Stereoselective Conversion of Aucubin into Polyfunctionalized Tetrahydro-1*H*-cyclopenta[*c*]furan Glucosides

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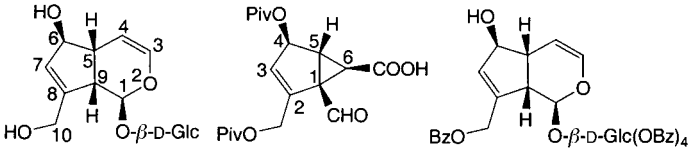
Mitsunobu reaction of 2′,3′,4′,6′,10-penta-*O*-pivaloylaucubin (**6**) with phthalimide, triphenylphosphine, and diethyl azodicarboxylate gave (6*R*)-6-phthalimido-perpivaloylbartsioside (**10**) (*Scheme 1*). Selective oxidation reactions performed with perpivaloylaucubin (**12**) yielded (1*R*)- and (1*S*)-3(β-D-glucopyranosyloxy)-1*H*-cyclopenta[*c*]furan-1-carboxaldehydes **13** and **14** respectively (*Scheme 2*). Similarly, perpivaloyl-6-epiaucubin (**9**) and **10** afforded the corresponding (1*S*)-carboxaldehyde **15** and (1*R*)-carboxaldehyde **16**, respectively. The protected cyclopentafuran glycosides obtained in this way are versatile synthons, which may prove useful for further chemical diversification.

1. Introduction. – The use of natural iridoid glycosides as starting materials for the chiral pool synthesis of cyclopentanoid compounds of biological interest has received considerable attention in recent years. Actually, apart from their classical applications in prostaglandin synthesis [1–6], iridoids were recently employed as natural precursors of several carbocyclic nucleoside analogues [7–9] and insect antifeedants [10]. In this context, aucubin (=(1*S*,4a*R*,5*S*,7a*S*)-1,4a,5,7a-tetrahydro-5-hydroxy-7-(hydroxmethyl)-cyclopenta[*c*]pyran-1-yl β-D-glucopyranoside; **1**), readily available in large amounts from the fresh fruits and leaves of *Aucuba japonica* THUNB. (Cornaceae) [11], appears particularly suitable for the development of new chiral synthons. For our part, we recently reported the conversion of aucubin to conformationally restricted cyclopropa-fused analogues of mannostatins [12], and to new heterocyclic systems derived from 8,9-diazatricyclo[4.4.0.$0^{1,5}$]decane [13]. In both cases, a similar successful strategy permitted differentiation of the two masked aldehydic functions present in aucubin aglycone, after rearrangement to the pivaloyl ester **2** of (1*S*,4*R*,5*R*,6*R*)-4-hydroxy-2-(hydroxymethyl)-1-formylbicyclo[3.1.0]hex-2-ene-6-carboxylic acid, in which the two corresponding C-atoms occur at different oxidation levels. In a continuation of our work, we were interested in the conversion of aucubin to different dihydroxy- and amino-hydroxy-substituted tetrahydrocyclopenta[*c*]furan-carboxaldehydes, with conservation of the sugar unit. Indeed, such compounds should be suitable for further chemical diversification [14] and may also prove useful intermediates for the synthesis of novel guaiane derivatives of biological relevance [15–17].

2. Results and Discussion. – The oxidative ring contraction of 3,4-dihydro-2*H*-pyrans to the corresponding tetrahydrofuran-2-carboxaldehydes by use of thallium-(III) nitrate trihydrate is well-documented [18][19]. Thus, a suitable entry to our target



1 **2** **5**

compounds could be envisioned through oxidation of the dihydropyran C=C bond present in aucubin and related iridoid glycosides. To ensure the desired chemical diversification, the oxidation reaction should be performed on protected aucubin, but also on compounds suitably modified at C(6), derived from the rare 6-epiaucubin (**3**) and its unnatural amino counterpart **4**.

2.1. *Conversion of Aucubin* (**1**) *to 6-Epiaucubin* (**3**) *and Amino Derivative* **4**. The conversion of aucubin (**1**) to 6-epiaucubin (**3**) (see *Scheme 1*), first described by *Bianco et al.* [20], was recently developed on a preparative scale in our group through a *Mitsunobu* reaction carried out with 2′,3′,4′,6′,10-penta-*O*-benzoylaucubin (**5**), which permitted us to achieve the required configuration inversion at C(6) [21]. A significant improvement in terms of yield has now been obtained, by performing the same reaction with 2′,3′,4′,6′,10-penta-*O*-pivaloylaucubin (**6**) instead of **5**. Thus, 6-*O*-acetylaucubin (**7**), readily obtained from **1** [21], was treated with pivaloyl chloride to afford 6-*O*-acetyl-2′,3′,4′,6′,10-penta-*O*-pivaloylaucubin (**8**) (*Scheme 1*). Selective deprotection of the acetyl group of **8** to give **6** was ensured by use of potassium cyanide, previously shown to permit selective deacetylation reactions in the field of sugar chemistry [22].

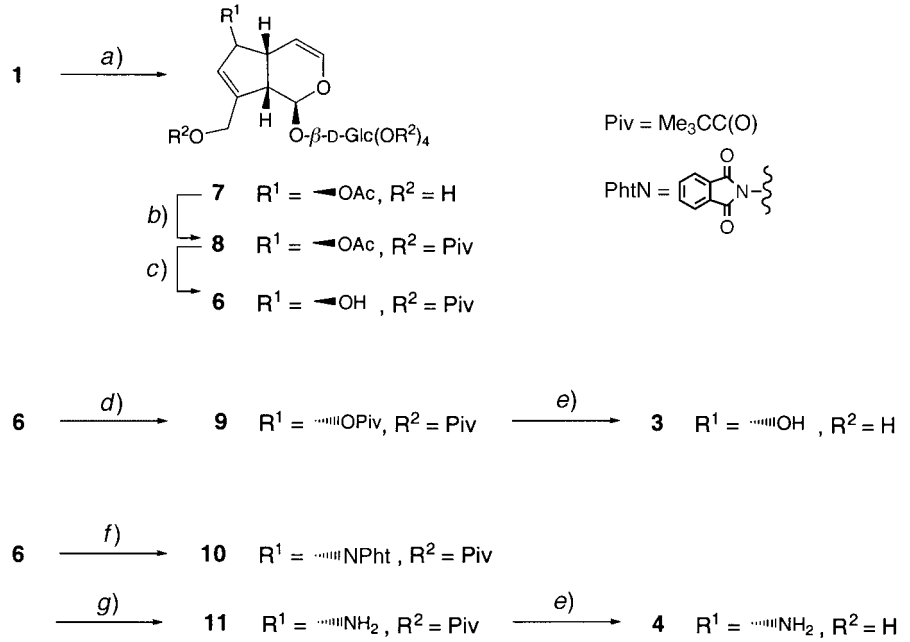
Configuration inversion at C(6) was achieved by a modified *Mitsunobu* reaction of **6**, involving pivalic acid in the presence of Ph_3P and diethyl azodicarboxylate (=diethyl diazenedicarboxylate; DEAD) in anhydrous tetrahydrofuran [23] (*Scheme 1*). Perpivaloyl-6-epiaucubin (**9**) obtained under these conditions could be further fully deprotected to **3** upon treatment with lithium hydroxide. This reaction sequence furnished **3** in 35% overall yield from **1**, instead of 20% when **5** was used as key intermediate.

The same approach was applied to the preparation of the amino derivative **4** with phthalimide (PhtN) as the N-donor in the course of the modified *Mitsunobu* reaction performed with **6** [24] (*Scheme 1*). Accordingly, treatment of **6** with phthalimide under the conditions described above gave (6*R*)-6-phthalimido-perpivaloylbartsioside (**10**) in 81% yield. Deprotection of the amino group with hydrazine in EtOH afforded (6*R*)-6-amino-2′,3′,4′,6′,10-*O*-pivaloylbartsioside (**11**) in 90% yield [25]. Final removal of the pivaloyl protecting groups was achieved upon treatment of **11** with lithium hydroxide, which gave the desired (6*R*)-6-aminobartsioside (**4**) in 80% yield.

In the ^{1}H-NMR spectra of **4**, **9**, **10**, and **11**, which belong to the 6-epi series, large ^3J(5,6) and ^3J(1,9) coupling constants, ranging from 7 to 8 Hz and from 5.5 to 7.5 Hz, respectively, give evidence for the configuration at C(6), in excellent agreement with previous observations [21][26][27].

