Stereocontrolled synthesis of glucosidic damascenone precursors

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A stereocontrolled synthesis of optically active β-D-glucopyranosides **7**–**10** and **11**–**14**, glucosidic damascenone precursors, was accomplished utilizing an asymmetric transfer hydrogenation to α,β-acetylenic ketones catalyzed by chiral ruthenium complexes as the key step.

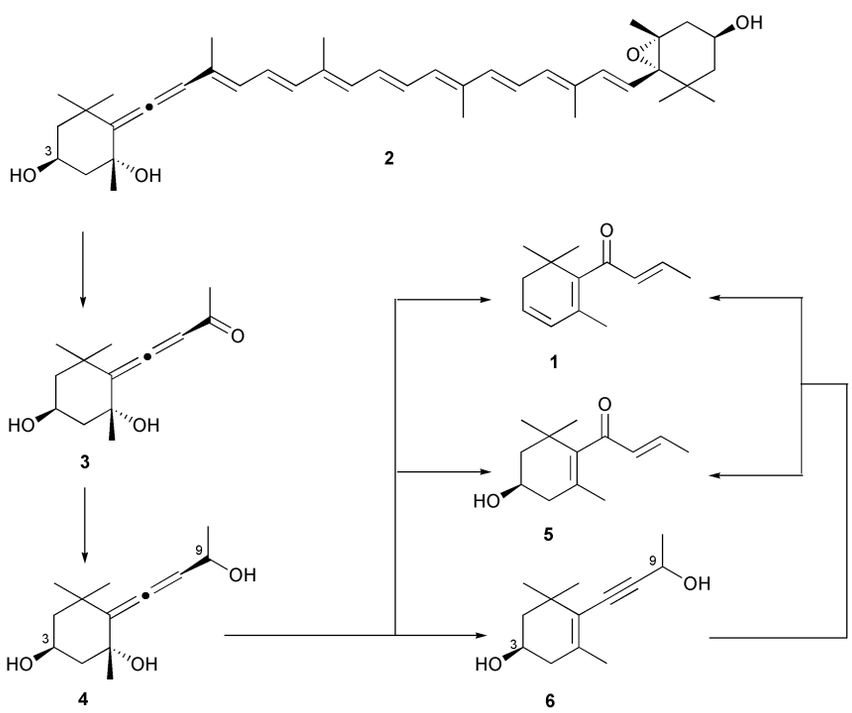
Introduction

Damascenone **1** (Scheme 1) is one of the most important flavor compounds, first identified in Bulgarian rose (*Rosa damascena*) oil in 1970.[1] Since then, **1** has also been identified[2] in various types of plant tissues and beverages. It is believed[3] to be formed in nature from the hydrolytic breakdown of complex secondary metabolites derived from carotenoids such as neoxanthin **2**. It was described in the literature[4] that **1** can be formed *in vivo*, as shown in Scheme 1. However, the direct progenitors of **1** are not completely clarified. The β-D-glucopyranosides of C_{13}-acetylenic diol **6** and -allenic triol **4** have been isolated[5–9] as glucosidic aroma precursors. The role of the glucosyl moiety in these glucosides is recognized as stabilization of the hydroxy group against hydrolysis. In intact plants, not only the position of the glucosyl moiety but also the stereochemistries of the hydroxy groups in these glucosides are considered to have an influence on the behavior against enzymatic hydrolysis. Their C-3 hydroxy groups are considered to be of β-configuration, because most xantophylls have β-configuration for C-3 hydroxy groups. However, their stereochemistries at C-9 have not been confirmed yet. In order to clarify their roles as aroma precursors in plants, both the confirmation of their stereochemistries including absolute configurations and the preparation of a diastereomerically pure samples are required. In a previous communication,[10] we reported stereocontrolled synthesis of (3*R*,9*S*)- and (3*R*,9*R*)-9-*O*-β-D-glucopyranosides **7** and **8** as well as the corresponding 3-*O*-β-D-glucopyranosides **9** and **10** (Fig. 1) utilizing an asymmetric transfer hydrogenation[11] to α,β-acetylenic ketones catalyzed by chiral ruthenium complexes as the key step. Afterwards, conversion of these acetylenic diol-glucosides into the corresponding allenic triol glucosides **11**–**14** was accomplished. In the present paper, we describe their details including relevant work.

Results and discussion

Synthesis of acetylenic diol-glucosides 7–10

Although the 9-*O*-β-glucoside of acetylenic diol **6** has been prepared[12] as a diastereomeric mixture, there has been so far reported no stereocontrolled synthesis for the optically active



Scheme 1

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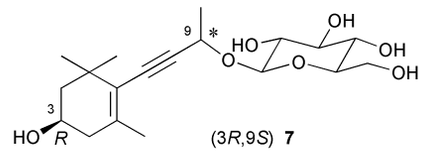
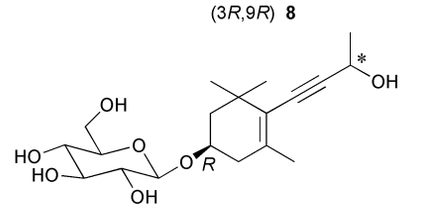


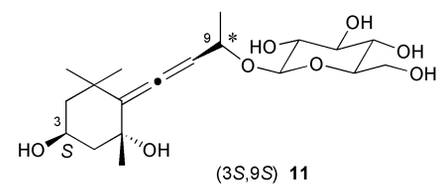
(3*R*,9*S*) **7**

(3*R*,9*R*) **8**



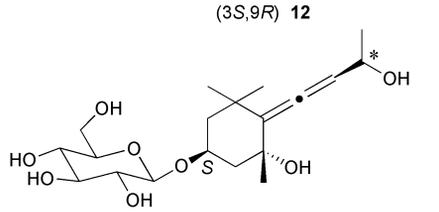
(3*R*,9*S*) **9**

(3*R*,9*R*) **10**



(3*S*,9*S*) **11**

(3*S*,9*R*) **12**



(3*S*,9*S*) **13**

(3*S*,9*R*) **14**

Fig. 1

glucoside. In order to synthesize diastereomeric pure glucosides **7**–**10**, diastereomeric pure alcohols **21a**,**b** and **24a**,**b**, key intermediates, were prepared applying Ru^{II}-promoted asymmetric transfer hydrogenation[11] to α,β-acetylenic ketones **19** and **17** as shown in Scheme 2.

The known (3*R*)-3-hydroxy terminal alkyne **15**,[13] prepared (66%) from (4*R*,6*R*)-4-hydroxy-2,2,6-trimethylcyclohexanone,[14] was silylated (99%) to give the *tert*-butyldimethylsilyl (TBS) ether **16**. Reaction of the lithium derivative prepared from *n*-BuLi and **16** with acetaldehyde, followed by oxidation with MnO_2 provided α,β-acetylenic ketone **17** (88%), which was deprotected (99%) and then acetylated (96%) to give the acetate **19**. Asymmetric transfer hydrogenation[11] of α,β-acetylenic ketones **17** and **19** using Ru^{II} catalysts **20a** or **20b**[15] and 2-propanol as the hydrogen donor quantitatively afforded the diastereomeric pure (>98% de) alcohol **21a** or **21b** as well as **24a** or **24b**, respectively. The absolute stereochemistries at C-9 of these alcohols were determined by the modified Mosher's method.[16] The (*S*)- and (*R*)-MTPA [α-methoxy-α-(trifluoromethyl)phenyl acetic acid] esters of **21a** and **24a** obtained by use of (*S,S*)-**20a** were prepared. The positive $\Delta\delta$ values of $\delta S - \delta R$ were observed on all protons except for the 9-methyl protons (see Experimental section), indicating that **21a** and **24a** had *S* configuration for C-9. In the case of TBS ether **17**, the (*S*)- or (*R*)-alcohol **24a** or **24b** could be also prepared *via in situ* formation of **20a** or **20b** by mixing $[RuCl_2(p\text{-cymene})]_2$, (1*S*,2*S*)- or (1*R*,2*R*)-*N*-(*p*-toluenesulfonyl)-1,2-diphenylethylethylenediamine (TsDPEN) and KOH in 2-propanol (Ru:diamine:KOH=1:1:2.5).[11] The compounds **24a** and **24b** were transformed into **27a** (99%) and **27b** (93%), precursors of the desired glucosides, by acetylation and subsequent desilylation.

Next, the glucosidation of the alcohol **21a** was investigated to prepare the (3*R*,9*S*)-9-*O*-β-D-glucopyranoside **7** (Scheme 3). We have previously reported[17] that the reaction of 3-hydroxy-β-ionone with tetra-*O*-benzoyl-α-D-glucopyranosyl bromide **37** using silver triflate as an activator and *N*,*N*-tetramethylurea as a proton acceptor gave the ortho ester, whereas the desired β-glucoside was obtained in the absence of *N*,*N*-tetramethylurea. In the case of the alcohol **21a**, reaction with **37** using silver triflate in the absence of *N*,*N*-tetramethylurea provided complex mixtures, probably due to its instability against acidic conditions, whereas the ortho ester **28** (61%) was obtained in the presence of *N*,*N*-tetramethylurea as reported[17] previously. β-Glucosidation of **21a** was achieved (95%) by use of tetra-*O*-pivaloyl (Piv)-α-D-glucopyranosyl bromide **38**[18] possessing a sterically bulky acyl group at C-2 position as a glucosyl donor and silver triflate as an activator in the presence of *N*,*N*-tetramethylurea. The acyl groups of **29** were removed under basic conditions to give the free alcohol **7** (98%). Since natural glucosides were isolated[5,6] as pentaacetates, the pentaol **7** was then acetylated to provide the pentaacetate **30** (95%).

(3*R*,9*R*)-9-*O*-, (3*R*,9*S*)-3-*O*- and (3*R*,9*R*)-3-*O*-β-D-glucopyranosides **31** (93%), **33** (81%) and **35** (79%) were also prepared (Scheme 3) by a similar glucosidation of alcohols **21b**, **24a** and **24b**, respectively. Deacylation (**8**: 99%; **9**: 93%; **10**: 99%) of these glucosides followed by acetylation afforded pentaacetates **32** (quant.), **34** (82%) and **36** (91%), respectively.

^1H and ^{13}C NMR spectra of 9-*O*-glucosides **30** and **32** were similar to each other but indicated characteristic differences around C-9 as shown in the Table 1. Spectral data of the (9*S*)-glucoside **30** were identical with those of the 9-*O*-glucoside isolated[5] from Riesling wine except for the chemical shift of the methyl carbon at C-9 (this[5] is probably misprint), while those of the (9*R*)-glucoside **32** were in accordance with those of the 9-*O*-gluccoside isolated[6] from rose petals. On the other hand, comparison of both ^1H and ^{13}C NMR spectra for 3-*O*-glucosides **34** and **36** showed no difference, but their optical rotation data (Table 1) and CD spectra (Fig. 2) were quite different.

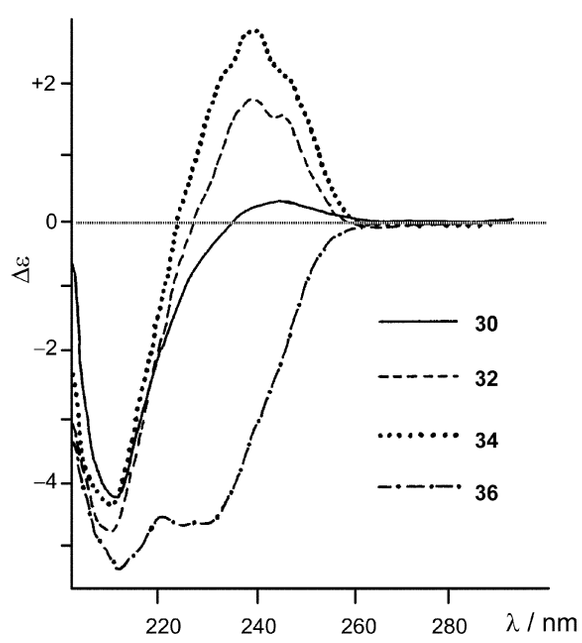


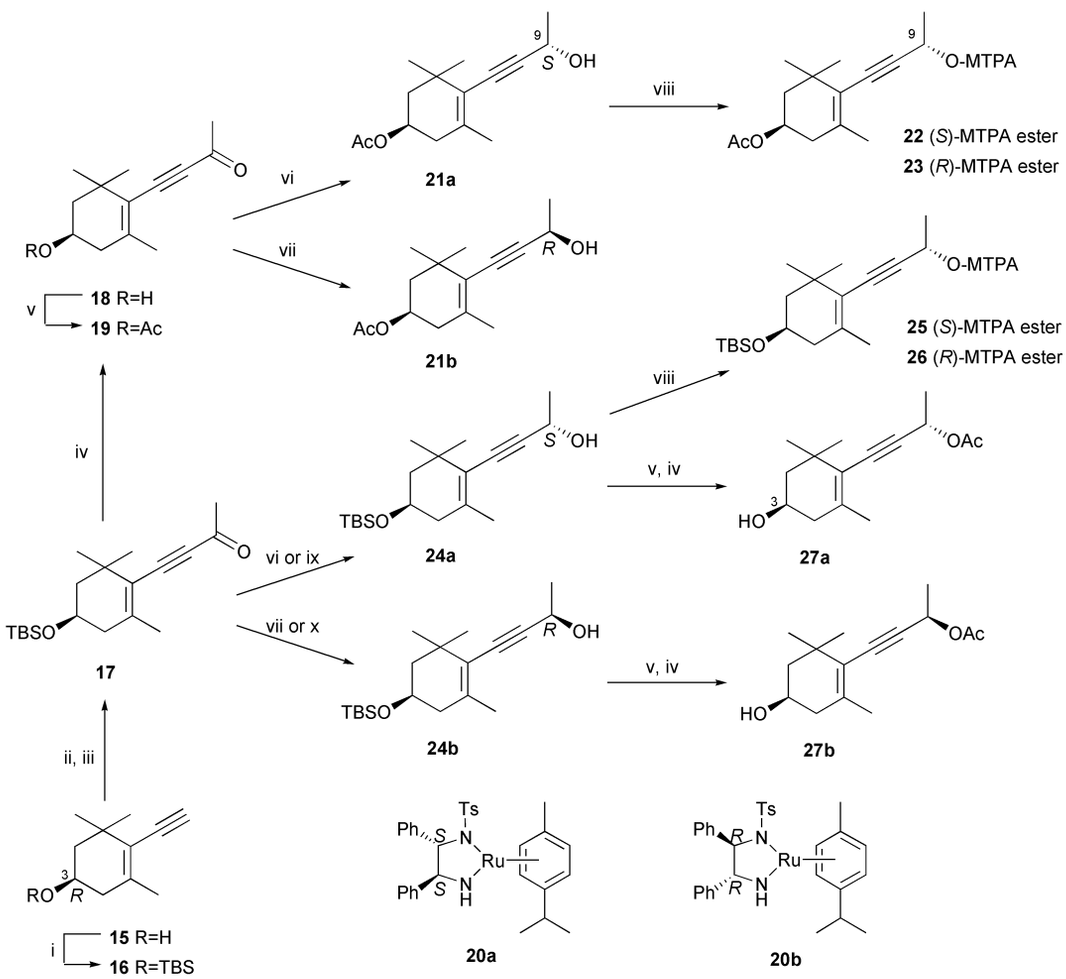
Fig. 2 CD spectra in MeOH of acetylenic diol-glucoside pentaacetates **30**, **32**, **34** and **36**.

Although the ^1H NMR data for the 3-*O*-glucosides isolated[5] from Riesling wine were in good agreement with those of **34** and **36**, the stereochemistry at C-9 is not confirmed yet as its chiroptical data were not reported.

In order to facilitate the confirmation of the stereochemistries of natural glucosides, separation of synthetic four isomers by HPLC was investigated. As a result, simultaneous separation using a chiral column (CHIRALPAK AD-H; DAICEL) was completely achieved as shown in Fig. 3.

