiCl_4$	A 0 °C, 5 min hexane–AcOEt (6:1)	 (**24**) 79%
(2)	R = OBz (**25**)	$TiCl_4$	A 0 °C, 15 min hexane–AcOEt (2:1)	 (**26**) 70%
(2)	R = SO_2Ph (**22**)	$TiCl_4$	A 0 °C, 3 min hexane–AcOEt (7:3)	 (**27**) 89%
 (3)	R = OAc (**20**)	$SnCl_4$	B −20 °C, 1 h; then room temp., 15 min hexane–AcOEt–CH_2Cl_2 (32:18:50)	 (**28**) 66%
 (4)	R = OAc (**20**)	$SnCl_4$	B −20 °C, 25 min; then room temp., 10 min hexane–AcOEt–CH_2Cl_2 (35:15:50)	 (**29**) 62%

when alkylations could be performed at 0 °C. This could be done by use of $TiCl_4$ or $SnCl_4$ instead of $EtAlCl_2$ as described in our preliminary report.[1] These new conditions led to higher yields and afforded exclusively the α-anomer.

Encouraged by our success in 1,1-disubstituted olefin C-glycosidation we examined applications to the trisubstituted homologues in order to investigate the effect of asymmetric induction on the aglycone moiety (Table 3).

Condensation of 2-methylbut-2-ene (**30**) with triacetyl-D-glucal (**1**) and diacetyl-L-rhamnal (**2**) afforded a 63% yield of

Table 3. Reaction of trisubstituted olefins with glycals.

Glycals	Olefin	Lewis acid	Procedure (T/°C, time, chromatography)	*C*-Glycoside [yield/% (α/β)]
 (1)	 (30)	BF_3·Et_2O	C room temp., 20 min hexane–AcOEt (96:4)	 (31) 63%(100/0)
 (2)	(30)	BF_3·Et_2O	C room temp., 20 min hexane–AcOEt (96:4)	 (32) 63%(100/0)
 (3)	(30)	$EtAlCl_2$	B −20 °C, 20 min; then −20 °C to room temp., 40 min hexane–AcOEt (96:4)	 80%(100/0) (33a) (S) C-3 (33b) (R) C-3
 (4)	(30)	$EtAlCl_2$	B −20 °C, 20 min; then −20 °C to room temp., 40 min hexane–AcOEt (96:4)	 75%(100/0) (34a) (R) C-3 (34b) (S) C-3
(1)	 (35)	$SnBr_4$	A room temp., 5 min hexane–AcOEt (95:5)	 (36) 85%(100/0)
(2)	(35)	$SnBr_4$	A room temp., 5 min pentane–Et_2O (5:1)	 (37a) + (37b) 80%(92/8)
(3)	(35)	$SnBr_4$	B room temp., 5 min hexane–AcOEt (87:13)	 (38) 75%(100/0)
(4)	(35)	BF_3·Et_2O	C 0 °C, 45 min hexane–AcOEt (96:4)	 (39) 50%(100/0)

α-*C*-glycosides (**31**) and (**32**) as a 1:1 mixture of diastereoisomers (at C-3). Variation of both Lewis acid and solvent had a major effect on chemoselectivity. Thus treatment of peracetylated glycals with compound (**30**) and $EtAlCl_2$ in dichloromethane afforded a complex mixture of chloro and unsaturated products.[1] In contrast, catalysis by BF_3·Et_2O in acetonitrile resulted in the exclusive formation of α-1,2′-diunsaturated *C*-glycosides.

The detailed ^1H assignment was established from 1D and 2D NOESY ^1H NMR data. The 1D spectrum clearly indicated the presence of the terminal vinyl group, identified by the two-proton olefinic multiplets at δ ~4.8. The 3-H signals appeared as two doublets of doublets: (**31**) 2.47 [0.5 H, dd, *J* 6.97 and 9.15 Hz, 3-H (*R*)], 2.58 [dd, 0.5 H, *J* 6.88 and 8.88 Hz, 3-H (*S*)]; (**32**) 2.39 [1 H, dd, *J* 5.46 and 6.81 Hz, 3-H (*S*)], 2.52 [1 H, dd, *J* 6.93 and 7.02 Hz, 3-H (*R*)]. This demonstrates the existence of a mixture of diastereoisomers and suggests an *anti* relationship between 1′-H and 3-H ascertained by the weak NOEs associated with 3-H and 5′-H. The 2′-H assignment was deduced from the 2D NOESY spectrum which revealed a correlation between

Table 4. ^1H and ^{13}C NMR data for '2-chloro-2,3-dimethylpropan-3-yl' and methylcyclohexenyl *C*-glycosides.

Compound	$J_{1',3}$	$\delta_{1'\text{-H}}$	$\delta_{C\text{-}1'}$	C-3	Compound	$J_{1',6}$	$\delta_{1'\text{-H}}$	$\delta_{C\text{-}1'}$
(33a)	2.2	4.96	76.99	(*S*)	**(38)**	3.4	4.70	77.42
(33b)	5.48	4.36	80.47	(*R*)	**(38)**	2.96	4.33	80.60
(34a)	1.68	4.83	75.16	(*R*)	**(39)**	3.28	4.58	75.12
(34b)	5.42	4.27	79.71	(*S*)	**(39)**	2.92	4.20	79.13

1'-H and the most deshielded olefinic resonances. NOE between 2'-H and the C-3 methyl was observed only for one diastereoisomer. Using Dreiding molecular models, it was established that this correlation should be only observable for the (*S*)-(**31**) and (*R*)-(**32**) isomers.

With 2-hydroxy glycals the use of boron trifluoride led to a partial reaction with a low yield of oxo *C*-glycoside. On the other hand, alkylation of glycal (**1**) performed with ethylaluminium dichloride afforded, after purification, α-*C*-glycosides (**33a**) (60%) and (**33b**) (20%). In the same fashion 2-oxo α-L-*C*-glycosides (**34a**) and (**34b**) were obtained in 50 and 25% yield, respectively.

Structural assignment was based upon ^1H and ^{13}C NMR data (Table 4). Thus between compounds (**33a**) and (**33b**) a 0.6 Hz difference for 1'-H and a 3.48 Hz difference for C-1' was noted. The same downfield shift could be observed for epimers (**34a**) and (**34b**). These deshielding effects would be consistent with a (3*S*) configuration for compounds (**33a**) and (**34b**) and a (3*R*) configuration for compounds (**33b**) and (**34a**) in which the anisotropic effect of the chlorine was induced by the *syn* relationship between the carbonyl at C-2' and the 3-H proton dictated by the $J_{1',3}$ coupling constants.

Reaction of methylcyclohexene (**35**) with (**1**) in the presence of tin(IV) bromide afforded an 85% yield of the methylcyclohexenyl α-*C*-glycoside (**36**) as a 6:4 mixture of stereoisomers (at C-6 of methylcyclohexene) as evidenced by the six olefinic resonances [δ_H 5.85 (0.4 H, ddd, *J* 2.51, 4.19, and 10.51 Hz, 3'-H), 5.82 (0.6 H, ddd, *J* 2.54, 4.40, and 10.43 Hz, 3'-H), 5.74 (0.6 H, ddd, *J* 0.95, 1.87, and 10.43 Hz, 2'-H), 5.58 (0.4 H, ddd, *J* 0.91, 1.89, and 10.51 Hz, 2'-H), 5.58 (m, 0.4 H, 2-H), and 5.51 (m, 0.6 H, 2-H)].

Similar alkylation with diacetyl-L-rhamnal (**2**) proceeded once again with a somewhat lower selectivity giving, after chromatography, the α and β anomers (**37a**) and (**37b**) (*R*:*S* 1:1) in 73.6 and 6.4% yield, respectively. For compound (**37a**), the ^1H NMR spectrum closely resembled that of compound (**36**) for the six olefinic signals but revealed a better selectivity at C-6 (*S*:*R* 3:1).

The detailed ^1H NMR study of *C*-glycosides (**36**), (**37a**), and (**37b**) was supported by the 300 MHz spectra. The NMR data were fully consistent with the methylcyclohexenyl structure. In addition each proton appeared as two signals, indicating the presence of a mixture of (6*R*) and (6*S*) isomers. Rigorous identification of all the resonances was supported by the $J_{1',6}$ coupling constants and by NOESY spectroscopy. Thus observation of the $J_{1',6}$ 4–5.4 Hz coupling constants clearly demonstrated a *syn* relationship between 1'-H and 6-H. Based on Dreiding molecular models, it was anticipated that in this configuration an interaction should be observable for the D(*R*) and the L(*S*) diastereoisomers between 2'-H and the methyl at C-1. As expected, the NOESY spectra showed this connection for only one of the two isomers. By these means the (6*R*):(6*S*) ratio was unequivocally determined.

Alkylation of glycals (**3**) and (**4**) with methylcyclohexene (**35**) showed no asymmetric induction at C-1. 2'-Oxo *C*-glycosides (**38**) and (**39**) were isolated as a 1:1 mixture of (6*R*) and (6*S*) diastereoisomers in 75 and 50% yield, respectively.

Once again 1'-H and C-1' chemical shifts were relied upon to make the stereochemical assignments of products (**38**) and (**39**) (Table 4). The data suggested an anisotropic effect of the double bond induced by the *syn* relationship between the carbonyl at C-2' and the 6-H proton dictated by the $J_{1',6}$ coupling constant. Unfortunately examination of molecular models did not permit an unambiguous determination of the stereochemistry at C-6.

Variation of the steric hindrance had a marked effect upon alkylation, affording a large amount of thermodynamically more stable β-*C*-glycosides (Table 5). Treatment of 2,3-dimethylbut-2-ene (**40**) with glycal (**1**) produced a mixture of α- and β-unsaturated *C*-glycosides (**41a**) (23%) and (**41b**) (47%) and of the α-chloro *C*-glycoside (**41c**) (15%). Similar alkylation of diacetyl-L-rhamnal (**2**) with compound (**40**) afforded α- and β-unsaturated *C*-glycosides (**42a**) and (**42b**) in 15 and 25% yield respectively, thus confirming the marked sensitivity to sterically encumbered nucleophiles.

Finally the reaction was performed with hexene and cyclohexene. Condensation of triacetyl-D-glucal (**1**) or diacetylrhamnal (**2**) with hex-1-ene (**43**) in the presence of tin(IV) chloride led to a mixture with unsaturated and chloro *C*-glycosides. Assignment of the diene structure of products (**44b**) and (**45b**) was based upon the ^1H NMR spectrum. Thus the two-proton signal at δ_H 5.5 indicated the presence of a C-2–C-3 double bond in the aglycone. Reaction of dimethylbutene (**40**) with 2-hydroxyglycal led to very poor yields (~10%). Hex-1-ene was found to be unreactive with this glycal.

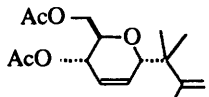
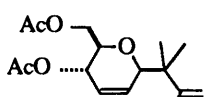
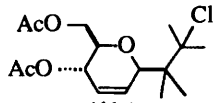
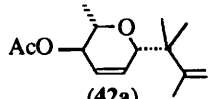
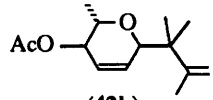
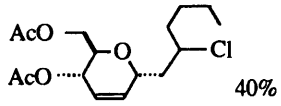
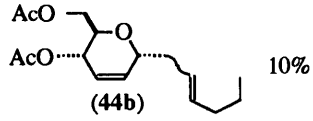
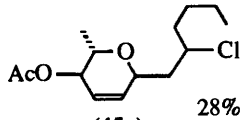
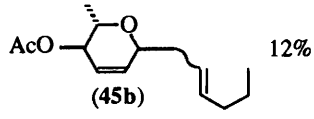
Structural Assignment.—(a) 2,3-*Unsaturated* C-*glycosides.* The structural assignment was based on NMR data. Observance of a two-proton multiplet around δ_H 5.8 assigned to 2'-H and 3'-H, and the presence of a single acetyl signal for 6-deoxy-L-*C*-glycosides or two acetyl resonances for the D-derivatives, indicated regioselective addition of the aglycone at C-1.

