Organic & Biomolecular Chemistry

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2016, **14**, 10238

Synthesis of 28a-homoselenolupanes and 28a-homoselenolupane saponins†

Katarzyna Sidoryk,[a,b] Lucie Rárová,[c] Jana Oklešťková,[d] Zbigniew Pakulski,*[a] Miroslav Strnad,*[d] Piotr Cmoch[a] and Roman Luboradzki[e]

Received 2nd September 2016,
Accepted 7th October 2016

DOI: 10.1039/c6ob01938b

www.rsc.org/obc

A practical synthesis of 28a-homo-28a-selenolupane triterpenes and the corresponding selenosaponins containing D-mannose, L-arabinose, L-rhamnose, and D-idose moieties is described. Selenium containing triterpenes were obtained from the readily available 3-*O*-allyl-homobetulin mesylate by nucleophilic substitution with the selenocyanate ion which upon reduction of the –SeCN group afforded the free selenol. Glycosylation using classical Schmidt donors gave 1,2-*trans* selenosaponins as the main product as well as minute amounts of 1,2-*cis* isomers. This is one of the very few examples of the synthesis of selenoglycosides by direct glycosylation of free selenols. The studied selenol showed high resistance to air oxidation resulting in good stability during the synthesis of selenolupane derivatives. Cytotoxic activities of new homoselenolupane derivatives were also evaluated *in vitro* and revealed that some triterpenes exhibited an interesting profile against human cancer cell lines.

Introduction

In the last few decades, the application of organoselenium compounds,[1] including steroid derivatives,[2] in cancer prevention and treatment became an objective of investigations of many scientific groups. These studies show that organoselenium compounds display a high cytotoxic activity against different cancer cell lines. Moreover, in some cases a positive effect on the cytotoxic properties was achieved by replacing the sulphur atom with selenium without modifying the basic structure of the compound.[3] Additionally, some heterocycles containing selenium possess an interesting anti-inflammatory activity profile with a significant analgesic effect.[4] Furthermore, many organoselenium derivatives demonstrate antimicrobial, antiviral and antifungal activities.[5]

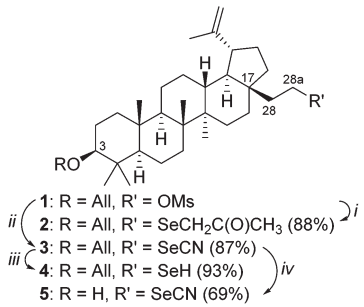
Previously, we reported the structure–activity relationships of the cytotoxic activity of ichopanol (28a-homobetulin) and ichopanothiol (28a-homothiobetulin) derivatives and saponins based on a homobetulin scaffold. We found, that the heteroatom (oxygen or sulphur) located on the C-17 side-chain is necessary for the anticancer activity of the studied compounds.[6–8] Based on the high biological activity of selenium derivatives, we reasoned that replacing these heteroatoms on the C-17 side-chain of the lupane core with selenium could enhance their anticancer effect. These results will broaden our knowledge regarding the synthesis, reactivity and stability of selenium-containing triterpenes and steroids as they are virtually unknown in the literature.[2,9] Herein, we report the first synthesis of homobetulin and homobetulin based saponins bearing a selenium atom. Furthermore, cytotoxic activities of all new derivatives were investigated.

Results and discussion

Mesylate **1**, readily prepared *via* the reaction of 3-*O*-allyl-ichopanol and mesyl chloride,[8] was used for the synthesis of selenolupane triterpenes. Standard synthesis of selenocyanate **3** involves the nucleophilic replacement of sulfonyl ester with potassium selenocyanate. Our first attempt using acetone as a solvent failed giving only selenide **2**. However, changing the solvent from acetone to DMF resulted in the formation of the desired product **3** in 87% yield; a small amount of by-product selenol **4** (7%) was also isolated. Reduction of **3** with $LiAlH_4$ gave the corresponding selenol **4** in 93% yield. Compound **5**,

[a]*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland. E-mail: zbigniew.pakulski@icho.edu.pl*
[b]*Pharmaceutical Research Institute, Rydygiera 8, 01-793 Warsaw, Poland*
[c]*Department of Chemical Biology and Genetics, Centre of the Region Haná for Biotechnological and Agricultural Research, Palacký University, Šlechtitelů 27, 783 71 Olomouc, Czech Republic*
[d]*Laboratory of Growth Regulators, Centre of the Region Haná for Biotechnological and Agricultural Research, Institute of Experimental Botany ASCR & Palacký University, Šlechtitelů 27, 783 71 Olomouc, Czech Republic. E-mail: miroslav.strnad@upol.cz*
[e]*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*

†Electronic supplementary information (ESI) available: Copies of ^{1}H and ^{13}C NMR spectra of the synthesized compounds. CCDC 1422676. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6ob01938b



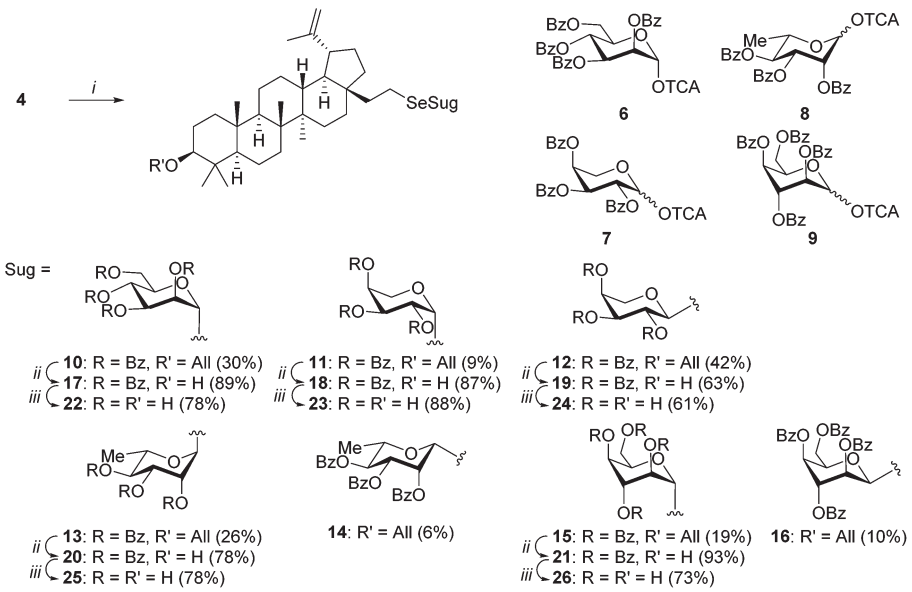
Scheme 1 Reagents and conditions: (i) KSeCN (5 equiv.), acetone, 60 °C; (ii) KSeCN (5 equiv.), DMF, 60 °C; (iii) $LiAlH_4$ (2 equiv.), THF; (iv) $PdCl_2$, CH_3OH, CH_2Cl_2.

needed for SAR studies, was prepared in 69% yield from allyl ether **3** by treatment with palladium(II) chloride (Scheme 1).

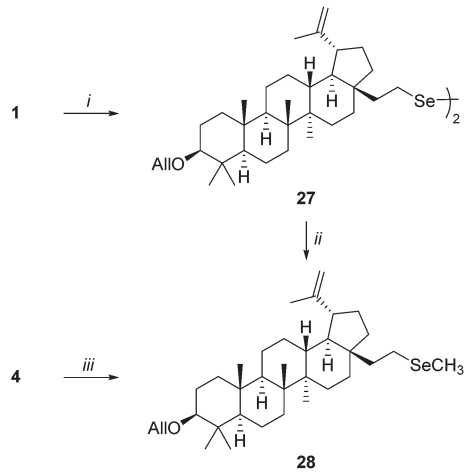
Synthesis of selenoglycosides by direct glycosylation of selenols is rarely found in the literature. Due to high susceptibility of selenols to oxidation the introduction of selenium at the anomeric position of a monosaccharide is achieved by the treatment of the sugar component with alkyl or aryl selenolates usually generated *in situ* from the corresponding diselenides in the presence of a reducing agent.[10] Free selenols were used occasionally to react with anomeric halogenides,[11] acetates,[11b,12] orthoesters,[13] or Schmidt donors.[11a,14]

For the synthesis of lupane-type selenoglycosides we chose the Schmidt methodology. TMSOTf promoted glycosylation was carried out by the treatment of selenol **4** with perbenzoylated glycosyl trichloroacetimidates **6**,[15] **7**,[16] **8**,[16] and **9**,[17] which gave the desired selenoglycosides in 29–51% yield. A significant amount of unreacted starting selenol **4** was also recovered (13–40%). Although yields were rather moderate, further manipulation of the reaction conditions did not improve the yields of the selenoglycosides. As expected, the presence of the benzoyl protecting groups in the donor molecules directed the anomeric selectivity of glycosylation.[18] Regioselectivity was, however, slightly lower than that in the case of the corresponding sulfur analogues.[8] With the exception of α-D-mannopyranoside **10**, mixtures of α and β anomers **11–16** of L-arabino, L-rhamno, and D-ido derivatives were obtained as specified in Scheme 2.

Selenols are considered highly susceptible to air oxidation leading to diselenides, however, selenol **4** was relatively resistant to oxidation. Recovered selenol **4** was reused for glycosylation without any significant decrease in the reaction yields. It must be noted, however, that prolonged storage slowly decreased its reactivity, although the physicochemical properties of **4** did not change. Considering the above observations which are crucial criteria in the synthesis of selenolupane derivatives, a study examining the stability of selenol **4** was undertaken. First, the independent synthesis of diselenide **27**, the expected product of the air oxidation of **4**, was conducted. The homogeneous product was prepared by the reaction of mesylate **1** with dilithium diselenide (Li_2Se_2)[19] affording compound **27** in 88% yield (Scheme 3). The same compound containing inseparable unknown byproducts, may also be obtained by the oxidation of selenol **4** with hydrogen peroxide in the presence of NaOH (79%) and from the equimolar mixture of selenocyanide **3** and selenol **4** in the presence of a base (94%) according to Krief's method.[20] Surprisingly, in all cases, the physichochemical properties of **27**, including ^{77}Se NMR, were identical as found for selenol **4** but differences in reactivity were observed. In contrast to compound **4**, compound **27** did not react with Schmidt donors. On the other hand, both derivatives were alkylated by treatment with methyl



Scheme 2 Reagents and conditions: (i) **6–9**, CH_2Cl_2, TMSOTf, −40 °C; (ii) (a) $[Ir(COD)(PMePh_2)]PF_6$, H_2, THF; (b) *p*-TsOH, $CHCl_3$, CH_3OH; (iii) K_2CO_3, CH_3OH.



Scheme 3 Reagents and conditions: (i) Se, Super Hydride, THF, 88%; (ii) NaH, CH_3I, THF, rt, 5 days, 70%; (iii) NaH, CH_3I, THF, rt, 12 h, 74%.

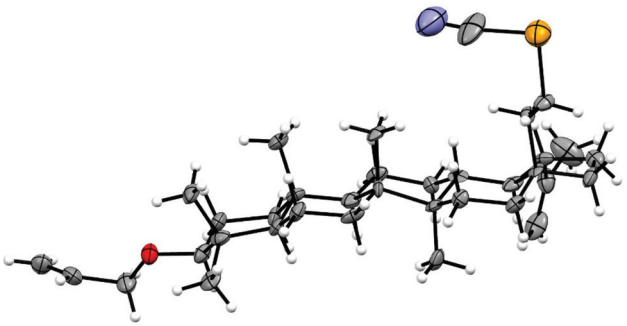


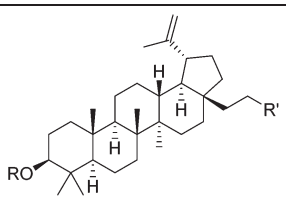
Fig. 1 X-ray structure of 3β-*O*-allyl-28a-selenocyanato-28a-homolup-20(29)-ene (**3**).

iodide to afford selenide **28**. However, in the case of the reaction of compound **27** with methyl iodide a longer reaction time was required (5 days, 70%), whereas the alkylation of freshly prepared selenol **4** in the presence of sodium hydride was complete within a few hours giving compound **28** in 74% yield (Scheme 3).