2.2. *Oxidation of the Dihydropyran Double Bond.* To demonstrate the feasibility of the oxidative dihydropyran-ring contraction with conservation of the sugar unit, perpivaloylaucubin (**12**) was first submitted to thallium(III) nitrate oxidation [18][19].

Scheme 1



a) 1. Ac_2O, *N,N*-demethylpyridin-4-amine (DMAP), pyridine; 2. KCN, CH_2Cl_2/MeOH 1:2. *b*) PivCl, pyridine/CH_2Cl_2 (1:1. *c*) KCN, CH_2Cl_2/MeOH 1:2. *d*) PivCOOH, DEAD, PPh_3, THF. *e*) LiOH, meCN/H_2O 7:3- *f*) PhtNH, DEAD, PPh_3, THF. *g*) NH_2NH_2, EtOH, reflux.

When conducted in MeCN, the reaction resulted in the formation of a 4:1 mixture of the desired (1*R*)- and (1*S*)-3-(β-D-glucopyranosyloxy)-1*H*-cyclopenta[*c*]furan-1-carboxaldehydes **13** and **14**, respectively, in 38% overall yield (*Scheme 2*; see also *Table 1*, *Method A*). The configuration at C(1) of **13** and **14** was deduced from NOE correlations and the ^3J(6a,1) values in the ^{1}H-NMR spectra (*Table 1*). When the same oxidation reaction was applied to **9**, the corresponding (1*S*)-carboxaldehyde **15** was obtained in 80% yield as single reaction product (*Scheme 2*).

In contrast, treatment of **10** with thallium(III) nitrate only gave the (1*R*)-carboxaldehyde **16** in 71% yield (*Scheme 3*). Typical NMR features of compounds **13**–**16** are summarized in *Table 1*.

These promising results prompted us to seek other oxidation conditions able to give similar results (*Table 1*), but that avoid the use of the highly toxic thallium nitrate, which is not suitable for large-scale preparative experiments. The treatment of **12** with *N*-iodosuccinimide (NIS) in THF/H_2O, followed by oxidation had been previously shown to afford the corresponding iodolactones in high yield [12]. Consequently, we envisioned developing for our purpose a two-step approach involving oxidation of the dihyropyran C=C bond to an iodolactol, followed by conversion of this latter in alkaline medium to the corresponding tetrahydrofuran-1-carboxaldehyde. As expected, reaction of **12** with NIS in MeCN/H_2O, followed by treatment in anhydrous DMF of

Scheme 2

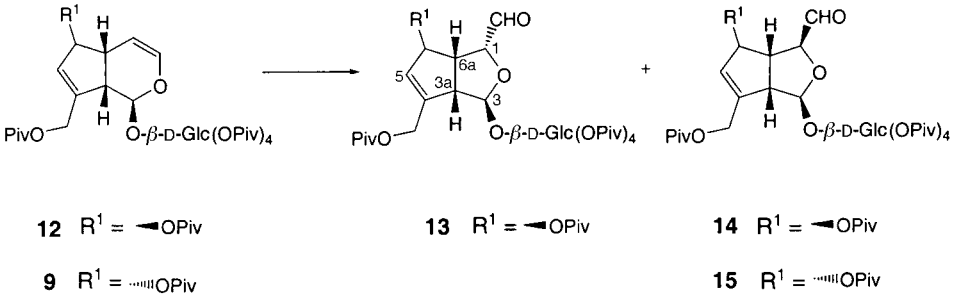
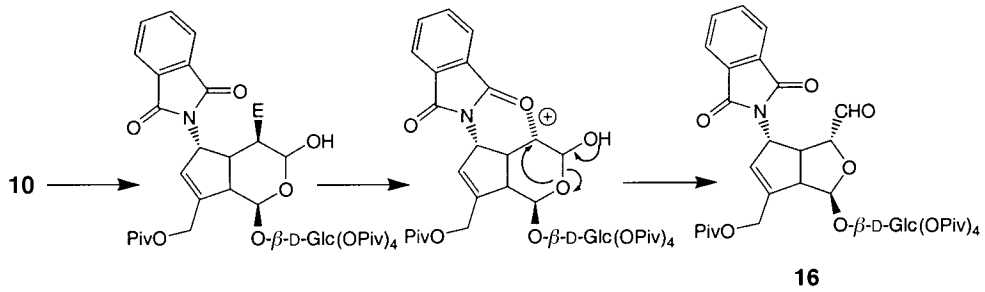


Table 1. *^{1}H-NMR Data of 1*H*-Cyclopenta[1,2-*c*]furan-1-carboxaldehydes* **13**–**16**

	^3J(6a,1) [Hz]	NOE[a])	(1*R*)/(1*S*)			Yield [%]		
			A[b])	*B*[c])	*C*[d])	*A*[b])	*B*[c])	*C*[d])
13	7.5	H–C(3)/H–C(3a), H–C(6)/H–C(6a)	4:1	3:1	4:1	38	78	95
14	3	H–C(1)/H–C(6)						
15	4.5	H–C(1)/H–C(6a), CH=0/H–C(6)	(1*S*)	(1*S*)	(1*S*)	80	89	83
16	6.5	H–C(1)/H–C(6), H–C(1)/H–C(6a), H–C(3a)/H–C(6), H–C(6)/H–C(6a)	(1*R*)	(1*R*)	(1*R*)	71	83	70

[a]) Correlations H–C(3a)/H–C(6a) and H–C(3)/CH_2–C(4) are observed for all compounds. [b]) *Method A*; [c]) *Method B*; [d]) *Method C*.

Scheme 3



the crude resulting diastereoisomeric iodolactols with potassium phthalimide, chosen as a weakly nucleophilic base, gave a 3:1 mixture of the desired carboxaldehydes **13** and **14** in 78% overall yield (*Table 1*, *Method B*). Under similar conditions, **9** and **10** were converted to carboxaldehydes **15** and **16**, in 89 and 83% yield, respectively. In a further improvement, the reaction sequence was envisaged as a one-pot experiment under phase-transfer-catalyzed conditions. Indeed, addition of toluene, 0.1M aqueous potassium hydrogencarbonate, and Bu_4NBr to the solution of the intermediate

iodolactols in MeCN readily afforded a 4:1 mixture **13**/**14** in 95% overall yield from **12**, **15** in 83% yield from **9**, and **16** in 70% yield from **10** (*Table 1*, *Method C*).

To rationalize the above results in terms of stereochemistry, the complex iodolactol mixtures obtained from **12**, **9**, and **10** were oxidized to the corresponding iodolactones to facilitate the ^{1}H-NMR analysis (*Table 2*). Under those conditions, a 7:3 mixture of iodolactones **17** (4*R*) and **18** (4*S*) was obtained from **12**, whereas both **9** and **10** gave the corresponding (4*R*)-iodolactones **19** and **20**, respectively, as single reaction products. In both **19** and **20**, the configuration at C(4) was deduced from the NOE between H–C(1) and H–C(4). Coupling constants clearly indicate that the conformation adopted by the cyclopenta[*c*]pyran system of 6-epi compounds **19** and **20** strongly differ from that of **17** [12]. The configuration at C(1) of the final ring-contraction products appears to be independent from the initial electrophlic attack of the C=C bond by the oxidizing reagent. Therefore, the final ring contraction most probably depends on the nature and the configuration of the substituent at C(6). Interestingly, in the case of **10**, the departure of the electrophile appears to be assisted by the carbonyl O-atom of the phthalimido substitutent, as depicted in *Scheme 3*.

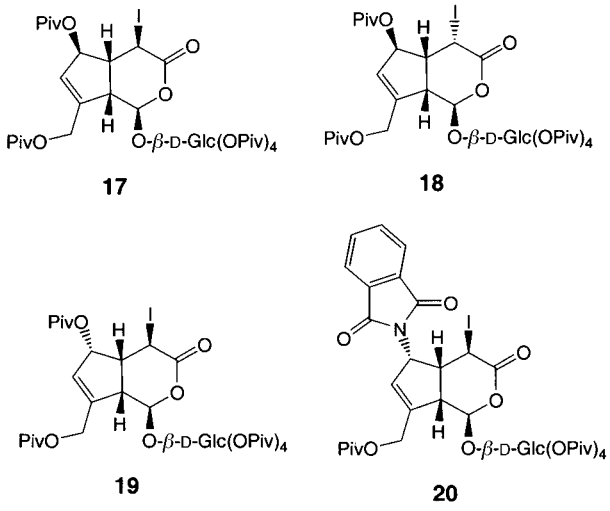


Table 2. *^{1}H-NMR Data of Iodolactones* **17**–**20**

	^3J(4,5) [Hz]	NOE	(4*R*)/(4*S*)	Yield [%]
17/**18** (from **12**)		see [12]	7:3	
19 (from **9**)	8	H–C(1)/H–C(4), H–C(9)/H–C(5)	(4*R*)	79
20 (from **10**)	11.5	H–C(1)/H–C(4), H–C(9)/H–C(5)	(4*R*)	83

In summary, we have described here an efficient access to a variety of tetrahydrocyclopenta[*c*]furancarboxaldehyde glucosides. The key step is an oxidation reaction performed on substrates easily accessible from a natural iridoid precursor. The

protected cyclopentafuran glycosides obtained in this way are versatile synthons, which may prove useful for further chemical diversification.