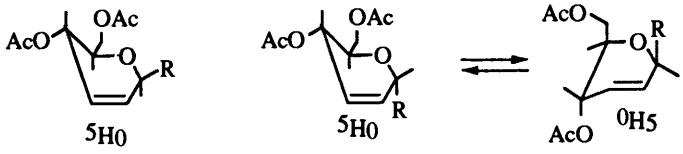
Assignment of the stereochemistry at the anomeric centre was based on examination of the $J_{4',5'}$ coupling constants (Table 6). The conformationally stable β-*C*-glycosides with all groups in an equatorial orientation were characterized by the large value of the coupling constants[21] ($J_{4',5'}$ 9–10 Hz). Confirmation of these assignments come from 2D NOE experiments.[8g,9b,9c] Thus examination of the NOESY spectra of the β-*C*-glycosides (**7b**) and (**37b**) revealed a connection between the 1'-H and the 5'-H protons in agreement with their *syn* relationship. For the α-anomers two cases must be considered. On the one hand for methylcyclohexenyl or dimethylbutenyl *C*-glycosides the equatorial orientation of the aglycone which locked the conformation as $^5H_0$ for the D series and as $^0H_5$ for the L series was dictated by the $J_{4',5'}$ 2–3.4 Hz coupling constants. On the other hand for most of the α-*C*-glycosides $J_{4',5'}$ coupling constants ranging from 5.5–7 Hz were observed. According to the work of Achmatowicz[21] these constants reflect an equilibrium between the $^0H_5$ and the $^5H_0$ conformations with a higher contribution of the conformer with the axial aglycone (L $^5H_0$, D $^0H_5$).

Once again NOESY data contributed to these assignments. Thus the detection of a cross-peak between 1'-H and 6'-H established that the methylcyclohexenyl α-L-*C*-glycoside (**37a**) was in the $^0H_5$ conformation. For the cyclohexenylmethyl α-*C*-glycoside (**7a**) the value of $J_{4',5'}$ 5.48 Hz indicated an equilibrating mixture of $^0H_5$ and the $^5H_0$ conformers. As expected the presence of $^0H_5$ conformers was dictated by a 1'-H–6'-H NOESY correlation. This observation is, to the best of our knowledge, the first experimental demonstration of the Achmatowicz hypothesis.

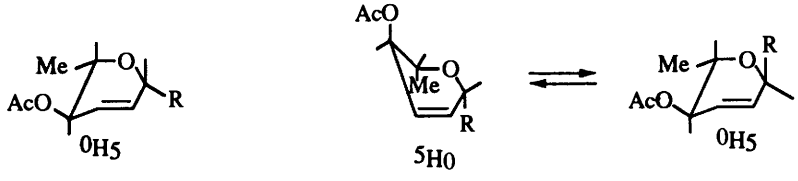
The proposed structures was also ascertained by chemical derivatization. Thus *C*-glucosides (**14a**), (**14b**), (**15a**), and (**15b**) were first deacetylated with sodium methoxide, then the double bond was stereoselectively oxidized with *m*-chloroperbenzoic acid (MCPBA)[22] (Scheme 1). Acetylation of the epoxy alcohols afforded finally the epoxy esters. Examination of the NMR

Table 5. Reaction of linear and tetrasubstituted olefins with glycals.

Glycal	Olefin	Lewis acid	Procedure (*T*/°C, time, chromatography)	*C*-Glycoside (yield/%)
(1)	 (40)	$SnCl_4$	A −20 °C, 5 min CH_2Cl_2–pentane (3:2)	 (41a) 23%  (41b) 15%  (41c) 47%
(2)	(40)	TmsOtf	A −20 °C, 5 min hexane–AcOEt (25:1)	 (42a) 15%  (42b) 25%
(1)	 (43)	$SnCl_4$	A −20 °C, 5 min hexane–Et_2O–AcOEt (6:1:0.5)	 (44a) 40%  (44b) 10%
(2)	(43)	$SnCl_4$	A −20 °C, 5 min pentane–Et_2O (15:1)	 (45a) 28%  (45b) 12%



β–D-C-glycosides α–D-C-glycosides



β–L-C-glycosides α–L-C-glycosides

spectra of compounds (**49a**) and (**51a**) indicated a $J_{1',2'}$ 4 Hz coupling constant characteristic[23] of a *cis* relationship between 1′-H and 2′-H, consistent with the α-configuration. For the corresponding isomers (**49b**) and (**51b**) the β-configuration was ascertained from the $J_{1',2'}$ 0 Hz coupling constant typical of a *trans* relationship between 1′H and 2′-H (Table 7).

Assignment of the 2′-H and 3′-H signals at 300 MHz was supported by 1D or 2D NOE spectroscopy and it was found that the chemical shift was solvent dependent. The key to this analysis lay in NOEs associated with the 1′-H and the 2′-H protons. For all the compounds examined in $CDCl_3$ at 300 MHz the 2′-H is deshielded relative to 3′-H, contrary to the results reported in the case of malonyl *C*-glycosides.[8f,8g] However, the ^1H 300 MHz NMR spectrum of some *C*-glycosides such as (**37a**), (**37b**), or (**41a**) in C_6D_6 revealed that in this solvent 3′-H was more deshielded than was 2′-H.

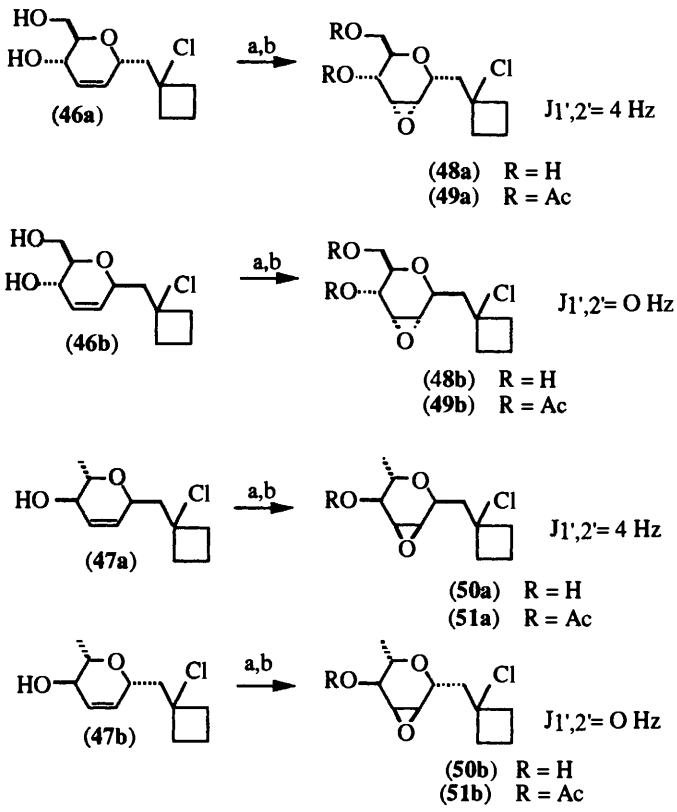
(b) *2-Oxo unsaturated C-glycosides.* ^1H and ^{13}C 300 MHz NMR spectra of the product were completely consistent with an α,β-unsaturated ketone structure, with characteristic olefinic resonances at δ_H 6.2 and 7 and the C-2 carbon resonating at δ_C 195. Structural investigation using 2D NOESY spectroscopy revealed the absence of connectivity between 1′-H and 5′-H (Table 8a). This result supported strongly an α-configuration at the anomeric carbon. Moreover, in the L series (Table 8b) this assignment was ascertained by a NOE between 1′-H and 6′-H (Figure 1).

Table 6. Analytical data for the 2,3-unsaturated *C*-glycosides.

Compound (formula)	$[\alpha]_D^{20}$ (°)	$J_{4',5'}$ (Hz)	Found (%) (Requires) C	H	Cl	S
(6) ($C_{17}H_{24}O_5 \cdot H_2O$)	+67.5[a]	6.57[c]	62.5 (62.55)	7.5 (8.02)		
(7a) ($C_{15}H_{22}O_3 \cdot H_2O$)	−70[a]	5.48[c]	66.8 (67.13)	8.65 (9.01)		
(7b) ($C_{15}H_{22}O_3 \cdot 0.5H_2O$)	−52.5[a]	8.81[c]	69.5 (69.47)	8.7 (8.94)		
(11) ($C_{21}H_{32}O_5 \cdot H_2O$)	+75[b]	6.5[c]	65.7 (65.92)	8.9 (8.96)		
(12a) ($C_{19}H_{30}O_3$)	−62.5[b]	6[c]	74.45 (74.45)	9.9 (9.87)		
(12b) ($C_{19}H_{30}O_3$)	−160[b]	9.5[c]	74.6 (74.45)	10.0 (9.87)		
(14a) ($C_{15}H_{21}ClO_5$)	+75[b]	7[c]	57.0 (56.85)	6.7 (6.68)	11.2 (11.19)	
(14b) ($C_{15}H_{21}ClO_5$)	+100[b]	9[c]	56.9 (56.85)	6.6 (6.68)	11.3 (11.19)	
(15a) ($C_{13}H_{19}ClO_3$)	−83.75[b]	6[c]	60.6 (60.36)	7.5 (7.30)	13.9 (13.71)	
(15b) ($C_{13}H_{19}ClO_3$)	−93.75[b]	9.5[c]	60.6 (60.36)	7.5 (7.30)	13.6 (13.71)	
(19) ($C_{15}H_{23}ClO_6 \cdot H_2O$)	+35[a]	7.26[c]	53.0 (52.40)	6.8 (7.04)	11.0 (10.31)	
(21) ($C_{17}H_{25}ClO_7$)	+71.25[a]	6[c]	54.2 (54.16)	6.7 (6.69)	9.4 (9.41)	
(23) ($C_{21}H_{27}ClO_7S$)	+30[a]	6[c]	54.9 (54.93)	6.1 (5.93)	7.5 (7.33)	7.1 (6.99)
(24) ($C_{13}H_{21}ClO_4$)	−85[a]	6[c]	56.3 (56.39)	7.7 (7.65)	13.0 (12.81)	
(26) ($C_{20}H_{25}ClO_5$)	−60[a]	6.5[c]	63.5 (63.05)	6.7 (6.62)	8.9 (9.31)	
(27) ($C_{19}H_{25}ClO_5S$)	−40[a]	6.5[c]	56.85 (56.90)	6.35 (6.29)	8.0 (8.85)	8.0 (8.0)
(31) ($C_{15}H_{22}O_5$)	+45[a]	6.36, 6.82[c]	64.1 (63.81)	8.0 (7.85)		
(32) ($C_{13}H_{20}O_3$)	−137.5[b]	6.36, 6.60[c]	69.5 (69.59)	9.0 (8.99)		
(36) ($C_{17}H_{24}O_5$)	+71[b]	2.39, 3.4[d]	66.2 (66.19)	7.85 (7.85)		
(37a) ($C_{15}H_{22}O_3 \cdot H_2O$)	−95[b]	2.21, 3.02[d]	67.4 (67.14)	8.3 (9.01)		
(37b) ($C_{15}H_{22}O_3 \cdot 0.5H_2O$)	−145[a]	8.46, 8.76[d]	69.3 (69.47)	8.7 (8.94)		
(41a) ($C_{16}H_{24}O_5$)	+60[a]	2.41[c]	64.7 (64.82)	8.2 (8.17)		
(41b) ($C_{16}H_{24}O_5$)	+175[b]	9.5[c]	64.8 (64.82)	8.2 (8.17)		
(41c) ($C_{16}H_{25}ClO_5$)	+92.5[a]	7[c]	57.6 (57.72)	7.6 (7.57)	10.35 (10.55)	
(42a) ($C_{14}H_{22}O_3$)	−125[a]	2.12[c]	70.6 (70.54)	9.3 (9.31)		
(42b) ($C_{14}H_{22}O_3$)	−115[a]	9.5[c]	70.6 (70.54)	9.3 (9.31)		
(44a) ($C_{16}H_{25}ClO_5$)	+52.5[b]	6[c]	57.9 (57.72)	7.7 (7.57)	10.6 (10.66)	
(44b) ($C_{16}H_{24}O_5$)	+55[a]	6[c]	64.8 (64.82)	8.2 (8.17)		
(45a) ($C_{14}H_{23}ClO_3$)	−75[b]	6.5[c]	61.3 (61.17)	8.6 (8.44)	13.15 (12.91)	
(45b) ($C_{14}H_{22}O_3$)	−55[a]	6[c]	70.6 (70.54)	9.35 (9.31)		

[a] $CHCl_3$, *c* 0.1. [b] MeOH, *c* 0.1. [c] $CDCl_3$. [d] C_6D_6.