There are two possible explanations for such unusual behaviour. The first is that both compounds (**4** and **27**) have identical spectroscopic properties but they are different compounds. This speculation may be supported by the result of alkylation described above. In the first case (considering diselenide **27**) sodium hydride acting first as a reducing agent (breaking Se–Se bond) and then as a base was required for alkylation.[21] It significantly prolonged the reaction time. On the other hand, when the formation of the Se–Se bond was not possible due to high steric hindrance, selenol was formed in both cases. However, reaction conditions and/or long storage time promoted the aggregation of selenol and the formation of relatively unreactive polymeric forms which caused a decrease in reactivity. Similar aggregation of betulin derivatives was described in the literature.[22]

Attempts to remove the allyl block from 3-*O*-allylselenosaponins with palladium(II) chloride were unsuccessful and caused decomposition of the starting materials. Therefore, deallylation was performed under neutral conditions by isomerisation of the allyl double bond in the presence of the hydrogen activated iridium complex $[Ir(COD)(PMePh_2)]PF_6$ followed by hydrolysis of 1-propenyl ether in the presence of *p*-TsOH.[17] Deallylated saponins **17–21** were obtained in high yields (78–93%) with the exception of **19** which was isolated in slightly lower yield (63%). Debenzoylation with potassium carbonate in methanol gave free saponins **22–26** in good yields (61–88%, Scheme 2).

Table 1 IC_{50} (μM) values obtained from Calcein AM assays with the tested cancer and normal cell lines; means ± SD obtained from three independent experiments performed in triplicate. Betulinic acid was used as a positive control



Comp. no.	R	R′	IC_{50} [μM] CEM	MCF7	HeLa	G-361	BJ
2	All	$SeCH_2COCH_3$	>50	>50	>50	>50	>50
5	H	SeCN	2.0 ± 0.6	5.2 ± 1.4	3.4 ± 0.6	3.8 ± 0.8	3.7 ± 0.8
29 [8]	H	SCN	4.4 ± 1.8	13.6 ± 4.8	6.7 ± 0.0	3.0 ± 0.1	4.6 ± 0.5
30 [7]	H	OH	15.3 ± 1.4	>50	>50	10.2 ± 0.9	>50
22	H	Se-α-D-Man*p*	>50	46.4 ± 5.2	>50	>50	>50
23	H	Se-β-L-Ara*p*	>50	>50	>50	>50	>50
24	H	Se-α-L-Ara*p*	>50	>50	>50	>50	>50
25	H	Se-α-L-Rha*p*	32.5 ± 4.4	45.4 ± 3.0	42.3 ± 0.0	41.0 ± 2.5	46.9 ± 0.1
26	H	Se-α-D-Ido*p*	>50	>50	>50	>50	>50
Betulinic acid	—	—	40.0 ± 2.8	>50	47.6 ± 1.9	>50	>50

Structures of all new compounds were confirmed by extended 1D and 2D NMR experiments, as well as elemental analysis and mass spectroscopy. Stereochemistry at the anomeric center was proven by measuring $^1J_{C1,H1}$ coupling constants. Observed $^1J_{C1,H1}$ coupling constants for **11** (170.4 Hz), **13** (171.0 Hz), and **15** (168.0 Hz) proved the equatorial position of the anomeric proton, whereas $^1J_{C1,H1}$ measured for **12** (158.0 Hz), **14** (153.0 Hz), and **16** (154.0 Hz) indicated the presence of axially oriented anomeric protons.[23] In the case of rhamnosides **13** and **14** (6-deoxy-hexopyranosides) the configuration at the anomeric carbon atom was additionally confirmed by the almost forgotten Sinclair–Sleeter rule.[24] The signal for the H-6 protons of **13** in which aglycon is in the axial position was observed upfield (1.39 ppm) in comparison with its epimer in which the signal for the H-6 protons appeared downfield (1.46 ppm). In addition, the structure of 3β-*O*-allyl-28a-selenocyanato-28a-homolup-20(29)-ene (**3**) was unequivocally confirmed by X-ray analysis (Fig. 1).

Antiproliferative activities of the studied derivatives of homobetulin were tested *in vitro*. Activity against normal human BJ fibroblasts was compared with cytotoxicity on cancer cell lines of various histopathological origins, including T-lymphoblastic leukaemia (CEM), breast adenocarcinoma (MCF7), malignant melanoma (G-361) and cervical carcinoma (HeLa) lines. The cells of all these lines were exposed to six serial 3-fold dilutions of each drug for 72 h, the proportions of surviving cells were then estimated and IC_{50} values (50% inhibitory concentrations) were calculated. A detailed procedure for the cytotoxicity assay was described previously.[7] The results obtained from Calcein AM assays are presented in Table 1.

Selenosaponins were practically inactive, except L-rhamnoside **25** which showed low activity (IC_{50} 32.5–45.4 μM). Similar results were obtained for oxygen[7] and sulphur analogs[8] which suggest that homobetulin saponins do not affect the growth of the cancer lines. Compound **30** was selective against malignant melanoma and leukemia cell lines (IC_{50} 10.2 or 15.3 μM) without affecting the growth of normal human fibroblasts and other cancer cells which suggested a high therapeutic index. By comparison, selenocyanate **5** showed the highest cytotoxic activity of all compounds tested (IC_{50} 2.0–5.2 μM). Its cytotoxicity was also higher than that measured for the appropriate sulphur analogue **29**, and much higher than those observed for ichopanol (**30**). Sulphur analogue **29** showed an interesting profile as much more higher activity was determined for G-361 melanoma cells than for other cancer cell lines and fibroblasts. Both compounds, however, exhibit a relatively low therapeutic index.

Conclusions

In conclusion, a series of 28a-homo-28a-selenolupane triterpenes and the corresponding homoselenosaponins bearing D-mannose, L-arabinose, L-rhamnose, and D-idose moieties were synthesised. Required selenol was obtained by a nucleophilic substitution of the corresponding mesylate with potassium selenocyanate followed by the reduction of the –SeCN group. Its unusual stability to air oxidation was discussed. Further glycosylation of selenol with Schmidt donors under the standard conditions followed by deprotection afforded homoselenosaponins. All new compounds were evaluated for their cytotoxic activities towards normal and cancer cell lines. Homobetulin selenocyanate was the most cytotoxic compound, whereas the corresponding saponins were mostly inactive. To our best knowledge this is the first synthesis of lupane-type triterpenes containing selenium as the core component.

Experimental section

General procedures

Silica gel HF_{254} and silica gel 230–400 mesh (E. Merck) were used for TLC and column chromatography, respectively. ^1H, ^{13}C and ^{77}Se NMR spectra were recorded at 298 K with a Varian NMR-vnmrs600 or vnmrs500 spectrometer, using standard experimental conditions and Varian software (ChemPack 4.1). Configurational assignments were based on the NMR measurements, generated using two-dimensional techniques like COSY and ^1H–^{13}C gradient selected HSQC (*g*-HSQC), as well as ^1H–^{13}C gradient selected HMBC (*g*-HMBC). TMS was used as the internal standard for determining ^1H and ^{13}C NMR chemical shifts. *J* values are given in hertz. High-resolution mass spectra (HRMS-ESI) were acquired with Mariner and MaldiSYNAPT G2-S HDMS (Waters) mass spectrometers. Optical rotations were measured with a Jasco P-2000 automatic polarimeter. IR spectra were recorded on a Jasco 6200 FT-IR spectrophotometer.

Single crystal X-ray diffraction measurements were carried out on an Agilent Supernova diffractometer, at 100 K with monochromated Cu Kα radiation (1.54184 Å). The data reduction was made by using CrysAlisPRO software.[25] The structures were solved by direct methods and refined on F^2 by full-matrix least-squares by using SHELXS97 and SHELXL97.[26] All non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed in calculated positions, and refined in riding mode. Crystals of **3** suitable for X-ray analysis were obtained by cooling of a hot methanol solution: monoclinic, $P2_1$, a = 13.729(2), b = 8.3619(9), c = 14.594(3) Å, β = 114.96(2), V = 1518.9(5) Å^3, Z = 2, D_{calc} = 1.279 g cm^{-1}, μ = 1.864 mm^{-1}, R_1 = 0.0894 for 2177 [$F_o > 4\sigma(F_o)$] and 0.1157 for all data, wR_2 = 0.2644, S = 1.046. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary material (deposition numbers: CCDC 1422676).

1-[3β-*O*-Allyl-28a-homolup-20(29)-en-28a-selenoyl]-2-propanone (2). A solution of **1** (50 mg, 0.087 mmol) and KSeCN (63 mg, 0.43 mmol) in acetone (1 mL) was stirred at 60 °C for 48 h. Then the solvents were evaporated, and the residue was dissolved in DCM and washed twice with water. An organic layer was evaporated to dryness; column chromatography of the residue (hexane–ethyl acetate, 40 : 1 → 10 : 1) gave **2** as a white

solid (45 mg, 88%). M.p. 166–167 °C; $[\alpha]_D^{20}$ 14.2 (*c* 0.3, chloroform); ν_{max} (film): 2942, 2868, 1700, 1641, 1455, 1230, 1072, 757 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 5.90–5.96 (m, C*H*═), 5.24–5.27 (m, ═CH_2), 5.11–5.13 (m, ═CH_2), 4.68 (H-29), 4.57 (H-29), 4.10–4.13 (m, OCH_2), 3.87–3.90 (m, OCH_2), 3.23 (m, SeCH_2COCH_3), 2.80 (dd, *J* 4.1, 11.7 Hz, H-3), 2.52 (H-28a), 2.42 (H-28a), 2.40 (H-19), 2.35 (s, SeCH_2COCH_3), 1.92 (H-21), 1.85 (H-28), 1.76 (H-13), 1.71 (H-2), 1.71 (H-16), 1.68 (H-1), 1.68 (s, H-30), 1.64 (H-12), 1.64 (H-22), 1.59 (H-15), 1.50 (H-6), 1.48 (H-18), 1.47 (H-2), 1.42 (H-11), 1.38 (H-6), 1.38 (H-7), 1.35 (H-21), 1.30 (H-28), 1.26 (H-9), 1.24 (H-11), 1.17 (H-16), 1.06 (H-12), 1.05 (s, H-26), 1.01 (H-15), 1.00 (H-22), 0.95 (s, H-23), 0.95 (s, H-27), 0.83 (s, H-25), 0.82 (H-1), 0.78 (s, H-24), 0.67 (H-5). ^{13}C NMR ($CDCl_3$) δ: 203.5 (SeCH_2*C*OCH_3), 150.6 (C-20), 135.9 (*C*H═), 115.9 (═*C*H_2), 109.5 (C-29), 86.3 (C-3), 70.6 (O*C*H_2), 55.8 (C-5), 50.4 (C-9), 49.9 (C-18), 47.2 (C-19), 46.8 (C-17), 42.5 (C-14), 40.4 (C-8), 38.8 (C-4), 38.6 (C-1), 37.1 (C-10), 37.1 (C-13), 35.4 (C-22), 34.2 (C-7), 31.6 (Se*C*H_2COCH_3), 30.7 (C-16), 29.9 (C-21), 28.4 (C-28), 28.1 (C-23), 27.4 (SeCH_2CO*C*H_3), 27.1 (C-15), 24.9 (C-12), 23.1 (C-2), 20.8 (C-11), 20.1 (C-28a), 19.3 (C-30), 18.2 (C-6), 16.3 (C-24), 16.1 (C-25), 16.0 (C-26), 14.8 (C-27). ^{77}Se NMR ($CDCl_3$, 114.4 MHz) δ: 209.8. HR-MS (ESI) calc. for $C_{37}H_{61}O_2Se$ $[M + H]^+$: 616.3759. Found: 616.3758. Anal. Calcd for $C_{37}H_{60}O_2Se$ (615.85): C, 72.16; H, 9.82. Found: C 71.90; H 10.25.