Experimental Part

General. Column chromatography (CC): flash silica gel *60 Merck* (35–70 μm). M.p.: *Leica* melting-point microscope; uncorrected. Optical rotations: *c* in g/100 ml; *Perkin-Elmer 241* polarimeter. IR Spectra: in cm^{-1}; *Perkin-Elmer FT-IR-1600* spectrometer; film, NaCl. NMR Spectra: *Bruker AC-300* at 300 (^1H) and 75 MHz (^{13}C); δ in ppm rel. to solvent peaks as internal standards ($\delta(CD_3OD)$ 3.4, $\delta(D_2O)$ 4.95, $\delta(CDCl_3)$ 7.27), *J* in Hz; assignments by 1D homonuclear decoupling and by NOESY experiments, C,H shift-correlation spectra (HETCOR and COLOC). MS: in *m/z*; *Nermag R10-10C* (DCI-MS with NH_3 as reagent gas), with an *Analytica* source (ESI-MS). Microanalyses were performed at the I.C.S.N. (CNRS, Gif-sur-Yvette, France).

*6-*O*-Acetyl-2′,3′,4′,6′,10-penta-*O*-pivaloylaucubin* (= *(1*S*,4a*R*,5*S*,7a*S*)-5-(Acetyloxy)-7-[(2,2-dimethyl-1-oxopropoxy)methyl]-1,4a,5,7a-tetrahydrocyclopenta[c]pyran-1-yl 2,3,4,6-Tetrakis-*O*-(2,2-dimethyl-1-oxopropyl)-β-*D*-glucopyranoside;* **8**). To a cooled soln. of 6-*O*-acetylaucubin (**7**; 1.2 g, 3.1 mmol) [20] in anh. pyridine/CH_2Cl_2 1:1 (80 ml), pivaloyl chloride (= 2,2-dimethylpropanoyl chloride; 11 ml, 89.9 mmol) was added carefully. The mixture was stirred under Ar at r.t. for 4 days. The mixture was quenched with ice (10 g), stirred for 30 min, and extracted with CH_2Cl_2 (3 × 150 ml). The combined org. layer was washed with 10% aq. HCl soln. until neutral, H_2O (150 ml), and brine (150 ml), dried (Na_2SO_4), and evaporated. CC (cyclohexane/AcOEt 5:1) afforded **8** (2.2 g, 88%). Colorless foam. IR: 2973*s*, 2930*s*, 1730*s*, 1659*m*, 1475*s*, 1458*s*, 1393*m*, 1366*s*, 1279*s*, 1154 (br.), 1035*s*, 894*m*. ^1H-NMR ($CDCl_3$): 1–1.3 (5 *s*, Piv); 2.05 (*s*, Ac); 2.78 (*m*, H–C(5)); 3.06 (*m*, H–C(9)); 3.75 (*ddd*, $^3J(5',4') = 9.5$, $^3J(5',6'b) = 5.5$, $^3J(5',6'a) = 1.5$, H–C(5′)); 4.05 (*dd*, $^2J(6'a,6'b) = 12.5$, $^3J(5',6'b) = 5.5$, H_b–C(6′)); 4.18 (*dd*, $^2J(6'a,6'b) = 12.5$, $^3J(5',6'a) = 1.5$, H_a–C(6′)); 4.68 (*d*, $^2J(10b,10a) = 14$, H–C(10)); 4.75 (*d*, $^2J(10a,10b) = 14$, Ha–C(10)); 4.89 (*d*, $^3J(1',2') = 8$, H–C(1′)); 4.91 (*dd*, $^3J(4,3) = 6$, $^3J(4,5) = 3.5$, H–C(4)); 5.05 (*dd*, $^3J(2',3') = 9.5$, $^3J(2',1') = 8$, H–C(2′)); 5.10 (*d*, $^3J(1,9) = 5$, H–C(1)); 5.11 (*t*, $^3J(4',3') = {}^3J(4',5') = 9.5$, H–C(4′)); 5.27 (*m*, H–C(6)); 5.34 (*t*, $^3J(3',2') = {}^3J(3',4') = 9.5$, H–C(3′)); 5.78 (*m*, H–C(7)); 6.18 (*dd*, $^3J(3,4) = 6$, $^4J(3,5) = 2$, H–C(3)). ^{13}C-NMR ($CDCl_3$): 21.1 ((*Me*CO); 27.1 (*Me*$_3$CCO); 38.6 (Me$_3$*C*CO); 39.5 (C(5)); 46.8 (C(9)); 61.3 (C(10)); 61.8 (C(6′)); 67.9 (C(4′)); 70.6 (C(2′)); 72.2 (C(3′)); 72.3 (C(5′)); 82.8 (C(6)); 93.5 (C(1)); 95.8 (C(1′)); 103.9 (C(4)); 126.5 (C(7)); 140.1 (C(3)); 144.8 (C(8)); 170.8 (Me*C*O); 177.9, 177.5, 177.1, 176.4 (2C) (Me$_3$C*C*O). ESI-MS: 831 ($[M + Na]^+$). Anal. calc. for $C_{42}H_{64}O_{15}$ (808.42): C 62.36, H 7.97; found: C 62.34, H 8.02.

*2′,3′,4′,6′,10-Penta-*O*-pivaloylaucubin* (= *(1*S*,4a*R*,5*S*,7a*S*)-5-7-[(2,2-Dimethyl-1-oxopropoxy)methyl]-1,4a,5,7a-tetrahydro-5-hydroxycyclopenta[c]pyran-1-yl 2,3,4,6-Tetrakis-*O*-(2,2-dimethyl-1-oxopropyl)-β-*D*-glucopyranoside*; **6**). To a soln. of **8** (3 g, 3.7 mmol) in anh. MeOH/CH_2Cl_2 2:1 (120 ml), anh. KCN (650 mg, 10 mmol) was added under Ar. The soln. was stirred at 60° for 48 h. Then, the reaction was stopped by filtration through silica gel. The solvent was evaporated. CC (cyclohexane/AcOEt 2:1) gave **6** (2 g, 70%). Colorless prisms from cyclohexane/AcOEt 2:1. M.p. 112°. $[\alpha]_D^{20} = -57.5$ ($c = 1$, $CHCl_3$) IR: 3471 (br.), 3060*w*, 2973*s*, 2936*s*, 2903*s*, 2874*m*, 1743 (br.), 1661*w*, 1480*s*, 1460*m*, 1398*m*, 1367*m*, 1281 (br.), 1228*m*, 1143(br.), 1052*s*, 1013*m*, 964*m*, 738*m*. ^1H-NMR ($CDCl_3$): 1–1.3 (5 *s*, Piv); 2.63 (*m*, H–C(5)); 2.94 (br. *t*, $^3J(9,1) = {}^3J(9,5) = 6$, H–C(9)); 3.72 (*ddd*, $^3J(5',4') = 9.5$, $^3J(5',6'b) = 5.5$, $^3J(5',6'a) = 1.5$, H–C(5′)); 4.02 (*dd*, $^2J(6'b,6'a) = 12.5$, $^3J(6'b,5') = 5.5$, H_b–C(6′)); 4.16 (*dd*, $^2J(6'a,6'b) = 12.5$, $^3J(5',6'a) = 1.5$, H_a–C(6′)); 4.41 (*m*, H–C(6)); 4.65 (br. *d*, $^2J(10b,10a) = 15$, H_b–C(10)); 4.72 (br. *d*, $^2J(10a,10b) = 15$, H_a–C(10)); 4.89 (*d*, $^3J(1',2') = 8$, H–C(1′)); 4.92 (*d*, $^3J(1,9) = 6$, H–C(1)); 4.95 (*dd*, $^3J(4,3) = 6$, $^3J(4,5) = 3.5$, H–C(4)); 5.05 (*dd*, $^3J(2',3') = 9.5$, $^3J(2',1') = 8$, H–C(2′)); 5.10 (*t*, $^3J(4',3') = {}^3J(4',5') = 9.5$, H–C(4′)); 5.32 (*t*, $^3J(3',2') = {}^3J(3',4') = 9.5$, H–C(3′)); 5.77 (*m*, H–C(7)); 6.18 (*dd*, $^3J(3,4) = 6$, $^4J(3,5) = 2$, H–C(3)). ^{13}C-NMR ($CDCl_3$): 27.1 (*Me*$_3$CCO); 38.7 (Me$_3$*C*CO); 43.7 (C(5)); 46.6 (C(9)); 61.7 (C(6′), C(10)); 67.8 (C(4′)); 70.6 (C(2′)); 72.1 (C(3′)); 72.3 (C(5′)); 81.6 (C(6)); 94.6 (C(1)); 96 (C(1′)); 104.6 (C(4)); 130.5 (C(7)); 139.9 (C(3)); 142.2 (C(8)); 177.9, 177.8, 177.1, 176.4 (2C) (Me$_3$C*C*O). ESI-MS: 789 ($[M + Na]^+$). Anal. calc. for $C_{40}H_{62}O_{14}$ (766.41): C 62.64, H 8.15; found: C 62.64, H 8.21.