The direct addition of an alkene to a peracetylated glycal represents a convenient stereocontrolled approach to unsaturated *C*-glycosides. The majority of the reactions led mostly or only to the α-*C*-glycoside in accord with the Danishefsky model [14] which postulated an *anti* S_N2' addition at the anomeric centre. However, addition of bulky olefins led to a mixture of *C*-glycosides with an non-negligible amount of β-isomer, following the mechanism depicted by Ferrier which involved an oxo-



Scheme 1. Synthesis of 2',3'-epoxy *C*-glycosides. [a] MCPBA. [b] Pyridine–acetic anhydride.

Table 7. ^{1}H 60 MHz NMR data[a] for 4'-*O*-acetyl-2',3'-epoxy *C*-glycosides (pyranose moieties).

	$\delta_{1'\text{-H}}$	$\delta_{2'\text{-H}}$	$\delta_{3'\text{-H}}$	$\delta_{4'\text{-H}}$	$\delta_{5'\text{-H}}$	$\delta_{6'\text{-H}}$	δ_{AcO}	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6'}$
(49a)	4.43	2.9	3.4	5.06	3.73	4.43	1.73	4	4	2	9.5	
(49b)	4.27	2.83	3.4	5.13	3.73	4.27	1.69, 1.73	0	4	2	9.5	6.5
(51a)	4.4	2.90	3.35	4.84	3.8	1.1	1.64	4	4	2	9.5	6
(51b)	4.37[b]	2.93	3.63	4.96	3.63	1.1	1.7	0	4	2	9.5	6.5

[a] C_6D_6. [b] $J_{1,1'}$ 5 and 8.5 Hz.

carbenium ion.[11] From all these results we suggest that alkene condensation with peracetylated glycals proceeded either by the fast S_N2' substitution or by the slow oxocarbenium pathway (Scheme 2). This hypothesis is consistent with the diminished stereoselectivity observed for 6-deoxy derivatives. This drop may reflect a difference in complexation between the catalyst and the glycal which induced a higher reactivity of the Lewis acid allowing for an increased formation of oxocarbenium ion. Reaction with 2,2-dimethylbut-2-ene led to an important yield of β-*C*-glycosides. Considering that hexene and 2-methylbut-2-ene afforded only α-derivatives it is clear that this drop in stereoselectivity is the consequence of steric hindrance. Structural examination of the glycal with all the substituents in *trans* positions suggested an interaction between the bulky olefin and the C-4 acetates, which decreased the rate of S_N2' substitution and promoted β-*C*-glycoside formation by olefin condensation with oxocarbenium carbocations.

Alkylation afforded *C*-glycosides with an unsaturated alglycone or *C*-glycosides containing a halogen. These results suggested strongly that the formation of the C–C bond at the anomeric centre induced the generation of a carbocation on the aglycone. This ion reacted with the most nucleophilic reagent present in the medium or led to unsaturated derivatives by elimination of hydrogen. The formation of acetate derivatives (**52**) and (**53**) when reactions were performed in the presence of trimethylsilyl triflate supported this hypothesis (Scheme 3). Postulation of hydrogen halide elimination provided a possible pathway for diunsaturated *C*-glycoside preparation, but the chemoselective formation of 2,3-hexenyl derivatives make this hypothesis unlikely. However, in the light of this result the synthesis of *C*-glycosides with an unsaturated aglycone by a concerted ene-like process must be considered.

The ratio of ene adduct to chloride is a function of alkene structure. Formation of the halide derivative requires that chlorine transfer be faster than bond rotation. Accordingly, cyclohexene derivatives led to unsaturated *C*-glycosides whereas methylenecyclobutene gave only chlorocyclobutyl *C*-glycosides. In the same fashion, condensation of 2-methylbut-2-ene in the presence of tin(IV) chloride in dichloromethane produced mostly the chloro derivative[1] but yielded dienyl *C*-glycosides when the reaction was catalysed by boron trifluoride–diethyl ether in acetonitrile. Polyfunctional olefins led only to halogeno *C*-glycosides, suggesting that it is difficult for a proton to reach a proper alignment relative to the tertiary carbocation.

Alkylation of peracetylated 2-hydroxy glycals with olefins afforded, in a first step, the enol ester. Lewis acid-induced

Table 8.

Compound (formula)	$[\alpha]_D^{20}$ (°)	NOE 1′,5′	NOE 1′,6′	Found (%) (Requires) C	H	Cl
(a) Analytical data for 2′-oxo D-*C*-glycosides.						
(8) ($C_{15}H_{20}O_4 \cdot H_2O$)	+4[a]	–	–	64.3 (64.0)	7.5 (7.88)	
(16) ($C_{13}H_{17}ClO_4 \cdot 0.5H_2O$)	−7.5[a]	–	–	55.8 (55.50)	6.3 (6.44)	12.6 (12.60)
(28)[b] ($C_{13}H_{19}ClO_4$)	−30[a]	–	–	[*M* + 1]		333.112[c] (333.1104)
(33a) ($C_{13}H_{19}ClO_4$)	−45[a]	–	+	56.3 (56.62)	7.0 (7.31)	12.0 (12.85)
(33b) ($C_{15}H_{21}ClO_6$)	−87.5[a]	–	+	[*M* + 1]		275.1071[c] (275.1050)
(38) ($C_{15}H_{20}O_4 \cdot 0.5H_2O$)	−55[a]	–	–	65.3 (65.90)	7.5 (7.74)	
(b) Analytical data for 2′-oxo L-*C*-glycosides.						
(9) ($C_{13}H_{18}O_2$)	+35[a]	–	+	74.9 (75.69)	8.75 (8.7)	
(17) ($C_{11}H_{15}ClO_2$)	+52.5[a]	–	+	61.8 (61.42)	7.0 (7.04)	16.3 (16.51)
(29)[b] ($C_{13}H_{19}ClO_4$)	+30[a]	–	+	57.0 (56.83)	7.0 (6.97)	12.6 (12.90)
(34a) ($C_{11}H_{17}ClO_2$)	+80[a]	–	+	60.9 (60.68)	8.0 (8.33)	16.3 (16.28)
(34b) ($C_{11}H_{17}ClO_2$)	+40[a]	–	+	61.0 (60.68)	7.9 (8.33)	16.4 (16.28)
(39) ($C_{13}H_{18}O_2 \cdot 0.5H_2O$)	+45[a]	–	+	72.0 (72.52)	8.5 (8.89)	

For both parts of the Table: [a] $CHCl_3$, *c* 0.1. [b] NOESY experiments were performed in C_6D_6. [c] High-resolution mass spectra.

transesterification followed by β-elimination gave the unsaturated oxo *C*-glycoside. One rationale for this interconversion derives from the isolation of an enol ester and unsaturated oxo *C*-glycoside mixture and from the observation of a strong smell of acetic anhydride (Scheme 4).

Although the catalyst had been chosen on an experimental basis some conclusions may be drawn. Tin(IV) bromide is a very useful catalyst leading to a high degree of stereoselectivity. However, its use is limited to cyclic olefins because it gave complex mixtures of halogenated and acetylated *C*-glycosides with other alkenes. $SnCl_4$, $EtAlCl_2$, and boron trifluoride–diethyl ether in dichloromethane have been used with a wide range of olefins. The results suggested that the right choice of catalyst is dependent on the glycal reactivity. Titanium(IV) chloride* is less reactive with olefins and also with glycals, for this reason it is a very interesting reagent for the alkylation of 6-deoxyglycals with polyfunctional 1,1-disubstituted olefins. In acetonitrile, $BF_3 \cdot Et_2O$ is a very useful catalyst which promoted the stereoselective formation of *C*-glycosides with an unsaturated aglycone. Unsaturated *C*-glycoside have been also produced in the presence of methyl trifluoromethanesulphonate; however, with this strong Lewis acid catalyst it is very difficult to control the reaction.

Experimental

^1H NMR spectra were recorded with a Varian T60 (60 MHz) or a Bruker MSL 300 (300.13 MHz) spectrometer. ^{13}C NMR spectra were obtained with a Varian CFT 20 (20 MHz) or a Bruker MSL 300 (75.37 MHz) spectrometer with tetramethylsilane as internal standard. Microanalysis and mass spectra were performed by the Laboratoire central de Microanalyse du CNRS, Vernaison France. Triacetyl-D-glucal and all the olefins except 4-t-butyl(methylene)cyclohexane[24] and 2-methylbut-2-ene derivatives[25] were commercial samples and were used without further purification. Diacetyl-L-rhamnal,[26] 2-hydroxy-D-glucal tetra-acetate,[27] and 2-hydroxy-L-fucal triacetate[28] were prepared according to published procedures. Dichloromethane and acetonitrile were distilled from P_2O_5 and stored over 4Å molecular sieves. Flash chromatography[20] was carried out on silica gel 60 (30–60 μ) in the indicated solvents. TLC was performed on silica gel 60 F254 (E. Merck). Optical rotations were measured on a Roussel-Jouan 'Quick' polarimeter. All reactions were run under nitrogen in flame-dried glassware with magnetic stirring. Reagents were added *via* syringe through septa.

Procedure for the Condensation of Olefins with Peracetylated Glycals (*Tables* 1, 2, 3, *and* 5).—*Procedure A*. A round-bottom flask equipped with a magnetic stirring bar was filled successively with glycal, dichloromethane (1.5–3 ml/mol equiv.), and alkene (1.2 mol equiv.), then the reaction mixture was cooled to the indicated temperature. Lewis acid (1.5 mol equiv.) was added and the reaction was followed by TLC. When all the starting material had disappeared the reaction mixture was poured into a 1:1 mixture of diethyl ether and saturated aq. disodium hydrogen phosphate (10 ml/mmol). The aqueous layer was extracted twice with diethyl ether (5 ml/mmol). The organic layer was washed successively with aq. sodium hydrogen carbonate (5 ml/mmol) and water (5 ml/mmol) then dried ($MgSO_4$). Removal of the solvent under reduced pressure, then flash chromatography of the residue in the indicated solvents, furnished the pure *C*-glycoside.

* Glycal alkylation with olefins is a reaction very sensitive to hydrogen halide. In order to limit hydrolysis, $SnCl_4$ and $TiCl_4$ were used as 1M-solutions in dichloromethane or 1,2-dichloroethane.