Table 1 Characteristic spectral data for acetylenic diol-glucoside pentaacetates

		9-*O*-Glucosides				3-*O*-Glucosides		
		30 (3*R*,9*S*)	**32** (3*R*,9*R*)	Glucoside from Riesling wine[5]	Glucoside from rose petals[6]	**34** (3*R*,9*S*)	**36** (3*R*,9*R*)	Glucoside from Riesling wine[5]
^{1}H NMR	3-H	5.03	5.01	5.03	5.00	3.92	3.92	3.92
($CDCl_3$)	9-H	4.80	4.74	4.80	4.74	5.60	5.59	5.60
δ: ppm	9-Me	1.48	1.51	1.48	1.51	1.52	1.52	1.53
	1′-H	4.88	4.86	4.89	4.86	4.62	4.62	4.61
^{13}C NMR	C3	67.74	67.77	67.72	67.8	73.07	73.07	—
($CDCl_3$)	C9	64.30	67.52	64.29	67.5	61.10	61.10	—
δ: ppm	9-Me	22.35	23.12	27.0	23.1	21.67	21.68	—
	C1′	97.78	98.88	97.79	98.9	99.61	99.60	—
$[\alpha]_D$ (MeOH)		−62.1	−6.9	−32.6	—	−108.6	+14.6	—

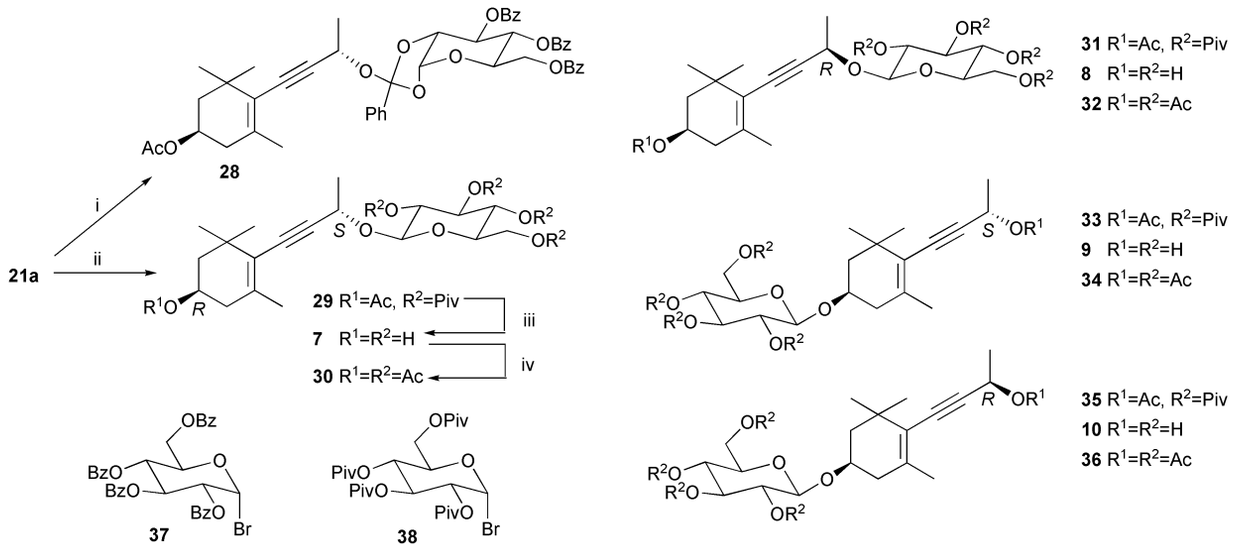


Scheme 2 *Reagents*: i, TBSCl, DMAP, Et_3N; ii, *n*-BuLi then CH_3CHO; iii, MnO_2; iv, HF; v, Ac_2O, Py; vi, cat. (*S*,*S*)-**20a**, 2-PrOH; vii, cat. (*R*,*R*)-**20b**, 2-PrOH; viii, (*S*)- or (*R*)-MTPA, EDC, DMAP; ix, cat. $[RuCl_2(p\text{-cymene})]_2$, cat. (*S*,*S*)-TsDPEN, cat. KOH, 2-PrOH; x, cat. $[RuCl_2(p\text{-cymene})]_2$, cat. (*R*,*R*)-TsDPEN, cat. KOH, 2-PrOH.

Synthesis of allenic triol-glucosides 11–14

We have recently synthesized[9] a diastereoisomeric mixture of allenic triol-9-*O*-glucosides **11** and **12** *via* the direct glucosidation (Scheme 4) of allenic diol **39** derived from grasshopper ketone **3**,[19] in order to identify natural allenic triol-glucosides in rose petals. However, the glucosidation of **39** under the same conditions as those (Scheme 3) described for the acetylenic alcohol **21a** unfortunately resulted in a complex mixture involving only a trace amount of glucoside **40**. It was proposed that the allenic alcohol **39** was extremely unstable even in the slightly acidic medium. Thus, acetylenic diol-glucoside derivatives depicted in Scheme 3 were converted into the corresponding allenic triol-glucosides **11**–**14** as shown in Scheme 4, according to the synthetic procedure[19] for grasshopper ketone.

Epoxidation of (9*S*)-9-*O*-glucoside **29** with MCPBA provided a mixture of *anti*-epoxide **41a** (37%) and *syn*-one **41b** (49%), which was cleanly separated by low-pressure liquid chromatography. The relative configurations between the acetoxy and epoxy groups in the two isomers were confirmed from chemical shifts for 2-Hs (**41a**: 2_{ax}-H δ 1.39, 2_{eq}-H δ 1.63; **41b**: 2_{ax}-H δ 1.55, 2_{eq}-H δ 1.41) in both isomers on the basis of the empirical rule.[20] Treatment of *anti*-epoxide **41a** with excess amounts of DIBAL-H gave a crude product, which was acetylated and purified by silica gel column chromatography to afford the pentaacetate **42** in 29% for 2 steps. The acyl groups of **42** were removed under basic conditions to provide the free alcohol **11** in 90%. The stereochemistries of aglycone parts in **42** and **11** were chemically proved by hydrolysis of **11** with β-glucosidase followed by MnO_2-oxidation affording



Scheme 3 *Reagents*: i, **37**, AgOTf, $Me_2NC(O)NMe_2$; ii, **38**, AgOTf, $Me_2NC(O)NMe_2$; iii, LiOH–MeOH; iv, Ac_2O, Py.

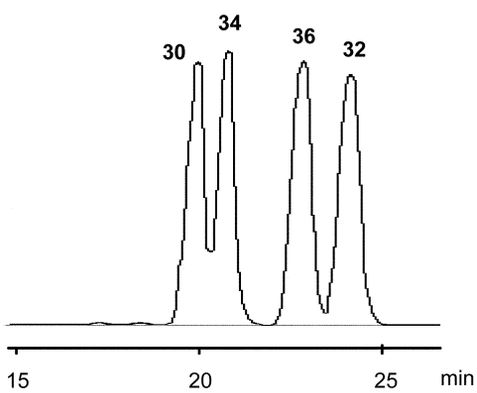


Fig. 3 HPLC elution profile of a mixture of acetylenic diol-glucoside pentaacetates **30**, **32**, **34** and **36**. Column: CHIRALPAK AD-H 0.46 × 25 cm; eluent: 2-PrOH–hexane (5:95); flow rate: 0.7 ml min^{-1}; UV detection: 250 nm.

grasshopper ketone **3**, whose ^{1}H NMR data were identical with those reported.[19] Thus, it was found that the α-hydroxyallene moiety in **11** was formed *via* the same pathway (S_N2'hydride reduction of ethynylepoxy group in **41a**) as reported[19] for the preparation of grasshopper ketone **3**.

(3*S*,9*R*)-9-*O*-, (3*S*,9*S*)-3-*O*- and (3*S*,9*R*)-3-*O*-β-glucoside **12**–**14** were also prepared by a similar method as shown in Scheme 4. In the case of preparation of **13**, the pentabenzoylated epoxide **47a** was employed, because epoxy-isomers derived from tetrapivalate **33** could not be separated. The stereochemistries of aglycone parts in these three glucosides were also chemically confirmed by transformation into grasshopper ketone **3**.

The allenic triol-9-*O*-glucosides were previously isolated from the leaves of *Lycium halimifolium Mill.*[7] as its pentaacetate and from the leaves of *Premna subscandens*[8] as a free alcohol. However, the absolute stereochemistry of aglycone parts in these glucosides has not been completely confirmed. ^{1}H NMR spectra of the pentaacetylated glucoside isolated from *Lycium halimifolium Mill.*[7] were identical with those of the synthetic (3*S*,9*R*)-**45**, while ^{1}H and ^{13}C NMR spectra of the glucoside isolated from *Premna subscandens*[8] were in accordance with those of (3*S*,9*R*)-**12**. On the other hand, we have recently identified[9] both (3*S*,9*S*)- and (3*S*,9*R*)-9-*O*-glucosides **11** and **12** in rose flowers, based on their synthesis (diastereoisomeric mixture; as described before) and the HPLC-MS analytical data. Therefore, its was found that these natural glucosides have the same configuration as the allenic part of proposed parent carotenoid, neoxanthin (Scheme 1).

The allenic triol-3-*O*-glucosides have not been isolated; however, it is considered that these are distributed in nature because the 3-*O*-glucoside of grasshopper ketone **3** was found[21] in several plants. In the case of allenic triol-3-*O*-glucosides, characteristic differences between both free alcohols **13** and **14** and their pentaacetates **48** and **51** are not observed in their ^{1}H and ^{13}C NMR spectra. Thus, separation of these two 3-*O*-glucosides **13** and **14** together with 9-*O*-glucosides **11** and **12** by HPLC was investigated. Since these four glucosides **11**–**14** did not show a remarkable UV absorption, they are detected as pentabenzoates **43**, **46**, **49** and **52**, respectively (Scheme 4). Simultaneous separation using a chiral column (CHIRALPAK AD-H; DAICEL) was performed as shown in Fig. 4.

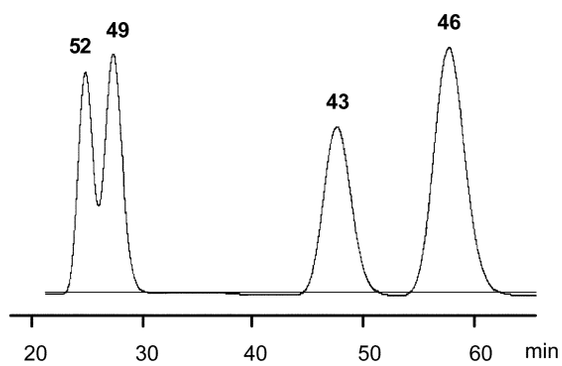
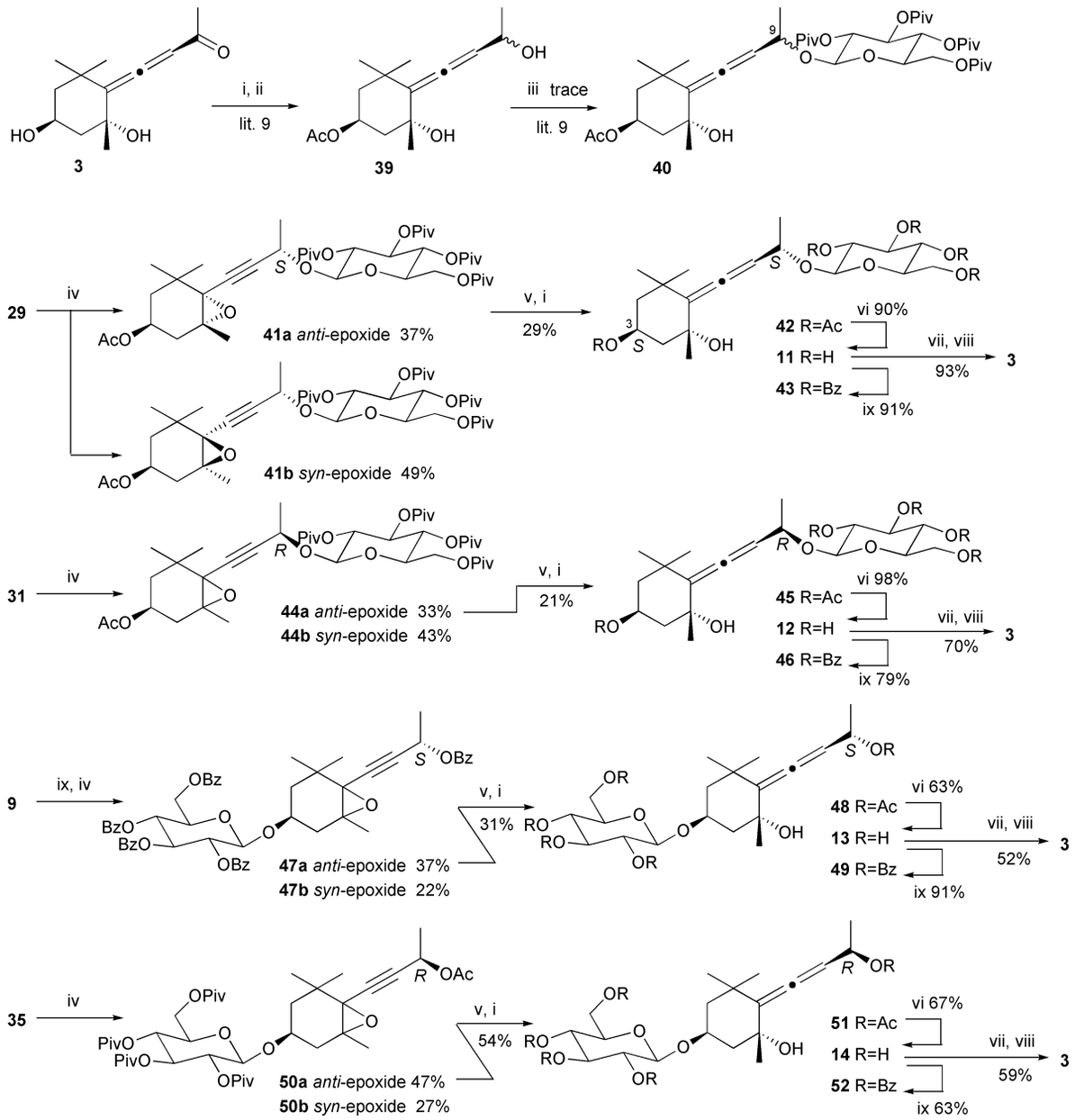


Fig. 4 HPLC elution profile of a mixture of allenic triol-glucoside pentabenzoates **43**, **46**, **49** and **52**. Column: CHIRALPAK AD-H 0.46 × 25 cm; eluent: EtOH–hexane (1:4); flow rate: 0.7 ml min^{-1}; UV detection: 230 nm.

In summary, we have accomplished a stereocontrolled synthesis of optically active β-D-glucopyranosides **7**–**10** and **11**–**14** of the acetylenic diol **6** and the allenic triol **4**, which are suggested to be glucosidic damascenone precursors. Investigation toward the clarification of their role as aroma precursors are now in progress.

Experimental

UV spectra were recorded on a JASCO Ubest-55 instrument. IR spectra were measured on a Perkin Elmer FT-IR spectrometer, model Paragon 1000, for chloroform solutions. ^{1}H NMR and ^{13}C NMR spectra were determined on a Varian Gemini-300 or a Varian VXR-500 superconducting FT-NMR spectrometer, for deuteriochloroform solutions unless otherwise stated (tetramethylsilane or MeOH as internal reference).



Scheme 4 *Reagents*: i, Ac_2O, Py; ii, $NaBH_4$; iii, **38**, AgOTf, $Me_2NC(O)NMe_2$; iv, MCPBA; v, DIBAL-H; vi, NaOMe–MeOH; vii, β-glucosidase; viii, MnO_2; ix, BzCl, Py.

J-Values are given in Hz. Mass spectra were taken on a Hitachi M-4100 spectrometer. Optical rotations were measured on a JASCO DIP-181 polarimeter ($[a]_D$ values are in units of 10^{-1} deg cm^2 g^{-1}) and CD spectra on a Shimadzu-AVIN 62A DS circular dichroism spectrometer.