Perpivaloyl-6-epiaucubin (= *(1*S*,4a*R*,5*R*,7a*S*)-5-(2,2-Dimethyl-1-oxopropoxy)-7-[(2,2-dimethyl-1-oxopropoxy)methyl]-1,4a,5,7a-tetrahydrocyclopenta[c]pyran-1-yl 2,3,4,6-Tetrakis-*O*-(2,2-dimethyl-1-oxopropyl)-β-*D*-glucopyranoside;* **9**). DEAD (diethyl azodicarboxylate; 0.06 ml, 0.4 mmol) was added dropwise at 0° under Ar to a soln. of PPh_3 (105 mg, 0.4 mmol), **6** (76 mg, 0.1 mmol) and pivalic acid (31.3 mg, 0.3 mmol) in anh. THF (5 ml). The mixture was allowed to stand 15 min at 0° and stirred at r.t. for 1 h 40 min. The solvent was evaporated. CC (cyclohexane/Me_2CO 9:1) afforded **9** (84 mg, 99%). Colorless needles from MeOH. M.p. 117°.

$[\alpha]_D^{20} = -31.25$ ($c = 0.8$, CH_2Cl_2). IR: 2973*s*, 1733*s*, 1661*w*, 1480*m*, 1461*w*, 1397*w*, 1367*w*, 1283*s*, 1139 (br.), 1074*m*, 973*w*, 719*w*. ^{1}H-NMR ($CDCl_3$): 1–1.3 (6 *s*, Piv); 2.62 (br. *t*, $^3J(1,9) = {}^3J(5,9) = 7.5$, H–C(9)); 2.95 (*dddd*, $^3J(5,6) = 7$, $^3J(5,9) = 7.5$, $^3J(5,4) = 4$, $^4J(5,3) = 2$, H–C(5)); 3.75 (*m*, $^3J(5',4') = 9.5$, $^3J(5',6'b) = 5.5$, $^3J(5',6'a) = 1.5$, H–C(5')); 4.05 (*dd*, $^2J(6'a,6'b) = 12$, $^3J(5',6'b) = 5.5$, H_b–C(6')); 4.18 (*dd*, $^2J(6'a,6'b) = 12$, $^3J(5',6'a) = 1.5$, H_a–C(6')); 4.78 (*dd*, $^3J(4,3) = 6.5$, $^3J(4,5) = 4$, H–C(4)); 4.8 (br. *s*, 2 H–C(10)); 4.82 (*d*, $^3J(1,9) = 7.5$, H–C(1)); 4.98 (*d*, $^3J(1',2') = 8$, H–C(1')); 5.08 (*dd*, $^3J(2',3') = 9.5$, $^3J(2',1') = 8$, H–C(2')); 5.19 (*t*, $^3J(4',3') = {}^3J(4',5') = 9.5$, H–C(4')); 5.35 (*t*, $^3J(3',2') = {}^3J(3',4') = 9.5$, H–C(3')); 5.6 (br. *d*, $^3J(6,5) = 7$, H–C(6)); 5.82 (*m*, H–C(7)); 6.35 (*dd*, $^3J(3,4) = 6.5$, $^4J(3,5) = 2$, H–C(3)). ^{13}C-NMR ($CDCl_3$): 27.1 (*Me*$_3$CCO); 38.7 (Me_3*C*CO); 39.2 (C(5)); 47.0 (C(9)); 61.6 (C(6')); 62.0 C(10); 67.7 (C(4')); 70.7 (C(2')); 72.0 (C(3')); 72.5 (C(5')); 77.2 (C(6)); 97.0 (C(1)); 97.5 (C(1')); 100.7 (C(4)); 126.6 (C(7)); 142.1 (C(3)); 147.2 (C(8)); 177.9, 177.8, 177.7, 177.1, 176.4, 176.3 (Me_3*C*CO). ESI-MS: 889 ($[M+K]^+$). Anal. calc. for $C_{45}H_{70}O_{15}$ (850.47): C 63.51, H 8.29; found: C 63.34, H 8.31.

6-Epiaucubin (**3**). To a soln. of **9** (70.5 mg, 0.08 mmol) in MeCN (7 ml) and H_2O (3 ml), LiOH (84 mg, 2 mmol) was added. The mixture was stirred for 8 h at r.t. CC (CH_2Cl_2/MeOH 4:1) afforded **3** (28.4 mg, 99%) as a colorless oil [21].

(*6*R*)-6-Phthalimido-perpivaloylbartsioside* (= *(1*S*,4a*R*,5*R*,7a*S*)-5-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)-7-[(2,2-dimethyl-1-oxopropoxy)methyl]-1,4a,5,7a-tetrahydrocyclopenta[c]pyran-1-yl 2,3,4,6-Tetrakis*-O*-(2,2-dimethyl-1-oxopropyl)-β-*D*-glucopyranoside;* **10**). DEAD (0.12 ml, 0.72 mmol) was added dropwise at 0° under Ar to a soln. of Ph_3P (189 mg, 0.72 mmol), **6** (140 mg, 0.18 mmol), and phthalimide (81 mg, 0.54 mmol) in anh. THF (10 ml). The mixture was allowed to stand 15 min at 0° and stirred at r.t. for 1 h 40 min. The solvent was evaporated. CC (cyclohexane/AcOEt 8:2) afforded **10** (133 mg, 81%). Colorless prisms from cyclohexane/AcOEt 7:3. M.p. 86°. $[\alpha]_D^{20} = -74.5$ ($c = 0.55$, $CHCl_3$). IR: 3062*w*, 2973*s*, 2934*s*, 2873*m*, 1773*m*, 1714 (br.), 1661*m*, 1612*w*, 1480*s*, 1461*m*, 1397*s*, 1367*s*, 1283*s*, 1139 (br.), 1074*s*, 973*m*, 719*m*. ^{1}H-NMR ($CDCl_3$): 1–1.3 (5 *s*, Piv); 2.95 (br. *t*, $^3J(9,5) = {}^3J(9,1) = 6$, H–C(9)); 3.25 (*dddd*, $^3J(5,6) = 8$, $^3J(5,9) = 6$, $^3J(5,4) = 3.5$, $^4J(5,3) = 2$, H–C(5)); 3.8 (*ddd*, $^3J(5',4') = 9.5$, $^3J(5',6'b) = 5$, $^3J(5',6'a) = 1.5$, H–C(5')); 4.1 (*dd*, $^2J(6'a,6'b) = 12$, $^3J(5',6'b) = 5$, H_b–C(6')); 4.3 (*dd*, $^2J(6'a,6'b) = 12$, $^3J(5',6'a) = 1.5$, H_a–C(6')); 4.5 (*dd*, $^3J(4,3) = 6$, $^3J(4,5) = 3.5$, H–C(4)); 4.8 (br. *d*, $^2J(10b,10a) = 15$, H_b–C(10)); 4.89 (br. *d*, $^2J(10a,10b) = 15$, H_a–C(10)); 4.95 (*d*, $^3J(1',2') = 8$, H–C(1')); 5.1 (*dd*, $^3J(2',3') = 9.5$, $^3J(2',1') = 8$, H–C(2')); 5.19 (*t*, $^3J(4',3') = {}^3J(4',5') = 9.5$, H–C(4')); 5.35 (*t*, $^3J(3',2') = {}^3J(3',4') = 9.5$, H–C(3')); 5.36 (*d*, $^3J(6,5) = 8$, H–C(6)); 5.45 (*d*, $^3J(1,9) = 6$, H–C(1)); 5.86 (*m*, H–C(7)); 6.2 (*dd*, $^3J(3,4) = 6.5$, $^3J(3,5) = 2$, H–C(3)); 7.8–7.65 (*m*, 4 arom. H). ^{13}C-NMR ($CDCl_3$): 26.9 (*Me*$_3$CCO); 36.2 (C(5)); 38.7 (Me_3*C*CO); 47.4 (C(9)); 58.2 (C(6)); 61.7 (C(6'), C(10)); 67.7 (C(4')); 70.7 (C(2')); 72.3 (C(3'), C(5')); 93.7 (C(1)); 96.7 (C(1')); 100.6 (C(4)); 123.2 (arom. C); 125.6 (C(7)); 131.7 (arom. C); 134 (arom. C); 141.2 (C(3)); 141.8 (C(8)); 168.2 (2 *C*O(PhtN)); 178.1, 177.6, 177.2, 176.8, 176.5 (Me_3*C*CO). ESI-MS: 918 ($[M+Na]^+$). Anal. calc. for $C_{48}H_{65}NO_{15}$ (895.44): C 64.34, H 7.31, N 1.56; found: C 64.13, H 7.31, N 1.65.