3β-*O*-Allyl-28a-selenocyanato-28a-homolup-20(29)-ene (3). A solution of **1** (984 mg, 1.71 mmol) and KSeCN (1.245 mg, 8.55 mmol) in DMF (15 mL) was stirred under an argon atmosphere at 60 °C for 24 h. Then the solvents were evaporated, and the residue was dissolved in DCM (50 mL) and washed with water (20 mL). An organic layer was evaporated to dryness; column chromatography of the residue (hexane–ethyl acetate, 40 : 1 → 20 : 1) gave selenol **4** (63 mg, 7%) as a side product and selenocyanate **3** as a cream-white solid (872 mg, 87%). M.p. 178–179 °C; $[\alpha]_D^{20}$ 7.9 (*c* 0.2, chloroform); ν_{max} (film): 2943, 2869, 2150 (SeCN), 1641, 1456, 1376, 1070, 883, 756, 548 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 5.90–5.96 (m, C*H*═), 5.24–5.27 (m, ═CH_2), 5.11–5.13 (m, ═CH_2), 4.70 (H-29), 4.60 (H-29), 4.10–4.13 (m, OCH_2), 3.87–3.90 (m, OCH_2), 3.03 (H-28a), 2.88 (H-28a), 2.79 (dd, *J* 4.2, 11.7 Hz, H-3), 2.43 (H-19), 2.12 (H-28), 1.92 (H-21), 1.78 (H-13), 1.72 (H-2), 1.68 (H-1), 1.68 (H-16), 1.68 (s, H-30), 1.65 (H-12), 1.60 (H-22), 1.59 (H-15), 1.59 (H-28), 1.52 (H-18), 1.50 (H-6), 1.48 (H-2), 1.42 (H-11), 1.40 (H-6), 1.40 (H-21), 1.38 (H-7), 1.26 (H-9), 1.26 (H-16), 1.24 (H-11), 1.08 (H-22), 1.07 (s, H-26), 1.06 (H-12), 1.05 (H-15), 0.96 (s, H-27), 0.95 (s, H-23), 0.84 (s, H-25), 0.82 (H-1), 0.78 (s, H-24), 0.67 (H-5). ^{13}C NMR ($CDCl_3$) δ: 150.0 (C-20), 135.9 (*C*H═), 115.9 (═*C*H_2), 109.9 (C-29), 101.5 (Se*C*N), 86.3 (C-3), 70.6 (O*C*H_2), 55.8 (C-5), 50.4 (C-9), 50.0 (C-18), 47.1 (C-17), 47.0 (C-19), 42.5 (C-14), 40.9 (C-8), 38.8 (C-4), 38.6 (C-1), 37.1 (C-10), 37.1 (C-13), 35.2 (C-22), 34.2 (C-7), 30.6 (C-16), 29.7 (C-21), 30.1 (C-28), 28.1 (C-23), 27.1 (C-15), 25.5 (C-28a), 25.1 (C-12), 23.1 (C-2), 20.8 (C-11), 19.3 (C-30), 18.2 (C-6), 16.3 (C-24), 16.1 (C-25), 16.0 (C-26), 14.8 (C-27). ^{77}Se NMR ($CDCl_3$, 114.4 MHz) δ: 232.1. HR-MS (ESI) calc. for $C_{35}H_{56}NOSe$ $[M + H]^+$: 585.3449. Found: 585.3450. Anal. Calcd for $C_{35}H_{55}NOSe$ (584.79): C, 71.89; H, 9.48; N, 2.40. Found: C, 71.80; H, 9.45; N, 2.39.

3β-*O*-Allyl-28a-homolup-20(29)-en-28a-selenol (4). To a suspension of $LiAlH_4$ (115 mg, 3.00 mmol) in THF (2 mL) cooled in an ice bath, a solution of selenocyanate **3** (341 mg, 0.58 mmol) in THF (5 mL) was added dropwise and left to warm to room temp. Then the reaction was quenched by the addition of ethyl acetate (2 mL) and saturated NH_4Cl (0.5 mL). After 15 min an additional portion of ethyl acetate (10 mL) was added and the solvents were removed by evaporation. Column chromatography of the residue (hexane–ethyl acetate, 40 : 1) afforded 302 mg (93%) of the title compound as a light yellow powder. M.p. 210–213 °C; $[\alpha]_D^{20}$ 41.6 (*c* 0.2, chloroform); ν_{max} (film): 3072, 2943, 2868, 1642, 1456, 1376, 1216, 1135, 1106, 1086, 1071, 920, 883, 758 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 5.90–5.96 (m, C*H*═), 5.24–5.27 (m, ═CH_2), 5.11–5.13 (m, ═CH_2), 4.68 (H-29), 4.58 (H-29), 4.10–4.13 (m, OCH_2), 3.87–3.90 (m, OCH_2), 2.88 (H-28a), 2.79 (dd, *J* 4.1, 11.7 Hz, H-3), 2.72 (H-28a), 2.42 (H-19), 2.00 (H-28), 1.92 (H-21), 1.81 (H-13), 1.71 (H-2), 1.70 (H-16), 1.69 (s, H-30), 1.68 (H-1), 1.64 (H-15), 1.64 (H-22), 1.60 (H-28), 1.51 (H-6), 1.49 (H-18), 1.47 (H-2), 1.39 (H-6), 1.36 (H-21), 1.35 (H-7), 1.26 (H-9), 1.21 (H-16), 1.08 (s, H-26), 1.03 (H-22), 1.01 (H-15), 0.97 (s, H-27), 0.96 (s, H-23), 0.85 (s, H-25), 0.83 (H-1), 0.79 (s, H-24), 0.68 (H-5). ^{13}C NMR ($CDCl_3$) δ: 150.6 (C-20), 109.6 (C-29), 86.3 (C-3), 55.8 (C-5), 50.5 (C-9), 49.9 (C-18), 47.3 (C-19), 46.8 (C-17), 42.5 (C-14), 41.0 (C-8), 38.8 (C-4), 38.6 (C-1), 37.2 (C-13), 37.1 (C-10), 35.6 (C-22), 34.3 (C-7), 30.7 (C-16), 30.2 (C-28), 30.0 (C-21), 28.1 (C-23), 27.2 (C-15), 25.2 (C-11 or 12), 24.9 (C-28a), 23.1 (C-2), 21.0 (C-11 or 12), 19.3 (C-30), 18.3 (C-6), 16.3 (C-24), 16.2 (C-25), 16.2 (C-26), 14.9 (C-27). ^{77}Se NMR ($CDCl_3$, 114.4 MHz) δ: 325.6. HR-MS (ESI) calc. for $C_{34}H_{56}OSe$ $[M]^+$: 560.3496. Found: 560.3511. Anal. Calcd for $C_{34}H_{56}OSe$ (559.78): C, 72.95; H, 10.08. Found: C, 73.50; H, 10.48.

28a-Selenocyanato-28a-homolup-20(29)-en-3β-ol (5). To a solution of selenocyanate **3** (77 mg, 0.13 mmol) in a mixture of methanol (1 mL) and DCM (0.5 mL) $PdCl_2$ (10 mg) was added and stirred at room temperature for 24 h until no more starting material was detected by TLC. The solvents were evaporated under diminished pressure. Column chromatography of the residue (hexane–ethyl acetate, 20 : 1 → 7 : 3) gave the title compound as a white solid (49 mg, 69%). M.p. 232–236 °C; $[\alpha]_D^{20}$ −3.2 (*c* 0.1, chloroform). ν_{max} (film): 2943, 2870, 2148 (SeCN), 1455, 1377, 1043, 1033, 882, 757, 547, 521 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 4.71 (H-29), 4.60 (H-29), 3.18 (dd, *J* 4.8, 11.5 Hz, H-3), 3.04 (H-28a), 2.88 (H-28a), 2.43 (H-19), 2.14 (H-28), 1.92 (H-21), 1.79 (H-13), 1.68 (H-16), 1.68 (s, H-30), 1.67 (H-1), 1.66 (H-12), 1.60 (H-2), 1.60 (H-15), 1.60 (H-22), 1.60 (H-28), 1.56 (H-2), 1.52 (H-6), 1.52 (H-18), 1.43 (H-11), 1.41 (H-6), 1.40 (H-21), 1.39 (H-7), 1.27 (H-9), 1.26 (H-16), 1.24 (H-11), 1.08 (H-22), 1.07 (H-12), 1.07 (s, H-26), 1.06 (H-15), 0.97 (s, H-27), 0.96 (s, H-23), 0.90 (H-1), 0.83 (s, H-25), 0.76 (s, H-24), 0.68 (H-5). ^{13}C NMR ($CDCl_3$) δ: 150.0 (C-20), 109.9 (C-29), 101.5 (Se*C*N), 79.0 (C-3), 55.3 (C-5), 50.4 (C-9), 50.0 (C-18), 47.2 (C-17), 47.1 (C-19), 42.5 (C-14), 40.9 (C-8), 38.8 (C-4), 38.7 (C-1), 37.2 (C-10), 37.1 (C-13), 35.3 (C-22), 34.2 (C-7), 30.6 (C-16), 30.1

(C-28), 29.7 (C-21), 27.9 (C-23), 27.2 (C-15), 25.5 (C-28a), 25.1 (C-12), 27.4 (C-2), 20.8 (C-11), 19.3 (C-30), 18.3 (C-6), 16.1 (C-25), 16.0 (C-26), 15.3 (C-24), 14.9 (C-27). ^{77}Se NMR ($CDCl_3$, 114.4 MHz) δ: 232.4. HR-MS (ESI) calc. for $C_{32}H_{51}NNaOSe$ $[M + Na]^+$: 568.3034. Found: 568.3029.

General procedure for glycosylation

A solution of glycosyl donor (**6–9**, 1.00 mmol) and selenol **4** (280 mg, 0.5 mmol) in DCM (10 mL) was stirred for 20 min at room temperature over molecular sieves (4 Å, 400 mg, finely ground), then cooled to −40 °C and TMSOTf (76 μL, 0.42 mmol) was added. After 60 min the reaction was quenched with Et_3N (1 mL), and the solvents were removed under diminished pressure. Column chromatography (hexane–ethyl acetate, 40 : 1 → 5 : 1) of the residue gave the protected saponins as white foams.

3β-*O*-Allyl-28a-Se-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-28a-seleno-28a-homolup-20(29)-ene (10). Recovered starting selenol **4** (112 mg, 40%) and the title compound (171 mg, 30%) were obtained. Data for **10**: $[\alpha]_D^{20}$ 59.7 (*c* 0.25, chloroform); ν_{max} (film): 2944, 2869, 1730, 1602, 1452, 1282, 1264, 1105, 1094, 757, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 6.24 (t, *J* 9.8 Hz, H-4′), 5.90–5.96 (m, C*H*═), 5.95 (br s, H-1′), 5.89 (H-3′), 5.87 (d, *J* 3.3 Hz, H-2′), 5.24–5.27 (m, ═CH_2), 5.11–5.13 (m, ═CH_2), 4.76 (H-5′), 4.68 (H-29), 4.64 (dd, *J* 2.5, 12.3 Hz, H-6′), 4.56 (H-29), 4.48 (dd, *J* 3.8, 12.3 Hz, H-6′), 4.10–4.13 (m, OCH_2), 3.87–3.90 (m, OCH_2), 2.73 (H-3), 2.72 (H-28a), 2.53 (H-28a), 2.41 (H-19), 1.99 (H-28), 1.90 (H-21), 1.74 (H-13), 1.66 (H-2), 1.66 (H-16), 1.65 (s, H-30), 1.61 (H-22), 1.59 (H-1), 1.59 (H-12), 1.54 (H-15), 1.43 (H-18), 1.41 (H-28), 1.40 (H-2), 1.34 (H-21), 1.33 (H-11), 1.20 (H-7), 1.18 (H-6), 1.14 (H-7), 1.14 (H-9), 1.11 (H-11), 1.11 (H-16), 1.00 (H-12), 0.99 (H-22), 0.90 (H-6), 0.90 (H-15), 0.88 (s, H-27), 0.87 (s, H-23), 0.82 (s, H-26), 0.73 (H-1), 0.67 (s, H-24), 0.55 (s, H-25), 0.53 (H-5). ^{13}C NMR ($CDCl_3$) δ: 150.4 (C-20), 135.9 (*C*H═), 115.9 (═*C*H_2), 109.6 (C-29), 86.2 (C-3), 76.3 (C-1′), 72.6 (C-3′), 71.1 (C-2′), 70.6 (C-5′), 70.6 (O*C*H_2), 66.8 (C-4′), 62.3 (C-6′), 55.7 (C-5), 50.3 (C-9), 50.0 (C-18), 47.2 (C-19), 46.7 (C-17), 42.3 (C-14), 40.9 (C-8), 38.8 (C-4), 38.5 (C-1), 37.1 (C-13), 37.0 (C-10), 35.3 (C-22), 34.0 (C-7), 30.7 (C-16), 29.9 (C-21), 28.3 (C-28), 28.0 (C-23), 27.0 (C-15), 25.0 (C-12), 23.1 (C-2), 20.8 (C-11), 19.5 (C-28a), 19.3 (C-30), 18.0 (C-6), 16.2 (C-24), 15.9 (C-25), 15.6 (C-26), 14.8 (C-27). ^{77}Se NMR ($CDCl_3$, 114.4 MHz) δ: 227.8. HR-MS (ESI) calc. for $C_{68}H_{82}NaO_{10}Se$ $[M + Na]^+$: 1161.4971. Found: 1161.4980. Anal. Calcd for $C_{68}H_{82}O_{10}Se \times H_2O$ (1156.38): C, 70.63; H, 7.32. Found: C, 70.58; H, 7.17.