Column chromatography (CC) was performed on silica gel (Merck Art. 7734). Short-column chromatography (SCC) was conducted on silica gel (Merck Art. 7739) under reduced pressure. Solid phase extraction (SPE) CC was performed using injector on the very short column (Mallinckrodt Baker) packed by small particle of silica gel. Low-pressure CC was carried out on a Yamazen Low pressure Liquid Chromatography System using a Lobar column (Merck LiChroprep Si 60). PTLC was performed on silica gel plate (Merck silica gel $60F_{254}$ precoated plate, 0.25 mm thickness). PHPLC was carried out on a Shimadzu LC-6A with a UV-VIS detector.

All operations were carried out under nitrogen or argon. Evaporation of the extract or the filtrate was carried out under reduced pressure. Ether refers to diethyl ether, and hexane to *n*-hexane. NMR assignments are given using the carotenoid numbering system.

1,1-Dimethylethyl{[(1*R*)-4-ethynyl-3,5,5-trimethylcyclohex-3-enyl]oxy}dimethylsilane 16

A solution of TBSCl (8.25 g, 54.7 mmol) in dry CH_2Cl_2 (10 ml) was added slowly to a stirred solution of (3*R*)-3-hydroxy terminal alkyne **15**[13] (8.16 g, 50.0 mmol), DMAP (7.28 g, 59.7 mmol) and Et_3N (8.34 ml, 59.7 mmol) in dry CH_2Cl_2 (30 ml) at 0 °C. The mixture was stirred at rt for 1.5 h, poured into chilled water and extracted with ether. The extracts were washed successively with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried solution gave a residue, which was purified by CC (ether–hexane, 5:95) to afford the TBS ether **16** (13.65 g, 99%) as a pale yellow oil; $[a]_D^{25}$ −61.0 (*c.* 1.20, MeOH); ν_{max}/cm^{-1} 3307 (≡CH), 2086 (C≡C); δ_H(300 MHz) 0.07 (6H, s, SiMe × 2), 0.89 (9H, s, *tert*-Bu), 1.12 and 1.16 (each 3H, s, *gem*-Me), 1.44 (1H, t, *J* 12, 2-H_{ax}), 1.71 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 1.89 (3H, s, 5-Me), 2.05 (1H, ddquint., *J* 17.5, 9 and 1, 4-H_{ax}), 2.25 (1H, br dd, *J* 17.5 and 5.5, 4-H_{eq}), 3.08 (1H, br s, 8-H), 3.92 (1H, m, 3-H); *m*/*z* (EI) 278.2071 (M^+, $C_{17}H_{30}OSi$ requires 278.2065).

4-({(4*R*)-4-[(1,1-Dimethylethyl)dimethylsilyl]oxy}-2,6,6-trimethylcyclohex-1-enyl)but-3-yn-2-one 17

To a solution of the terminal alkyne **16** (5.00 g, 18.0 mmol) in dry THF (50 ml) was added *n*-BuLi (1.56 M in hexane; 13.8 ml, 21.5 mmol) at −40 °C and the mixture was stirred for a further 15 min. Acetaldehyde (2 ml) was added to this mixture and the mixture was stirred at −40 °C for 10 min and rt for 15 min. After being quenched with saturated aq. NH_4Cl, the mixture was extracted with ether. The extracts were washed with brine, dried and evaporated to give the crude adduct which, without purification, was dissolved in ether–hexane (1:5) and shaken with active MnO_2 (160 g) at rt for 15 h. The mixture was filtered through Celite. Evaporation of the filtrate gave a residue, which was purified by CC (ether–hexane, 15:85) to provide the acetylenic ketone **17** (4.82 g, 84%) as a pale yellow oil; $[\alpha]_D^{26}$ −61.8 (*c*. 1.09, MeOH); λ_{max}/nm 212, 283; ν_{max}/cm^{-1} 2178 (C≡C), 1664 (conj. C=O), 1607 (C=C); δ_H(300 MHz) 0.08 (6H, s, SiMe × 2), 0.90 (9H, s, *tert*-Bu), 1.13 and 1.18 (each 3H, s, *gem*-Me), 1.47 (1H, t, *J* 12.5, 2-H_{ax}), 1.73 (1H, ddd, *J* 12.5, 3.5 and 2, 2-H_{eq}), 1.96 (3H, s, 5-Me), 2.11 (1H, ddq, *J* 18, 9 and 1, 4-H_{ax}), 2.34 (1H, ddd-like, *J* 18, 6 and 1, 4-H_{eq}), 2.38 (3H, s, 9-Me), 3.94 (1H, m, 3-H); *m*/*z* (EI) 320.2165 (M^+, $C_{19}H_{32}O_2Si$ requires 320.2170).

4-[(4*R*)-4-Hydroxy-2,6,6-trimethylcyclohex-1-enyl]but-3-yn-2-one 18

Aq. 47% HF (1 ml) was added to a solution of the silyl ether **17** (5.64 g, 17.6 mmol) in CH_3CN (50 ml) at 0 °C. The mixture was stirred at rt for 30 min and then neutralized with saturated aq. $NaHCO_3$. After CH_3CN was evaporated off, the organics were extracted with ether. The extracts were washed with brine, dried and evaporated to give a residue, which was purified by SCC (acetone–hexane, 3:7) to afford the 3-hydroxy compound **18** (3.61 g, 99%) as a pale yellow oil; $[\alpha]_D^{26}$ −100.7 (*c*. 1.10, MeOH); λ_{max}/nm 212, 283; ν_{max}/cm^{-1} 3608 and 3482 (OH), 2180 (C≡C), 1664 (conj. C=O), 1613 (C=C); δ_H(300 MHz) 1.14 and 1.20 (each 3H, s, *gem*-Me), 1.46 (1H, t, *J* 12, 2-H_{ax}), 1.85 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 1.97 (3H, s, 5-Me), 2.10 (1H, ddd, *J* 18, 9 and 1, 4-H_{ax}), 2.39 (3H, s, 9-Me), 2.48 (1H, ddd, *J* 18, 6 and 2, 4-H_{eq}), 3.99 (1H, m, 3-H); *m*/*z* (EI) 206.1311 (M^+, $C_{13}H_{18}O_2$ requires 206.1306).

4-[(4*R*)-4-Acetyloxy-2,6,6-trimethylcyclohex-1-enyl]but-3-yn-2-one 19

Ac_2O (7 ml) was added to a solution of the 3-hydroxy ketone **18** (3.16 g, 17.5 mmol) in pyridine (Py) (20 ml) and the reaction mixture was stirred at rt for 2 h, poured into ice-water and extracted with ether. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue, which was purified by CC (acetone–hexane, 1:3) to afford the acetate **19** (4.18 g, 96%) as a pale yellow solid; $[\alpha]_D^{29}$ −58.2 (*c*. 1.08, EtOH); λ_{max}/nm 212, 280; ν_{max}/cm^{-1} 2181 (C≡C), 1732 (COO), 1665 (conj. C=O), 1615 (C=C); δ_H(300 MHz) 1.18 and 1.21 (each 3H, s, *gem*-Me), 1.58 (1H, t, *J* 12.5, 2-H_{ax}), 1.85 (1H, ddd, *J* 12.5, 3.5 and 2, 2-H_{eq}), 1.97 (3H, s, 5-Me), 2.05 (3H, s, AcO), 2.16 (1H, ddq, *J* 18, 9 and 1.5, 4-H_{ax}), 2.39 (3H, s, 9-Me), 2.56 (1H, ddd, *J* 18, 6 and 1, 4-H_{eq}), 5.03 (1H, m, 3-H); *m*/*z* (CI) 249.1485 (M^+ + H, $C_{15}H_{21}O_3$ requires 249.1489).

Asymmetric transfer hydrogenation of α,β-acetylenic ketones 17 and 19 using (*S*,*S*)-Ru^{II} catalyst 20a or (*R*,*R*)-Ru^{II} catalyst 20b; typical procedure

To a solution of the 3-acetoxy acetylenic ketone **19** (2.61 g, 10.5 mmol) in 2-propanol (105 ml) was added the (*S*,*S*)-Ru^{II} catalyst **20a**[15] (126 mg, 0.21 mmol) and the mixture was stirred at rt for 2 h. After evaporation of 2-propanol, the residue was purified by CC (acetone–hexane, 1:3) to provide the (3*R*,9*S*)-alcohol **21a** (2.63 g, quant.; 98% de) as a pale yellow oil.

The optical purity of **21a** and **21b** was calculated by analytical HPLC (CHIRALPAK AS; DAICEL IND., Ltd., 0.46 × 25 cm; 2-propanol–hexane, 4:96, 0.7 ml min^{-1}; 25 °C; 250 nm detect.) and that of **24a** and **24b** by analytical HPLC (CHIRALPAK AS; DAICEL IND., Ltd., 0.46 × 25 cm; 2-propanol–hexane, 0.5:99.5, 0.5 ml min^{-1}; 25 °C; 250 nm detect.).

Compound 21a. $[\alpha]_D^{25}$ −72.4 (*c*. 1.00, MeOH); ν_{max}/cm^{-1} 3603 and 3436 (OH), 2210 (C≡C), 1729 (COO); δ_H(300 MHz) 1.15 and 1.17 (each 3H, s, *gem*-Me), 1.51 (3H, d, *J* 6.5, 9-Me), 1.54 (1H, t, *J* 12, 2-H_{ax}), 1.81 (1H, ddd, *J* 12, 4 and 2, 2-H_{eq}), 1.87 (3H, s, 5-Me), 2.04 (3H, s, AcO), 2.09 (1H, br dd, *J* 18 and 9.5, 4-H_{ax}), 2.46 (1H, br dd, *J* 18 and 5.5, 4-H_{eq}), 4.71 (1H, q, *J* 6.5, 9-H), 5.01 (1H, m, 3-H); *m*/*z* (EI) 250.1577 (M^+, $C_{15}H_{22}O_3$ requires 250.1568).

Compound 21b. $[\alpha]_D^{25}$ −33.2 (*c*. 1.06, MeOH); ν_{max}/cm^{-1} 3602 and 3466 (OH), 2210 (C≡C), 1730 (COO); δ_H(300 MHz) 1.14 and 1.17 (each 3H, s, *gem*-Me), 1.51 (3H, d, *J* 6.5, 9-Me), 1.54 (1H, t, *J* 12, 2-H_{ax}), 1.81 (1H, d, *J* 5.5, OH), 1.81 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 1.87 (3H, s, 5-Me), 2.04 (3H, s, AcO), 2.10 (1H, br dd, *J* 18 and 9.5, 4-H_{ax}), 2.46 (1H, br dd, *J* 18 and 4, 4-H_{eq}), 4.71 (1H, quint.-like, *J* 6.5, 9-H), 5.01 (1H, m, 3-H); *m*/*z* (EI) 250.1567 (M^+, $C_{15}H_{22}O_3$ requires 250.1568).

Compound 24a. $[\alpha]_D^{29}$ −75.2 (*c*. 1.01, MeOH); ν_{max}/cm^{-1} 3604 and 3446 (OH), 2209 (C≡C); δ_H(300 MHz) 0.07 (6H, s, SiMe × 2), 0.89 (9H, s, *tert*-Bu), 1.10 and 1.13 (each 3H, s, *gem*-Me), 1.44 (1H, t, *J* 12.5, 2-H_{ax}), 1.50 (3H, d, *J* 6.5, 9-Me), 1.70 (1H, ddd, *J* 12.5, 3.5 and 2, 2-H_{eq}), 1.86 (3H, s, 5-Me), 1.96 (1H, d, *J* 5, OH), 2.05 (1H, br dd, *J* 17.5 and 9.5, 4-H_{ax}), 2.24 (1H, br dd, *J* 17.5 and 5.5, 4-H_{eq}), 3.91 (1H, m, 3-H), 4.70 (1H, quint.-like, *J* 6.5, 9-H); *m*/*z* (EI) 322.2337 (M^+, $C_{19}H_{34}O_2Si$ requires 322.2326).

Compound 24b. $[\alpha]_D^{27}$ −43.1 (*c*. 1.04, MeOH); ν_{max}/cm^{-1} 3607 and 3446 (OH), 2209 (C≡C); δ_H(300 MHz) 0.07 (6H, s, SiMe × 2), 0.89 (9H, s, *tert*-Bu), 1.10 and 1.14 (each 3H, s, *gem*-Me), 1.44 (1H, t, *J* 12, 2-H_{ax}), 1.50 (3H, d, *J* 6.5, 9-Me), 1.70 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 1.86 (3H, s, 5-Me), 1.90 (1H, br s, OH), 2.05 (1H, dd, *J* 17.5 and 9, 4-H_{ax}), 2.24 (1H, br dd, *J* 17.5 and 5.5, 4-H_{eq}), 3.91 (1H, m, 3-H), 4.70 (1H, q, *J* 6.5, 9-H); *m*/*z* (EI) 322.2308 (M^+, $C_{19}H_{34}O_2Si$ requires 322.2326).

Asymmetric transfer hydrogenation of the α,β-acetylenic ketone 17 *via in situ* formation of (*S*,*S*)-Ru^{II} catalyst 20a or (*R*,*R*)-Ru^{II} catalyst 20b

To a solution of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (12 mg, 0.020 mmol) and (*S*,*S*)-TsDPEN or (*R*,*R*)-TsDPEN (14.6 mg, 0.040 mmol) in 2-propanol (4 ml) were added KOH (5.6 mg, 0.10 mmol) and then a solution of acetylenic ketone **17** (648 mg, 2.02 mmol) in 2-propanol (12 ml). The mixture was stirred at rt for 2 h. After evaporation of 2-propanol, the residue was purified by SCC (ether–hexane, 1:4) to provide the (3*R*,9*S*)-alcohol **24a** or the (3*R*,9*R*)-alcohol **24b**, quantitatively.

Preparation of (*S*)- and (*R*)-MTPA esters of (3*R*,9*S*)-9-hydroxy compounds 21a and 24a; typical procedure

To a solution of the (3*R*,9*S*)-alcohol **21a** (50 mg, 0.20 mmol) and (*S*)-MTPA (70 mg, 0.30 mmol) and DMAP (37 mg, 0.30 mmol) in dry CH_2Cl_2 (5 ml) was added EDC {1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride} (58 mg, 0.30 mmol) at 0 °C. After being stirred at rt for 30 min, the reaction mixture was diluted with ether. The organic layer was washed successively with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried solution gave a residue,

which was purified by SCC (ether–hexane, 3:7 to acetone–hexane, 3:7) to afford the (*S*)-MTPA ester **22** (37 mg, 40%) and the recovered alcohol **21a** (22 mg, 44%).

Compound 22 [(*S*)-MTPA ester of 21a]. ν_{max}/cm^{-1} 2218 (C≡C), 1748 and 1732 (COO); δ_H(300 MHz) 1.136 (6H, s, *gem*-Me), 1.534 (1H, t, *J* 12, 2-H$_{ax}$), 1.573 (3H, d, *J* 6.5, 9-Me), 1.813 (1H, ddd, *J* 12, 3.5 and 1.5, 2-H$_{eq}$), 1.848 (3H, s, 5-Me), 2.036 (3H, s, AcO), 2.099 (1H, br dd, *J* 18 and 9, 4-H$_{ax}$), 2.466 (1H, br dd, *J* 18 and 5, 4-H$_{eq}$), 3.589 (3H, s, OMe), 5.012 (1H, m, 3-H), 5.829 (1H, q, *J* 6.5, 9-H), 7.34–7.42 (3H, m, Ar–H), 7.54–7.59 (2H, m, Ar–H); *m*/*z* (EI) 466.1961 (M$^+$, $C_{25}H_{29}O_5F_3$ requires 466.1965).