*(6*R*)-6-Amino-2',3',4',6',10-*O*-pivaloylbartsioside* (= *(1*S*,4a*R*,5*R*,7a*S*)-5-Amino-7-[(2,2-dimethyl-1-oxopropoxy)methyl]-1,4a,5,7a-tetrahydrocyclopenta[c]pyran-1-yl 2,3,4,6-Tetrakis*-O*-(2,2-dimethyl-1-oxopropyl)-β-*D*-glucopyranoside;* **11**). A 0.31M soln. of hydrazine in EtOH (1.9 ml, 0.6 mmol) was added dropwise to a soln. of **10** (178.5 mg, 0.2 mmol) in EtOH (2.5 ml). The mixture was stirred at 95° for 3 h 30 min, and the solvent was evaporated. CC (CH_2Cl_2/MeOH/NH_4OH 95:5:1) gave **11** (137 mg, 90%). Glassy solid. $[\alpha]_D^{20} = -34.5$ ($c = 0.55$, $CHCl_3$). IR: 3062*w*, 2972*s*, 2935*m*, 2908*m*, 2873*m*, 1744*s*, 1655*m*, 1480*s*, 1461*m*, 1397*m*, 1367*m*, 1281*s*, 1228*m*, 1144 (br.). ^{1}H-NMR ($CDCl_3$): 1–1.3 (5 *s*, Piv); 2.8 (br. *t*, $^3J(9,5) = {}^3J(9,1) = 5.5$, H–C(9)); 2.88 (br. *ddd*, $^3J(5,9) = 5.5$, $^3J(5,6) = 7.5$, $^4J(5,3) = 2$, H–C(5)); 3.75 (*ddd*, $^3J(5',4') = 9.5$, $^3J(5',6'b) = 5.5$, $^3J(5',6'a) = 1.5$, H–C(5')); 4.00 (br. *d*, $^3J(6,5) = 7.5$, H–C(6)); 4.05 (*dd*, $^2J(6'b,6'a) = 12$, $^3J(6'b,5') = 5.5$, H_b–C(6')); 4.2 (*dd*, $^2J(6'a,6'b) = 12$, $^3J(6'a,5') = 1.5$, H_a–C(6')); 4.68 (br. *d*, $^2J(10b,10a) = 14_b$, H–C(10)); 4.75 (br. *d*, $^2J(10a,10b) = 14$, H_a–C(10)); 4.82 (*dd*, $^3J(4,3) = 6.5$, $^3J(4,5) = 3.5$, H–C(4)); 4.93 (*d*, $^3J(1',2') = 8$, H–C(1')); 5.08 (*d*, $^3J(1,9) = 5.5$, H–C(1)); 5.08 (*dd*, $^3J(2',3') = 9.5$, $^3J(2',1') = 8$, H–C(2')); 5.15 (*t*, $^3J(4',3') = {}^3J(4',5') = 9.5$, H–C(4')); 5.35 (*t*, $^3J(3',2') = {}^3J(3',4') = 9.5$, H–C(3')); 5.72 (*m*, H–C(7)); 6.38 (*dd*, $^3J(3,4) = 6.5$, $^4J(3,5) = 2$, H–C(3)). ^{13}C-NMR ($CDCl_3$): 27.1 (*Me*$_3$CCO); 38.1 (Me_3*C*CO); 38.7 (C(5)); 47.2 (C(9)); 58.4 (C(6)); 61.7 (C(6'), C(10)); 67.8 (C(4')); 70.7 (C(2')); 72.2 (C(3')); 72.3 (C(5')); 94.6 (C(1)); 95.9 (C(1')); 101.4 (C(4)); 133.3 (C(7)); 139.6 (C(3)); 141.6 (C(8)); 177.9 (2C), 177.1, 176.4 (2C) (Me_3*C*CO). ESI-MS: 766 ($[M+H]^+$). Anal. calc. for $C_{40}H_{63}NO_{13}$ (765.43): C 62.73, H 8.29, N 1.83; found: C 62.56, H 8.34, N 1.75.

*(6*R*)-6-Aminobartsioside* (= *(1*S*,4a*R*,5*R*,7a*S*)-5-Amino-7-(hydroxymethyl)]-1,4a,5,7a-tetrahydrocyclopenta[c]pyran-1-yl β-*D*-glucopyranoside*; **4**). Compound **11** (23 mg, 0.03 mmol) was dissolved in MeCN/H_2O 7:3 (10 ml), and LiOH (18.8 mg, 0.45 mmol) was added at r.t. The soln. was stirred at 60° for 48 h and filtered at r.t. on *Dowex 50X8 200* (H^+ form, MeCN/H_2O 7:3, then 0.05M NH_4OH: **4** (9.4 mg, 80%). Glassy solid. $[\alpha]_D^{20} = -33.6$ ($c = 0.5$, MeOH). IR: 3348 (br.); 2922*m*, 1654*m*, 1576*m*, 1458*m*, 1378*m*, 1228*m*, 1078*s*, 1048*s*, 1019*s*, 964*m*.

^{1}H-NMR (CD_3OD): 2.8 (br. *t*, $^3J(9,1) = {}^3J(9,5) = 7.5$, H–C(9)); 3.1 (*dddd*, $^3J(5,9) = 7.5$, $^3J(5,6) = 7$, $^3J(5,4) = 3.5$, $^4J(5,3) = 2$, H–C(5)); 3.6–3.2 (*m*, H–C(2′), H–C(3′), H–C(4′), H–C(5′)); 3.7 (*dd*, $^2J(6'b,6'a) = 12$, $^3J(6'b,5') = 6.5$, H_b–C(6′)); 4.0 (*dd*, $^2J(6'a,6'b) = 12$, $^3J(5',6'a) = 2$, H_a–C(6′)); 4.08 (br. *d*, $^3J(6,5) = 7$, H–C(6)); 4.25 (br. *d*, $^2J(10b,10a) = 15$, H_b–C(10)); 4.50 (br. *d*, $^2J(10a,10b) = 15$, H_a–C(10)); 4.8 (*d*, $^3J(1',2') = 8$, H–C(1′)); 5.05 (*dd*, $^3J(4,3) = 6.5$, $^3J(4,5) = 3.5$, H–C(4)); 5.15 (*d*, $^3J(1,9) = 7.5$, H–C(1)); 5.92 (*m*, H–C(7)); 6.60 (*dd*, $^3J(3,4) = 6.5$, $^4J(3,5) = 2$, H–C(3)). ^{13}C-NMR (CD_3OD): 40.1 (C(5)); 48.7 (C(9)); 58.9 (C(6)); 61.4 (C(10)); 62.9 (C(6′)); 71.8 (C(4′)); 74.9 (C(2′)); 77.9 (C(3′)); 78.5 (C(5′)); 97.9 (C(1)); 99.9 (C(1′)); 101.8 (C(4)); 129.8 (C(7)); 144.2 (C(3)); 149.1 (C(8)). ESI-MS: 368 ($[M + Na]^+$). Anal. calc. for $C_{15}H_{23}NO_8$ (345.35): C 52.17, H 6.71, N 4.06; found: C 52.13, H 6.56, N 4.72.