3β-*O*-Allyl-28a-Se-(2,3,4-tri-*O*-benzoyl-β-L-arabinopyranosyl)-28a-seleno-28a-homolup-20(29)-ene (11) and 3β-*O*-allyl-28a-Se-(2,3,4-tri-*O*-benzoyl-α-L-arabinopyranosyl)-28a-seleno-28a-homolup-20(29)-ene (12). Recovered starting selenol **4** (36 mg, 13%), **11** (44 mg, 9%) and **12** (212 mg, 42%) were obtained.

*Data for **11**.* $[\alpha]_D^{20}$ 125.8 (*c* 0.3, chloroform); ν_{max} (film): 2943, 2868, 1729, 1603, 1451, 1281, 1262, 1108, 1086, 1069, 757, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 6.23 (d, *J* 5.3 Hz, H-1′), 5.90–5.96 (m, C*H*═), 5.86 (dd, *J* 5.3, 10.0 Hz, H-2′), 5.77 (dd, *J* 3.5, 10.0 Hz, H-3′), 5.75 (H-4′), 5.24–5.27 (m, ═CH_2), 5.11–5.13 (m, ═CH_2), 4.66 (H-29), 4.56 (H-29), 4.52 (dd, *J* 1.0, 13.1 Hz, H-5′), 4.04 (dd, *J* 2.3, 13.1 Hz, H-5′), 4.10–4.13 (m, OCH_2), 3.87–3.90 (m, OCH_2), 2.78 (dd, *J* 4.1, 11.7 Hz, H-3), 2.58 (H-28a), 2.45, (H-28a), 2.35 (H-19), 1.92 (H-13), 1.88 (H-28), 1.71 (H-2), 1.68 (H-1), 1.68 (H-16), 1.66 (s, H-30), 1.63 (H-22), 1.60 (H-11), 1.60 (H-12), 1.52 (H-15), 1.48 (H-2), 1.48 (H-6), 1.44 (H-18), 1.36 (H-6), 1.35 (H-7), 1.34 (H-28), 1.32 (H-21), 1.26 (H-21), 1.29 (H-11), 1.24 (H-9), 1.15 (H-16), 1.02 (H-12), 0.99 (s, H-26), 0.98 (H-22), 0.96 (H-15), 0.95 (s, H-23), 0.93 (s, H-27), 0.83 (s, H-25), 0.81 (H-1), 0.78 (s, H-24), 0.66 (H-5). ^{13}C NMR ($CDCl_3$) δ: 150.5 (C-20), 109.5 (C-29), 86.3 (C-3), 79.8 (C-1′, $^1J_{C1,H1}$ 170.4 Hz), 69.6 (C-4′), 69.5 (C-2′), 69.3 (C-3′), 62.5 (C-5′), 55.8 (C-5), 50.4 (C-9), 49.9 (C-18), 47.2 (C-19), 46.8 (C-17), 42.4 (C-14), 40.8 (C-8), 38.8 (C-4), 38.6 (C-1), 37.0 (C-10), 37.0 (C-13), 35.3 (C-22), 34.2 (C-7), 30.6 (C-16), 29.9 (C-21), 28.9 (C-28), 28.0 (C-23), 27.1 (C-15), 25.1 (C-12), 23.1 (C-2), 20.8 (C-11), 19.3 (C-30), 18.5 (C-28a), 18.2 (C-6), 16.2 (C-24), 16.1 (C-25), 15.9 (C-26), 14.8 (C-27). ^{77}Se NMR ($CDCl_3$, 114.4 MHz) δ: 191.5. HR-MS (ESI) calc. for $C_{60}H_{76}NaO_8Se$ $[M + Na]^+$: 1027.4603. Found: 1027.4601.

*Data for **12**.* $[\alpha]_D^{20}$ 45.6 (*c* 0.2, chloroform); ν_{max} (film): 2943, 2868, 1729, 1602, 1452, 1261, 1108, 1092, 1069, 757, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 5.90–5.96 (m, C*H*═), 5.81 (t, *J* 6.4 Hz, H-2′), 5.75 (H-4′), 5.71 (dd, *J* 6.9, 3.3 Hz, H-3′), 5.29 (H-1′), 5.24–5.27 (m, ═CH_2), 5.11–5.13 (m, ═CH_2), 4.69 (H-29), 4.57 (H-29), 4.46 (dd, *J* 6.1, 12.2 Hz, H-5′), 4.10–4.13 (m, OCH_2), 3.95 (dd, *J* 2.9, 12.2 Hz, H-5′), 3.87–3.90 (m, OCH_2), 2.79 (dd, *J* 4.2, 11.7 Hz, H-3), 2.71 (H-28a), 2.42 (H-19), 1.92 (H-28), 1.86 (H-21), 1.76 (H-16), 1.74 (H-13), 1.70 (H-2), 1.67 (H-1), 1.67 (s, H-30), 1.64 (H-22), 1.62 (H-12), 1.57 (H-15), 1.48 (H-6), 1.46 (H-2), 1.46 (H-18), 1.40 (H-11), 1.39 (H-28), 1.35 (H-7), 1.33 (H-6), 1.30 (H-21), 1.24 (H-9), 1.19 (H-11), 1.18 (H-16), 1.04 (H-12), 1.00 (H-15), 0.98 (H-22), 0.96 (s, H-26), 0.95 (s, H-23), 0.94 (s, H-27), 0.81 (H-1), 0.80 (s, H-25), 0.77 (s, H-24), 0.66 (H-5). ^{13}C NMR ($CDCl_3$) δ: 150.6 (C-20), 109.5 (C-29), 86.3 (C-3), 78.9 (C-1′, $^1J_{C1,H1}$ 158.0 Hz), 70.9 (C-2′), 69.9 (C-3′), 68.1 (C-4′), 64.3 (C-5′), 55.8 (C-5), 50.4 (C-9), 49.9 (C-18), 47.2 (C-19), 46.9 (C-17), 42.5 (C-14), 40.9 (C-8), 38.8 (C-4), 38.6 (C-1), 37.1 (C-10), 37.0 (C-13), 35.3 (C-22), 34.2 (C-7), 30.7 (C-16), 29.9 (C-21), 29.2 (C-28), 28.1 (C-23), 27.2 (C-15), 25.1 (C-12), 23.1 (C-2), 20.9 (C-11), 20.5 (C-28a), 19.3 (C-30), 18.2 (C-6), 16.3 (C-24), 16.1 (C-25), 16.0 (C-26), 14.8 (C-27). ^{77}Se NMR ($CDCl_3$, 114.4 MHz) δ: approx. 292. HR-MS (ESI) calc. for $C_{60}H_{76}NaO_8Se$ $[M + Na]^+$: 1027.4603. Found: 1027.4592.

3β-*O*-Allyl-28a-Se-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-28a-seleno-28a-homolup-20(29)-ene (13) and 3β-*O*-allyl-28a-Se-(2,3,4-tri-*O*-benzoyl-β-L-rhamnopyranosyl)-28a-seleno-28a-homolup-20(29)-ene (14). Recovered starting selenol **4** (84 mg, 30%), **13** (132 mg, 26%) and **14** (31 mg, 6%) were obtained.

*Data for **13**.* $[\alpha]_D^{20}$ 12.4 (*c* 0.2, chloroform); ν_{max} (film): 2943, 2869, 1731, 1602, 1452, 1280, 1262, 1104, 1094, 1069, 757, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 5.90–5.96 (m, C*H*═), 5.85 (H-2′), 5.83 (H-3′), 5.76 (br s, H-1′), 5.73 (t, *J* 9.7 Hz, H-4′), 5.24–5.27 (m, ═CH_2), 5.11–5.13 (m, ═CH_2), 4.71 (H-29), 4.58 (H-29), 4.42 (dq, *J* 6.2, 9.7 Hz, H-5′), 4.10–4.13 (m, OCH_2), 3.87–3.90 (m, OCH_2), 2.79 (dd, *J* 4.0, 11.7 Hz, H-3), 2.69 (H-28a), 2.46 (H-19),

2.00 (H-28), 1.92 (H-21), 1.79 (H-13), 1.76 (H-16), 1.72 (H-2), 1.68 (H-1), 1.68 (s, H-30), 1.66 (H-22), 1.65 (H-12), 1.59 (H-15), 1.48 (H-18), 1.47 (H-2), 1.47 (H-28), 1.46 (H-6), 1.43 (H-11), 1.39 (d, *J* 6.2 Hz, H-6′), 1.36 (H-21), 1.35 (H-7), 1.32 (H-6), 1.26 (H-9), 1.24 (H-11), 1.20 (H-16), 1.05 (H-12), 1.02 (H-15), 1.02 (H-22), 1.02 (s, H-26), 0.96 (s, H-27), 0.95 (s, H-23), 0.82 (H-1), 0.81 (s, H-25), 0.77 (s, H-24), 0.66 (H-5). ^{13}C NMR ($CDCl_3$) δ: 150.6 (C-20), 109.6 (C-29), 86.3 (C-3), 77.8 (C-1′, $^1J_{C1,H1}$ 171.0 Hz), 73.4 (C-2′), 70.6 (C-3′), 71.8 (C-4′), 69.5 (C-5′), 55.8 (C-5), 50.4 (C-9), 49.9 (C-18), 47.1 (C-19), 46.9 (C-17), 42.5 (C-14), 40.9 (C-8), 38.8 (C-4), 38.6 (C-1), 37.1 (C-10), 37.1 (C-13), 35.3 (C-22), 34.2 (C-7), 30.7 (C-16), 29.9 (C-21), 29.2 (C-28), 28.0 (C-23), 27.2 (C-15), 25.1 (C-12), 23.1 (C-2), 20.9 (C-11), 20.6 (C-28a), 19.3 (C-30), 18.2 (C-6), 17.6 (C-6′), 16.3 (C-24), 16.1 (C-25), 16.2 (C-26), 14.8 (C-27). ^{77}Se NMR ($CDCl_3$, 114.4 MHz) δ: 243.6. HR-MS (ESI) calc. for $C_{61}H_{78}NaO_8Se$ $[M + Na]^+$: 1041.4760. Found: 1041.4764.

Data for ***14****.* $[\alpha]_D^{20}$ 95.8 (*c* 0.3, chloroform); ν_{max} (film): 2941, 2868, 1730, 1602, 1452, 1280, 1261, 1120, 1092, 1069, 757, 711 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 6.03 (d, *J* 3.0 Hz, H-2′), 5.90–5.96 (m, C*H*═), 5.63 (dd, *J* 9.4, 10.1 Hz, H-4′), 5.60 (dd, *J* 3.4, 10.1 Hz, H-3′), 5.30 (s, H-1′), 5.24–5.27 (m, ═CH_2), 5.11–5.13 (m, ═CH_2), 4.68 (H-29), 4.57 (H-29), 4.10–4.13 (m, OCH_2), 3.87–3.90 (m, OCH_2), 3.87 (H-5′), 2.79 (H-3), 2.77 (H-28a), 2.66 (H-28a), 2.43 (H-19), 1.86 (H-21), 1.78 (H-13), 1.72 (H-2), 1.72 (H-16), 1.68 (H-1), 1.68 (s, H-30), 1.64 (H-22), 1.55 (H-15), 1.55 (H-28), 1.51 (H-6), 1.48 (H-2), 1.48 (H-18), 1.46 (d, *J* 6.1 Hz, H-6′), 1.45 (H-28), 1.43 (H-11), 1.39 (H-6), 1.38 (H-7), 1.36 (H-21), 1.27 (H-9), 1.24 (H-11), 1.20 (H-16), 1.05 (H-12), 1.05 (s, H-26), 1.03 (H-22), 1.02 (H-15), 0.96 (s, H-27), 0.95 (s, H-23), 0.85 (s, H-25), 0.82 (H-1), 0.79 (s, H-24), 0.68 (H-5). ^{13}C NMR ($CDCl_3$) δ: 150.4 (C-20), 109.6 (C-29), 86.3 (C-3), 77.0 (C-1′, $^1J_{C1,H1}$ 153.0 Hz), 76.6 (C-5′), 72.5 (C-3′), 72.4 (C-2′), 71.3 (C-4′), 55.8 (C-5), 50.5 (C-9), 49.8 (C-18), 47.2 (C-19), 46.8 (C-17), 42.5 (C-14), 40.9 (C-8), 38.8 (C-4), 38.6 (C-1), 37.1 (C-10), 37.1 (C-13), 35.4 (C-22), 34.3 (C-7), 30.5 (C-16), 29.9 (C-21), 29.0 (C-28), 28.1 (C-23), 27.2 (C-15), 25.0 (C-12), 23.1 (C-2), 20.9 (C-11), 20.3 (C-28a), 19.3 (C-30), 18.2 (C-6), 18.1 (C-6′), 16.3 (C-24), 16.3 (C-26), 16.1 (C-25), 14.8 (C-27). ^{77}Se NMR ($CDCl_3$, 114.4 MHz) δ: 326.6. HR-MS (ESI) calc. for $C_{61}H_{78}NaO_8Se$ $[M + Na]^+$: 1041.4760. Found: 1041.4757.