Compound 23 [(*R*)-MTPA ester of 21a]. ν_{max}/cm^{-1} 2218 (C≡C), 1747 and 1731 (COO); δ_H(300 MHz) 1.100 and 1.111 (each 3H, s, *gem*-Me), 1.523 (1H, t, *J* 12, 2-H$_{ax}$), 1.632 (3H, d, *J* 6.5, 9-Me), 1.800 (1H, ddd, *J* 12, 3.5 and 1.5, 2-H$_{eq}$), 1.818 (3H, s, 5-Me), 2.036 (3H, s, AcO), 2.088 (1H, brdd, *J* 18 and 9, 4-H$_{ax}$), 2.454 (1H, br dd, *J* 18 and 5, 4-H$_{eq}$), 3.564 (3H, s, OMe), 5.002 (1H, m, 3-H), 5.820 (1H, q, *J* 6.5, 9-H), 7.33–7.43 (3H, m, Ar–H), 7.52–7.58 (2H, m, Ar–H); *m*/*z* (EI) 466.1966 (M$^+$, $C_{25}H_{29}O_5F_3$ requires 466.1965).

Compound 25 [(*S*)-MTPA ester of 24a]

ν_{max}/cm^{-1} 2214 (C≡C), 1749 (COO); δ_H(300 MHz) 0.068 (6H, s, SiMe × 2), 0.893 (9H, s, *tert*-Bu), 1.088 and 1.106 (each 3H, s, *gem*-Me), 1.432 (1H, t, *J* 12, 2-H$_{ax}$), 1.568 (3H, d, *J* 6.5, 9-Me), 1.698 (1H, ddd, *J* 12.5, 3.5 and 1.5, 2-H$_{eq}$), 1.840 (3H, s, 5-Me), 2.053 (1H, dd, *J* 17.5 and 9, 4-H$_{ax}$), 2.253 (1H, ddd, *J* 17.5, 5.5 and 1.5, 4-H$_{eq}$), 3.591 (3H, s, OMe), 3.912 (1H, m, 3-H), 5.832 (1H, t, *J* 6.5 Hz, 9-H), 7.34-7.41 (3H, m, Ar–H), 7.53-7.59 (2H, m, Ar–H); *m*/*z* (EI) 538.2740 (M$^+$, $C_{29}H_{41}F_3O_4Si$ requires 538.2724).

Compound 26 [(*R*)-MTPA ester of 24a]. ν_{max}/cm^{-1} 2215 (C≡C), 1748 (COO); δ_H(300 MHz) 0.062 (6H, s, SiMe × 2), 0.887 (9H, s, *tert*-Bu), 1.052 and 1.080 (each 3H, s, *gem*-Me), 1.416 (1H, t, *J* 12, 2-H$_{ax}$), 1.622 (3H, d, *J* 6.5, 9-Me), 1.685 (1H, ddd, *J* 12, 3.5 and 2, 2-H$_{eq}$), 1.801 (3H, s, 5-Me), 2.037 (1H, dd, *J* 18 and 9.5, 4-H$_{ax}$), 2.238 (1H, br dd, *J* 18 and 5, 4-H$_{eq}$), 3.562 (3H, s, OMe), 3.898 (1H, m, 3-H), 5.815 (1H, t, *J* 6.5, 9-H), 7.33–7.42 (3H, m, Ar–H), 7.51–7.57 (2H, m, Ar–H); *m*/*z* (EI) 538.2714 (M$^+$, $C_{29}H_{41}F_3O_4Si$ requires 538.2724).

(1*R*)-4-[(3*S*)-3-Acetyloxybut-1-ynyl]-3,5,5-trimethylcyclohex-3-enol 27a

According to the procedure described in the preparation of the 3-acetoxy acetylenic ketone **19**, acetylation of the 9-hydroxy compound **24a** (1.51 g) afforded the acetate, which without purification was desilylated in the same manner as described for the preparation of the 3-hydroxy acetylenic ketone **18**. The resulting crude product was purified by SCC (acetone–hexane, 3:7) to provide the 3-hydroxy compound **27a** (1.15 g, 99% from **24a**) as a pale yellow oil; $[a]_D^{27}$ −209.5 (*c*. 1.01, MeOH); ν_{max}/cm^{-1} 3607 and 3450 (OH), 2221 (C≡C), 1732 (COO), 1627 (C=C); δ_H(300 MHz) 1.11 and 1.15 (each 3H, s, *gem*-Me), 1.41 (1H, t, *J* 12, 2-H$_{ax}$), 1.53 (3H, d, *J* 6.5, 9-Me), 1.76 (1H, br s, OH), 1.81 (1H, ddd, *J* 12, 3.5 and 2, 2-H$_{eq}$), 1.87 (3H, s, 5-Me), 2.02 (1H, br dd, *J* 17.5 and 9.5, 4-H$_{ax}$), 2.07 (3H, s, AcO), 2.38 (1H, ddd, *J* 17.5, 5.5 and 2, 4-H$_{eq}$), 3.95 (1H, m, 3-H), 5.60 (1H, q, *J* 6.5, 9-H); *m*/*z* (EI) 250.1582 (M$^+$, $C_{15}H_{22}O_3$ requires 250.1568).

(1*R*)-4-[(3*R*)-3-Acetyloxybut-1-ynyl]-3,5,5-trimethylcyclohex-3-enol 27b

According to the procedure described in the preparation of the compound **27a**, acetylation of the 9-hydroxy compound **24b** (2.65 g) followed by desilylation afforded the 3-hydroxy compound **27b** (1.91 g, 93%) as a pale yellow oil; $[a]_D^{26}$ +50.6 (*c*. 0.97, MeOH); ν_{max}/cm^{-1} 3606 and 3453 (OH), 2221 (C≡C), 1732 (COO), 1625 (C=C); δ_H(300 MHz) 1.10 and 1.16 (each 3H, s, *gem*-Me), 1.42 (1H, t, *J* 12, 2-H$_{ax}$), 1.53 (3H, d, *J* 6.5, 9-Me), 1.70 (1H, br s, OH), 1.81 (1H, ddd, *J* 12, 3.5 and 2, 2-H$_{eq}$), 1.88 (3H, s, 5-Me), 2.02 (1H, br dd, *J* 17 and 9.5, 4-H$_{ax}$), 2.07 (3H, s, AcO), 2.39 (1H, ddd, *J* 17, 5.5 and 2, 4-H$_{eq}$), 3.96 (1H, m, 3-H), 5.60 (1H, q, *J* 6.5, 9-H); *m*/*z* (EI) 250.1571 (M$^+$, $C_{15}H_{22}O_3$ requires 250.1568).

1,2-*O*-({(1*S*)-4-[(4*R*)-4-Acetyloxy-2,6,6-trimethylcyclohex-1-enyl]but-3-yn-2-yl}phenylmethylene)-3,4,6-tri-*O*-benzoyl-α-D-glucopyranose 28

To a stirred suspension of tetra-*O*-benzoyl-α-D-glucosyl bromide **37** (1.80 g, 2.73 mmol), (3*R*,9*S*)-9-hydroxy compound **21a** (530 mg, 2.12 mmol), *N,N*-tetramethylurea (0.76 ml, 6.35 mmol) and powdered molecular sieves 4 Å (7 g) in dry CH_2Cl_2 (25 ml) was added AgOTf (1.08 g, 4.20 mmol) at 0 °C. After being stirred at 0 °C for 15 min, the reaction was quenched with saturated aq. $NaHCO_3$. The reaction mixture was diluted with AcOEt and filtered through Celite. The organic layer of the filtrate was washed with brine, dried and evaporated to give a residue, which was purified by CC (CH_2Cl_2–hexane–ether, 5:4:0.7) to afford the ortho ester **28** (1.07 g, 61%) as a colorless foam; $[a]_D^{23}$ −83.6 (*c*. 0.99, MeOH); λ_{max}/nm 231, 274; ν_{max}/cm^{-1} 1727 (COO); δ_H(300 MHz) 1.05 and 1.10 (each 3H, s, *gem*-Me), 1.37 (3H, d, *J* 6.5, 9-Me), 1.47 (1H, t, *J* 12, 2-H$_{ax}$), 1.73 (1H, ddd, *J* 12, 3.5 and 1.5, 2-H$_{eq}$), 1.80 (3H, s, 5-Me), 2.01 (3H, s, AcO), 2.02 (1H, m, 4-H$_{ax}$), 2.40 (1H, br dd, *J* 18 and 6, 4-H$_{eq}$), 4.12 (1H, ddd, *J* 12, 4.5 and 3, 5′-H), 4.33 (1H, q, *J* 6.5, 9-H), 4.37 (1H, dd, *J* 12 and 4.5, 6′-H), 4.51 (1H, dd, *J* 12 and 3, 6′-H), 4.92 (1H, ddd, *J* 5, 3 and 1, 2′-H), 4.96 (1H, m, 3-H), 5.52 (1H, br d, *J* 9, 4′-H), 5.79 (1H, dd, *J* 3 and 1, 3′-H), 6.10 (1H, d, *J* 5, 1′-H), 7.17–7.65 (12H, m, Ar–H), 7.83–8.10 (8H, m, Ar–H); *m*/*z* (SIMS) 851.3061 (M$^+$ + Na, $C_{49}H_{48}O_{12}Na$ requires 851.3041).

β-Glucosidation of alcohols 21a, 21b, 27a and 27b; typical procedure

To a stirred suspension of tetra-*O*-pivaloyl-α-D-glucosyl bromide **38** (8.18 g, 14.6 mmol), (3*R*,9*S*)-9-hydroxy compound **21a** (1.83 g, 7.32 mmol), *N,N*-tetramethylurea (3.40 ml, 28.4 mmol) and powdered molecular sieves 4 Å (20 g) in dry CH_2Cl_2 (70 ml) was added AgOTf (5.64 g, 21.9 mmol) at 0 °C. After being stirred at 0 °C for 30 min and rt for 2 h, the reaction was quenched with saturated aq. $NaHCO_3$. The reaction mixture was diluted with AcOEt and filtered through Celite. The organic layer of the filtrate was washed with brine, dried and evaporated to give a residue which was purified by CC (CH_2Cl_2–hexane–ether, 5:4:0.7) to afford the β-glucoside **29** (5.22 g, 95%) as a colorless foam.

Compound 29 [β-glucoside of 21a]. $[a]_D^{27}$ −46.7 (*c*. 0.92, MeOH); λ_{max}/nm 230; ν_{max}/cm^{-1} 2211 (C≡C), 1739 (COO); δ_H(300 MHz) 1.11, 1.15, 1.16 and 1.22 (each 9H, s, *tert*-Bu × 4), 1.15 and 1.17 (each 3H, s, *gem*-Me), 1.45 (3H, d, *J* 6.5 Hz, 9-Me), 1.56 (1H, t, *J* 12, 2-H$_{ax}$), 1.84 (1H, ddd, *J* 12, 3.5 and 2, 2-H$_{eq}$), 1.87 (3H, s, 5-Me), 2.05 (3H, s, AcO), 2.12 (1H, br dd, *J* 17.5 and 9, 4-H$_{ax}$), 2.49 (1H, br dd, *J* 17.5, 5.5, 4-H$_{eq}$), 3.71 (1H, ddd, *J* 9.5, 6 and 1.5, 5′-H), 4.06 (1H, dd, *J* 12 and 6, 6′-H), 4.22 (1H, dd, *J* 12 and 1.5, 6′-H), 4.81 (1H, q, *J* 6.5, 9-H), 4.92 (1H, d, *J* 8, 1′-H), 5.02 (1H, m, 3-H), 5.05 (1H, dd, *J* 9.5 and 8, 2′-H), 5.10 (1H, t, *J* 9.5, 4′-H), 5.30 (1H, t, *J* 9.5, 3′-H); *m*/*z* (SIMS) 771.4308 (M$^+$ + Na, $C_{41}H_{64}O_{12}Na$ requires 771.4291).

Compound 31 [β-glucoside of 21b]. $[a]_D^{26}$ +5.9 (*c*. 1.02, MeOH); λ_{max}/nm 231; ν_{max}/cm^{-1} 2212 (C≡C), 1736 (COO); δ_H(300 MHz) 1.11, 1.15, 1.16 and 1.21 (each 9H, s, *tert*-Bu × 4),

1.14 and 1.17 (each 3H, s, *gem*-Me), 1.50 (3H, d, *J* 6.5, 9-Me), 1.55 (1H, t, *J* 12, 2-H_{ax}), 1.82 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 1.87 (3H, s, 5-Me), 2.05 (3H, s, AcO), 2.10 (1H, br dd, *J* 17.5 and 9.5, 4-H_{ax}), 2.46 (1H, br dd, *J* 17.5 and 5, 4-H_{eq}), 3.72 (1H, ddd, *J* 9.5, 5.5 and 2, 5′-H), 4.04 (1H, dd, *J* 12.5 and 5.5, 6′-H), 4.19 (1H, dd, *J* 12.5 and 2, 6′-H), 4.72 (1H, q, *J* 6.5, 9-H), 4.89 (1H, d, *J* 8, 1′-H), 5.02 (1H, m, 3-H), 5.06 (1H, dd, *J* 9.5 and 8, 2′-H), 5.12 (1H, t, *J* 9.5, 4′-H), 5.30 (1H, t, *J* 9.5, 3′-H); *m*/*z* (SIMS) 771.4312 (M^+ + Na, $C_{41}H_{64}O_{12}Na$ requires 771.4291).

Compound 33 [β-glucoside of 27a]. $[\alpha]_D^{27}$ −77.1 (*c*. 1.04, MeOH); λ_{max}nm 231; ν_{max}/cm^{-1} 2211 (C≡C), 1739 (COO); δ_H(300 MHz) 1.08 and 1.12 (each 3H, s, *gem*-Me), 1.11 (9H, s, *tert*-Bu), 1.15 (18H, s, *tert*-Bu × 2), 1.22 (9H, s, *tert*-Bu), 1.48 (1H, t, *J* 12, 2-H_{ax}), 1.52 (3H, d, *J* 6.5, 9-Me), 1.84 (3H, s, 5-Me), 1.89 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 2.01 (1H, br dd, *J* 17 and 9, 4-H_{ax}), 2.07 (3H, s, AcO), 2.30 (1H, br dd, *J* 17 and 5, 4-H_{eq}), 3.73 (1H, ddd, *J* 9.5, 6.5 and 2, 5′-H), 3.93 (1H, m, 3-H), 3.99 (1H, dd, *J* 12 and 6.5, 6′-H), 4.26 (1H, dd, *J* 12 and 2, 6′-H), 4.66 (1H, d, *J* 8, 1′-H), 4.99 (1H, dd, *J* 9.5 and 8, 2′-H), 5.06 (1H, t, *J* 9.5, 4′-H), 5.32 (1H, t, *J* 9.5, 3′-H), 5.59 (1H, q, *J* 6.5, 9-H); *m*/*z* (SIMS) 771.4297 (M^+ + Na, $C_{41}H_{64}O_{12}Na$ requires 771.4291).

Compound 35 [β-glucoside of 27b]. $[\alpha]_D^{24}$ +24.6 (*c*. 0.98, MeOH); λ_{max}/nm 231; ν_{max}/cm^{-1} 2221 (C≡C), 1739 (COO); δ_H(300 MHz) 1.07 and 1.13 (each 3H, s, *gem*-Me), 1.11, 1.15, 1.16 and 1.22 (each 9H, s, *tert*-Bu × 4), 1.48 (1H, t, *J* 12, 2-H_{ax}), 1.52 (3H, d, *J* 6.5, 9-Me), 1.84 (3H, s, 5-Me), 1.89 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 2.01 (1H, br dd, *J* 17 and 9, 4-H_{ax}), 2.07 (3H, s, AcO), 2.30 (1H, br dd, *J* 17 and 5, 4-H_{eq}), 3.73 (1H, ddd, *J* 9.5, 6.5 and 2, 5′-H), 3.92 (1H, m, 3-H), 3.98 (1H, dd, *J* 12 and 6.5, 6′-H), 4.26 (1H, dd, *J* 12 and 2, 6′-H), 4.66 (1H, d, *J* 8, 1′-H), 4.99 (1H, dd, *J* 9.5 and 8, 2′-H), 5.06 (1H, t, *J* 9.5, 4′-H), 5.32 (1H, t, *J* 9.5, 3′-H), 5.59 (1H, q, *J* 6.5, 9-H); *m*/*z* (SIMS) 771.4311 (M^+ + Na, $C_{41}H_{64}O_{12}Na$ requires 771.4291).