*(1*R*,3*S*,3a*S*,6R,6a*R*)- and (1*S*,3*S*,3a*S*,6R,6a*R*)-6-(2,2-Dimethyl-1-oxopropoxy)-4-[(2,2-dimethyl-1-oxopropoxy)methyl]-3,3a,6,6a-tetrahydro-3-[2,3,4,6-tetrakis*-O-*(2,2-dimethyl-1-oxopropyl)-β-*D*-glucopyranosyloxy]-1*H*-cyclopenta[*c*]furan-1- carboxaldehyde* (**13** and **14**, resp.). *Method A:* Thallium(III) nitrate trihydrate (TTN; 137.8 mg, 0.31 mmol) was added carefully to a soln. of perpivaloylaucubin (**12**, 236 mg, 0.28 mmol) in MeCN (15 ml). The mixture was stirred for 3 h 30 min at 0°. H_2O (15 ml) was added and the soln. extracted with AcOEt (3 × 15 ml). The org. extract was washed with H_2O (2 × 15 ml), sat. aq. $NaHSO_3$ soln. (2 × 15 ml), and brine (2 × 15 ml), dried (Na_2SO_4), and evaporated. CC (cyclohexane/AcOEt 85:15) afforded a 4:1 mixture (by ^{1}H-NMR) **13**/**14** (92 mg, 38%).

Method B: NIS (14 mg, 0.062 mmol) was added to a soln. of **12** (35.1 mg, 0.041 mmol) in MeCN (5.5 ml) and H_2O (1 ml). The mixture was stirred for 4 h at r.t. and extracted with CH_2Cl_2 (7 ml). The org. layer was washed with 0.1M aq. $Na_2S_2O_4$ (5 ml), dried (Na_2SO_4), and evaporated. The residue of crude iodolactols (48 mg) was dissolved in anh. DMF (2 ml). Potassium phthalimide (7.6 mg, 0.041 mmol) was added and the mixture was stirred for 30 min at r.t. CH_2Cl_2 (5 ml) was added, and the org. layer was washed with H_2O (2 × 5 ml) and brine (5 ml), dried (Na_2SO_4), and evaporated. CC (cyclohexane/AcOEt 85:15) afforded a 3:1 mixture (by ^{1}H-NMR) **13**/**14** (27.7 mg, 78%).

Method C: A soln. of NIS (24.8 mg, 0.11 mmol) and **12** (62.4 mg, 0.073 mmol) in MeCN (7 ml) and H_2O (3 ml) was stirred for 2 h 30 min at r.t. Toluene (10 ml), 0.1M aq. $KHCO_3$ (11 ml), and Bu_4NBr (9.4 mg, 0.029 mmol) were added, and the mixture was stirred vigorously at r.t. for 20 h. The org. layer was separated and washed with 0.1M aq. $Na_2S_2O_4$ (30 ml) and brine (30 ml), dried (Na_2SO_4), and evaporated. CC (cyclohexane/AcOEt 85:15) afforded a 4:1 mixture (by ^{1}H-NMR) **13**/**14** (60 mg, 95%).

For anal. purposes, pure samples of compounds **13** and **14** were prepared from the above mixtures by repeated CC (cyclohexane/AcOEt 9:1).

Data of **13**: Amorphous glassy solid. $[\alpha]_D^{20} = -31.1$ ($c = 4.4$, $CHCl_3$). IR: 2964*s*, 2923*m*, 2872*m*, 1733*s*, 1477*m*, 1456*m*, 1395*w*, 1364*w*, 1277*m*, 1133*s*, 1062*m*, 1031*m*, 964*w*. ^{1}H-NMR ($CDCl_3$): 1–1.3 (6 *s*, Piv); 3.1 (*td*, $^3J(6a,1) = {}^3J(6a,3a) = 7.5$, $^3J(6a,6) = 2.5$, H–C(6a)); 3.55 (br. *d*, $^3J(3a,6a) = 7.5$, H–C(3a)); 3.75 (*ddd*, $^3J(5',4') = 9.5$, $^3J(5',6'b) = 5$, $^3J(5',6'a) = 1.5$, H–C(5′)); 4.08 (*dd*, $^2J(6'a,6'b) = 12.5$, $^3J(6'a,5') = 5$, H_a–C(6′)); 4.2 (*dd*, $^2J(6'b,6'a) = 12.5$, $^3J(6'b,5') = 1.5$, H_b–C(6′)); 4.55 (br. *d*, $^3J(1,6a) = 7.5$, H–C(1)); 4.68 (br. *d*, $^2J = 15$, 1 H, CH_2–C(4)); 4.72 (br. *d*, $^2J = 15$, 1 H, CH_2–C(4)); 4.88 (*d*, $^3J(1',2') = 8$, H–C(1′)); 5.05 (*dd*, $^3J(2',3') = 9.5$, $^3J(2',1') = 8$, H–C(2′)); 5.12 (*t*, $^3J(4',3') = {}^3J(4',5') = 9.5$, H–C(4′)); 5.3 (*t*, $^3J(3',2') = {}^3J(3',4') = 9.5$, H–C(3′)); 5.38 (*m*, H=C(6)); 5.52 (br. *s*, H–C(3)); 5.7 (*m*, H–C(5)); 9.85 (br. *s*, CH=O). ^{13}C-NMR ($CDCl_3$): 27.2 (Me_3CCO); 38.7 (Me_3CCO); 50.9 (C(6a)); 57.9 (C(3a)); 61.2 (CH_2–C(4)); 61.7 (C(6′)); 67.8 (C(4′)); 70.9 (C(2′)); 72.5 (C(3′)); 72.6 (C(5′)); 79.4 (C(6)); 82.9 (C(1)); 95.7 (C(1′)); 100.6 (C(3)); 127.3 (C(5)); 143.7 (C(4)); 178.2, 177.9, 177.7, 177.1, 176.4 (2C) (Me_3CCO); 198.1 (CH=O). ESI-MS: 889 ($[M + Na]^+$). Anal. calc. for $C_{45}H_{70}O_{16}$ (866.47): C 62.34, H 8.14; found: C 61.67, H 8.33.

Data of **14**: Amorphous glassy solid. $[\alpha]_D^{20} = -59.3$ ($c = 4$, $CHCl_3$). IR: 2964*m*, 2923*m*, 2872*w*, 1733*s*, 1477*m*, 1475s,1395*w*, 1364*w*, 1277*m*, 1144*s*, 1067*m*, 1031*w*. ^{1}H-NMR (C_6D_6): 0.99–1.3 (6 *s*, Piv); 3.08 (*ddd*, $^3J(5',4') = 9$, $^3J(5',6'a) = 5.5$, $^3J(5',6'b) = 1.5$, H–C(5′)); 3.18 (*ddd*, $^3J(6a,3a) = 7.5$, $^3J(6a,1) = 3$, $^3J(6a,6) = 2.5$, H–C(6a)); 3.22 (br. *d*, $^3J(3a,6a) = 7.5$, H–C(3a)); 3.95 (*dd*, $^2J(6'a,6'b) = 12.5$, $^3J(6'a,5') = 5.5$, H_a–C(6′)); 4.12 (*dd*, $^2J(6'b,6'a) = 12.5$, $^3J(6'b,5') = 1.5$, H_b–C(6′)); 4.22 (br. *d*, $^3J(1,6a) = 3$, H–C(1)); 4.38 (br. *d*, $^2J = 14$, 1 H, CH_2–C(4)); 4.42 (br. *d*, $^2J = 14$, 1 H, CH_2–C(4)); 4.68 (*d*, $^3J(1',2') = 8$, H–C(1′)); 5.2 (*t*, $^3J(4',3') = {}^3J(4',5') = 9$, H–C(4′)); 5.25 (*dd*, $^3J(2',3') = 9$, $^3J(2',1') = 8$, H–C(2′)); 5.38 (*t*, $^3J(3',2') = {}^3J(3',4') = 9$, H–C(3′)); 5.4 (*m*, H–C(6)); 5.55 (*m*, H–C(5)); 5.65 (*s*, H–C(3)); 9.6 (*s*, CH=O). ^{13}C-NMR ($CDCl_3$): 26.9 (Me_3CCO); 38.8 (Me_3CCO); 49.8 (C(6a)); 57.7 (C(3a)); 61.2 (CH_2–C(4)); 61.7 (C(6′)); 68.1 (C(4′)); 71.2 (C(2′)); 72.5 (C(3′)); 72.7 (C(5′)); 83.8 (C(6)); 88.7 (C(1)); 96.1 (C(1′)); 101.7 (C(3)); 126.7 (C(5)); 144.2 (C(4)); 179.0–177.1 (6 C, Me_3CCO); 199.8 (CH=O). ESI-MS: 889 ($[M + Na]^+$). Anal. calc. for $C_{45}H_{70}O_{16}$ (866.47): C 62.34, H 8.14; found: C 61.85, H 8.24.