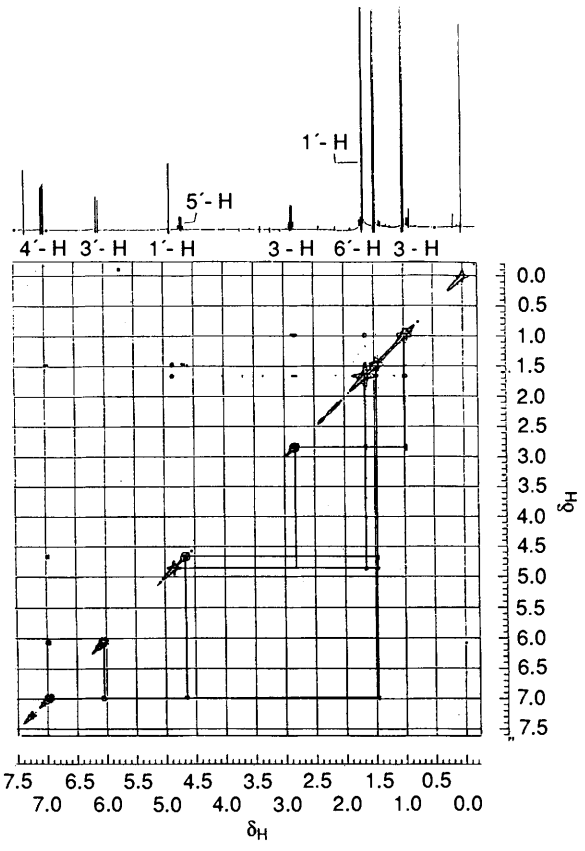


Figure 1. Contour plot of (3*R*)-2-chloro-2-methyl-3-(3,4,6-trideoxy-α-L-*glycero*-hex-3-enopyran-2-ulosyl)butane (**34a**) 2D NOESY spectrum. The 1D 300 MHz ^{1}H NMR spectrum is shown above.

Procedure B. A round-bottom flask equipped with a magnetic stirring bar was filled successively with glycal, dichloromethane (1.5–3 ml/mol equiv.), and alkene (1.2 mol equiv.) then the reaction mixture was cooled to the indicated temperature. Lewis acid (1.5 mol equiv.) was added and the reaction was followed by TLC. When all the starting material had disappeared the reaction mixture was poured into a 1:1 mixture of diethyl ether and saturated aq. sodium hydrogen carbonate (10 ml/mmol). The aqueous layer was extracted twice with diethyl ether (5 ml/mmol). The organic layer was washed successively with aq. sodium hydrogen carbonate (5 ml/mmol) and water (5 ml/mmol) then dried ($MgSO_4$). Removal of the solvent under reduced pressure, then flash chromatography of the residue in the indicated solvents, furnished the pure *C*-glycoside.

Procedure C. A round-bottom flask equipped with a magnetic stirring bar was filled successively with glycal, acetonitrile (1.5–3 ml/mol equiv.) and alkene (1.2 mol equiv.), then the reaction mixture was cooled to −20 °C and boron trifluoride–diethyl ether (1.5 mol equiv.) was added. The cooling bath was removed and the reaction was followed by TLC. When all the starting material had disappeared the reaction mixture was poured into a 1:1 mixture of diethyl ether and saturated aq. sodium hydrogen carbonate (10 ml/mmol). The aqueous layer was extracted twice with diethyl ether (5 ml/mmol). The organic layer was washed successively with aq. sodium hydrogen carbonate (5 ml/mmol) and water (5 mol/mmol), then dried ($MgSO_4$). Removal of the solvent under reduced pressure, then flash chromatography of the residue in the indicated solvents, furnished the pure *C*-glycoside.

NMR data. (a) *Methylenecyclohexyl derivatives.*

Compound (**6**) δ_H(300 MHz; $CDCl_3$) 1.62 (4 H, m, 4- and 5-H_2), 2.00 (4 H, m, 3- and 6-H_2), 2.14 (1 H, dd, *J* 5.97 and 13.7 Hz, 1-C*H*H), 2.17 (6 H, s, 2 × Ac), 2.35 (1 H, dd, *J* 2.53 and 13.7 Hz, C-1 CH*H*), 3.96 (1 H, ddd, *J* 3.39, 6.57, and 6.57 Hz, 5'-H), 4.14 (1 H, dd, *J* 3.39 and 11.83 Hz, 6'-H), 4.24 (1 H, dd, *J* 6.57 and 11.83 Hz, 6'-H), 4.34 (1 H, ddddd, *J* 1.63, 2.07, 2.49, 2.53, and 5.97 Hz, 1'-H), 5.13 (1 H, dddd, *J* 2.07, 2.16, 2.64, and 6.57 Hz, 4'-H), 5.5 (1 H, m, 2-H), 5.76 (1 H, ddd, *J* 2.16, 2.49, and 10.41 Hz, 3'-H), and 5.93 (1 H, ddd, *J* 1.63, 2.64, and 10.41 Hz, 2'-H); δ_C(75.47 MHz; $CDCl_3$) 20.82 (q, *Me*CO), 21.06 (q, *Me*CO), 22.34 and 22.97 (t, C-4 and -5), 25.37 and 28.62 (t, C-3 and -6), 41.76 (t, 1-CH_2), 63.07 (t, C-6'), 65.23 (d, C-4'), 69.63 (d, C-5'), 70.73 (d, C-1'), 123.38 (d, C-3'), 124.30 (d, C-2), 133.64 (d, C-2'), 134.03 (s, C-1), 170.49 (s, Me*C*O), and 171.20 (s, Me*C*O).

Compound (**7a**) δ_H(300 MHz; $CDCl_3$) 1.22 (3 H, d, *J* 6.56 Hz, 6'-H_3), 1.52–1.68 (4 H, m, 4- and 5-H_2), 1.95–2.08 (4 H, m, 3- and 6-H_2), 2.10 (3 H, s, Ac), 2.12 (1 H, dd, *J* 6.95 and 14.26 Hz, 1-C*H*H), 2.32 (1 H, dd, *J* 6.95 and 14.26 Hz, 1-CH*H*), 3.97 (1 H, dd, *J* 5.48 and 6.56 Hz, 5'-H), 4.23 (1 H, ddddd, *J* 1.36, 1.99, 2.19, 6.95, and 6.95 Hz, 1'-H), 4.89 (1 H, dddd, *J* 1.46, 2.19, 3.29, and 5.48 Hz, 4'-H), 5.34 (1 H, m, 2-H), 5.77 (1 H, ddd, *J* 1.36, 3.29, and 10.24 Hz, 3'-H), and 5.93 (1 H, ddd, *J* 1.46, 1.99, and 10.24 Hz, 2'-H); δ_C(75.47 MHz; $CDCl_3$) 16.93 (q, C-6'), 21.11 (q, *Me*CO), 22.22 and 22.81 (t, C-4 and -5), 25.20 and 28.51 (t, C-3 and -6), 42.16 (t, 1-CH_2), 68.21 (d, C-5'), 68.92 (d, C-4'), 69.70 (d, C-1'), 122.58 (d, C(2), 123.99 (d, C-3'), 133.88 (d, C-2'), 133.88 (s, C-1), and 170.58 (s, Me*C*O).

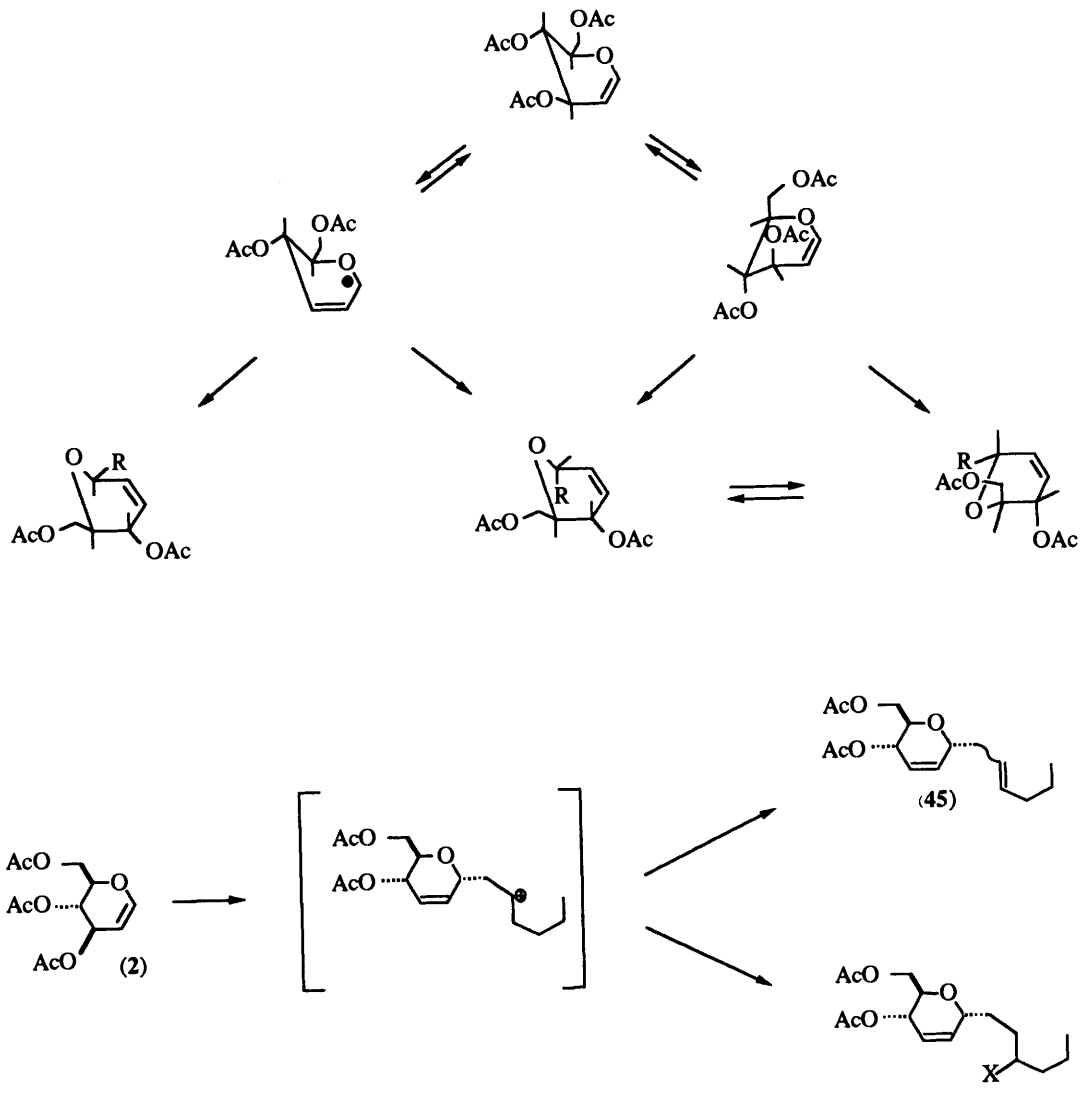
Compound (**7b**) δ_H(300 MHz; $CDCl_3$) 1.24 (3 H, d, *J* 6.04 Hz, 6'-H_3), 1.7–1.65 (4 H, m, 4- and 5-H_2), 1.92–2.04 (4 H, m, 3- and 6-H_2), 2.07 (3 H, s, Ac), 2.085 (1 H, dd, *J* 7.86 and 13.60 Hz, 1-C*H*H), 2.26 (1 H, dd, *J* 6.64 and 13.60 Hz, 1-CH*H*), 3.58 (1 H, dd, *J* 6.04 and 8.81 Hz, 5'-H), 4.23 (1 H, ddddd, *J* 2.31, 2.42, 3.02, 6.64, and 7.86 Hz, 1'-H), 5.05 (1 H, dddd, *J* 1.51, 1.82, 3.02, and 8.81 Hz, 4'-H), 5.38 (1 H, m, 2-H), 5.66 (1 H, ddd, *J* 1.51, 2.42, and 10.58 Hz, 3'-H), and 5.93 (1 H, ddd, *J* 1.82, 2.31, and 10.58 Hz, 2'-H).