Methanolysis of tetrapivalates 29, 31, 33 and 35; typical procedure

To a solution of the tetrapivalate **29** (955 mg, 1.28 mmol) in MeOH (25 ml) was added $LiOH·H_2O$ (134 mg, 3.19 mmol) and the mixture was stirred at rt for 20 h. To this mixture was added Dowex 50W-X8 (H^+) (4 g) and stirring continued at rt for a further 10 min. After Dowex was filtered off, the filtrate was evaporated to give a residue, which was purified by SCC (CH_2Cl_2–MeOH, 85:15) to yield the pentaol **7** (463 mg, 98%) as a colorless foam.

(3*R*,9*S*)-9-*O*-Glucoside 7

$[\alpha]_D^{27}$ −169.2 (*c*. 0.98, MeOH); δ_H(500 MHz, D_2O) 1.06 and 1.11 (each 3H, s, *gem*-Me), 1.38 (1H, t, *J* 12, 2-H_{ax}), 1.48 (3H, d, *J* 6.5, 9-Me), 1.78 (1H, ddd, *J* 12, 3 and 2, 2-H_{eq}), 1.84 (3H, s, 5-Me), 2.00 (1H, dd, *J* 17.5 and 10, 4-H_{ax}), 2.38 (1H, br dd, *J* 17.5 and 5, 4-H_{eq}), 3.26 (1H, dd, *J* 9.5 and 8.5, 2′-H), 3.35 (1H, t-like, *J* 9.5, 4′-H), 3.39 (1H, ddd, *J* 9.5, 5.5 and 2, 5′-H), 3.44 (1H, t, *J* 9.5, 3′-H), 3.67 (1H, dd, *J* 12 and 5.5, 6′-H), 3.86 (1H, dd, *J* 12 and 2, 6′-H), 3.95 (1H, m, 3-H), 4.72 (1H, d, *J* 8.5, 1′-H), 4.93 (1H, q, *J* 6.5, 9-H); δ_C(125 MHz, D_2O) 21.63 (9-CH_3), 21.85 (5-CH_3), 27.84 (1-CH_3), 29.76 (1-CH_3), 35.92 (C1), 39.86 (C4), 45.03 (C2), 60.83 (C6′), 64.37 (C3), 64.83 (C9), 69.77 (C4′), 73.03 (C2′), 76.02 and 76.25 (C3′ and C5′), 84.62 (C7), 92.63 (C8), 99.64 (C1′), 122.31 (C6), 140.50 (C5); *m*/*z* (SIMS) 393.1910 (M^+ + Na, $C_{19}H_{30}O_7Na$ requires 393.1887).

(3*R*,9*R*)-9-*O*-Glucoside 8. $[\alpha]_D^{27}$ −23.5 (*c*. 0.89, MeOH); δ_H(500 MHz, D_2O) 1.06 and 1.11 (each 3H, s, *gem*-Me), 1.38 (1H, t, *J* 12, 2-H_{ax}), 1.49 (3H, d, *J* 6.5, 9-Me), 1.77 (1H, ddd, *J* 12, 3 and 2, 2-H_{eq}), 1.84 (3H, s, 5-Me), 2.00 (1H, br dd, *J* 17.5 and 9.5, 4-H_{ax}), 2.38 (1H, br dd, *J* 17.5 and 5, 4-H_{eq}), 3.23 (1H, dd, *J* 9 and 8.5, 2′-H), 3.38–3.45 (2H, m, 4′-H and 5′-H), 3.44 (1H, t, *J* 9, 3′-H), 3.70 (1H, dd, *J* 12.5 and 4, 6′-H), 3.81 (1H, br d, *J* 12.5, 6′-H), 3.95 (1H, m, 3-H), 4.62 (1H, d, *J* 8.5, 1′-H), 4.81 (1H, q, *J* 6.5, 9-H); δ_C(125 MHz, D_2O) 21.80 (5-CH_3), 21.89 (9-CH_3), 27.84 (1-CH_3), 29.70 (1-CH_3), 35.91 (C1), 39.84 (C4), 45.02 (C2), 60.69 (C6′), 64.38 (C3), 67.49 (C9), 69.44 (C4′), 73.39 (C2′), 75.86 (C3′), 76.08 (C5′), 84.09 (C7), 93.45 (C8), 101.33 (C1′), 122.35 (C6), 140.51 (C5); *m*/*z* (SIMS) 393.1903 (M^+ + Na, $C_{19}H_{30}O_7Na$ requires 393.1887).

(3*R*,9*S*)-3-*O*-Glucoside 9. $[\alpha]_D^{27}$ −75.4 (*c*. 0.92, MeOH); δ_H(500 MHz, D_2O) 1.07 and 1.11 (each 3H, s, *gem*-Me), 1.43 (3H, d, *J* 6.5, 9-Me), 1.47 (1H, t, *J* 12, 2-H_{ax}), 1.84 (3H, s, 5-Me), 1.91 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 2.06 (1H, br dd, *J* 18 and 9.5, 4-H_{ax}), 2.50 (1H, ddd, *J* 18, 5.5 and 2, 4-H_{eq}), 3.19 (1H, dd, *J* 9 and 8, 2′-H), 3.34 (1H, dd, *J* 9.5 and 9, 4′-H), 3.40 (1H, ddd, *J* 9.5, 5.5 and 2, 5′-H), 3.44 (1H, t, *J* 9, 3′-H), 3.67 (1H, dd, *J* 12.5 and 5.5, 6′-H), 3.86 (1H, dd, *J* 12.5 and 2, 6′-H), 4.11 (1H, m, 3-H), 4.56 (1H, d, *J* 8, 1′-H), 4.70 (1H, q, *J* 6.5, 9-H); δ_C(125 MHz, D_2O) 21.67 (5-CH_3), 23.58 (9-CH_3), 27.64 (1-CH_3), 29.61 (1-CH_3), 35.97 (C1), 37.32 (C4), 43.55 (C2), 58.27 (C9), 60.85 (C6′), 69.79 (C4′), 73.08 (C3), 73.28 (C2′), 75.93 and 76.04 (C3′ and C5′), 82.08 (C7), 95.90 (C8), 100.76 (C1′), 122.58 (C6), 139.35 (C5); *m*/*z* (SIMS) 393.1894 (M^+ + Na, $C_{19}H_{30}O_7Na$ requires 393.1887).

(3*R*,9*R*)-3-*O*-Glucoside 10. $[\alpha]_D^{26}$ −46.3 (*c*. 0.93, MeOH); δ_H(500 MHz, D_2O) 1.06 and 1.11 (each 3H, s, *gem*-Me), 1.43 (3H, d, *J* 6.5, 9-Me), 1.47 (1H, t, *J* 12, 2-H_{ax}), 1.83 (3H, s, 5-Me), 1.90 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 2.06 (1H, br dd, *J* 18 and 9.5, 4-H_{ax}), 2.51 (1H, ddd, *J* 18, 5.5 and 2, 4-H_{eq}), 3.19 (1H, dd, *J* 9.5 and 8, 2′-H), 3.34 (1H, dd, *J* 9.5 and 9, 4′-H), 3.39 (1H, ddd, *J* 9.5, 5.5 and 2, 5′-H), 3.44 (1H, t, *J* 9.5, 3′-H), 3.67 (1H, dd, *J* 12.5 and 5, 6′-H), 3.86 (1H, dd, *J* 12.5 and 2, 6′-H), 4.11 (1H, m, 3-H), 4.55 (1H, d, *J* 8, 1′-H), 4.70 (1H, q, *J* 6.5, 9-H); δ_C(125 MHz, D_2O) 21.67 (5-CH_3), 23.59 (9-CH_3), 27.65 (1-CH_3), 29.61 (1-CH_3), 35.97 (C1), 37.32 (C4), 43.55 (C2), 58.27 (C9), 60.85 (C6′), 69.79 (C4′), 73.07 (C3), 73.27 (C2′), 75.93 and 76.03 (C3′ and C5′), 82.08 (C7), 95.89 (C8), 100.76 (C1′), 122.58 (C6), 139.31 (C5); *m*/*z* (SIMS) 393.1910 (M^+ + Na, $C_{19}H_{30}O_7Na$ requires 393.1887).

Acetylation of pentaols 7, 8, 9 and 10; typical procedure

To a solution of the pentaol **7** in Py (5 ml) was added Ac_2O (1.5 ml) and the reaction mixture was stirred at rt for 20 h, poured into ice-water and extracted with AcOEt. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue, which was purified by SCC (ether–CH_2Cl_2, 13:87) to afford the pentaacetate **30** (448 mg, 95%) as a colourless foam. ^1H and ^{13}C NMR data of the synthetic (3*R*,9*S*)-9-*O*-glucoside **30** were in agreement with those of the 9-*O*-glucoside isolated[5] from Riesling wine, except for the methyl carbon at C-9 (lit.[5]: δ 27.0). While those of the synthetic (3*R*,9*R*)-9-*O*-glucoside **31** were in accordance with those of 9-*O*-glucosde isolated[6] from rose petals, except for C-2′ (lit.[6]: δ 71.8).

(3*R*,9*S*)-9-*O*-Glucoside pentaacetate 30. $[\alpha]_D^{26}$ −62.1 (*c*. 0.98, MeOH); λ_{max}/nm (MeOH) 230; ν_{max}/cm^{-1} 2212 (C≡C), 1755 (COO); δ_H(500 MHz) 1.16 and 1.18 (each 3H, s, *gem*-Me), 1.48 (3H, d, *J* 6.5, 9-Me), 1.56 (1H, t, *J* 12, 2-H_{ax}), 1.84 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 1.88 (3H, s, 5-Me), 2.01, 2.02, 2.03, 2.05 and 2.09 (each 3H, s, AcO × 5), 2.12 (1H, br dd, *J* 17.5 and 9, 4-H_{ax}), 2.48 (1H, br dd, *J* 17.5 and 5.5, 4-H_{eq}), 3.69 (1H, ddd, *J* 9.5, 4.5 and 2.5, 5′-H), 4.14 (1H, dd, *J* 12.5 and 2.5,

6′-H), 4.28 (1H, dd, *J* 12.5 and 4.5, 6′-H), 4.80 (1H, q, *J* 6.5, 9-H), 4.88 (1H, d, *J* 8, 1′-H), 5.03 (1H, m, 3-H), 5.04 (1H, dd, *J* 9.5 and 8, 2′-H), 5.10 (1H, t, *J* 9.5, 4′-H), 5.21 (1H, t, *J* 9.5, 3′-H); δ_C(125 MHz) 20.61, 20.75 and 21.36 (CH_3COO × 3), 20.64 (CH_3COO × 2), 22.30 (5-CH_3), 22.35 (9-CH_3), 28.52 (1-CH_3), 30.09 (1-CH_3), 35.93 (C1), 37.33 (C4), 42.15 (C2), 61.91 (C6′), 64.30 (C9), 67.74 (C3), 68.53 (C4′), 71.08 (C2′), 71.87 (C5′), 73.07 (C3′), 83.80 (C7), 91.83 (C8), 97.78 (C1′), 123.16 (C6), 137.84 (C5), 169.38, 169.42, 170.33, 170.67 and 170.69 (CH_3COO × 5); *m*/*z* (SIMS) 603.2432 (M^+ + Na, $C_{29}H_{40}O_{12}Na$ requires 603.2415).

(3*R*,9*R*)-9-*O*-Glucoside pentaacetate 32. $[\alpha]_D^{27}$ −6.9 (*c*. 0.87, MeOH); λ_{max}/nm (MeOH) 231; ν_{max}/cm^{-1} 2212 (C≡C), 1756 (COO); δ_H(500 MHz) 1.15 and 1.17 (each 3H, s, *gem*-Me), 1.51 (3H, d, *J* 7, 9-Me), 1.55 (1H, t, *J* 12, 2-H_{ax}), 1.82 (1H, ddd, *J* 12, 3.5 and 1.5, 2-H_{eq}), 1.88 (3H, s, 5-Me), 2.01, 2.02, 2.03, 2.05 and 2.06 (each 3H, s, AcO × 5), 2.11 (1H, br dd, *J* 17.5 and 9, 4-H_{ax}), 2.47 (1H, br dd, *J* 17.5 and 5.5, 4-H_{eq}), 3.71 (1H, ddd, *J* 9.5, 4.5 and 2.5, 5′-H), 4.10 (1H, dd, *J* 12 and 2.5, 6′-H), 4.25 (1H, dd, *J* 12 and 4.5, 6′-H), 4.74 (1H, q, *J* 7, 9-H), 4.86 (1H, d, *J* 8, 1′-H), 5.01 (1H, m, 3-H), 5.02 (1H, dd, *J* 9.5 and 8, 2′-H), 5.10 (1H, t, *J* 9.5, 4′-H), 5.21 (1H, t, *J* 9.5, 3′-H); δ_C(125 MHz) 20.60, 20.70 and 21.36 (CH_3COO × 3), 20.63 (CH_3COO × 2), 22.30 (5-CH_3), 23.12 (9-CH_3), 28.52 (1-CH_3), 30.08 (1-CH_3), 35.96 (C1), 37.33 (C4), 42.17 (C2), 62.04 (C6′), 67.52 (C9), 67.77 (C3), 68.41 (C4′), 71.48 (C2′), 71.89 (C5′), 72.99 (C3′), 84.05 (C7), 91.96 (C8), 98.88 (C1′), 123.22 (C6), 137.89 (C5), 169.27, 169.38 and 170.34 (CH_3COO × 3), 170.66 (CH_3COO × 2); *m*/*z* (SIMS) 603.2406 (M^+ + Na, $C_{29}H_{40}O_{12}Na$ requires 603.2415).

(3*R*,9*S*)-3-*O*-Glucoside pentaacetate 34. $[\alpha]_D^{27}$ −108.6 (*c*. 0.87, MeOH); λ_{max}/nm (MeOH) 231; ν_{max}/cm^{-1} 2212 (C≡C), 1755 (COO); δ_H(500 MHz) 1.10 and 1.13 (each 3H, s, *gem*-Me), 1.50 (1H, t, *J* 12.5, 2-H_{ax}), 1.52 (3H, d, *J* 6.5, 9-Me), 1.86 (3H, s, 5-Me), 1.90 (1H, ddd, *J* 12.5, 3.5 and 1.5, 2-H_{eq}), 2.01, 2.03, 2.04, 2.07 and 2.08 (each 3H, s, AcO × 5), 2.02 (1H, 4-H_{ax}), 2.32 (1H, brdd, *J* 17 and 5, 4-H_{eq}), 3.71 (1H, ddd, *J* 9.5, 5.5 and 2.5, 5′-H), 3.92 (1H, m, 3-H), 4.13 (1H, dd, *J* 12.5 and 2.5, 6′-H), 4.24 (1H, dd, *J* 12.5 and 5.5, 6′-H), 4.62 (1H, d, *J* 8, 1′-H), 4.96 (1H, dd, *J* 9.5 and 8, 2′-H), 5.06 (1H, t, *J* 9.5, 4′-H), 5.21 (1H, t, *J* 9.5, 3′-H), 5.60 (1H, q, *J* 6.5, 9-H); δ_C(125 MHz) 20.61, 20.63, 20.67, 20.75 and 21.13 (CH_3COO × 5), 21.67 (9-CH_3), 22.37 (5-CH_3), 28.53 (1-CH_3), 30.09 (1-CH_3), 36.17 (C1), 37.89 (C4), 44.06 (C2), 61.10 (C9), 62.30 (C6′), 68.62 (C4′), 71.51 (C2′), 71.83 (C5′), 72.86 (C3′), 73.07 (C3), 82.44 (C7), 92.06 (C8), 99.61 (C1′), 123.48 (C6), 137.65 (C5), 169.23, 169.42, 169.98, 170.32 and 170.63 (CH_3COO × 5); *m*/*z* (SIMS) 603.2433 (M^+ + Na, $C_{29}H_{40}O_{12}Na$ requires 603.2415).