*(1*S*,3*S*,3a*S*,6S,6a*R*)-6-(2,2-Dimethyl-1-oxopropoxy)-4-[(2,2-dimethyl-1-oxopropoxy)methyl]-3,3a,6,6a-tetrahydro-3-{[2,3,4,6-tetrakis-*O*-(2,2-dimethyl-1-oxopropyl)-β-*D*-glucopyranosyl]oxy}-1-*H*-cyclopenta[*c*]furan-1-carboxaldehyde* (**15**). *Method A:* As described for **13**/**14**, with **9** (100 mg, 0.12 mmol) and TTN (57.8 mg, 0.13 mmol): **15** (83 mg, 80%).

Method B: As described for **13**/**14**, with **9** (100 mg, 0.12 mmol) and potassium phthalimide (22 mg, 0.12 mmol): **15** (93 mg, 89%).

Method C: As described for **13**/**14**, with **9** (29 mg, 0.034 mmol): **15** (24.5 mg, 83%).

Data of **15**: Amorphous glassy solid. $[\alpha]_D^{20} = -46.3$ ($c = 1$, $CHCl_3$). IR: 2974*s*, 2936*s*, 2875*m*, 1733*s*, 1481*s*, 1462*s*, 1399*m*, 1368*m*, 1280*m*, 1143*s*, 1063*m*, 1036*m*, 964*m*. ^{1}H-NMR (C_6D_6): 1–1.4 (6 *s*, Piv); 2.88 (br. *d*, ^3J(6a,3a) = 7, H–C(3a)); 3.1 (*ddd*, ^3J(5′,4′) = 9, ^3J(5′,6′b) = 5.5, ^3J(5′,6′a) = 1.5, H–C(5′)); 3.18 (*td*, ^3J(6a,1) = 4.5, ^3J(6a,3a) = ^3J(6a,6) = 7, H–C(6a)); 3.98 (*dd*, ^2J(6′a,6′b) = 12.5, ^3J(6′a,5′) = 5.5, H_a–C(6′)); 4.12 (*dd*, ^2J(6′a,6′b) = 12.5, ^3J(5′,6′b) = 1.5, H_b–C(6′)); 4.31 (br. *d*, ^2J = 14, 1 H, CH_2–C(4)); 4.4 (br. *d*, ^2J = 14, 1 H, CH_2–C(4)); 4.68 (*dd*, ^3J(1,6a) = 4.5, ^3J(1, CH=O) = 1.5, H–C(1)); 4.72 (*d*, ^3J(1′,2′) = 8, H–C(1′)) 5.25 (*t*, ^3J(4′,3′) = ^3J(4′,5′) = 9, H–C(4′)); 5.3 (*dd*, ^3J(2′,3′) = 9, ^3J(2′,1′) = 8, H–C(2′)); 5.38 (*t*, ^3J(3′,2′) = ^3J(3′,4′) = 9, H–C(3′)); 5.41 (*m*, H–C(5)); 5.52 (*dm*, ^3J(6, 6a) = 7, H–C(6)); 5.83 (*s*, H–C(3)); 9.72 (*d*, ^3J(1, (CH=O) = 1.5, CH=O). ^{13}C-NMR ($CDCl_3$): 26.9 (*Me*$_3$CCO); 38.6 (Me$_3$*C*CO); 44.9 (C(6a)); 57.4 (C(3a)); 60.9 (*C*H$_2$–C(4)); 61.0 (C(6′)); 68.1 (C(4′)); 71.1 (C(2′)); 72.5 (C(3′)); 72.6 (C(5′)); 77.0 (C(6)); 84.4 (C(1)); 95.7 (C(1′)); 101.7 (C(3)); 128.6 (C(5)); 140.8 (C(4)); 178.2–176.4 (Me$_3$*C*CO); 200.8 (CH=O). ESI-MS: 889 ([*M* + Na]$^+$). Anal. calc. for $C_{45}H_{70}O_{16}$ (866.47): C 62.34, H 8.14; found: C 62.13, H 8.26.

*(1R,3S,3aS,6S,6aR)-6-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)-4-[(2,2-dimethyl-1-oxopropoxy)methyl]-3,3a,6,6a-tetrahydro-3-{[2,3,4,6-tetrakis-*O*-(2,2-dimethyl-1-oxopropyl)-β-*D*-glucopyranosyl]oxy}-1*H*-cyclopenta[*c*]furan-1-carboxaldehyde* (**16**). *Method A:* As described for **13**/**14**, with **10** (85 mg, 0.095 mmol) and TTN (46.2 mg, 0.104 mmol): **16** (61 mg, 71%).

Method B: As described for **13**/**14**, with **10** (52 mg, 0.058 mmol) and potassium phthalimide (10.8 mg, 0.058 mmol): **16** (44 mg, 83%).

Method C: As described for **13**/**14**, with **10** (1 g, 1.1 mmol): **16** (704 mg, 70%).

Data of **16**: Colorless prisms from cyclohexane/AcOEt 85:15. M.p. 80°. $[\alpha]_D^{20} = -46$ ($c = 0.5$, $CHCl_3$). IR: 3450 (br.), 2974*m*, 2937*s*, 2911*m*, 2875*m*, 1736*s*, 1717*s*, 1646*w*, 1481*m*, 1282*m*, 1142*s*. ^{1}H-NMR ($CDCl_3$): 1–1.3 (5 *s*, Piv); 3.38 (*q*, ^3J(6a,1) = ^3J(6a,3a) = ^3J(6a,6) = 6.5, H–C(6a)); 3.45 (br. *d*, ^3J(3a,6a) = 6.5, H–C(3a)); 3.8 (*ddd*, ^3J(5′,4′) = 9.5, ^3J(5′,6′b) = 5.5, ^3J(5′,6′a) = 1.5, H–C(5′)); 4.09 (*dd*, ^2J(6′a,6′b) = 12.5, ^3J(6′a, 5′) = 5.5, H_a–C(6′)); 4.22 (*dd*, ^2J(6′b,6′a) = 12.5, ^3J(6′b,5′) = 1.5, H_b–C(6′)); 4.42 (*dd*, ^3J(1,6a) = 6.5, ^3J(1, CH=O) = 1.5, H–C(1)); 4.71 (br. *d*, ^2J = 14, 1 H, CH_2–C(4)); 4.80 (br. *d*, ^2J = 14, 1 H, CH_2–C(4)); 5.00 (*d*, ^3J(1′,2′) = 8, H–C(1′)); 5.05 (*dd*, ^3J(2′,3′) = 9.5, ^3J(2′,1′) = 8, H–C(2′)); 5.12 (*t*, ^3J(4′,3′) = ^3J(4′,5′) = 9.5, H–C(4′)); 5.33 (*t*, ^3J(3′,2′) = ^3J(3′,4′) = 9.5, H–C(3′)); 5.38 (*m*, H–C(6)); 5.82 (*s*, H–C(3)); 6.10 (*m*, H–C(5)); 7.88–7.7, (*m*, 4 arom. H); 9.59 (*d,* ^3J(1, CH=O) = 1.5, CH=O).^{13}C-NMR ($CDCl_3$): 27.2 (*Me*$_3$CCO); 38.8 (Me$_3$*C*CO); 46.6 (C(6a)); 57.3 (C(3a)); 61.0 (*C*H$_2$–C(4)); 61.7 (C(6′)); 68.0 (C(2′)); 71.1 (C(4′)); 72.5 (C(3′), C(5′)); 85.6 (C(1)); 95.8 (C(1′)); 101.9 (C(3)); 123.4 (2 arom. C); 127.9 (C(5)); 131.7 (2 arom. C); 134.2 (2 arom. C); 137.0 (C(4)); 168.4 (2 CO (PhtN)); 177.8, 177.6, 177.1, 176.6, 176.4 (Me$_3$*C*CO); 202.0 (CH=O). ESI-MS: 934 ([*M* + Na]$^+$). Anal. calc. for $C_{48}H_{65}NO_{16}$ (911.43): C 63.21, H 7.18, N 1.54; found: C 63.02, H 7.17, N 1.55.