Compound (**8**) δ_H(300.13 MHz; $CDCl_3$) 1.5–1.7 (4 H, m, 4- and 5-H_2), 1.9–2.05 (4 H, m, 3- and 6-H_2), 2.08 (3 H, s, Ac), 2.23 (1 H, dd, *J* 9.46 and 14.99, 1-C*H*H), 2.38 (1 H, dd, *J* 4.58 and 14.99, 1-CH*H*), 4.16 (1 H, dd, *J* 4 and 11.71 Hz, 6'-H), 4.32 (1 H, dd, *J* 6.52 and 11.71 Hz, 6'-H), 4.36 (1 H, dd, *J* 4.58 and 9.96 Hz, 1'-H), 4.66 (1 H, dddd, *J* 2.31, 2.34, 4, and 6.52 Hz, 5'-H), 5.48 (1 H, m, 2-H), 6.32 (1 H, dd, *J* 2.31 and 10.51 Hz, 3'-H), and 6.86 (1 H, dd, *J* 2.34 and 10.51 Hz, 4'-H); δ_C(75.47 MHz; $CDCl_3$) 20.74 (q, *Me*CO), 22.27 and 22.85 (t, C-4 and -5), 25.35 and 27.98 (t, C-3 and -6), 37.64 (t, 1-CH_2), 64.10 (t, C-6'), 66.07 (d, C-5'), 76.89 (d, C-1'), 124.46 (d, C-2), 127.28 (d, C-3'), 133.30 (s, C-1), 145.10 (d, C-4'), 170.58 (s, Me*C*O), and 195.91 (s, C-2').

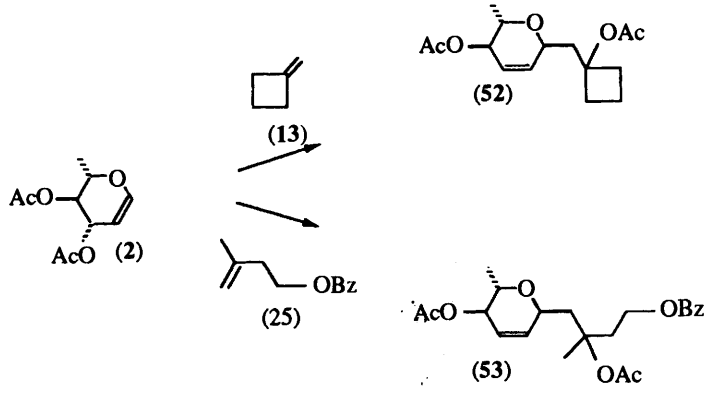
Compound (**9**) δ_H(300.13 MHz; $CDCl_3$) 1.36 (3 H, d, *J* 6.94 Hz, 6'-H_3), 1.5–1.7 (4 H, m, 4- and 5-H_2), 1.92–2.03 (2 H, m, 3- and 6-H_2), 2.30 (1 H, dd, *J* 4.39 and 14.98 Hz, 1-C*H*H), 2.40 (1 H, dd, *J* 10.24 and 14.98 Hz, 1-CH*H*), 4.30 (1 H, dd, *J* 4.39 and 10.24 Hz, 1'-H), 4.62 (1 H, ddd, *J* 2.19, 2.20, and 6.94 Hz, 5'-H), 5.52 (1 H, m, 2-H), 6.01 (1 H, dd, *J* 2.20 and 10.60 Hz, 3'-H), and 6.90 (1 H, dd, *J* 2.19 and 10.60 Hz, 4'-H); δ_C(75.47 MHz; $CDCl_3$) 19.20 (q, C-6'), 22.23 and 22.79 (t, C-4 and -5), 25.29 and 27.93 (t, C-3 and -6), 37.54 (t, 1-CH_2), 65.40 (d, C-5'), 76.26 (d, C-1'), 124.18 (d, C-2), 124.88 (d, C-3'), 133.56 (s, C-1), 151.83 (d, C-4'), and 198.76 (s, C-2').

Compound (**11**) δ_H(60 MHz; $CDCl_3$) 0.9 (9 H, s, Bu^t), 2.1 (6 H, s, 2 × Ac), 1.4–2.4 (9 H, m, 1-CH_2 and 7 × cyclohexenyl H), 3.95 (1 H, dd, *J* 6 and 6.5 Hz, 5'-H), 4.0 (1 H, ddd, *J* 4, 6.5, and 6.5 Hz, 6'-H), 4.23 (2 H, m, 1'- and 6'-H), 5.2 (1 H, ddd, *J* 1, 2 and 6.5 Hz, 4'-H), 5.6 (1 H, m, cyclohexenyl), and 5.9 (2 H, m, 2'- and 3'-H).

Compound (**12a**) δ_H(60 MHz; $CDCl_3$) 0.88 (9 H, s, Bu^t), 1.23 (3 H, d, *J* 6.5 Hz, 6'-H_3), 2.11 (3 H, s, Ac), 2.16–2.41 (9 H, m, CH_2 and 7 × cyclohexenyl H), 3.95 (1 H, dd, *J* 6 and 6.5 Hz, 5'-H), 4.25 (1 H, br dd, *J* 7 and 7 Hz, 1'-H), 4.96 (1 H, ddd, *J* 2, 2.5, and



Scheme 2. Mechanism of the addition of olefins.



Scheme 3. Reaction of diacetyl-L-rhamnal (**2**) with olefin in the presence of trimethylsilyl triflate.

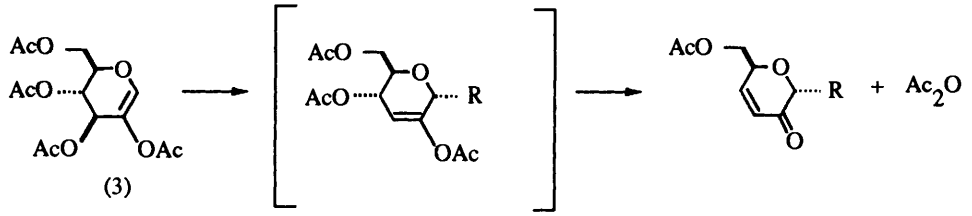
6 Hz, 4′-H), 5.55 (1 H, m, cyclohexenyl), and 5.86 (2 H, m, 2′- and 3′-H).

Compound (**12b**) δ_H(60 MHz; $CDCl_3$) 0.86 (9 H, s, Bu^t), 1.25 (3 H, d, *J* 6 Hz, 6′-H_3), 2.13 (3 H, s, Ac), 1.66–2.33 (9 H, m, CH_2 and 7 × cyclohexenyl H), 3.60 (1 H, dd, *J* 6 and 9.5 Hz, 5′-H), 4.3 (1 H, br dd, *J* 7 and 7 Hz, 1′-H), 5.13 (1 H, ddd, *J* 2, 2.5, and 9.5 Hz, 4′-H), 5.6 (1 H, m, cyclohexenyl), and 5.83 (2 H, m, 2′- and 3′-H).

(b) *Cyclobutyl C-glycosides.*

Compound (**14a**) δ_H(60 MHz; $CDCl_3$) 2.10 and 2.13 (6 H, 2 s, Ac), 1.8–2.3 (2 H, m, 3-H_2), 2.60 (6 H, m, 1-CH_2 and 2- and 4-H_2), 4.0 (1 H, m, 5′-H), 4.2 (2 H, d, *J* 5 Hz, 6′-H_2), 4.7 (1 H, m, 1′-H), 5.2 (1 H, ddd, *J* 1, 3, and 7 Hz, 4′-H), and 5.8 (2 H, m, 2′- and 3′-H).

Compound (**14b**) δ_H(60 MHz; $CDCl_3$) 2.10 (6 H, s, Ac), 1.80–



Scheme 4. Formation of 2′-oxo *C*-glycosides.

2.3 (2 H, m, 3-H_2), 2.16 (m, 6 H, 1-CH_2 and 2- and 4-H_2), 3.8 (1 H, dt, *J* 5 and 9 Hz, 5′-H), 4.2 (2 H, d, *J* 5 Hz, 6′-H_2), 4.6 (1 H, m, 1′-H), 5.36 (1 H, ddd, *J* 1, 3, and 9 Hz, 4′-H), and 5.8 (2 H, m, 2′- and 3′-H).

Compound (**15a**) δ_H(60 MHz; $CDCl_3$) 1.20 (3 H, d, *J* 6.5 Hz, 6′-H_3), 2.08 (3 H, s, Ac), 1.66–2.73 (8 H, m, 1-CH_2 and cyclobutyl), 3.8 (1 H, dq, *J* 6 and 6.5 Hz, 5′-H), 4.58 (1 H, m, 1′-H), 4.93 (1 H, ddd, *J* 2, 2, and 6 Hz, 4′-H), and 5.8 (2 H, m, 2′- and 3′-H); δ_C(20 MHz; $CDCl_3$) 13.7 (t, C-3), 16.3 (q, C-6′), 19.0 (q, *Me*CO), 37.3 and 38.6 (t, C-2 and -4), 38.5 (t, 1-CH_2), 66.2 (d, C-4′), 68.2 (d, C-5′), 68.7 (d, C-1′), 69.8 (s, C-1), 123 (d, C-3′), 132.1 (d, C-2′), and 168.9 (s, Me*C*O).

Compound (**15b**) δ_H(60 MHz; $CDCl_3$) 1.20 (3 H, d, *J* 6.5 Hz, 6′-H_3), 2.1 (3 H, s, Ac), 1.6–2.9 (8 H, m, 1-CH_2 and cyclobutyl), 3.6 (1 H, dq, *J* 6.5 and 9.5 Hz, 5′-H), 4.5 (1 H, m, 1′-H), 5.06 (1 H, ddd, *J* 1, 3, and 9.5 Hz, 4′-H), and 5.75 (2 H, m, 2′- and 3′-H); δ_C(20 MHz; $CDCl_3$) 13.3 (t, C-3), 16.9 (q, C-6′), 19.5 (q, *Me*CO), 36.9 and 38.5 (t, C-2 and -4), 35.7 (t, 1-CH_2), 69.3 (d, C-4′), 69.5 (d, C-5′), 70.6 (d, C-1′), 71.3 (s, C-1), 123.9 (d, C-2′), 131.6 (d, C-3′), and 168.9 (s, Me*C*O).

Compound (**16**) δ_H(300.13 MHz; $CDCl_3$) 1.8 (2 H, m, 3-H_2), 2.08 (3 H, s, Ac), 2.23 (1 H, dd, *J* 9.46 and 14.99 Hz, 1-C*H*H), 2.38 (1 H, dd, *J* 2.7 and 14.99 Hz, 1-CH*H*), 2.1–2.60 (4 H, m, 2- and 4-H_2), 4.24 (1 H, dd, *J* 4.07 and 11.88 Hz, 6′-H), 4.54 (1 H, dd, *J* 6.75 and 11.88 Hz, 6′-H), 4.66 (1 H, dddd, *J* 2.16, 3.02, 4.07, and 6.75 Hz, 5′-H), 4.71 (1 H, dd, *J* 2.7 and 9.46 Hz, 1′-H), 6.18 (1 H, dd, *J* 2.16 and 10.49 Hz, 3′-H), and 6.93 (1 H, dd, *J* 3.02 and 10.49 Hz, 4′-H); δ_C(75.47 MHz; $CDCl_3$) 15.80 (t, C-3), 20.74 (q, *Me*CO), 38.71 and 39.30 (t, C-2 and -4), 40.80 (t, 1-CH_2), 63.12 (t, C-6′), 69.13 (d, C-5′), 70.25 (s, C-1), 75.64 (d, C-1′), 127.57 (d, C-3′), 145.85 (d, C-4′), 170.57 (s, Me*C*O), and 195.1 (s, C-2′).