(3*R*,9*R*)-3-*O*-Glucoside pentaacetate 36. $[\alpha]_D^{26}$ +14.6 (*c*. 1.02, MeOH); λ_{max}/nm (MeOH) 231; ν_{max}/cm^{-1} 2221 (C≡C), 1755 (COO); δ_H(500 MHz) 1.09 and 1.14 (each 3H, s, *gem*-Me), 1.50 (1H, t, *J* 12, 2-H_{ax}), 1.52 (3H, d, *J* 7, 9-Me), 1.86 (3H, s, 5-Me), 1.90 (1H, ddd, *J* 13, 3.5 and 2, 2-H_{eq}), 2.01, 2.03, 2.04, 2.07 and 2.08 (each 3H, s, AcO × 5), 2.02 (1H, 4-H_{ax}), 2.32 (1H, br dd, *J* 17.5 and 5.5, 4-H_{eq}), 3.71 (1H, ddd, *J* 9.5, 5.5 and 2, 5′-H), 3.92 (1H, m, 3-H), 4.13 (1H, dd, *J* 12 and 2, 6′-H), 4.24 (1H, dd, *J* 12 and 5.5, 6′-H), 4.62 (1H, d, *J* 8, 1′-H), 4.95 (1H, dd, *J* 9.5 and 8, 2′-H), 5.06 (1H, t, *J* 9.5, 4′-H), 5.21 (1H, t, *J* 9.5, 3′-H), 5.59 (1H, q, *J* 7, 9-H); δ_C(125 MHz) 20.61, 20.63, 20.67, 20.75 and 21.13 (CH_3COO × 5), 21.68 (9-CH_3), 22.37 (5-CH_3), 28.54 (1-CH_3), 30.09 (1-CH_3), 36.17 (C1), 37.89 (C4), 44.05 (C2), 61.10 (C9), 62.29 (C6′), 68.62 (C4′), 71.51 (C2′), 71.83 (C5′), 72.86 (C3′), 73.07 (C3), 82.44 (C7), 92.04 (C8), 99.60 (C1′), 123.48 (C6), 137.66 (C5), 169.24, 169.43, 170.00, 170.33 and 170.64 (CH_3COO × 5); *m*/*z* (SIMS) 603.2406 (M^+ + Na, $C_{29}H_{40}O_{12}Na$ requires 603.2415).

Epoxidation of tetrapivalates 29, 31 and 35; typical procedure

A solution of MCPBA (74%, 3.49 g, 15.0 mmol) in CH_2Cl_2 (130 ml) was added dropwise to an ice-cooled solution of the tetrapivalate **29** (7.42 g, 9.92 mmol) and the mixture was stirred at 0 °C for 1 h and rt for 5 h. After the reaction mixture was quenched with aq. 10% $Na_2S_2O_3$, CH_2Cl_2 was evaporated off and the organics were extracted with AcOEt. The extracts were washed with saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue, which was purified by CC (CH_2Cl_2–hexane–ether, 5:4:0.8) and then low-pressure CC (CH_2Cl_2–hexane–ether, 3:6:1) to afford the *anti*-epoxide **41a** (2.83 g, 37%) and the *syn*-epoxide **41b** (3.74 g, 49%) as colorless foams, respectively.

Separation of epoxides **50a**,**b** was conducted by low-pressure CC (ether–benzene, 7.5:92.5).

Compound 41a. $[\alpha]_D^{27}$ −24.7 (*c*. 1.01, MeOH); ν_{max}/cm^{-1} 1739 (COO); δ_H(300 MHz) 1.11 and 1.22 (each 9H, s, *tert*-Bu × 2), 1.16 (18H, s, *tert*-Bu × 2), 1.15 and 1.25 (each 3H, s, *gem*-Me), 1.39 (1H, dd, *J* 13.5 and 8, 2-H_{ax}), 1.42 (3H, d, *J* 6.5, 9-Me), 1.48 (3H, s, 5-Me), 1.63 (1H, br dd, *J* 13.5 and 3, 2-H_{eq}), 1.81 (1H, dd, *J* 15 and 6.5, 4-H_{ax}), 2.02 (3H, s, AcO), 2.39 (1H, br dd, *J* 15 and 6, 4-H_{eq}), 3.71 (1H, ddd, *J* 9.5, 6 and 1.5, 5′-H), 4.05 (1H, dd, *J* 12 and 6, 6′-H), 4.22 (1H, dd, *J* 12 and 1.5, 6′-H), 4.69 (1H, q, *J* 6.5, 9-H), 4.85 (1H, d, *J* 8, 1′-H), 4.87 (1H, m, 3-H), 5.04 (1H, dd, *J* 9.5 and 8, 2′-H), 5.10 (1H, t, *J* 9.5, 4′-H), 5.30 (1H, t, *J* 9.5, 3′-H); *m*/*z* (SIMS) 787.4247 (M^+ + Na, $C_{41}H_{64}O_{13}Na$ requires 787.4241).

Compound 41b. $[\alpha]_D^{26}$ −49.2 (*c*. 1.02, MeOH); ν_{max}/cm^{-1} 1740 (COO); δ_H(300 MHz) 1.11 (9H, s, *tert*-Bu), 1.16 (18H, s, *tert*-Bu × 2), 1.18 (3H, s, 1-Me), 1.22 (12H, s, *tert*-Bu and 1-Me), 1.41 (1H, ddd, *J* 12.5, 4.5 and 1.5, 2-H_{eq}), 1.43 (3H, d, *J* 6.5, 9-Me), 1.47 (3H, s, 5-Me), 1.55 (1H, t, *J* 12.5, 2-H_{ax}), 1.83 (1H, dd, *J* 14.5 and 9.5, 4-H_{ax}), 2.02 (3H, s, AcO), 2.33 (1H, ddd, *J* 14.5, 7.5 and 1.5, 4-H_{eq}), 3.69 (1H, ddd, *J* 9.5, 6 and 2, 5′-H), 4.06 (1H, dd, *J* 12.5 and 6, 6′-H), 4.21 (1H, dd, *J* 12.5 and 2, 6′-H), 4.68 (1H, q, *J* 6.5, 9-H), 4.81 (1H, d, *J* 8.5, 1′-H), 4.87 (1H, m, 3-H), 5.04 (1H, dd, *J* 9.5 and 8.5, 2′-H), 5.10 (1H, t, *J* 9.5, 4′-H), 5.28 (1H, t, *J* 9.5, 3′-H); *m*/*z* (SIMS) 787.4248 (M^+ + Na, $C_{41}H_{64}O_{13}Na$ requires 787.4241).

Compound 44a. $[\alpha]_D^{26}$ +19.8 (*c*. 1.01, MeOH); × ν_{max}/cm^{-1} 1737 (COO); δ_H(300 MHz) 1.11, 1.15, 1.16 and 1.22 (each 9H, s, *tert*-Bu × 4), 1.13 and 1.24 (each 3H, s, *gem*-Me), 1.37 (1H, dd, *J* 13.5 and 8, 2-H_{ax}), 1.46 (3H, d, *J* 6.5, 9-Me), 1.48 (3H, s, 5-Me), 1.60 (1H, ddd, *J* 13.5, 3.5 and 1, 2-H_{eq}), 1.79 (1H, dd, *J* 15 and 6.5, 4-H_{ax}), 2.01 (3H, s, AcO), 2.36 (1H, ddd, *J* 15, 5.5 and 1, 4-H_{eq}), 3.71 (1H, ddd, *J* 9.5, 5 and 2, 5′-H), 4.06 (1H, dd, *J* 12.5 and 5, 6′-H), 4.18 (1H, dd, *J* 12.5 and 2, 6′-H), 4.55 (1H, q, *J* 6.5, 9-H), 4.76 (1H, d, *J* 8, 1′-H), 4.86 (1H, m, 3-H), 5.04 (1H, dd, *J* 9.5 and 8, 2′-H), 5.14 (1H, t, *J* 9.5, 4′-H), 5.29 (1H, t, *J* 9.5, 3′-H); *m*/*z* (SIMS) 787.4243 (M^+ + Na, $C_{41}H_{64}O_{13}Na$ requires 787.4241).

Compound 44b. $[\alpha]_D^{25}$ +14.1 (*c*. 1.06, MeOH); ν_{max}/cm^{-1} 1737 (COO); δ_H(300 MHz) 1.11 (9H, s, *tert*-Bu), 1.15 (18H, s, *tert*-Bu × 2), 1.17 (3H, s, 1-Me), 1.22 (12H, s, *tert*-Bu and 1-Me), 1.39 (1H, ddd, *J* 12.5, 4 and 1.5, 2-H_{eq}), 1.45 (3H, d, *J* 6.5, 9-Me), 1.45 (3H, s, 5-Me), 1.53 (1H, t, *J* 12.5, 2-H_{ax}), 1.81 (1H, dd, *J* 15 and 9.5, 4-H_{ax}), 2.00 (3H, s, AcO), 2.31 (1H, br dd, *J* 15 and 7.5, 4-H_{eq}), 3.71 (1H, ddd, *J* 9.5, 5 and 2, 5′-H), 4.07 (1H, dd, *J* 12.5 and 5, 6′-H), 4.19 (1H, dd, *J* 12.5 and 2, 6′-H), 4.55 (1H, q, *J* 6.5, 9-H), 4.76 (1H, d, *J* 8, 1′-H), 4.86 (1H, m, 3-H), 5.04 (1H, dd, *J* 9.5 and 8, 2′-H), 5.14 (1H, t, *J* 9.5, 4′-H), 5.29 (1H, t, *J* 9.5, 3′-H); *m*/*z* (SIMS) 787.4250 (M^+ + Na, $C_{41}H_{64}O_{13}Na$ requires 787.4241).

Compound 50a. $[a]_D^{23}$ +37.9 (*c.* 1.06, MeOH); ν_{max}/cm^{-1} 1740 (COO); δ_H(300 MHz) 1.08 and 1.20 (each 3H, s, *gem*-Me), 1.10, 1.15, 1.16 and 1.21 (each 9H, s, *tert*-Bu × 4), 1.32 (1H, dd, *J* 13 and 9.5, 2-H$_{ax}$), 1.44 (3H, s, 5-Me), 1.48 (3H, d, *J* 7, 9-Me), 1.64 (1H, dd, *J* 14.5 and 8, 4-H$_{ax}$), 1.65 (1H, 2-H$_{eq}$), 2.05 (3H, s, AcO), 2.24 (1H, br dd, *J* 14.5 and 5, 4-H$_{eq}$), 3.69 (1H, ddd, *J* 9.5, 6.5 and 1.5, 5′-H), 3.75 (1H, m, 3-H), 3.97 (1H, dd, *J* 12 and 6, 6′-H), 4.24 (1H, dd, *J* 12 and 2, 6′-H), 4.55 (1H, d, *J* 8, 1′-H), 4.95 (1H, dd, *J* 9.5 and 8, 2′-H), 5.05 (1H, t, *J* 9.5, 4′-H), 5.29 (1H, t, *J* 9.5, 3′-H), 5.45 (1H, q, *J* 7, 9-H); *m*/*z* (SIMS) 765.4417 (M^+ + H, $C_{41}H_{65}O_{13}$ requires 765.4422).

Compound 50b. $[a]_D^{23}$ +15.1 (*c.* 0.99, MeOH); ν_{max}/cm^{-1} 1740 (COO); δ_H(300 MHz) 1.13 and 1.14 (each 3H, s, *gem*-Me), 1.10 and 1.22 (each 9H, s, *tert*-Bu × 2), 1.15 (18H, s, *tert*-Bu × 2), 1.42 (3H, s, 5-Me), 1.44 (2H, m, 2-H$_2$), 1.48 (3H, d, *J* 6.5, 9-Me), 1.75 (1H, dd, *J* 14.5 and 9.5, 4-H$_{ax}$), 2.05 (3H, s, AcO), 2.12 (1H, dd, *J* 14.5 and 7.5, 4-H$_{eq}$), 3.70 (1H, ddd, *J* 10, 6 and 2, 5′-H), 3.81 (1H, m, 3-H), 3.97 (1H, dd, *J* 12 and 6, 6′-H), 4.27 (1H, dd, *J* 12 and 2, 6′-H), 4.58 (1H, d, *J* 8, 1′-H), 4.94 (1H, dd, *J* 10 and 8, 2′-H), 5.06 (1H, t, *J* 10, 4′-H), 5.30 (1H, t, *J* 10, 3′-H), 5.45 (1H, q, *J* 6.5, 9-H); *m*/*z* (SIMS) 765.4413 (M^+ + H, $C_{41}H_{65}O_{13}$ requires 765.4422).

Synthesis of epoxide 47a,b

BzCl (4.85 ml, 41.8 mmol) was added to a solution of the pentaol **9** (1.55 g, 4.19 mmol) in Py (6.5 ml) and the reaction mixture was stirred at rt for 16 h, poured into ice-water and extracted with AcOEt. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue, which was purified by SCC (AcOEt–hexane, 1:3) to afford the pentabenzoate (2.96 g, 79%) as a colorless foam; $[a]_D^{22}$ −14.1 (*c.* 0.99, $CHCl_3$); λ_{max}/nm 230, 273; ν_{max}/cm^{-1} 2217 (C≡C), 1732 (COO); δ_H(300 MHz) 1.02 and 1.05 (each 3H, s, *gem*-Me), 1.48 (1H, t, *J* 12, 2-H$_{ax}$), 1.64 (3H, d, *J* 6.5, 9-Me), 1.71 (3H, s, 5-Me), 1.92 (1H, ddd, *J* 12, 3.5 and 2, 2-H$_{eq}$), 1.95 (1H, br dd, *J* 18 and 9, 4-H$_{ax}$), 2.24 (1H, br dd, *J* 18 and 5, 4-H$_{eq}$), 3.98 (1H, m, 3-H), 4.19 (1H, ddd, *J* 10, 6 and 3, 5′-H), 4.50 (1H, dd, *J* 12 and 6, 6′-H), 4.63 (1H, dd, *J* 12 and 3, 6′-H), 4.96 (1H, d, *J* 8, 1′-H), 5.50 (1H, dd, *J* 10 and 8, 2′-H), 5.61 (1H, t, *J* 10, 4′-H), 5.84 (1H, q, *J* 6.5, 9-H), 5.91 (1H, t, *J* 10, 3′-H), 7.25–7.59 (15H, m, Ar–H), 7.81–8.07 (10H, m, Ar–H); *m*/*z* (SIMS) 913.3202 (M^+ + Na, $C_{54}H_{50}O_{12}Na$ requires 913.3197). According to the procedure described in the epoxidation of tetrapivalates **29**, **31** and **35**, this pentabenzoate (641 mg) was treated with MCPBA. The resulting crude products were purified by SCC (AcOEt–hexane, 1:3) and then low-pressure CC (CH_2Cl_2–hexane–AcOEt, 4:6:0.7) to afford the *anti*-epoxide **47a** (308 mg, 47%; 37% from **9**) and the *syn*-epoxide **47b** (183 mg, 28%; 22% from **9**) as colourless foams, respectively.

Compound 47a. $[a]_D^{22}$ −10.7 (*c.* 1.03, $CHCl_3$); ν_{max}/cm^{-1} 1731 (COO); δ_H(300 MHz) 1.02 and 1.15 (each 3H, s, *gem*-Me), 1.26 (3H, s, 5-Me), 1.33 (1H, dd, *J* 13.5 and 10, 2-H$_{ax}$), 1.55 (1H, dd, *J* 14.5 and 8, 4-H$_{ax}$), 1.58 (3H, d, *J* 6.5, 9-Me), 1.68 (1H, ddd, *J* 13.5, 3.5 and 1, 2-H$_{eq}$), 2.17 (1H, ddd, *J* 14.5, 3.5 and 1, 4-H$_{eq}$), 3.80 (1H, m, 3-H), 4.15 (1H, ddd, *J* 10, 6 and 3, 5′-H), 4.49 (1H, dd, *J* 12 and 6, 6′-H), 4.61 (1H, dd, *J* 12 and 3, 6′-H), 4.87 (1H, d, *J* 8, 1′-H), 5.47 (1H, dd, *J* 10 and 8, 2′-H), 5.62 (1H, t, *J* 10, 4′-H), 5.70 (1H, q, *J* 6.5, 9-H), 5.90 (1H, t, *J* 10, 3′-H), 7.24–7.59 (15H, m, Ar–H), 7.81–8.05 (10H, m, Ar–H); *m*/*z* (SIMS) 929.3151 (M^+ + Na, $C_{54}H_{50}O_{13}Na$ requires 929.3146).