3β-*O*-Allyl-28a-Se-(2,3,4,6-tetra-*O*-benzoyl-α-D-idopyranosyl)-28a-seleno-28a-homolup-20(29)-ene (15) and 3β-*O*-allyl-28a-Se-(2,3,4,6-tetra-*O*-benzoyl-β-D-idopyranosyl)-28a-seleno-28a-homolup-20(29)-ene (16). Recovered starting selenol **4** (104 mg, 37%), **15** (108 mg, 19%) and **16** (57 mg, 10%) were obtained.

Data for ***15****.* $[\alpha]_D^{20}$ 83.1 (*c* 0.2, chloroform); ν_{max} (film): 2943, 2869, 1726, 1602, 1452, 1265, 1105, 1093, 1067, 1027, 757, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 5.94 (br s, H-1′), 5.90–5.96 (m, C*H*═), 5.66 (br s, H-3′), 5.41 (br s, H-2′), 5.40 (m, H-4′), 5.24–5.27 (m, ═CH_2), 5.25 (m, H-5′), 5.11–5.13 (m, ═CH_2), 4.73 (dd, *J* 7.7, 11.6 Hz, H-6′), 4.68 (H-29), 4.57 (H-29), 4.56 (H-6′), 4.10–4.13 (m, OCH_2), 3.87–3.90 (m, OCH_2), 2.78 (dd, *J* 4.3, 11.7 Hz, H-3), 2.73 (H-28a), 2.52 (H-28a), 2.40 (H-19), 1.86 (H-21), 1.76 (H-13), 1.72 (H-16), 1.70 (H-2), 1.66 (s, H-30), 1.65 (H-12), 1.64 (H-1), 1.64 (H-22), 1.54 (H-15), 1.54 (H-28), 1.45 (H-2), 1.43 (H-11), 1.42 (H-18), 1.41 (H-28), 1.41 (H-6), 1.31 (H-21), 1.28 (H-7), 1.24 (H-11), 1.20 (H-9), 1.20 (H-16), 1.16 (H-6), 1.05 (H-12), 1.02 (H-22), 0.94 (s, H-23), 0.91 (H-15), 0.91 (s, H-27), 0.90 (s, H-26), 0.78 (H-1), 0.75 (s, H-24), 0.66 (s, H-25), 0.62 (H-5). ^{13}C NMR ($CDCl_3$) δ: 150.5 (C-20), 109.6 (C-29), 86.3 (C-3), 77.1 (C-1′, $^1J_{C1,H1}$ 168.0 Hz), 69.7 (C-2′), 66.7 (C-4′), 66.3 (C-3′), 66.3 (C-5′), 63.3 (C-6′), 55.8 (C-5), 50.3 (C-9), 49.9 (C-18), 47.2 (C-19), 46.6 (C-17), 42.3 (C-14), 40.9 (C-8), 38.8 (C-4), 38.5 (C-1), 37.0 (C-10), 37.0 (C-13), 35.3 (C-22), 34.2 (C-7), 30.5 (C-16), 29.9 (C-21), 28.8 (C-28), 28.1 (C-23), 27.1 (C-15), 25.1 (C-12), 23.1 (C-2), 20.9 (C-11), 20.3 (C-28a), 19.3 (C-30), 18.2 (C-6), 16.3 (C-24), 16.0 (C-25), 15.9 (C-26), 14.8 (C-27). ^{77}Se NMR ($CDCl_3$, 114.4 MHz) δ: 265.9. HR-MS (ESI) calc. for $C_{68}H_{82}NaO_{10}Se$ $[M + Na]^+$: 1161.4971. Found: 1161.4962. Anal. Calcd for $C_{68}H_{82}NaO_{10}Se$ (1138.33): C, 71.75; H, 7.26. Found: C, 71.88; H, 7.35.

Data for ***16****.* $[\alpha]_D^{20}$ −9.2 (*c* 0.5, chloroform); ν_{max} (film): 2942, 2868, 1727, 1602, 1452, 1264, 1107, 1093, 1068, 1027, 756, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 5.90–5.96 (m, C*H*═), 5.69 (t, *J* 2.7 Hz, H-3′), 5.54 (d, *J* 1.4 Hz, H-1′), 5.44 (br s, H-4′), 5.40 (br s, H-2′), 5.24–5.27 (m, ═CH_2), 5.11–5.13 (m, ═CH_2), 4.67 (H-6′), 4.65 (H-29), 4.58 (H-29), 4.57 (H-6′), 4.54 (H-5′), 4.10–4.13 (m, OCH_2), 3.87–3.90 (m, OCH_2), 2.78 (H-3), 2.78 (H-28a), 2.40 (H-19), 1.95 (H-28), 1.90 (H-21), 1.74 (H-13), 1.72 (H-16), 1.70 (H-2), 1.67 (s, H-30), 1.65 (H-1), 1.65 (H-12), 1.64 (H-22), 1.54 (H-15), 1.49 (H-6), 1.47 (H-18), 1.45, (H-2), 1.43 (H-11), 1.39 (H-28), 1.38 (H-21), 1.35 (H-6), 1.34 (H-7), 1.24 (H-9), 1.24 (H-11), 1.20 (H-16), 1.05 (H-12), 1.02 (H-22), 1.00 (s, H-26), 0.96 (H-15), 0.95 (s, H-23), 0.94 (s, H-27), 0.80 (H-1), 0.77 (s, H-25), 0.75 (s, H-24), 0.66 (H-5). ^{13}C NMR ($CDCl_3$) δ: 150.3 (C-20), 109.8 (C-29), 86.3 (C-3), 76.6 (C-1′, $^1J_{C1,H1}$ 154.0 Hz), 75.0 (C-5′), 69.7 (C-2′), 67.1 (C-3′), 65.7 (C-4′), 63.2 (C-6′), 55.8 (C-5), 50.4 (C-9), 49.7 (C-18), 47.3 (C-19), 46.9 (C-17), 42.5 (C-14), 40.9 (C-8), 38.8 (C-4), 38.6 (C-1), 37.1 (C-10), 37.1 (C-13), 35.4 (C-22), 34.3 (C-7), 30.6 (C-16), 30.0 (C-21), 28.7 (C-28), 28.1 (C-23), 27.2 (C-15), 25.1 (C-12), 23.1 (C-2), 20.9 (C-11), 19.7 (C-28a), 19.2 (C-30), 18.2 (C-6), 16.3 (C-24), 16.2 (C-26), 16.1 (C-25), 14.8 (C-27). ^{77}Se NMR ($CDCl_3$, 114.4 MHz) δ: 324.1. HR-MS (ESI) calc. for $C_{68}H_{82}NaO_{10}Se$ $[M + Na]^+$: 1161.4971. Found: 1161.5000.

General procedure for the deallylation reaction

A solution of iridium complex was prepared from [Ir(COD)($MePPh_2$)$_2$]PF_6 (3–5 mg) according to the literature procedure[17] and transferred to a solution of the corresponding saponin in THF (3 mL), stirred at room temperature for 12 h, and then concentrated. The crude vinyl ether was dissolved in a chloroform (2.0 mL) and methanol (2.0 mL) mixture, and then *p*-TsOH (70 mg) was added. The mixture was stirred for 1 h and concentrated. Column chromatography (hexane–ethyl acetate, 20 : 1 → 7 : 3) of the residue gave the title compound as foam.

28a-Se-(2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl)-28a-seleno-28a-homolup-20(29)-en-3β-ol (17). Starting from **10** (95 mg, 0.083 mmol) the title compound was obtained (81 mg, 89%). $[\alpha]_D^{20}$ 64.5 (*c* 0.3, chloroform); ν_{max} (film): 2942, 2868, 1729,

1602, 1451, 1281, 1264, 1104, 1094, 1068, 756, 709 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 6.23 (t, *J* 9.8 Hz, H-4′), 5.97 (br s, H-1′), 5.90 (H-2′), 5.88 (H-3′), 4.77 (H-5′), 4.69 (H-29), 4.66 (dd, *J* 2.4, 12.3 Hz, H-6′), 4.57 (H-29), 4.50 (dd, *J* 3.8, 12.3 Hz, H-6′), 3.13 (dd, *J* 4.2, 11.5 Hz, H-3), 2.74 (H-28a), 2.53 (H-28a), 2.42 (H-19), 1.99 (H-28), 1.91 (H-21), 1.75 (H-13), 1.67 (H-16), 1.66 (s, H-30), 1.62 (H-22), 1.61 (H-12), 1.58 (H-1), 1.56 (H-2), 1.55 (H-15), 1.49 (H-2), 1.44 (H-18), 1.42 (H-28), 1.35 (H-21), 1.34 (H-11), 1.23 (H-7), 1.21 (H-6), 1.18 (H-9), 1.16 (H-7), 1.13 (H-11), 1.12 (H-16), 1.01 (H-12), 1.00 (H-22), 0.93 (H-6), 0.91 (H-15), 0.90 (s, H-23), 0.89 (s, H-27), 0.83 (s, H-26), 0.82 (H-1), 0.66 (s, H-24), 0.56 (s, H-25), 0.56 (H-5). ^{13}C NMR ($CDCl_3$) δ: 150.4 (C-20), 109.6 (C-29), 78.9 (C-3), 76.3 (C-1′), 72.6 (C-2′), 71.1 (C-3′), 70.7 (C-5′), 66.8 (C-4′), 62.6 (C-6′), 55.2 (C-5), 50.3 (C-9), 50.0 (C-18), 47.2 (C-19), 46.7 (C-17), 42.4 (C-14), 40.8 (C-8), 38.8 (C-4), 38.6 (C-1), 37.1 (C-13), 37.0 (C-10), 35.3 (C-22), 34.0 (C-7), 30.7 (C-16), 29.9 (C-21), 28.3 (C-28), 27.9 (C-23), 27.4 (C-2), 27.1 (C-15), 25.0 (C-12), 20.8 (C-11), 19.6 (C-28a), 19.3 (C-30), 18.1 (C-6), 15.9 (C-25), 15.6 (C-26), 15.3 (C-24), 14.4 (C-27). ^{77}Se NMR ($CDCl_3$, 114.4 MHz) δ: 227.9. HR-MS (ESI) calc. for $C_{65}H_{78}NaO_{10}Se$ $[M + Na]^+$: 1121.4658. Found 1121.4677. Anal. Calcd for $C_{65}H_{78}O_{10}Se \times H_2O$ (1116.32): C, 69.94; H, 7.22. Found: C, 70.05; H, 7.23.

28a-Se-(2,3,4-Tri-*O*-benzoyl-β-L-arabinopyranosyl)-28a-seleno-28a-homolup-20(29)-en-3β-ol (18). Starting from **11** (85 mg, 0.084 mmol) the title compound was obtained (56 mg, 87%). $[\alpha]_D^{20}$ 160.5 (*c* 0.2, chloroform); ν_{max} (film): 2942, 2867, 1729, 1451, 1280, 1261, 1108, 1087, 1069, 1027, 757, 710 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 6.23 (d, 1 H, *J* 5.2 Hz, H-1′), 5.87 (dd, 1 H, *J* 5.2, 10.0 Hz, H-2′), 5.78 (dd, 1 H, *J* 10.0, 3.4 Hz, H-3′), 5.75 (br s, 1H, H-4′), 4.66 (br s, 1 H, H-29), 4.56 (br s, 1 H, H-29), 4.53 (dd, 1 H, *J* 13.0 Hz, H-5′), 4.04 (dd, 1 H, *J* 2.2, 13.0 Hz, H-5′), 3.18 (dd, 1 H, *J* 4.9, 11.3 Hz, H-3), 2.56–2.60 (m, 1 H), 2.43–2.48 (m, 1 H), 2.31–2.38 (m, 1 H), 1.82–1.92 (m, 2 H), 1.66 (s, 3 H), 1.00 (s, 3 H), 0.96 (s, 3 H), 0.94 (s, 3 H), 0.82 (s, 3 H), 0.76 (s, 3 H), 0.79–1.75 (m, 24 H), 0.66–0.68 (m, 1 H, H-5). ^{13}C NMR ($CDCl_3$) δ: 150.5 (C-20), 109.6 (C-29), 79.8, 79.0, 69.6, 69.5, 69.3, 62.5 (C-5′), 55.3 (C-5), 50.5, 49.9, 47.2, 46.8 (C), 42.5 (C), 40.8 (C), 38.9 (C), 38.7 (CH_2), 37.2 (C), 37.0, 35.3 (CH_2), 34.2 (CH_2), 30.6 (CH_2), 29.9 (CH_2), 29.0 (CH_2), 28.0, 27.4 (CH_2), 27.2 (CH_2), 25.1 (CH_2), 20.9 (CH_2), 19.3, 18.5 (CH_2), 18.3 (CH_2), 16.1, 16.0, 15.4, 14.8. HR-MS (ESI) calc. for $C_{57}H_{72}NaO_8Se$ $[M + Na]^+$: 987.4290. Found: 987.4283.