Compound (**17**) δ_H(300.13 MHz; $CDCl_3$) 1.43 (3 H, d, *J* 6.97 Hz, 6′-H_3), 1.8 (2 H, m, 3-H_2), 2.24 (1 H, dd, *J* 9.32 and 15.1 Hz, 1-C*H*H), 2.39 (1 H, dd, *J* 2.82 and 15.1 Hz, 1-CH*H*), 2.1–2.60 (4 H, m, 2- and 4-H_2), 4.63 (1 H, ddd, *J* 1.95, 2.95, and 6.97 Hz, 5′-H), 4.63 (1 H, dd, *J* 2.82 and 9.32 Hz, 1′-H), 6.06 (1 H, dd, *J* 1.95 and 10.40 Hz, 3′-H), and 6.95 (1 H, dd, *J* 2.95 and 10.40 Hz, 4′-H); δ_C(75.47 MHz; $CDCl_3$) 15.76 (t, C-3), 17.63 (q, C-6′), 38.75 and 40.61 (t, C-2 and -4), 39.34 (t, 1-*C*H_2), 66.67 (d, C-5′), 70.45 (s, C-1), 74.48 (d, C-1′), 125.08 (d, C-3′), 151.79 (d, C-4′), and 195.92 (s, C-2′).

(c) 3-*Methylbut*-3-*en*-1-*ol derivatives.*

Compound (**19**) δ_H(300.13 MHz; $CDCl_3$) 1.69 and 1.72 (2 × 1.5 H, 2 s, 3-Me), 2.02 and 2.04 (2 × 1.5 H, 2 s, Ac), 2–2.3 (4 H, m, 2- and 4-H_2), 3.8 (2 H, m, 1-H_2), 3.9 (1 H, m, 5′-H), 4.17 (2 H, m, 6′-H_2), 4.60 (0.5 H, ddddd, *J* 2.12, 2.32, 2.40, 2.88, and 9.59 Hz, 1′-H), 4.62 (0.5 H, ddddd, *J* 2.12, 2.32, 2.40, 2.88, and 9.59 Hz, 1′-H), 5.08 (1 H, dddd, *J* 1.81, 2.32, 2.39, and 7.26 Hz, 4′-H), 5.77 (0.5 H, ddd, *J* 2.12, 2.35, and 10.35 Hz, 3′-H), 5.78 (0.5 H, ddd, *J* 2.12, 2.35, and 10.35 Hz, 3′-H), 5.85 (0.5 H, ddd, *J* 1.81, 2.88, and 10.35 Hz, 2′-H), and 5.86 (0.5 H, ddd, *J* 1.81, 2.88, and 10.35 Hz, 2′-H); δ_C(75.47 MHz; $CDCl_3$) 20.75 and 20.97 (q, *Me*CO), 29.75 and 31.50 (q, 3-Me), 44.60, 46.23, 46.53, and 47.32 (t, C-2 and -4), 59.42 (t, C-1), 62.69 and 64.61 (t, C-6′), 64.61 (d, C-4′), 69.45 (d, C-1′ and -5′), 72.15 (s, C-3), 123.69 (d, C-3′), 133.41 (d, C-2′), and 170.35 and 170.62 (s, Me*C*O).

Compound (**21**) δ_H(60 MHz; $CDCl_3$) 1.73 (3 H, s, 3-Me), 2.06 (3 H, s, Ac), 2.10 (3 H, s, Ac), 1.8–2.4 (4 H, m, 2- and 4-H_2), 3.95 (1 H, dt, *J* 4 and 6 Hz, 5′-H), 4.17 (2 H, d, *J* 4 Hz, 6′-H_2), 4.3 (2 H, dd, *J* 7 and 7 Hz, 1-H_2), 4.5 (1 H, m, 1′-H), 5.10 (1 H, ddd, *J* 1, 2, and 6 Hz, 4′-H), and 5.80 (2 H, m, 2′- and 3′-H).

Compound (**23**) δ_H(60 MHz; $CDCl_3$) 1.67 (3 H, s, 3-Me), 2.10 (6 H, s, Ac), 1.9–2.5 (4 H, m, 2- and 4-H_2), 3.4 (2 H, dd, *J* 7 and 7 Hz, 1-H_2), 3.9 (1 H, dt, *J* 4 and 6 Hz, 5′-H), 4.2 (2 H, m, 6′-H_2), 4.5 (1 H, m, 1′-H), 5.10 (1 H, dd, *J* 2 and 6 Hz, 4′-H), 5.80 (2 H, m, 2′- and 3′-H), 7.7 (3 H, m, ArH), and 8.0 (2 H, dd, *J* 2 and 8 Hz, ArH).

Compound (**24**) δ_H(60 MHz; $CDCl_3$) 1.26 (3 H, d, *J* 7 Hz, 6′-H_3), 1.7 (3 H, s, 3-Me), 2.00 (2 H, m, 2-H_2), 2.07 (3 H, s, Ac), 2.2 (2 H, dd, *J* 6 and 6 Hz, 4-H_2), 2.8 (1 H, m, OH), 4.0 (2 H, m, 5′- and 1-H), 4.4 (1 H, dd, *J* 7 and 7 Hz, 1-H), 4.5 (1 H, m, 1′-H), 4.83 (1 H, ddd, *J* 1, 2.5, and 6 Hz, 4′-H), and 5.76 (2 H, m, 2′- and 3′-H).

Compound (**26**) δ_H(60 MHz; $CDCl_3$) 1.21 (3 H, d, *J* 6.5 Hz, 6′-H_3), 1.76 (3 H, s, 3-Me), 2.06 (3 H, s, Ac), 1.9–2.4 (4 H, m, 2- and 4-H_2), 3.7 (1 H, dq, *J* 6.5 and 6.5 Hz, 5′-H), 4.4–4.6 (3 H, m, 1-H_2 and 1′-H), 4.8 (1 H, dd, *J* 2 and 6.5 Hz, 4′-H), 5.76 (2 H, m, 2′- and 3′-H), 7.4 (3 H, m, ArH), and 8.0 (2 H, m, ArH).

Compound (**27**) δ_H(60 MHz; $CDCl_3$) 1.21 (3 H, d, *J* 7 Hz, 6′-H_3), 1.63 (3 H, s, 3-Me), 2.2 (3 H, s, Ac), 2.0–2.6 (4 H, m, 2- and 4-H_2), 3.4 (2 H, m, 1-H_2), 3.8 (1 H, dq, *J* 6.5 and 7 Hz, 5′-H), 4.5 (1 H, m, 1′-H), 4.86 (1 H, dd, *J* 2 and 6.5 Hz, 4′-H), 5.8 (2 H, m, 2′- and 3′-H), 7.6 (3 H, m, ArH), and 7.96 (2 H, m, ArH).

Compound (**28**) δ_H(300 MHz; $CDCl_3$) 1.66 and 1.67 (2 × 1.5 H, s, 3-Me), 2.04 (3 H, s, Ac), 2.09 (3 H, s, Ac), 2.06–2.20 (3 H, m, 2- and 4-H), 2.28 (0.5 H, dd, *J* 6.68 and 14.62 Hz, 2-H), 2.46 (0.5 H, dd, *J* 2.82 and 15.34 Hz, 4-H), 4.2–4.3 (3 H, m, 1-H_2 and 6′-H), 4.40 (0.5 H, dd, *J* 6.93 and 11.92 Hz, 6′-H), 4.42 (0.5 H, dd, *J* 6.95 and 11.96 Hz, 6′-H), 4.68 (2 H, m, 1′- and 5′-H), 6.04 (0.5 H, dd, *J* 2.2 and 10.23 Hz, 3′-H), 6.17 (0.5 H, br d, *J* 10.23 Hz, 3′-H), and 6.92 (1 H, dd, *J* 3.10 and 10.23 Hz, 4′-H); δ_C(75.47 MHz; $CDCl_3$) 20.66 (q, *Me*CO), 20.90 (q, *Me*CO), 29.82 and 31.14 (q, 3-Me), 41.51, 42.91, and 43.31 (t, C-2 and -4), 60.28, 61.15, and 62.09 (t, C-1 and -6′), 69.29 (d, C-5′), 70.39 (s, C-3), 74.99 (d, C-1′), 127.50 (d, C-3′), 145.72 (d, C-4′), 170.5 and 170.83 (s, Me*C*O), and 194.36 (s, C-2′).

Compound (**29**) δ_H(300 MHz; $CDCl_3$) 1.46 (1.5 H, *J* 6.96 Hz, 6′-H_3), 1.47 (1.5 H, d, *J* 6.96 Hz, 6′-H_3), 1.68 (3 H, s, 3-Me), 2.051 (1.5 H, s, Ac), 2.055 (1.5 H, s, Ac), 2.10–2.20 (2 H, m, 2- and 4-H), 2.28 (1 H, dd, *J* 7.32 and 14.62 Hz, 2-H), 2.42 (0.5 H, dd, *J* 2.25 and 14.35 Hz, 4-H), 2.46 (0.5 H, dd, *J* 1.98 and 14.00 Hz, 4-H), 4.32 (2 H, m, 1-H_2), 4.57 (0.5 H, dd, *J* 2.25 and 5.85 Hz, 1′-H), 4.60 (0.5 H, dd, *J* 1.98 and 5.48 Hz, 1′-H), 4.63 (1 H, ddd, *J* 2.20, 2.92, and 6.96 Hz, 5′-H), 6.04 (0.5 H, dd, *J* 2.2 and 10.23 Hz, 3′-H), 6.042 (0.5 H, dd, *J* 2.2 and 10.23 Hz, 3′-H), and 6.95 (1 H, dd, *J* 2.92 and 10.23 Hz, 4′-H); δ_C(75.47 MHz; $CDCl_3$) 17.54 (q, C-6′), 20.83 (q, *Me*CO), 29.97 and 31.11 (q, 3-Me), 41.68, 42.68, and 43.31 (t, C-2 and -4), 61.15 (t, C-1), 66.93 (d, C-5′), 70.50 (s, C-3), 73.88 (d, C-1′), 125.0 (d, C-3′), 151.58 (d, C-4′), 170.5 (s, Me*C*O), and 192.5 (s, C-2′).

(d) 2-*Methylbut*-2-*ene derivatives.*

Compound (**31**) δ_H(300.13 MHz; $CDCl_3$) 1.065 [1.5 H, d, *J* 6.88 Hz, 3-Me(*S*)], 1.17 [1.5 H, d, *J* 6.97 Hz, 3-Me(*R*)], 1.73 [1.5 H, br d, *J* 1.10 Hz, 2-Me(*R*)], 1.76 [1.5 H, br d, *J* 1.01 Hz, 2-Me(*S*)], 2.079, 2.093, 2.098, and 2.104 (6 H, 4 s, Ac), 2.47

[0.5 H, dd, *J* 6.97 and 9.15 Hz, 3-H(*R*)], 2.58 [0.5 H, dd, *J* 6.88 and 8.88 Hz, 3-H(*S*)], 3.93 [0.5 H, ddd, *J* 3.61, 6.82, and 6.94 5′-H(*R*)], 3.98 [0.5 H, ddd, *J* 3.33, 6.36, and 6.48, 5′-H(*S*)], 4.12 (1 H, m, 1′-H), 4.22 (2 H, m, 6′-H_2), 4.76 (0.5 H, m, 1-H), 4.80 (1.5 H, m, 1-H), 5.12 (1 H, m, 4′-H), 5.76 [0.5 H, ddd, *J* 1.66, 2.77, and 10.54 Hz, 3′-H(*R*)], 5.83 [0.5 H, ddd, *J* 1.66, 3, and 10.54 Hz, 3′-H(*S*)], 5.96 [0.5 H, ddd, *J* 1.66, 3.5, and 10.54 Hz, 2′-H(*R*)], and 6.04 [0.5 H, ddd, *J* 1.19, 2.50, and 10.54 Hz, 2′-H(*S*)]; δ_C(75.47 MHz; $CDCl_3$) 15.70 and 16.38 (q, 3-Me), 18.94 and 20.00 (q, 2-Me), 20.75 and 21.01 (q, *Me*CO), 44.33 (d, C-3), 62.76 and 62.97 (t, C-6′), 65.05 (d, C-5′), 69.69 and 70.04 (d, C-4′), 73.37 and 74.24 (d, C-1′), 111.55 and 112.06 (t, C-1), 123.5 and 123.9 (d, C-3′), 132.02 and 131.51 (d, C-2′), 146.43 and 146.92 (s, C-2), and 170.35 and 170.72 (s, Me*C*O).