Compound 47b. $[a]_D^{21}$ +9.1 (*c.* 0.99, $CHCl_3$); λ_{max}/nm 230, 273; ν_{max}/cm^{-1} 1730 (COO); δ_H(300 MHz) 1.05 and 1.08 (each 3H, s, *gem*-Me), 1.32 (3H, s, 5-Me), 1.45 (2H, m, 2-H$_2$), 1.61 (3H, d, *J* 6.5, 9-Me), 1.69 (1H, dd, *J* 15 and 10, 4-H$_{ax}$), 2.06 (1H, dd, *J* 15 and 7, 4-H$_{eq}$), 3.86 (1H, m, 3-H), 4.16 (1H, ddd, *J* 10, 6 and 3, 5′-H), 4.49 (1H, dd, *J* 12 and 6, 6′-H), 4.62 (1H, dd, *J* 12 and 3, 6′-H), 4.87 (1H, d, *J* 8, 1′-H), 5.45 (1H, dd, *J* 10 and 8, 2′-H), 5.59 (1H, t, *J* 10, 4′-H), 5.69 (1H, q, *J* 6.5, 9-H), 5.88 (1H, t, *J* 10, 3′-H), 7.25–7.61 (15H, m, Ar–H), 7.80–8.07 (10H, m, Ar–H); *m*/*z* (SIMS) 929.3129 (M^+ + Na, $C_{54}H_{50}O_{13}Na$ requires 929.3146).

Synthesis of allenic triol-glucoside pentaacetates 42, 45, 48 and 51 from anti-epoxides 41a, 44a, 47a and 50a; typical procedure

A solution of DIBAL-H (1.0 M in CH_2Cl_2; 13.8 ml, 13.8 mmol) was added to a solution of the epoxide **41a** (680 mg, 0.89 mmol) in dry CH_2Cl_2 (20 ml) at 0 °C and the mixture was stirred at 0 °C for 1 h and rt for 1.5 h. After the excess DIBAL-H was destroyed by an addition of moist silica gel (SiO_2–H_2O, 10:1; 5 g), the mixture was diluted with MeOH and the resulting suspension was centrifuged at 3000*g* for 10 min. The residue was rinsed with MeOH twice. The combined supernatant was evaporated to give the crude product which, without purification, was dissolved in Py (20 ml) and Ac_2O (6 ml) was added to it. After being stirred at rt for 16 h, poured into ice-water and extracted with AcOEt. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue, which was purified by SCC (ether–CH_2Cl_2, 1:4) to afford the (3*S*,9*S*)-allenic triol-9-*O*-glucoside pentaacetate **42** (157 mg, 29% from **41a**) as a colorless foam. ^{1}H NMR data of the synthetic (3*S*,9*R*)-9-*O*-glucoside **45** were in accordance with those of 9-*O*-glucoside isolated[7] from *Lycium halimifolium Mill*.

(3*S*,9*S*)-9-*O*-Glucoside pentaacetate 42. $[a]_D^{26}$ −16.5 (*c.* 0.97, MeOH); ν_{max}/cm^{-1} 3596 and 3497 (OH), 1955 (C=C=C), 1754 (COO); δ_H(500 MHz) 1.06 and 1.36 (each 3H, s, *gem*-Me), 1.31 (3H, d, *J* 6.5, 9-Me), 1.36 (1H, t, *J* 12, 2-H$_{ax}$), 1.41 (3H, s, 5-Me), 1.45 (1H, dd, *J* 13 and 11.5, 4-H$_{ax}$), 1.95 (1H, ddd, *J* 12.5, 3.5 and 2, 2-H$_{eq}$), 2.01, 2.02, 2.03, 2.04 and 2.08 (each 3H, s, AcO × 5), 2.27 (1H, ddd, *J* 13, 4 and 2, 4-H$_{eq}$), 3.58 (1H, ddd, *J* 10, 5 and 2.5, 5′-H), 4.12 (1H, dd, *J* 12 and 2.5, 6′-H), 4.24 (1H, dd, *J* 12 and 5, 6′-H), 4.37 (1H, dq, *J* 8 and 6.5, 9-H), 4.71 (1H, d, *J* 8, 1′-H), 4.98 (1H, dd, *J* 9.5 and 8, 2′-H), 5.09 (1H, t, *J* 9.5, 4′-H), 5.13 (1H, d, *J* 8, 8-H), 5.18 (1H, t, *J* 9.5, 3′-H), 5.35 (1H, m, 3-H); δ_C(125 MHz) 20.57, 20.60, 20.66, 20.74 and 21.34 (*C*H$_3$COO × 5), 21.84 (9-CH$_3$), 29.18 (1-CH$_3$), 31.21 (5-CH$_3$), 32.20 (1-CH$_3$), 35.19 (C1), 45.03 and 45.08 (C2 and C4), 62.03 (C6′), 67.70 (C3), 68.44 (C4′), 71.42 (C2′), 71.76 (C5′), 71.89 (C5), 72.93 (C3′), 73.51 (C9), 96.52 (C8), 97.88 (C1′), 116.30 (C6), 169.21, 169.36, 170.31, 170.40 and 170.58 (CH$_3$*C*OO × 5), 199.01 (C7); *m*/*z* (SIMS) 621.2518 (M^+ + Na, $C_{29}H_{42}O_{13}Na$ requires 621.2521).

(3*S*,9*R*)-9-*O*-Glucoside pentaacetate 45. $[a]_D^{27}$ −2.0 (*c.* 0.99, MeOH); ν_{max}/cm^{-1} 3595 and 3487 (OH), 1958 (C=C=C), 1755 (COO); δ_H(500 MHz) 1.08 (3H, s, 1-Me), 1.25 (3H, d, *J* 6, 9-Me), 1.36 (6H, s, 1-Me and 5-Me), 1.36 (1H, t, *J* 12, 2-H$_{ax}$), 1.46 (1H, t, *J* 12.5, 4-H$_{ax}$), 1.96 (1H, ddd, *J* 12, 4 and 2.5, 2-H$_{eq}$), 2.01 (3H), 2.03 (3H), 2.04 (6H) and 2.08 (3H) (each s, AcO × 5), 2.24 (1H, ddd, *J* 12.5, 4 and 2.5, 4-H$_{eq}$), 3.64 (1H, ddd, *J* 9.5, 4.5 and 2.5, 5′-H), 4.11 (1H, dd, *J* 12.5 and 2.5, 6′-H), 4.25 (1H, dd, *J* 12.5 and 4.5, 6′-H), 4.28 (1H, quint., *J* 6, 9-H), 4.60 (1H, d, *J* 8, 1′-H), 4.96 (1H, dd, *J* 9.5 and 8, 2′-H), 5.08 (1H, t, *J* 9.5, 4′-H), 5.19 (1H, t, *J* 9.5, 3′-H), 5.35 (1H, m, 3-H), 5.39 (1H, d, *J* 6, 8-H); δ_C(125 MHz) 20.52, 20.61, 20.63, 20.64 and 20.76 (9-CH$_3$ and *C*H$_3$COO × 4), 21.40 (*C*H$_3$COO), 29.22 (1-CH$_3$), 31.16 (5-CH$_3$), 31.97 (1-CH$_3$), 35.19 (C1), 45.06 (C4), 45.26 (C2), 62.08 (C6′), 67.93 (C3), 68.45 (C4′), 71.52 (C2′), 71.85 (C5′), 72.27 (C5), 72.88 (C3′), 75.22 (C9), 97.57 (C8), 99.66 (C1′), 116.74 (C6), 169.14, 169.41, 170.37, 170.44 and 170.66 (CH$_3$*C*OO × 5), 198.70 (C7); *m*/*z* (SIMS) 621.2536 (M^+ + Na, $C_{29}H_{42}O_{13}Na$ requires 621.2520).

(3*S*,9*S*)-3-*O*-Glucoside pentaacetate 48. $[\alpha]_D^{20}$ −58.3 (*c*. 1.05, MeOH); ν_{max}/cm^{-1}: 3591 and 3508 (OH), 1960 (C=C=C), 1754 (COO); δ_H(500 MHz) 1.06 and 1.29 (each 3H, s, *gem*-Me), 1.30 (3H, d, *J* 6.5, 9-Me), 1.33 (1H, dd, *J* 13.5 and 11, 4-H_{ax}), 1.36 (3H, s, 5-Me), 1.39 (1H, t, *J* 12, 2-H_{ax}), 1.99 (1H, ddd, *J* 12, 4.5 and 2.5, 2-H_{eq}), 2.00 (3H), 2.03 (6H), 2.05 (3H) and 2.08 (3H) (each s, AcO × 5), 2.17 (1H, ddd, *J* 13.5, 4.5 and 2.5, 4-H_{eq}), 3.72 (1H, ddd, *J* 10, 5.5 and 2.5, 5′-H), 4.13 (1H, dd, *J* 12.5 and 2.5, 6′-H), 4.20 (1H, m, 3-H), 4.25 (1H, dd, *J* 12.5 and 5.5, 6′-H), 4.63 (1H, d, *J* 8, 1′-H), 4.95 (1H, dd, *J* 10 and 8, 2′-H), 5.06 (1H, t, *J* 10, 4′-H), 5.20 (1H, t, *J* 10, 3′-H), 5.35 (2H, m, 8-H and 9-H); δ_C(125 MHz) 19.85 (9-CH_3), 20.62, 20.63, 20.71, 20.76 and 21.27 (CH_3COO × 5), 29.37 (1-CH_3), 31.08 (5-CH_3), 32.05 (1-CH_3), 35.05 (C1), 45.44 (C4), 47.06 (C2), 62.27 (C6′), 68.37 (C9), 68.66 (C4′), 71.52 (C2′), 71.73 (C5′), 72.28 (C5), 72.94 (C3′), 73.40 (C3), 96.14 (C8), 100.01 (C1′), 117.43 (C6), 169.27, 169.45, 170.30, 170.33 and 170.65 (CH_3COO × 5), 199.26 (C7); *m*/*z* (SIMS) 621.2508 (M^+ + Na, $C_{29}H_{42}O_{13}Na$ requires 621.2520).

(3*S*,9*R*)-3-*O*-Glucoside pentaacetate 51. $[\alpha]_D^{20}$ +25.3 (*c*. 1.03, MeOH); ν_{max}/cm^{-1} 3593 and 3487 (OH), 1958 (C=C=C), 1754 (COO); δ_H(500 MHz) 1.06 and 1.29 (each 3H, s, *gem*-Me), 1.30 (3H, d, *J* 6.5, 9-Me), 1.31 (1H, 4-H_{ax}), 1.36 (3H, s, 5-Me), 1.38 (1H, t, *J* 12, 2-H_{ax}), 2.00, 2.02, 2.03, 2.05 and 2.08 (each 3H, s, AcO × 5), 2.00 (1H, 2-H_{eq}), 2.18 (1H, ddd, *J* 12.5, 3.5 and 2, 4-H_{eq}), 3.72 (1H, ddd, *J* 9.5, 5.5 and 2.5, 5′-H), 4.13 (1H, dd, *J* 12 and 2.5, 6′-H), 4.20 (1H, m, 3-H), 4.25 (1H, dd, *J* 12 and 5.5, 6′-H), 4.64 (1H, d, *J* 8, 1′-H), 4.95 (1H, dd, *J* 9.5 and 8, 2′-H), 5.06 (1H, t, *J* 9.5, 4′-H), 5.20 (1H, t, *J* 9.5, 3′-H), 5.37 (2H, m, 8-H and 9-H); δ_C(125 MHz) 19.78 (9-CH_3), 20.62, 20.64, 20.71, 20.76 and 21.26 (CH_3COO × 5), 29.33 (1-CH_3), 31.13 (5-CH_3), 31.89 (1-CH_3), 35.16 (C1), 45.52 (C4), 47.16 (C2), 62.27 (C6′), 68.08 (C9), 68.65 (C4′), 71.53 (C2′), 71.73 (C5′), 72.30 (C5), 72.94 (C3′), 73.49 (C3), 96.16 (C8), 100.07 (C1′), 117.60 (C6), 169.29, 169.47, 170.30, 170.32 and 170.67 (CH_3COO × 5), 199.05 (C7); *m*/*z* (SIMS) 621.2541 (M^-+Na, $C_{29}H_{42}O_{13}Na$ requires 621.2520).

Methanolysis of pentaacetates 42, 45, 48 and 51; typical procedure

To a solution of the pentaacetate **42** (101 mg, 0.17 mmol) in MeOH (5 ml) was added NaOMe (1 M in MeOH; 0.25 ml, 0.25 mmol) and the mixture was stirred at rt for 4 h. The mixture was concentrated to give a residue, which was purified by SPE CC (CH_2Cl_2–MeOH, 4:1) to yield the hexaol **11** (59 mg, 90%) as a colourless foam. ^1H and ^{13}C NMR data (in CD_3OD solution) of the synthetic (3*S*,9*S*)-9-*O*-glucosides **12** were identical with those of the glucoside isolated[8] from *Premna subscandes*, while those (in D_2O solution) of 9-*O*-glucosides **11** and **12** were accordance with those of glucosides previously prepared.[9]

(3*S*,9*S*)-9-*O*-Glucoside 11. $[\alpha]_D^{27}$ −29.1 (*c*. 1.00, MeOH); δ_H(500 MHz, CD_3OD) 1.05 and 1.30 (each 3H, s, *gem*-Me), 1.23 (1H, t, *J* 12, 2-H_{ax}), 1.32 (3H, d, *J* 6.5, 9-Me), 1.30 (1H, 4-H_{ax}), 1.39 (3H, s, 5-Me), 1.84 (1H, ddd, *J* 12.5, 4.5 and 2, 2-H_{eq}), 2.14 (1H, ddd, *J* 13, 4.5 and 2, 4-H_{eq}), 3.16 (1H, ddd, *J* 9, 6 and 2.5, 5′-H), 3.18 (1H, br t, *J* 8, 2′-H), 3.30 (2H, m, 3′-H and 4′-H), 3.65 (1H, dd, *J* 12 and 6, 6′-H), 3.83 (1H, dd, *J* 12 and 2.5, 6′-H), 4.16 (1H, tt-like, *J* 11.5 and 4.5, 3-H), 4.48 (1H, m, 9-H), 4.50 (1H, d, *J* 8, 1′-H), 5.21 (1H, d, *J* 8, 8-H); δ_C(125 MHz, CD_3OD) 22.56 (9-CH_3), 29.60 (1-CH_3), 31.79 (5-CH_3), 33.29 (1-CH_3), 36.17 (C1), 49.95 (C4), 50.34 (C2), 62.78 (C6′), 64.76 (C3), 71.65 (C4′), 72.70 (C5), 74.01 (C9), 75.08 (C2′), 78.08 (C5′), 78.26 (C3′), 97.79 (C8), 101.09 (C1′), 116.83 (C6), 201.15 (C7); δ_H(500 MHz, D_2O) 1.03 and 1.20 (each 3H, s, *gem*-Me), 1.24 (1H, t, *J* 12, 2-H_{ax}), 1.31 (3H, d, *J* 6.5, 9-Me), 1.36 (3H, s, 5-Me), 1.36 (1H, dd, *J* 13.5 and 12, 4-H_{ax}), 1.84 (1H, ddd, *J* 12, 4 and 2, 2-H_{eq}), 2.11 (1H, ddd, *J* 13.5, 4 and 2, 4-H_{eq}), 3.22 (1H, dd, *J* 9.5 and 8, 2′-H), 3.29 (1H, ddd, *J* 9.5, 5.5 and 2, 5′-H), 3.32 (1H, t, *J* 9.5, 4′-H), 3.40 (1H, t, *J* 9.5, 3′-H), 3.64 (1H, dd, *J* 12.5 and 5.5, 6′-H), 3.84 (1H, dd, *J* 12.5 and 2, 6′-H), 4.16 (1H, tt, *J* 12 and 4, 3-H), 4.49 (1H, dq, *J* 8 and 6.5, 9-H), 4.59 (1H, d, *J* 8, 1′-H), 5.23 (1H, d, *J* 8, 8-H); δ_C(125 MHz, D_2O) 21.09 (9-CH_3), 28.24 (1-CH_3), 30.49 (5-CH_3), 31.93 (1-CH_3), 34.61 (C1), 47.39 (C4), 47.75 (C2), 60.91 (C6′), 64.07 (C3), 69.74 (C4′), 72.01 (C5), 73.18 (C2′), 74.18 (C9), 76.05 (C3′), 76.30 (C5′), 95.84 (C8), 99.21 (C1′), 115.15 (C6), 200.57 (C7); *m*/*z* (SIMS) 411.1978 (M^+ + Na, $C_{19}H_{32}O_8Na$ requires 411.1993).