28a-Se-(2,3,4-Tri-*O*-benzoyl-α-L-arabinopyranosyl)-28a-seleno-28a-homolup-20(29)-en-3β-ol (19). Starting from **12** (110 mg, 0.109 mmol) the title compound was obtained (66 mg, 63%). $[\alpha]_D^{20}$ 37.5 (*c* 0.2, chloroform); ν_{max} (film): 2942, 2868, 1728, 1451, 1278, 1261, 1108, 1092, 1069, 1026, 756, 709 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 5.81 (m, 1 H, H-2′), 5.74–5.76 (m, 1 H, H-4′), 5.71 (dd, 1 H, *J* 6.9, 3.2 Hz, H-3′), 5.29 (d, 1 H, *J* 4.4 Hz, H-1′), 4.69 (br s, 1 H, H-29), 4.57 (br s, 1 H, H-29), 4.46 (dd, 1 H, *J* 12.2, 6.1 Hz, H-5′), 3.95 (dd, 1 H, *J* 3.0, 12.2 Hz, H-5′), 3.17 (dd, 1 H, *J* 4.8, 11.4 Hz, H-3), 2.69–2.73 (m, 2 H), 2.39–2.45 (m, 1 H), 1.81–1.96 (m, 2 H), 1.72–1.78 (m, 2 H), 1.66 (s, 3 H), 0.97 (s, 3 H), 0.96 (s, 3 H), 0.95 (s, 3 H), 0.79 (s, 3 H), 0.75 (s, 3 H), 0.74–1.70 (m, 22 H), 0.66–0.68 (m, 1 H, C-5). ^{13}C NMR ($CDCl_3$) δ: 150.5 (C-20), 109.6 (C-29), 79.0, 78.9, 70.9, 69.9, 68.1, 60.4 (C-5′), 55.3 (C-5), 50.4, 49.9, 47.2, 46.9 (C), 42.5 (C), 40.8 (C), 38.8 (C), 38.7 (CH_2), 37.1 (C), 37.0, 35.3 (CH_2), 34.2 (CH_2), 30.7 (CH_2), 29.9 (CH_2), 29.3 (CH_2), 28.0, 27.4 (CH_2), 27.2 (CH_2), 25.1 (CH_2), 21.0 (CH_2), 20.9 (CH_2), 18.3 (CH_2), 16.1, 16.0, 15.4, 14.9. HR-MS (ESI) calc. for $C_{57}H_{72}NaO_8Se$ $[M + Na]^+$: 987.4290. Found: 987.4295.

28a-Se-(2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl)-28a-seleno-28a-homolup-20(29)-en-3β-ol (20). Starting from **13** (77 mg, 0.075 mmol) the title compound was obtained (58 mg, 78%). $[\alpha]_D^{20}$ 1.8 (*c* 0.2, chloroform); ν_{max} (film): 2942, 2869, 1730, 1602, 1452, 1281, 1262, 1094, 1069, 757, 710 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 5.82–5.86 (m, 2 H, H-2′, H-3′), 5.77 (d, 1 H, *J* 0.7 Hz, H-1′), 5.73 (t, 1 H, *J* 9.8 Hz, H-4′), 4.71–4.72 (m, 1 H, H-29), 4.58 (br s, 1 H, H-29), 4.43 (dq, 1 H, *J* 6.2, 9.8, Hz, H-5′), 3.18 (dd, 1 H, *J* 4.8, 11.3 Hz, H-3), 2.68–2.71 (m, 2 H), 2.43–2.49 (m, 1 H), 1.88–2.00 (m, 2 H), 1.75–1.83 (m, 2 H), 1.68 (s, 3 H), 1.40 (d, 3 H, *J* 6.2 Hz, H-6′), 1.03 (s, 3 H), 0.96 (s, 3 H), 0.96 (s, 3 H), 0.80 (s, 3 H), 0.75 (s, 3 H), 0.83–1.66 (m, 22 H), 0.66–0.68 (m, 1 H, H-5). ^{13}C NMR ($CDCl_3$) δ: 150.5 (C-20), 109.6 (C-29), 78.9, 77.9, 73.4, 71.8, 70.7, 69.6, 55.3, 50.4, 49.9, 47.2, 46.9 (C), 42.5 (C), 40.9 (C), 38.8 (C), 38.7 (CH_2), 37.1 (C), 37.1, 35.3 (CH_2), 34.2 (CH_2), 30.7 (CH_2), 29.9 (CH_2), 29.2 (CH_2), 28.0, 27.4 (CH_2), 27.3 (CH_2), 25.1 (CH_2), 20.9 (CH_2), 20.7 (CH_2), 19.3, 18.3 (CH_2), 17.7, 16.2, 16.1, 15.3, 14.9. HR-MS (ESI) calc. for $C_{58}H_{74}NaO_8Se$ $[M + Na]^+$: 1001.4447. Found: 1001.4434.

28a-Se-(2,3,4,6-Tetra-*O*-benzoyl-α-D-idopyranosyl)-28a-seleno-28a-homolup-20(29)-en-3β-ol (21). Starting from **15** (102 mg, 0.089 mmol) the title compound was obtained (91 mg, 93%). $[\alpha]_D^{20}$ 74.4 (*c* 0.2, chloroform); ν_{max} (film): 2942, 2868, 1725, 1451, 1264, 1093, 1067, 1027, 756, 710 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 5.94 (br s, 1 H), 5.66 (br s, 1 H), 5.40–5.41 (m, 2 H), 5.24–5.26 (m, 1 H, H-5′), 4.73 (dd, 1 H, *J*7.6, 11.6 Hz, H-5′), 4.68 (br s, 1 H, H-29), 4.54–4.57 (m, 2 H, H-5′, H-29), 3.16 (dd, 1 H, *J* 4.6, 11.4 Hz, H-3), 2.70–2.76 (m, 1 H), 2.50–2.55 (m, 1 H), 2.37–2.43 (m, 1 H), 1.93–1.99 (m, 1 H), 1.82–1.90 (m, 1 H), 1.73–1.78 (m, 1 H), 1.66 (s, 3 H), 0.95 (s, 3 H), 0.91 (s, 3 H), 0.90 (s, 3 H), 0.73 (s, 3 H), 0.65 (s, 3 H), 0.75–1.68 (m, 23 H), 0.61–0.63 (m, 1 H, C-5). ^{13}C NMR ($CDCl_3$) δ: 150.5 (C-20), 109.6 (C-29), 78.9 (C-3), 77.1 (C-1′), 69.8, 66.7, 66.3, 66.3, 63.2 (C-6′), 55.2 (C-5), 50.4, 49.9, 47.2, 46.6 (C), 42.4 (C), 40.8 (C), 38.8 (C), 38.6 (CH_2), 37.1 (C), 37.0, 35.3 (CH_2), 34.1 (CH_2), 30.5 (CH_2), 29.9 (CH_2), 28.8 (CH_2), 28.0, 27.4 (CH_2), 27.2 (CH_2), 25.0 (CH_2), 20.9 (CH_2), 20.3 (CH_2), 19.3, 18.2 (CH_2), 16.0, 15.9, 15.3, 14.8. HR-MS (ESI) calc. for $C_{65}H_{78}NaO_{10}Se$ $[M + Na]^+$: 1121.4658. Found: 1121.4679. Anal. Calcd for $C_{65}H_{78}O_{10}Se$ (1098.30): C, 71.08; H, 7.16. Found: C, 71.45; H, 7.56.

General procedure for the debenzoylation reaction

A suspension of the protected saponin (0.10 mmol) and K_2CO_3 (20 mg) in MeOH (10 mL) was stirred for 2 h, then neutralized with Amberlyst 15 resin (H^+ form) and purified by column chromatography (hexane–ethyl acetate, 5 : 1 → 1 : 1, and then hexane–ethyl acetate–methanol, 5 : 3 : 1) to afford the unprotected saponin.

28a-Se-α-D-Mannopyranosyl-28a-seleno-28a-homolup-20(29)-en-3β-ol (22). Yield 78% (53 mg); m.p. 222–224 °C. $[\alpha]_D^{20}$ 100.8 (*c* 0.2, chloroform–methanol, 1 : 1); ν_{max} (film): 2941, 2868,

1640, 1454, 1377, 1104, 1066, 1032, 880, 795, 719 cm^{-1}. ^1H NMR ($CDCl_3/CD_3OD$, 1 : 1) δ: 5.63 (s, H-1′), 4.68 (H-29), 4.57 (H-29), 4.08 (d, *J* 2.2 Hz, H-2′), 3.91 (H-6′), 3.87 (H-5′), 3.85 (H-4′), 3.79 (H-6′), 3.78 (H-3′), 3.18 (H-3), 2.63 (H-28a), 2.52 (H-28a), 2.41 (H-19), 1.91 (H-28), 1.90 (H-21), 1.78 (H-13), 1.74 (H-16), 1.69 (s, H-30), 1.68 (H-1), 1.67 (H-22), 1.66 (H-12), 1.59 (H-2), 1.57 (H-15), 1.54 (H-6), 1.49 (H-18), 1.44 (H-11), 1.40 (H-6), 1.40 (H-7), 1.39 (H-28), 1.37 (H-21), 1.29 (H-9), 1.25 (H-11), 1.21 (H-16), 1.07 (H-12), 1.06 (s, H-26), 1.03 (H-22), 1.02 (H-15), 0.98 (s, H-27), 0.97 (s, H-23), 0.92 (H-1), 0.85 (s, H-25), 0.77 (s, H-24), 0.70 (H-5). ^{13}C NMR ($CDCl_3/CD_3OD$, 1 : 1) δ: 150.4 (C-20), 109.3 (C-29), 81.2 (C-1′), 78.6 (C-3), 74.1 (C-5′), 72.7 (C-2′), 72.1 (C-3′), 66.8 (C-4′), 61.1 (C-6′), 55.1 (C-5), 50.3 (C-9), 49.7 (C-18), 47.1 (C-19), 46.6 (C-17), 42.3 (C-14), 40.7 (C-8), 38.6 (C-4), 38.5 (C-1), 36.9 (C-10), 36.9 (C-13), 35.1 (C-22), 34.0 (C-7), 30.4 (C-16), 29.6 (C-21), 28.7 (C-28), 27.6 (C-23), 27.0 (C-15), 26.8 (C-2), 24.8 (C-12), 20.7 (C-11), 19.8 (C-28a), 19.0 (C-30), 18.1 (C-6), 15.8 (C-25), 15.7 (C-26), 15.1 (C-24), 14.6 (C-27). ^{77}Se NMR ($CD_3OD : CDCl_3$, 1 : 1, 114.4 MHz) δ: 226.3. HR-MS (ESI) calc. for $C_{37}H_{62}NaO_6Se$ $[M + Na]^+$: 705.3609. Found: 705.3611.