Compound (**32**) δ_H(300.13 MHz; $CDCl_3$) 1.09 [1.5 H, d, *J* 6.93 Hz, 3-Me(*R*)], 1.11 [1.5 H, d, *J* 5.46 Hz, 3-Me(*S*)], 1.18 [1.5 H, d, *J* 6.6 Hz, 6′-H_3(*S*)], 1.22 [1.5 H, d, *J* 6.36 Hz, 6′-H_3(*R*)], 1.71 [1.5 H, dd, *J* 0.95 and 1.42 Hz, 2-Me(*S*)], 1.74 [1.5 H, dd, *J* 0.95 and 1.65 Hz, 2-Me(*R*)], 2.04 (1.5 H, s, Ac), 2.06 (1.5 H, s, Ac), 2.39 [0.5 H, dd, *J* 5.46 and 6.81 Hz, 3-H(*S*)], 2.52 [0.5 H, dd, *J* 6.93 and 7.02 Hz, 3-H(*R*)], 3.86 [0.5 H, dq, *J* 5.18 and 6.36 Hz, 5′-H(*S*)], 3.90 [0.5 H, dq, *J* 4.95 and 6.60 Hz, 5′-H(*R*)], 4.01 [0.5 H, dddd, *J* 1.88 2.11, 2.11, and 6.81 Hz, 1′-H(*S*)], 4.04 [0.5 H, dddd, *J* 1.18, 1.88, 2.11, and 7.02 Hz, 1′-H(*R*)], 4.74 (0.5 H, m, 1-H), 4.78 (0.5 H, m, 1-H), 4.80 (1 H, m, 1-H), 4.88 (1 H, m, 4′-H), 5.74 [0.5 H, ddd, *J* 2.12, 3.30, and 10.60 Hz, 3′-H(*R*)], 5.81 [0.5 H, ddd, *J* 2.11, 3.54, and 10.60 Hz, 3′-H(*S*)], 5.92 [0.5 H, ddd, *J* 1.81, 2.11, and 10.6 Hz, 2′-H(*S*)], 6.00 [0.5 H, ddd, *J* 1.18, 2.36, and 10.60 Hz, 2′-H(*R*)]; δ_C(75.47 MHz; $CDCl_3$) 15.36 and 16.25 (q, 3-Me), 16.78 and 17.05 (q, C-6′), 19.56 and 20.18 (q, 2-Me), 21.14 (q, *Me*CO), 44.45 and 44.65 (t, C-3), 68.38 and 68.72 (d, C-5′), 69.63 and 69.73 (d, C-4′), 72.09 and 72.80 (d, C-1′), 111.34 and 111.60 (t, C-1), 123.05 and 123.46 (d, C-3′), 132.30 and 133.01 (d, C-2′), 147.01 and 147.11 (s, C-2), and 170.64 (Me*C*O).

Compound (**33a**) δ_H(300.13 MHz; $CDCl_3$) 0.97 (3 H, d, *J* 7.31 Hz, 3-Me), 1.64 (6 H, s, 1-H_3 and 2-Me), 2.09 (3 H, s, Ac), 2.80 (1 H, dd, *J* 2.20 and 7.31 Hz, 3-H), 4.28 (1 H, dd, *J* 3.74 and 12.12 Hz, 6′-H), 4.45 (1 H, dd, *J* 7.26 and 12.12 Hz, 6′-H), 4.7 (1 H, dddd, *J* 1.80, 3.74, 3.89, and 7.26 Hz, 5′-H), 4.96 (1 H, d, *J* 2.2 Hz, 1′-H), 6.18 (1 H, dd, *J* 1.80 and 10.50 Hz, 3′-H), and 6.92 (1 H, dd, *J* 3.89 and 10.50 Hz, 4′-H); δ_C(75.47 MHz; $CDCl_3$) 9.96 (q, 3-Me), 20.70 (q, *Me*CO), 29.22 and 31.71 (q, C-1 and 2-Me), 45.34 (d, C-3), 62.23 (t, C-6′), 70.54 (d, C-5′), 74.2 (s, C-2), 76.99 (d, C-1′), 128.24 (d, C-3′), 145.35 (d, C-4′), 170.50 (s, Me*C*O), and 195.06 (s, C-2′).

Compound (**33b**) δ_H(300.13 MHz; $CDCl_3$) 1.033 (3 H, d, *J* 6.94 Hz, 3-Me), 1.63 (6 H, s, 1-H_3 and 2-Me), 2.09 (3 H, s, Ac), 2.54 (1 H, dd, *J* 5.48 and 6.94 Hz, 3-H), 4.17 (1 H, dd, *J* 4.33 and 11.77 Hz, 6′-H), 4.36 (1 H, d, *J* 5.48 Hz, 1′-H), 4.42 (1 H, dd, *J* 7.28 and 11.77 Hz, 6′-H), 4.7 (1 H, dddd, *J* 1.47, 2.66, 4.33, and 7.28 Hz, 5′-H), 6.18 (1 H, dd, *J* 1.47 and 10.50 Hz, 4′-H), and 6.63 (1 H, dd, *J* 2.66 and 10.50 Hz, 3′-H); δ_C(75.47 MHz; $CDCl_3$) 13.77 (q, 3-Me), 20.69 (q, *Me*CO), 30.40 and 31.84 (q, C-1 and 2-Me), 43.39 (d, C-3), 63.88 (t, C-6′), 68.51 (d, C-5′), 73.72 (s, C-2), 80.47 (d, C-1′), 127.89 (d, C-3′), 145.05 (d, C-4′), 170.49 (s, Me*C*O), and 194.53 (s, C-2′).

Compound (**34a**) δ_H(300.13 MHz; $CDCl_3$) 0.97 (3 H, d, *J* 7.12 Hz, 3-Me), 1.44 (3 H, d, *J* 6.97 Hz, 6′-H_3), 1.63 and 1.64 (6 H, 2 s, 1-H_3 and 2-Me), 2.82 (1 H, dq, *J* 1.68 and 7.12 Hz, 3-H), 4.63 (1 H, ddd, *J* 2.70, 3.89, and 6.97 Hz, 5′-H), 4.83 (1 H, d, *J* 1.68 Hz, 1′-H), 6.05 (1 H, dd, *J* 2.70 and 10.41 Hz, 3′-H), and 6.98 (1 H, dd, *J* 3.89 and 10.41 Hz, 4′-H); δ_C(75.47 MHz; $CDCl_3$) 10.11 (q, 3-Me), 16.36 (q, C-6′), 29.43 and 31.84 (q, C-1 and 2-Me), 44.84 (d, C-3), 68.54 (d, C-5′), 74.53 (s, C-2), 75.16 (d, C-1′), 125.49 (d, C-3′), 151.71 (d, C-4′), and 195.96 (s, C-2′).

Compound (**34b**) δ_H(300.13 MHz; $CDCl_3$) 1.03 (3 H, d, *J* 7.12 Hz, 3-Me), 1.38 (3 H, d, *J* 6.52 Hz, 6′-H_3), 1.64 and 1.66 (6 H, 2 s, 1-H_3 and 2-Me), 2.58 (1 H, dq, *J* 5.42 and 7.12 Hz, 3-H), 4.27 (1 H, d, *J* 5.42 Hz, 1′-H), 4.68 (1 H, ddd, *J* 2.22, 2.56, and 6.52 Hz, 5′-H), 6.06 (1 H, dd, *J* 2.22 and 10.39 Hz, 3′-H), and 6.89 (1 H, dd, *J* 2.56 and 10.39 Hz, 4′-H); δ_C(75.47 MHz; $CDCl_3$) 13.83 (q, 3-Me), 19.06 (q, C-6′), 30.24 and 31.94 (q, C-1 and 2-Me), 43.34 (d, C-3), 66.04 (d, C-5′), 74.29 (s, C-2), 79.71 (d, C-1′), 125.49 (d, C-3′), 150.91 (d, C-4′), and 195.62 (s, C-2′).

(e) 1-*Methylcyclohexene C-glycosides.*

Compound (**36**) δ_H(300.13 MHz; C_6D_6), (6 H, m, cyclohexenyl), 1.70–1.76 (9 H, 1-Me and Ac), 2.04 (0.4 H, m, 6-H), 2.44 (0.6 H, m, 6-H), 4.0 (0.4 H, dd, *J* 4.27 and 11.11 Hz, 6′-H), 4.1 (0.6 H, dd, *J* 4.35 and 11.43 Hz, 6′-H), 4.2–4.35 (1.8 H, m, 1′-, 5′-, and 6′-H), 4.41 (0.6 H, dd, *J* 7.37 and 11.43 Hz, 6′-H), 4.5 (0.6 H, dddd, *J* 1.87, 2.23, 2.54, and 5.15 Hz, 1′-H), 4.98 (0.4 H, dddd, *J* 0.91, 2.33, 2.39, and 4.19 Hz, 4′-H), 5.09 (0.6 H, dddd, *J* 0.95, 2.23, 3.40, and 4.40 Hz, 4′-H), 5.51 (0.6 H, m, 2-H), 5.58 (0.4 H, m, 2-H), 5.58 (0.4 H, ddd, *J* 0.91, 1.89, and 10.51 Hz, 2′-H), 5.74 (0.6 H, ddd, *J* 0.95, 1.87, and 10.43 Hz, 2′-H), 5.82 (0.6 H, ddd, *J* 2.54, 4.40, and 10.43 Hz, 3′-H), and 5.85 (0.4 H, ddd, *J* 2.51, 4.19, and 10.51 Hz, 3′-H).

Compound (**37a**) δ_H(300.13 MHz; C_6D_6) 1.06 [0.75 H, d, *J* 6.55 Hz, 6′-H_3(*R*)], 1.14 [2.25 H, d, *J* 5.44 Hz, 6′-H_3(*S*)], 1.4–2.0 (6.25 H, m, cyclohexenyl), 1.65 (3 H, s, 1-Me), 1.73 and 1.75 (0.75 H and 2.25 H, 2 s, Ac), 2.5 [0.75 H, m, 6-H(*S*)], 4.10 [0.25 H, dd, *J* 2.21 and 6.55 Hz, 5′-H(*R*)], 4.17 [0.75 H, dd, *J* 3.02 and 5.44 Hz, 5′-H(*S*)], 4.26 [0.25 H, dddd, *J* 1.91, 2.12, 2.12, and 4.83 Hz, 1′-H(*R*)], 4.43 [0.75 H, dddd, *J* 1.82, 2.42, 2.42, and 4.53 Hz, 1′-H(*S*)], 4.84 [0.25 H, ddd, *J* 2.21, 2.42, and 4.83 Hz, 4′-H(*R*)], 4.90 [0.75 H, ddd, *J* 2.42, 3.02, and 4.53 Hz, 4′-H(*S*)], 5.52 [0.75 H, m, 2-H(*S*)], 5.61 [0.25 H, dd, *J* 1.91 and 10.27 Hz, 2′-H(*R*)], 5.61 [0.25 H, m, 2-H(*R*)], 5.78 [0.75 H, dd, *J* 1.82, and 10.28 Hz, 2′-H(*S*)], 5.88 [0.75 H, ddd, *J* 2.42, 2.42, and 10.28 Hz, 3′-H(*S*)], and 5.90 [0.25 H, ddd, *J* 2.12, 2.42, and 10.27 Hz, 3′-H(*R*)].