(3*S*,9*R*)-9-*O*-Glucoside 12. $[\alpha]_D^{23}$ 0 (*c*. 0.77, MeOH); δ_H(500 MHz, CD_3OD) 1.10 and 1.30 (each 3H, s, *gem*-Me), 1.24 (1H, t, *J* 12, 2-H_{ax}), 1.30 (3H, d, *J* 6.5, 9-Me), 1.31 (1H, 4-H_{ax}), 1.34 (3H, s, 5-Me), 1.85 (1H, ddd, *J* 12, 4 and 2, 2-H_{eq}), 2.14 (1H, ddd, *J* 12.5, 4 and 2, 4-H_{eq}), 3.16 (1H, dd, *J* 9 and 8, 2′-H), 3.23 (1H, ddd, *J* 9.5, 5.5 and 2.5, 5′-H), 3.31 (2H, m, 3′-H and 4′-H), 3.67 (1H, dd, *J* 12 and 5.5, 6′-H), 3.84 (1H, dd, *J* 12 and 2.5, 6′-H), 4.16 (1H, tt-like, *J* 11.5 and 4, 3-H), 4.39 (1H, d, *J* 8, 1′-H), 4.40 (1H, quint., *J* 6.5, 9-H), 5.47 (1H, d, *J* 6.5, 8-H); δ_C(125 MHz, CD_3OD) 19.89 (9-CH_3), 28.82 (1-CH_3), 30.84 (5-CH_3), 32.29 (1-CH_3), 35.53 (C1), 49.27 (C4), 49.83 (C2), 62.05 (C6′), 64.05 (C3), 70.86 (C4′), 72.09 (C5), 74.51 (C2′), 75.20 (C9), 77.24 (C5′), 77.46 (C3′), 98.32 (C8), 102.36 (C1′), 116.59 (C6), 199.43 (C7); δ_H(500 MHz, D_2O) 1.07 and 1.20 (each 3H, s, *gem*-Me), 1.25 (1H, t, *J* 12, 2-H_{ax}), 1.28 (3H, d, *J* 6.5, 9-Me), 1.32 (3H, s, 5-Me), 1.38 (1H, dd, *J* 12.5 and 12, 4-H_{ax}), 1.85 (1H, ddd, *J* 12, 4 and 2, 2-H_{eq}), 2.11 (1H, ddd, *J* 12.5, 4 and 2, 4-H_{eq}), 3.19 (1H, dd, *J* 9 and 8, 2′-H), 3.34 (2H, m, 4′-H and 5′-H), 3.41 (1H, t, *J* 9, 3′-H), 3.67 (1H, dd, *J* 12 and 5, 6′-H), 3.84 (1H, dd, *J* 12 and 0.5, 6′-H), 4.16 (1H, tt, *J* 12 and 4, 3-H), 4.44 (1H, quint., *J* 6.5, 9-H), 4.52 (1H, d, *J* 8, 1′-H), 5.41 (1H, d, *J* 6.5, 8-H); δ_C(125 MHz, D_2O) 19.83 (9-CH_3), 28.33 (1-CH_3), 30.38 (5-CH_3), 31.66 (1-CH_3), 34.70 (C1), 47.42 (C4), 47.91 (C2), 60.90 (C6′), 64.10 (C3), 69.69 (C4′), 72.23 (C5), 73.41 (C2′), 76.04, 76.21 and 76.40 (C3′, C5′ and C9), 96.93 (C8), 101.12 (C1′), 115.55 (C6), 199.76 (C7); *m*/*z* (SIMS) 411.1996 (M^+ + Na, $C_{19}H_{32}O_8Na$ requires 411.1993).

(3*S*,9*S*)-3-*O*-Glucoside 13. $[\alpha]_D^{20}$ −57.8 (*c*. 0.69, MeOH); δ_H(500 MHz, D_2O) 1.05 and 1.21 (each 3H, s, *gem*-Me), 1.23 (3H, d, *J* 6, 9-Me), 1.32 (3H, s, 5-Me), 1.37 (1H, t, *J* 12, 2-H_{ax}), 1.42 (1H, t, *J* 12.5, 4-H_{ax}), 1.97 (1H, br d, *J* 12, 2-H_{eq}), 2.23 (1H, br d, *J* 12.5, 4-H_{eq}), 3.18 (1H, dd, *J* 9 and 8, 2′-H), 3.34 (1H, t, *J* 9, 4′-H), 3.42 (1H, ddd, *J* 9, 6 and 2, 5′-H), 3.45 (1H, t, *J* 9, 3′-H), 3.67 (1H, dd, *J* 12 and 6, 6′-H), 3.87 (1H, dd, *J* 12 and 2, 6′-H), 4.28 (1H, m, 3-H), 4.34 (1H, quint., *J* 6, 9-H), 4.55 (1H, d, *J* 8, 1′-H), 5.37 (1H, d, *J* 6, 8-H); δ_C(125 MHz, D_2O) 21.81 (9-CH_3), 28.38 (1-CH_3), 30.08 (5-CH_3), 31.84 (1-CH_3), 34.54 (C1), 44.89 (C4), 46.46 (C2), 60.86 (C6′), 66.11 (C9), 69.81 (C4′), 72.06 (C5), 73.25 (C2′), 73.42 (C3), 75.96 and 76.01 (C3′ and C5′), 98.51 (C8), 100.86 (C1′), 115.71 (C6), 199.00 (C7); *m*/*z* (SIMS) 411.2007 (M^+ + Na, $C_{19}H_{32}O_8Na$ requires 411.1993).

(3*S*,9*R*)-3-*O*-Glucoside 14. $[\alpha]_D^{27}$ −26.3 (*c*. 0.99, MeOH); δ_H(500 MHz, D_2O) 1.05 and 1.21 (each 3H, s, *gem*-Me), 1.23 (3H, d, *J* 6.5, 9-Me), 1.33 (3H, s, 5-Me), 1.37 (1H, t, *J* 12.5, 2-H_{ax}), 1.43 (1H, dd, *J* 13 and 12, 4-H_{ax}), 1.96 (1H, ddd, *J* 12.5, 4 and 2, 2-H_{eq}), 2.24 (1H, ddd, *J* 13, 4 and 2, 4-H_{eq}), 3.18 (1H, dd, *J* 9.5 and 8, 2′-H), 3.34 (1H, t, *J* 9.5, 4′-H), 3.43 (1H, ddd, *J* 9.5, 6 and 2, 5′-H), 3.45 (1H, t, *J* 9.5, 3′-H), 3.67 (1H, dd, *J* 12 and 6 Hz, 6′-H), 3.87 (1H, dd, *J* 12 and 2, 6′-H), 4.29 (1H, m, 3-H), 4.34 (1H, quint, *J* 6.5, 9-H), 4.56 (1H, d, *J* 8, 1′-H), 5.37 (1H, d, *J* 6.5, 8-H); δ_C(125 MHz, D_2O) 21.83 (9-CH_3), 28.38 (1-CH_3), 30.25 (5-CH_3), 31.59 (1-CH_3), 34.67 (C1), 44.83 (C4), 46.52 (C2), 60.86 (C6′), 66.24 (C9), 69.81 (C4′), 72.08 (C5), 73.26 (C2′), 73.43 (C3), 75.96 and 76.01 (C3′ and C5′), 98.52

(C8), 100.86 (C1′), 115.69 (C6), 198.93 (C7); *m/z* (SIMS) 411.2011 (M^+ + Na, $C_{19}H_{32}O_8Na$ requires 411.1993).

Enzymatic hydrolysis of allenic triol-glucosides 11, 12, 13 and 14; typical procedure

β-Glucosidase from sweet almonds (Nacalai tesque Co., 30 mg) was added to a solution of the glucoside **11** (20 mg) in water (3 ml) and the mixture was stirred at 37 °C for 16 h. The mixture was concentrated in *vacuo* to furnish a residue, which was purified by SCC ($MeOH–CH_2Cl_2$, 15:85) to provide the aglycone. This was dissolved in AcOEt (3 ml) and active MnO_2 (160 mg) was added to it. After being stirred at rt for 4 h, the mixture was filtered through Celite. Evaporation of the filtrate gave a residue, which was purified by SPE CC (acetone–hexane, 1:3) to give grasshopper ketone **3** (10.7 mg, 93% from **11**). ^{1}H NMR data were identical with those reported.[19]

Benzoylation of allenic triol-glucosides 11, 12, 13 and 14; typical procedure

To a solution of the hexaol **11** (6.4 mg, 0.016 mmol) in Py (1 ml) was added BzCl (0.2 ml, 1.7 mmol) and the reaction mixture was stirred at rt for 24 h, poured into ice-water and extracted with AcOEt. The extracts were washed with aq. 5% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue, which was purified by SCC (ether–CH_2Cl_2, 1:4) and then PTLC (ether–CH_2Cl_2, 1:9) to afford the pentabenzoate **43** (13.6 mg, 91%) as a colorless foam.

(3*S*,9*S*)-9-*O*-Glucoside pentabenzoate 43. λ_{max}/nm 230, 273; ν_{max}/cm^{-1} 3594 (OH), 1957 (C=C=C), 1732 (COO); δ_H(300 MHz) 1.00 and 1.35 (each 3H, s, *gem*-Me), 1.31 (3H, d, *J* 6.5, 9-Me), 1.35–1.48 (2H, m, 2-H_{ax} and 4-H_{ax}), 1.44 (3H, s, 5-Me), 2.03 (1H, ddd, *J* 12, 4 and 2, 2-H_{eq}), 2.27 (1H, ddd, *J* 13, 4 and 2, 4-H_{eq}), 4.06 (1H, ddd, *J* 9.5, 6 and 3, 5′-H), 4.45 (1H, m, 9-H), 4.48 (1H, dd, *J* 12 and 6, 6′-H), 4.66 (1H, dd, *J* 12 and 3, 6′-H), 5.07 (1H, d, *J* 8, 1′-H), 5.09 (1H, d, *J* 8, 8-H), 5.53 (1H, dd, *J* 9.5 and 8, 2′-H), 5.55 (1H, m, 3-H), 5.64 (1H, t, *J* 9.5, 4′-H), 5.87 (1H, t, *J* 9.5, 3′-H), 7.26–7.60 (15H, m, Ar–H), 7.81–8.06 (10H, m, Ar–H); *m/z* (SIMS) 931.3301 (M^+ + Na, $C_{54}H_{52}O_{13}Na$ requires 931.3303).

(3*S*,9*R*)-9-*O*-Glucoside pentabenzoate 46. λ_{max}/nm 230, 273; ν_{max}/cm^{-1} 3593 (OH), 1963 (C=C=C), 1732 (COO); δ_H(300 MHz) 1.07 (3H, s, 1-Me), 1.20 (3H, d, *J* 6.5, 9-Me), 1.34 (6H, s, 1-Me and 5-Me), 1.43 (1H, t, *J* 12, 2-H_{ax}), 1.52 (1H, t, *J* 12, 4-H_{ax}), 2.05 (1H, ddd, *J* 12, 3.5 and 2, 2-H_{eq}), 2.30 (1H, ddd, *J* 12, 3.5 and 2, 4-H_{eq}), 4.12 (1H, ddd, *J* 9.5, 6 and 3, 5′-H), 4.37 (1H, quint., *J* 6.5, 9-H), 4.50 (1H, dd, *J* 12 and 6, 6′-H), 4.63 (1H, dd, *J* 12 and 3, 6′-H), 4.97 (1H, d, *J* 8, 1′-H), 5.44 (1H, d, *J* 6.5, 8-H), 5.52 (1H, dd, *J* 9.5 and 8, 2′-H), 5.57 (1H, m, 3-H), 5.65 (1H, t, *J* 9.5, 4′-H), 5.89 (1H, t, *J* 9.5, 3′-H), 7.25–7.58 (15H, m, Ar–H), 7.81–8.06 (10H, m, Ar–H); *m/z* (SIMS) 931.3307 (M^+ + Na, $C_{54}H_{52}O_{13}Na$ requires 931.3303).

(3*S*,9*S*)-3-*O*-Glucoside pentabenzoate 49. λ_{max}/mm 230, 273; ν_{max}/cm^{-1} 3592 (OH), 1962 (C=C=C), 1732 (COO); δ_H(300 MHz) 0.98, 1.20 and 1.24 (each 3H, s, *gem*-Me and 5-Me), 1.21 (1H, 4-H_{ax}), 1.29 (1H, t, *J* 12.5, 2-H_{ax}), 1.38 (3H, d, *J* 6, 9-Me), 1.96 (1H, br d, *J* 12.5, 2-H_{eq}), 2.08 (1H, br d, *J* 12, 4-H_{eq}), 4.18 (1H, ddd, *J* 9.5, 6 and 3, 5′-H), 4.25 (1H, m, 3-H), 4.50 (1H, dd, *J* 12 and 6, 6′-H), 4.62 (1H, dd, *J* 12 and 3, 6′-H), 4.98 (1H, d, *J* 8, 1′-H), 5.43 (1H, d, *J* 5.5, 8-H), 5.50 (1H, dd, *J* 9.5 and 8, 2′-H), 5.57 (1H, m, 9-H), 5.62 (1H, t, *J* 9.5, 4′-H), 5.89 (1H, t, *J* 9.5, 3′-H), 7.25–7.56 (15H, m, Ar–H), 7.81–8.05 (10H, m, Ar–H); *m/z* (SIMS) 931.3293 (M^+ + Na, $C_{54}H_{52}O_{13}Na$ requires 931.3303).

(3*S*,9*R*)-3-*O*-Glucoside pentabenzoate 52. λ_{max}/mm 230, 273; ν_{max}/cm^{-1} 3593 (OH), 1963 (C=C=C), 1732 (COO); δ_H(500 MHz) 1.01 (3H, s, 1-Me), 1.19 and 1.20 (each 3H, s, 1-Me and 5-Me), 1.2 (1H, 4-H_{ax}), 1.27 (1H, t, *J* 12.5, 2-H_{ax}), 1.39 (3H, d, *J* 6.5, 9-Me), 1.96 (1H, br d, *J* 12.5, 2-H_{eq}), 2.02 (1H, br d, *J* 12, 4-H_{eq}), 4.17 (1H, ddd, *J* 9.5, 6 and 3, 5′-H), 4.23 (1H, m, 3-H), 4.50 (1H, dd, *J* 12 and 6, 6′-H), 4.62 (1H, dd, *J* 12 and 3, 6′-H), 4.95 (1H, d, *J* 8, 1′-H), 5.42 (1H, d, *J* 4.5, 8-H), 5.48 (1H, dd, *J* 9.5 and 8, 2′-H), 5.60 (1H, m, 9-H), 5.61 (1H, t, *J* 9.5, 4′-H), 5.87 (1H, t, *J* 9.5, 3′-H), 7.2–7.6 (15H, m, Ar–H), 7.8–8.1 (10H, m, Ar–H); *m/z* (SIMS) 931.3320 (M^+ + Na, $C_{54}H_{52}O_{13}Na$ requires 931.3303).

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