(*4*R*)-3,4-Dihydro-4-iodo-3-oxo-perpivaloyl-6-epiaucubin* (= *(1*R*,4R,4a*R*,5*S*,7a*S*)-5-(2,2-Dimethyl-1-oxopropoxy)-7-[(2,2-dimethyl-1-oxopropoxy)methyl]-1,3,4,4a,5,7a-hexahydro-4-iodo-3-oxocyclopenta[*c*]pyran-1-yl 2,3,4,6-Tetrakis-*O*-(2,2-dimethyl-1-oxopropyl)-β-*D*-glucopyranoside*; **19**). NIS (9 mg, 0.04 mmol) was added to a soln. of **9** (22 mg, 0.026 mmol) in MeCN (8 ml) and H_2O (2 ml). The mixture was stirred at r.t. for 5 h. CH_2Cl_2 (10 ml) was added. The org. layer was washed with H_2O (10 ml), 0.1M aq. $Na_2S_2O_4$ (10 ml), brine (10 ml), and dried (Na_2SO_4). The solvent was evaporated. CC (cyclohexane/Me_2CO 3:1) afforded a mixture of the corresponding crude iodolactols (25 mg, 98%). To a soln. of these compounds (23 mg, 0.023 mmol) in anh. CH_2Cl_2 (5 ml), 4Å molecular sieves (152 mg), pyridinium dichromate (PDC; 10 mg, 0.028 mmol), and AcOH (0.1 ml) were added under Ar. The mixture was stirred at r.t. for 12 h and then filtered through *Celite*. The filtrate was evaporated. CC (cyclohexane/Me_2CO 95:5) afforded **19** (18 mg, 79%). Colorless needles from EtOH. M.p. 126°. $[\alpha]_D^{20} = +10.7$ ($c = 1$, CH_2Cl_2). IR: 2968*m*, 2936*m*, 2876*w*, 1736*s*, 1480*m*, 1399*w*, 1361*w*, 1279*m*, 1138*s*, 1073*w*, 1035*w*, 986*w*. ^{1}H-NMR ($CDCl_3$): 1–1.3 (6 *s*, Piv); 3.12 (br. *t*, ^3J(9,5) = ^3J(9,1) = 8, H–C(9)); 3.58 (br. *dt*, ^3J(5,6) = 6.5, ^3J(5,9) = ^3J(5,4) = 8, H–C(5)); 3.78 (*ddd*, ^3J(5′,4′) = 9.5, ^3J(5′,6′b) = 4.5, ^3J(5′,6′a) = 1.5, H–C(5′)); 4.01 (*dd*, ^2J(6′b,6′a) = 12.5, ^3J(6′b,5′) = 4.5, H_b–C(6′)); 4.25 (*dd*, ^2J(6′a,6′b) = 12.5, ^3J(6′a,5′) = 1.5, H_a–C(6′)); 4.65 (br. *d*, ^2J(10b,10a) = 16.5, H_b–C(10)); 4.75 (br. *d*, ^2J(10a,10b) = 16.5, H_a–C(10)); 4.86 (br. *d*, ^3J(4,5) = 8, H–C(4)); 5.02 (*d*, ^3J(1′,2′) = 8, H–C(1′)); 5.11 (*dd*, ^3J(2′,3′) = 9.5, ^3J(2′,1′) = 8, H–C(2′)); 5.19 (*t*, ^3J(4′,3′) = ^3J(4′,5′) = 9.5, H–C(4′)); 5.35 (*t*, ^3J(3′,2′) = ^3J(3′,4′) = 9.5, H–C(3′)); 5.42 (*d*, ^3J(1,9) = 8, H–C(1));

5.62 (*d*, $^3J(6,5)=7$, H–C(6)); 5.95 (*m*, H–C(7)). ^{13}C-NMR ($CDCl_3$): 13.2 (C(4)); 27.1 (Me_3CCO); 38.8 (Me_3CCO); 48.1 (C(5)); 48.7 (C(9)); 61.1 (C(10)); 61.3 (C(6′)); 67.4 (C(4′)); 70.5 (C(2′)); 71.8 (C(5′)); 72.9 (C(3′)); 75.9 (C(6)); 97.2 (C(1′)); 99.7 (C(1)); 127.3 (C(7)); 145.3 (C(8)); 165.2 (C(3)); 177.7–176.6 (6C, Me_3CCO). ESI-MS: 1015 ($[M+Na]^+$). Anal. calc. for $C_{45}H_{69}IO_{16}$ (992.92): C 54.43, H 7.00; found: C 54.66, H 7.22.

(4R,6S)-3,4-Dihydro-4-iodo-3-oxo-perpivaloyl-6-phthalimidobartsioside (= *(1*R*,4R,4a*R*,5*S*,7a*S*)-5-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)-7-[(2,2-dimethyl-1-oxopropoxy)methyl]-1,3,4,4a,5,7a-hexahydro-4-iodo-3-oxocyclopenta[*c*]pyran-1-yl 2,3,4,6-Tetrakis-*O*-(2,2-dimethyl-1-oxopropyl)-β-D-glucopyranoside*; **20**). As described for **19** with **10** (73 mg, 0.08 mmol) and NIS: intermediate iodolactols (68 mg, 81%) were oxidized with PDC. CC (cyclohexane/acetone 3:1) afforded **20** (56 mg, 83%). Colorless needles from cyclohexane/acetone (3:1). M.p. 105°. $[\alpha]_D^{20}=-30$ ($c=1$, CH_2Cl_2). IR: 2973*m*, 2930*w*, 2903*w*, 2876*w*, 1746*s*, 1714*s*, 1485*m*, 1399*m*, 1361*m*, 1268*m*, 1133*s*, 1084*m*, 981*m*, 720*w*. ^{1}H-NMR ($CDCl_3$): 1–1.3 (5 *s*, Piv); 3.12 (br. *t*, $^3J(9,5)=^3J(9,1)=9.5$, H–C(9)); 3.58 (*dt*, $^3J(5,6)=^3J(5,9)=9.5$, $^3J(5,4)=11.5$, H–C(5)); 3.83 (*ddd*, $^3J(5',4')=9.5$, $^3J(5',6'b)=4.5$, $^3J(5',6'a)=1.5$, H–C(5′)); 4.11 (*dd*, $^2J(6'a,6'b)=12.5$, $^3J(5',6'b)=4.5$, H_b–C(6′)); 4.42 (*dd*, $^2J(6'a,6'b)=12.5$, $^3J(5',6'a)=1.5$, H_a–C(6′)); 4.58 (*d*, $^3J(4,5)=11.5$, H–C(4)); 4.75 (br. *s*, 2 H–C(10)); 5.02 (*d*, $^3J(1',2')=8$, H–C(1′)); 5.12 (*dd*, $^3J(2',3')=9.5$, $^3J(2',1')=8$, H–C(2′)); 5.22 (*t*, $^3J(4',3')=^3J(4',5')=9.5$, H–C(4′)); 5.38 (*t*, $^3J(3',2')=^3J(3',4')=9.5$, H–C(3′)); 5.58 (*m*, H–C(7)); 5.66 (*m*, $^3J(6,5)=9.5$, $^3J(6,7)=2$, H–C(6)); 6.18 (*d*, $^3J(1,9)=9.5$, H–C(1)); 7.8–7.65 (*m*, 4 arom. H). ^{13}C-NMR ($CDCl_3$): 18.2 (C(4)); 26.9 (Me_3CCO); 38.7 (Me_3CCO); 45.1 (C(5)); 51.9 (C(9)); 55.8 (C(6)); 61.3 (C(10)); 61.7 (C(6′)); 67.5 (C(4′)); 70.6 (C(2′)); 71.9 (C(3′)); 72.8 (C(5′)); 97.8 (C(1′)); 98.2 (C(1)); 123.7 (2 arom. C); 125.3 (C(7)); 131.4 (2 arom. C); 134.6 (2 arom. C); 141.5 (C(8)); 164.7 (C(3)); 168.7 (2 *C*O (PhtN)); 178.0, 177.4, 177.0, 176.6, 176.3 (Me_3CCO). ESI-MS: 1060 ($[M+Na]^+$). Anal. calc. for $C_{48}H_{64}INO_{16}$ (1037.33): C 55.54, H 6.22, N 1.35; found: C 55.30, H 6.56, N 1.46.

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