28a-Se-β-L-Arabinopyranosyl-28a-seleno-28a-homolup-20(29)-en-3β-ol (23). Yield 88% (57 mg); m.p. 238–240 °C. $[\alpha]_D^{20}$ 108.3 (*c* 0.2, chloroform–methanol, 1 : 1); ν_{max} (film): 2940, 2868, 1640, 1459, 1377, 1083, 1031, 971, 880, 850, 792, 619 cm^{-1}. ^1H NMR ($CDCl_3/CD_3OD$, 1 : 1) δ: 5.70 (d, *J* 4.7 Hz, H-1′), 4.68 (H-29), 4.57 (H-29), 4.12 (dd, *J* 1.4, 12.4 Hz, H-5′), 3.98 (dd, *J* 4.7, 9.0 Hz, H-2′), 3.93 (H-4′), 3.73 (dd, *J* 3.0, 12.4 Hz, H-5′), 3.65 (dd, *J* 3.2, 9.0 Hz, H-3′), 3.17 (dd, *J* 7.7, 8.5 Hz, H-3), 2.57 (H-28a), 2.45 (H-28a), 2.41 (H-19), 1.93 (H-16), 1.91 (H-28), 1.89 (H-21), 1.77 (H-13), 1.68 (s, H-30), 1.67 (H-1), 1.64 (H-12), 1.58 (H-2), 1.56 (H-15), 1.56 (H-22), 1.52 (H-6), 1.48 (H-18), 1.43 (H-11), 1.40 (H-6), 1.38 (H-7), 1.38 (H-28), 1.34 (H-21), 1.28 (H-9), 1.23 (H-11), 1.18 (H-16), 1.08 (H-22), 1.06 (H-12), 1.06 (s, H-26), 0.99 (H-15), 0.96 (s, H-23), 0.96 (s, H-27), 0.90 (H-1), 0.83 (s, H-25), 0.75 (s, H-24), 0.68 (H-5). ^{13}C NMR ($CDCl_3/CD_3OD$, 1 : 1) δ: 150.4 (C-20), 109.2 (C-29), 83.8 (C-1′, $^1J_{C1,H1}$ 165.3 Hz), 78.5 (C-3), 71.1 (C-3′), 69.3 (C-2′), 68.0 (C-4′), 64.7 (C-5′), 55.1 (C-5), 50.2 (C-9), 49.6 (C-18), 47.0 (C-19), 46.6 (C-17), 42.2 (C-14), 42.2 (C-8), 38.5 (C-4), 38.5 (C-1), 36.8 (C-10), 36.8 (C-13), 35.1 (C-22), 33.9 (C-7), 30.3 (C-16), 29.6 (C-21), 28.8 (C-28), 27.6 (C-23), 26.9 (C-15), 26.7 (C-2), 24.8 (C-12), 20.6 (C-11), 18.9 (C-30), 18.1 (C-28a), 18.0 (C-6), 15.7 (C-25), 15.3 (C-26), 15.0 (C-24), 14.5 (C-27). ^{77}Se NMR ($CD_3OD : CDCl_3$, 1 : 1, 114.4 MHz) δ: 328.6. HR-MS (ESI) calc. for $C_{36}H_{60}NaO_5Se$ $[M + Na]^+$: 675.3504. Found: 675.3500.

28a-Se-α-L-Arabinopyranosyl-28a-seleno-28a-homolup-20(29)-en-3β-ol (24). Yield 61% (40 mg); m.p. 203–204 °C. $[\alpha]_D^{20}$ −14.1 (*c* 0.2, chloroform–methanol, 1 : 1); ν_{max} (film): 2942, 2868, 1453, 1376, 1081, 1043, 992, 883, 860, 798, 757 cm^{-1}. ^1H NMR ($CDCl_3/CD_3OD$, 1 : 1) δ: 4.76 (d, *J* 7.5 Hz, H-1′), 4.69 (H-29), 4.57 (H-29), 4.04 (dd, *J* 4.4, 12.1 Hz, H-5′), 3.95 (H-4′), 3.79 (t, *J* 7.5 Hz, H-2′), 3.61 (dd, *J* 3.3, 7.7 Hz, H-3′), 3.56 (dd, *J* 2.3, 12.1 Hz, H-5′), 3.16 (dd, *J* 5.1, 11.2 Hz, H-3), 2.62 (H-28a), 2.44 (H-19), 1.96 (H-28), 1.90 (H-21), 1.80 (H-13), 1.76 (H-16), 1.69 (s, H-30), 1.68 (H-1), 1.68 (H-22), 1.67 (H-12), 1.63 (H-15), 1.60 (H-2), 1.54 (H-6), 1.50 (H-18), 1.44 (H-11), 1.42 (H-6), 1.41 (H-7), 1.41 (H-28), 1.36 (H-21), 1.32 (H-9), 1.24 (H-11), 1.21 (H-16), 1.08 (H-12), 1.06 (s, H-26), 1.02 (H-15), 1.02 (H-22), 0.98 (s, H-27), 0.96 (s, H-23), 0.93 (H-1), 0.85 (s, H-25), 0.76 (s, H-24), 0.70 (H-5). ^{13}C NMR ($CDCl_3/CD_3OD$, 1 : 1) δ: 149.9 (C-20), 108.7 (C-29), 81.5 (C-1′, $^1J_{C1,H1}$ 156.8 Hz), 77.9 (C-3), 72.4 (C-3′), 71.1 (C-2′), 67.9 (C-5′), 67.2 (C-4′), 54.8 (C-5), 49.9 (C-9), 49.3 (C-18), 46.7 (C-19), 46.2 (C-17), 41.8 (C-14), 41.8 (C-8), 38.1 (C-4), 38.1 (C-1), 36.5 (C-10), 36.5 (C-13), 34.5 (C-22), 33.6 (C-7), 29.9 (C-16), 29.2 (C-21), 28.8 (C-28), 27.0 (C-23), 26.5 (C-15), 26.2 (C-2), 24.5 (C-12), 20.2 (C-11), 18.5 (C-28a), 18.2 (C-30), 17.6 (C-6), 15.3 (C-26), 15.2 (C-25), 14.5 (C-24), 13.9 (C-27). ^{77}Se NMR ($CD_3OD : CDCl_3$, 1 : 1, 114.4 MHz) δ: 287.9. HR-MS (ESI) calc. for $C_{36}H_{60}NaO_5Se$ $[M + Na]^+$: 675.3504. Found: 675.3490.

28a-Se-α-L-Rhamnopyranosyl-28a-seleno-28a-homolup-20(29)-en-3β-ol (25). Yield 78% (52 mg); m.p. 201–202 °C. $[\alpha]_D^{20}$ −94.0 (*c* 0.2, chloroform–methanol, 1 : 1); ν_{max} (film): 2941, 2869, 1640, 1454, 1376, 1102, 1064, 973, 882, 756, 647 cm^{-1}. ^1H NMR ($CDCl_3/CD_3OD$, 1 : 1) δ: 5.55 (d, *J* 1.0 Hz, H-1′), 4.69 (H-29), 4.57 (H-29), 4.07 (dd, *J* 1.0, 3.4 Hz, H-2′), 3.92 (dq, *J* 6.2, 9.4 Hz, H-5′), 3.71 (dd, *J* 3.4, 9.4 Hz, H-3′), 3.46 (t, *J* 9.4 Hz, H-4′), 3.16 (dd, *J* 3.1, 10.2 Hz, H-3), 2.56 (H-28a), 2.42 (H-19), 1.92 (H-28), 1.91 (H-21), 1.78 (H-13), 1.76 (H-16), 1.69 (s, H-30), 1.68 (H-1), 1.68 (H-22), 1.66 (H-12), 1.60 (H-15), 1.59 (H-2), 1.54 (H-6), 1.49 (H-18), 1.44 (H-11), 1.41 (H-6), 1.40 (H-7), 1.40 (H-28), 1.36 (H-21), 1.34 (d, *J* 6.2 Hz, H-6′), 1.29 (H-9), 1.25 (H-11), 1.21 (H-16), 1.07 (H-12), 1.05 (s, H-26), 1.02 (H-15), 1.02 (H-22), 0.98 (s, H-27), 0.96 (s, H-23), 0.92 (H-1), 0.84 (s, H-25), 0.76 (s, H-24), 0.69 (H-5). ^{13}C NMR ($CDCl_3/CD_3OD$, 1 : 1) δ: 150.1 (C-20), 109.0 (C-29), 80.7 (C-1′), 72.6 (C-2′), 72.6 (C-4′), 72.2 (C-3), 71.7 (C-3′), 70.1 (C-5′), 55.0 (C-5), 50.1 (C-9), 49.5 (C-18), 46.8 (C-19), 46.4 (C-17), 42.0 (C-14), 40.4 (C-8), 38.8 (C-4), 38.4 (C-1), 36.7 (C-10), 36.7 (C-13), 34.8 (C-22), 33.8 (C-7), 30.2 (C-16), 29.5 (C-21), 28.6 (C-28), 27.3 (C-23), 26.8 (C-15), 26.4 (C-2), 24.7 (C-12), 20.5 (C-11), 19.1 (C-28a), 18.7 (C-30), 17.8 (C-6), 16.8 (C-6′), 15.6 (C-26), 15.5 (C-25), 14.8 (C-24), 14.3 (C-27). ^{77}Se NMR ($CD_3OD : CDCl_3$, 1 : 1, 114.4 MHz) δ: 229.2. HR-MS (ESI) calc. for $C_{37}H_{62}NaO_5Se$ $[M + Na]^+$: 689.3660. Found: 689.3656.

28a-Se-α-D-Idopyranosyl-28a-seleno-28a-homolup-20(29)-en-3β-ol (26). Yield 73% (50 mg); m.p. 206–208 °C. $[\alpha]_D^{20}$ 78.3 (*c* 0.2, chloroform–methanol, 1 : 1); ν_{max} (film): 2941, 2868, 1639, 1454, 1376, 1105, 1043, 982, 880, 733 cm^{-1}. ^1H NMR ($CDCl_3/CD_3OD$, 1 : 1) δ: 5.49 (br s, H-1′), 4.69 (H-29), 4.57 (H-29), 4.42 (ddd, *J* 1.5, 6.1, 6.1 Hz, H-5′), 3.87 (m, H-3′), 3.84 (m, H-2′), 3.81 (dd, *J* 5.8, 11.3 Hz, H-6′), 3.77 (dd, *J* 6.3, 11.3 Hz, H-6′), 3.71 (m, H-4′), 3.14 (dd, *J* 4.8, 11.5 Hz, H-3), 2.61 (H-28a), 2.52 (H-28a), 2.43 (H-19), 1.94 (H-21), 1.92 (H-28), 1.82 (H-13), 1.76 (H-16), 1.69 (H-1), 1.69 (s, H-30), 1.68 (H-22), 1.67 (H-12), 1.64 (H-15), 1.62 (H-2), 1.58 (H-2), 1.54 (H-6), 1.51 (H-18), 1.45 (H-28), 1.44 (H-11), 1.43 (H-6), 1.42 (H-7), 1.35 (H-21), 1.33 (H-9), 1.25 (H-11), 1.21 (H-16), 1.08 (H-12), 1.08 (s, H-26), 1.03 (H-15), 1.03 (H-22), 0.99 (s, H-27), 0.96 (s, H-23), 0.93 (H-1), 0.86 (s, H-25), 0.76 (s, H-24), 0.71 (H-5). ^{13}C NMR ($CDCl_3/CD_3OD$, 1 : 1) δ: 149.7 (C-20), 108.2 (C-29), 81.5 (C-1′), 77.6 (C-3), 71.7 (C-2′), 68.4 (C-4′), 68.3 (C-5′), 67.9 (C-3′), 60.5 (C-6′),

54.6 (C-5), 49.7 (C-9), 49.1 (C-18), 46.6 (C-19), 45.8 (C-17), 41.5 (C-8), 40.0 (C-14), 37.9 (C-1), 37.8 (C-4), 36.3 (C-13), 36.2 (C-10), 34.3 (C-22), 33.4 (C-7), 29.6 (C-16), 28.9 (C-21), 28.5 (C-28), 26.6 (C-23), 26.3 (C-15), 25.9 (C-2), 24.3 (C-12), 20.0 (C-11), 19.5 (C-28a), 17.7 (C-30), 17.4 (C-6), 14.8 (C-25), 14.7 (C-26), 14.1 (C-24), 13.5 (C-27). ^{77}Se NMR (CD_3OD : $CDCl_3$, 1 : 1, 114.4 MHz) δ: 267.7. HR-MS (ESI) calc. for $C_{37}H_{62}NaO_6Se$ $[M + Na]^+$: 705.3609. Found: 705.3605.

Attempt to di-(3β-*O*-allyl-28a-homolup-20(29)-en-28a-yl) diselenide (27). To grey elemental selenium (powder, 95 mg, 1.20 mmol) 1 M solution of Super Hydride in THF (1.2 mL, 1.20 mmol) was slowly added under an argon atmosphere. The mixture was allowed to stir at 50 °C for 1 h, cooled to room temp and ^{t}BuOH (200 μL) was added followed by THF (up to 5 mL total volume). The above suspension (1.0 mL) was added to a solution of mesylate **1** (58 mg, 0.10 mmol) in THF (2 mL) and stirred for 3 h at 50 °C. Solvents were removed under reduced pressure and the residue was purified by preparative TLC (hexane–ethyl acetate, 40 : 1). The product was suspended in a hot $CHCl_3$–MeOH (1 : 3) mixture, cooled to r.t. and the solid was decanted. Pure **27** (49 mg, 88%) was obtained as a yellow powder. All physicochemical properties were identical as desribed for selenol **4**. HR-MS (ESI) calc. for $C_{34}H_{56}OSe$ $[\frac{1}{2}M]^+$: 560.3496. Found: 560.3489. Anal. Calcd for $C_{68}H_{112}O_2Se_2 \times 2 \times$ MeOH (1183.65): C, 71.03; H, 10.22. Found: C, 71.25; H, 10.05.