Compound (**37b**) δ_H(300.13 MHz; C_6D_6) 1.24 [1.5 H, d, *J* 6.34 Hz, 6′-H_3(*R*)], 1.31 [1.5 H, d, *J* 6.34 Hz, 6′-H_3(*S*)], 1.4–2.1 (6.5 H, m, cyclohexenyl), 1.58 [1.5 H, s, 1-Me(*R*)], 1.70 and 1.72 (3 H, 2 s, Ac), 1.79 [1.5 H, s, 1-Me(*S*)], 2.5 [0.5 H, m, 6-H(*R*)], 3.59 (0.5 H, dd, *J* 6.34 and 8.46 Hz, 5′-H(*S*)], 3.70 [0.5 H, dd, *J* 6.34 and 8.76 Hz, 5′-H(*R*)], 4.32 [0.5 H, dddd, *J* 1.79, 2.72, 3.02, and 5.42 Hz, 1′-H(*S*)], 4.46 [0.5 H, dddd, *J* 1.79, 2.72, 3.32, and 4.94 Hz, 1′-H(*R*)], 5.33 [0.5 H, dddd, *J* 1.82, 1.82, 3.02, and 8.46 Hz, 4′-H(*S*)], 5.36 [0.5 H, dddd, *J* 1.82, 1.82, 3.32, and 8.76 Hz, 4′-H(*R*)], 5.48 [0.5 H, ddd, *J* 1.79, 1.82, and 10.28 Hz, 2′-H(*S*)], 5.54 [0.5 H, m, 2-H(*R*)], 5.61 [0.5 H, m, 2-H(*S*)], 5.66 [0.5 H, ddd, *J* 1.79, 1.82, and 10.28 Hz, 2′-H(*R*)], 5.84 [0.5 H, ddd, *J* 1.82, 2.72, and 10.28 Hz, 3′-H(*S*)], and 5.86 [0.5 H, ddd, *J* 1.82, 2.72, and 10.28 Hz, 3′-H(*R*)].

Compound (**38**) δ_H(300.13 MHz; $CDCl_3$) 1.4–1.75 (9 H, m, 3-, 4-, and 5-H_2, and 1-Me), 2.05 and 2.08 (2 × 1.5 H, 2 s, Ac), 2.84 and 2.95 (each 0.5 H, m, together 6-H), 4.14 (0.5 H, dd, *J* 3.80 and 11.70 Hz, 6′-H), 4.29 (0.5 H, dd, *J* 4.02 and 11.79 Hz, 6′-H), 4.33 (0.5 H, d, *J* 2.96 Hz, 1′-H), 4.53 (0.5 H, dd, *J* 6.58 and 11.70 Hz, 6′-H), 4.55 (0.5 H, dd, *J* 5.85 and 11.79 Hz, 6′-H), 4.70 (0.5 H, d, *J* 3.4 Hz, 1′-H), 4.71 (0.5 H, dddd, *J* 2.07, 4.0, 4.02, and 5.85 Hz, 5′-H), 4.78 (0.5 H, dddd, *J* 1.73, 3.62, 3.80, and 6.58 Hz, 5′-H), 5.54 (0.5 H, m, 3-H), 5.63 (0.5 H, m, 3-H), 6.21 (0.5 H, dd, *J* 1.73 and 10.31, 3′-H), 6.26 (0.5 H, dd, *J* 2.07 and 10.33 Hz, 3′-H), 6.92 (0.5 H, dd, *J* 3.62 and 10.38 Hz, 4′-H), and 6.97 (0.5 H, dd, *J* 4.00 and 10.33 Hz, 4′-H); δ_C(75.47 MHz; $CDCl_3$) 20.81 (s, *Me*CO), 22.69, 24.15, 25.27, and 25.75 (t, C-4 and -5), 26.86 (q, 1-Me), 28.13 and 32.23 (t, C-3), 39.12 and 40.60 (d, C-6), 62.47 and 63.27 (t, C-6′), 70.36 and 70.83 (d, C-5′), 77.42 and 80.60 (d, C-1′), 125.78 and 126.0 (d, C-2), 128.10 and 128.30 (d, C-3′), 145.18 and 145.99 (d, C-4′), 170.55 (s, Me*C*O), and 196.10 (s, C-2′).

Compound (**39**) δ_H(300.13 MHz; $CDCl_3$) 1.44 (1.5 H, d, *J* 6.95 Hz, 6′-H_3), 1.45 (1.5 H, d, *J* 6.24 Hz, 6′-H_3), 1.56–1.8 (7 H, m, 4- and 5-Hz, and 1-Me), 1.96–2.1 (2 H, m, 3-H_2), 2.85 (0.5 H, m, 6-H), 2.97 (0.5 H, m, 6-H), 4.20 (0.5 H, d, *J* 2.92 Hz, 1′-H), 4.58

(0.5 H, d, *J* 3.28 Hz, 1'-H), 4.65 (0.5 H, ddd, *J* 1.75, 3.61, and 6.95 Hz, 5'-H), 4.73 (0.5 H, ddd, *J* 1.87, 2.75, and 6.24 Hz, 5'-H), 5.54 (0.5 H, m, 2-H), 5.66 (0.5 H, m, 2-H), 6.06 (0.5 H, dd, *J* 1.75 and 10.23 Hz, 3'-H), 6.10 (0.5 H, dd, *J* 1.87 and 10.23 Hz, 3'-H), 6.96 (0.5 H, dd, *J* 3.61 and 10.23 Hz, 4'-H), and 7.02 (0.5 H, dd, *J* 2.75 and 10.23 Hz, 4'-H); δ_C(75.47 MHz; $CDCl_3$) 17.19 and 17.84 (q, C-6'), 21.32, 21.60, 22.78, and 23.12 (t, C-4 and -5), 23.55 and 25.35 (q, 1-Me), 28.25 and 32.32 (t, C-3), 38.60 and 40.07 (d, C-6), 67.99 and 68.23 (d, C-5'), 75.12 and 79.13 (d, C-1'), 125.26 and 126.20 (d, C-2), 125.47 and 125.76 (d, C-3'), 132.89 and 132.63 (s, C-1), 151.52 and 152.27 (d, C-4'), and 196.37 (s, C-2').

(f) 2,3-*Dimethylbut-2-ene* C-*glycosides*.

Compound (**41a**) δ_H(300.13 MHz; $CDCl_3$) 1.07 and 1.12 (6 H, 2 s, 3-Me_2), 1.79 (3 H, dd, *J* 0.76 and 1.53 Hz, 2-Me), 2.07 and 2.08 (6 H, 2 s, Ac), 4.07 (1 H, dd, *J* 4.83 and 11.18 Hz, 6'-H), 4.15 (2 H, m, 1'- and 5'-H), 4.34 (1 H, dd, *J* 7.52 and 11.18 Hz, 6'-H), 4.83 (1 H, dd, *J* 0.76 and 1.51 Hz, 1-H), 4.86 (1 H, dd, *J* 1.51 and 1.53 Hz, 1-H), 4.90 (1 H, dddd, *J* 0.76, 2.12, 2.41, and 4.84 Hz, 4'-H), 5.87 (1 H, dddd, *J* 0.71, 2.12, 4.84, and 10.27 Hz, 3'-H), and 6.01 (1 H, ddd, *J* 0.76, 1.81, and 10.27 Hz, 2'-H).

Compound (**41b**) δ_H(60 MHz; $CDCl_3$) 1.0 and 1.1 (6 H, 2 s, 3-Me_2), 1.76 (3 H, s, 2-Me), 2.07 (6 H, s, Ac), 3.6 (1 H, dt, *J* 4 and 9.5 Hz, 5'-H), 4.0 (1 H, m, 1'-H), 4.15 (2 H, d, *J* 4 Hz, 6'-H_2), 4.8 (2 H, m, 1-H_2), 5.2 (1 H, dd, *J* 3 and 9.5 Hz, 4'-H), and 5.76 (2 H, m, 2'- and 3'-H).

Compound (**41c**) δ_H(60 MHz; $CDCl_3$) 1.08 and 1.13 (6 H, 2 s, 3-Me_2), 1.57 and 1.63 (6 H, 2 s, 1-H_3 and 2-Me), 2.07 and 2.13 (6 H, 2 s, Ac), 3.83 (1 H, dt, *J* 4 and 7 Hz, 5'-H), 4.16 (2 H, d, *J* 5 Hz, 6'-H_2), 4.36 (1 H, m, 1'-H), 5.05 (1 H, dd, *J* 2 and 7 Hz, 4'-H), and 5.76 (2 H, m, 2'- and 3'-H).

Compound (**42a**) δ_H(300.13 MHz; $CDCl_3$) 1.07 and 1.12 (6 H, 2 s, 3-Me_2), 1.24 (3 H, d, *J* 6.95 Hz, 6'-H_3), 1.78 (3 H, dd, *J* 0.75 and 1.36 Hz, 2-Me), 2.06 (3 H, s, Ac), 4.1 (2 H, m, 1'- and 5'-H), 4.75 (1 H, dddd, *J* 0.66, 2.12, 2.12, and 4.83 Hz, 4'-H), 4.83 (1 H, dd, *J* 0.75 and 1.82 Hz, 1-H), 4.86 (1 H, dd, *J* 1.36 and 1.82 Hz, 1-H), 5.87 (1 H, dddd, *J* 0.91, 2.12, 4.83, and 10.57 Hz, 3'-H), and 6.01 (1 H, ddd, *J* 0.66, 1.51, and 10.57 Hz, 2'-H).

Compound (**42b**) δ_H(60 MHz; $CDCl_3$) 1.13 and 1.20 (6 H, 2 s, 3-Me_2), 1.24 (3 H, d, *J* 6.5 Hz, 6'-H_3), 1.8 (3 H, s, 2 × Me), 2.1 (3 H, s, Ac), 3.55 (1 H, dq, *J* 6.5 and 9.5 Hz, 5'-H), 4.1 (1 H, m, 1'-H), 4.8 (2 H, m, 1-H), 5.06 (1 H, dd, *J* 4 and 9.5 Hz, 4'-H), and 5.83 (2 H, m, 2'- and 3'-H).

(g) *Hex*-1-*ene* C-*glycosides*.

Compound (**44a**) δ_H(60 MHz; $CDCl_3$) 0.95 (3 H, m, 6-H_3), 1.2–1.95 (8 H, m, 1-, 3-, 4-, and 5-H_2), 2.23 (6 H, s, Ac), 3.80–4.4 (5 H, m, 2-, 1'-, 5'-H, and 6'-H_2), 5.2 (1 H, dd, *J* 2 and 6 Hz, 4'-H), and 5.9 (2 H, m, 2'- and 3'-H).

Compound (**44b**) δ_H(60 MHz; $CDCl_3$) 0.93 (3 H, m, CH_2*Me*), 1.3–1.7 (2 H, m, hexenyl CH_2), 1.9–2.6 (4 H, m, 2 × hexenyl CH_2), 2.1 (6 H, s, Ac), 4.23 (4 H, m, 1'- and 5'-H, and 6'-H_2), 5.2 (1 H, ddd, *J* 1, 2, and 6 Hz, 4'-H), 5.5 (2 H, m, hexenyl CH=CH), and 5.9 (2 H, m, 2'- and 3'-H).

Compound (**45a**) δ_H(60 MHz; $CDCl_3$) 1.0 (3 H, m, CH_2*Me*), 1.24 (1 H, d, *J* 6.5 Hz, 6'-H), 1.6–2.0 (8 H, m, 4 × hexenyl CH_2), 2.1 (3 H, s, Ac), 3.8–4.4 (3 H, m, 2-, 1'-, and 5'-H), 4.9 (1 H, ddd, *J* 1, 4, and 6.5 Hz, 4'-H), and 5.83 (2 H, m, 2'- and 3'-H).

Compound (**45b**) δ_H(60 MHz; $CDCl_3$) 0.9 (3 H, m, CH_2*Me*), 1.1 (1 H, d, *J* 6.5 Hz, 6'-H), 1.2–1.8 (2 H, m, hexenyl CH_2), 2.07 (3 H, s, Ac), 2.0–2.7 (4 H, m, 2 × hexenyl CH_2), 3.83–4.4 (2 H, m, 1'- and 5'-H), 4.87 (1 H, ddd, *J* 1, 4, and 6 Hz, 4'-H), 5.26 (2 H, m, hexenyl CH=CH), and 5.80 (2 H, m, 2'- and 3'-H).

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