Methyl 3β-*O*-allyl-28a-homolup-20(29)-en-28a-yl-selenide (28). To a solution of **4** (56 mg, 0.10 mmol) in THF (1 mL) 60% NaH (20 mg, 0.50 mmol) was added and stirred for 15 min. Then methyl iodide (31 μL, 0.50 mmol) was added and stirred at room temp overnight. The reaction was quenched by the addition of saturated solution of NH_4Cl (60 μL), solvents were coevaporated with toluene and the whole mixture was purified by preparative TLC (hexane–ethyl acetate, 40 : 1) to afford 42 mg (74%) of the title compound as light yellow foam. $[\alpha]_D^{20}$ 15.3 (*c* 0.2, chloroform); ν_{max} (film): 2942, 2868, 1642, 1455, 1376, 1135, 1086, 1071, 919, 882, 758 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 5.90–5.96 (m, C*H*═), 5.24–5.27 (m, ═CH_2), 5.11–5.13 (m, ═CH_2), 4.57 (H-29), 4.68 (H-29), 4.10–4.13 (m, OCH_2), 3.87–3.90 (m, OCH_2), 2.79 (dd, *J* 4.2, 11.7 Hz, H-3), 2.47 (H-28a), 2.42 (H-19), 2.39 (H-28a), 2.01 (s, $^2J_{Se,H}$ 10.0 Hz calculated from satellite signals, SeCH_3), 1.89 (H-21), 1.88 (H-28), 1.79 (H-13), 1.72 (H-2), 1.68 (H-1), 1.68 (s, H-30), 1.64 (H-22), 1.56 (H-15), 1.50 (H-6), 1.48 (H-2), 1.47 (H-18), 1.39 (H-6), 1.38 (H-7), 1.35 (H-21), 1.33 (H-28), 1.26 (H-9), 1.04 (s, H-26), 1.00 (H-15), 1.00 (H-22), 0.96 (s, H-27), 0.95 (s, H-23), 0.84 (s, H-25), 0.82 (H-1), 0.78 (s, H-24), 0.68 (H-5). ^{13}C NMR ($CDCl_3$) δ: 150.6 (C-20), 135.9 (*C*H═), 115.9 (═*C*H_2), 109.6 (C-29), 86.3 (C-3), 70.6 (O*C*H_2), 55.9 (C-5), 50.5 (C-9), 49.9 (C-18), 47.3 (C-19), 46.7 (C-17), 42.5 (C-14), 41.0 (C-8), 38.9 (C-4), 38.6 (C-1), 37.1 (C-10), 37.1 (C-13), 35.4 (C-22), 34.3 (C-7), 30.7 (C-16), 30.0 (C-21), 28.8 (C-28), 28.1 (C-23), 27.2 (C-15), 25.1 (C-12), 23.1 (C-2), 21.0 (C-11), 20.4 (C-28a), 19.4 (C-30), 18.3 (C-6), 16.3 (C-24), 16.1 (C-26), 16.1 (C-25), 14.9 (C-27), 4.1 (Se*C*H_3). ^{77}Se NMR ($CDCl_3$, 114.4 MHz) δ: 93.4. HR-MS (ESI) calc. for $C_{35}H_{58}OSe$ $[M]^+$: 574.3653. Found: 574.3662. Anal. Calcd for $C_{35}H_{58}OSe$ (573.81): C, 73.26; H, 10.19. Found: C, 72.97; H, 10.28.

Acknowledgements

This work was financed by grants from the National Science Centre, Poland (no. 2012/07/B/ST5/00823) and by the Czech Ministry of Education grant from the National Program for Sustainability I (LO1204) and grant GAČR 14-19590S. We thank Olga Hustáková for excellent technical assistance.

References

1 (*a*) Y. Xie, M. D. Short, P. B. Cassidy and J. C. Roberts, *Bioorg. Med. Chem. Lett.*, 2001, **11**, 2911–2915; (*b*) S. V. Madhunapantula, D. Desai, A. Sharma, S. J. Huh, S. Amin and G. P. Robertson, *Mol. Cancer Ther.*, 2008, **7**, 1297–1308; (*c*) E. Dominguez-Alvarez, D. Plano, M. Font, A. Calvo, C. Prior, C. Jacob, J. A. Palop and C. Sanmartin, *Eur. J. Med. Chem.*, 2014, **73**, 153–166; (*d*) Q. Guan, F. Yang, D. Guo, J. Xu, M. Jiang, Ch. Liu, K. Bao, Y. Wu and W. Zhang, *Eur. J. Med. Chem.*, 2014, **87**, 1–9; (*e*) P. Arsenyan, E. Paegle, I. Domracheva, A. Gulbe, I. Kanepe-Lapsa and I. Shestakova, *Eur. J. Med. Chem.*, 2014, **87**, 471–483; (*f*) V. Calcatierra, O. Lopez, J. G. Fernandez-Bolanos, G. B. Plata and J. M. Padron, *Eur. J. Med. Chem.*, 2015, **94**, 63–72; (*g*) M. Zhou, S. Ji, Z. Wu, Y. Li, W. Zheng, H. Zhou and T. Chen, *Eur. J. Med. Chem.*, 2015, **96**, 92–97; (*h*) I. L. Martins, C. Charneira, V. Gandin, J. L. Farreira da Silva, G. C. Justino, J. P. Telo, A. J. S. C. Vieira, C. Marzano and A. M. M. Antunes, *J. Med. Chem.*, 2015, **58**, 4250–4265.

2 (*a*) H.-J. Quan, J. Koyanagi, K. Ohmori, S. Uesato, T. Tsuchido and S. Saito, *Eur. J. Med. Chem.*, 2002, **37**, 659–669; (*b*) L. L. Romero-Hernández, P. Merino-Montiel, S. Montiel-Smith, S. Meza-Reyes, J. L. Vega-Báez, I. Abasolo, S. Schwartz Jr., O. López and J. G. Fernández-Bolaños, *Eur. J. Med. Chem.*, 2015, **99**, 67–81.

3 (*a*) D. Plano, C. Sanmartin, E. Moreno, C. Prior, A. Calvo and J. A. Palop, *Bioorg. Med. Chem. Lett.*, 2007, **17**, 6853–6859; (*b*) E. Ibanez, D. Plano, M. Font, A. Calvo, C. Prior, J. A. Palop and C. Sanmartin, *Eur. J. Med. Chem.*, 2011, **46**, 265–274; (*c*) E. Moreno, D. Plano, I. Lamberto, M. Font, I. Encio, J. A. Palop and C. Sanmartin, *Eur. J. Med. Chem.*, 2012, **47**, 283–298.

4 Sh. H. Abdel-Hafez, *Eur. J. Med. Chem.*, 2008, **43**, 1971–1977.

5 (*a*) G. Mugesh and H. Wolf-Walther du Mont Sies, *Chem. Rev.*, 2001, **101**, 2125–2179; (*b*) C. W. Nogueira, G. Zeni and J. B. T. Rocha, *Chem. Rev.*, 2004, **104**, 6255–6285; (*c*) M. Piętka-Ottlik, H. Wójtowicz-Młochowska, K. Kołodziejczyk, E. Piasecki and J. Młochowski, *Chem. Pharm. Bull.*, 2008, **56**, 1423–1427.

6 P. Cmoch, A. Korda, L. Rárová, J. Oklešťková, M. Strnad, R. Luboradzki and Z. Pakulski, *Tetrahedron*, 2014, **70**, 2717–2730.

7 K. Sidoryk, A. Korda, L. Rárová, J. Oklešťková, M. Strnad, P. Cmoch, Z. Pakulski, K. Gwardiak, R. Karczewski and R. Luboradzki, *Tetrahedron*, 2015, **71**, 2004–2012.

8 K. Sidoryk, A. Korda, L. Rárová, J. Oklešťková, Z. Pakulski, M. Strnad, P. Cmoch, K. Gwardiak and R. Karczewski, *Eur. J. Org. Chem.*, 2016, 373–383.

9 (*a*) S. A. Sadek, S. M. Shaw, W. V. Kessler and G. C. Wolf, *J. Org. Chem.*, 1981, **46**, 3259–3262; (*b*) H. J. Quan, J. Koyanagi, F. Komada and S. Saito, *Eur. J. Med. Chem.*, 2005, **40**, 662–673; (*c*) M. Ibrahim-Ouali, *Tetrahedron Lett.*, 2009, **50**, 1607–1609; (*d*) O. E. D. Rodrigues, D. de Souza, L. C. Soares, L. Dornelles, R. A. Burrow, H. R. Appelt, C. F. Alves, D. Alves and A. L. Braga, *Tetrahedron Lett.*, 2010, **51**, 2237–2240; (*e*) M. Ibrahim-Ouali, E. Romero and H. Bouleghlem, *Tetrahedron*, 2011, **67**, 3668–3676.

10 (*a*) R. Benhaddou, S. Czernecki and D. Randriamandimby, *Synlett*, 1992, 967–968; (*b*) C. Mukherjee, P. Tiwari and A. K. Misra, *Tetrahedron Lett.*, 2006, **47**, 441–445; (*c*) P. Tiwari and A. K. Misra, *Tetrahedron Lett.*, 2006, **47**, 2345–2348; (*d*) S. Valerio, A. Iadonisi, M. Adinolfi and A. Ravida, *J. Org. Chem.*, 2007, **72**, 6097–6106.

11 (*a*) S. Mehta, J. S. Andrews, B. D. Johnston and B. M. Pinto, *J. Am. Chem. Soc.*, 1994, **116**, 1569–1570; (*b*) H. Abe, S. Shuto and A. Matsuda, *J. Am. Chem. Soc.*, 2001, **123**, 11870–11882; (*c*) S. S. Weng, C. L. Li, C. S. Liao, T. A. Chen, C. C. Huang and K. T. Hung, *J. Carbohydr. Chem.*, 2010, **429**, 29–440.

12 (*a*) G. Stork, H. S. Suh and G. Kim, *J. Am. Chem. Soc.*, 1991, **113**, 7054–7056; (*b*) S. Mehta and B. M. Pinto, *Tetrahedron Lett.*, 1991, **32**, 4435–4438; (*c*) K. C. Nicolaou, H. J. Mitchell, K. C. Fylaktakidou, R. M. Rodriguez and H. Suzuki, *Chem. – Eur. J.*, 2000, **6**, 3116–3148; (*d*) S. C. Ennis, I. Cumpstey, A. J. Fairbanks, T. D. Butters, M. Mackeen and M. R. Wormald, *Tetrahedron*, 2002, **58**, 9403–9411.

13 (*a*) A. Düffels and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 1999, 375–378; (*b*) T. Bamhaoud, S. Sanchez and J. Prandi, *Chem. Commun.*, 2000, 659–660; (*c*) A. Düffels, L. G. Green, S. V. Ley and A. D. Miller, *Chem. – Eur. J.*, 2000, **6**, 1416–1430; (*d*) H. Abe, S. Shuto and A. Matsuda, *J. Org. Chem.*, 2000, **65**, 4315–4325; (*e*) M. Aloui, D. J. Chambers, I. Cumpstey, A. J. Fairbanks, A. J. Redgrave and C. M. P. Seward, *Chem. – Eur. J.*, 2002, **8**, 2608–2621.

14 (*a*) S. Mehta, J. S. Andrews, B. D. Johnston, B. Svensson and B. M. Pinto, *J. Am. Chem. Soc.*, 1995, **117**, 9783–9790; (*b*) K. C. Nicolaou, R. M. Rodriguez, H. J. Mitchell, H. Suzuki, K. C. Fylaktakidou, O. Baudoin and F. L. Van Delft, *Chem. – Eur. J.*, 2000, **6**, 3095–3115; (*c*) K. C. Nicolaou, K. C. Fylaktakidou, H. J. Mitchell, F. L. Van Delft, R. M. Rodriguez, S. R. Conley and Z. Jin, *Chem. – Eur. J.*, 2000, **6**, 3166–3185.

15 R. H. Furneaux, Z. Pakulski and P. C. Tyler, *Can. J. Chem.*, 2002, **80**, 964–972.

16 C. Gauthier, J. Legault, M. Lebrun, P. Dufour and A. Pichette, *Bioorg. Med. Chem.*, 2006, **14**, 6713–6725.

17 P. Cmoch, A. Korda, L. Rárová, J. Oklešťková, M. Strnad, K. Gwardiak, R. Karczewski and Z. Pakulski, *Eur. J. Org. Chem.*, 2014, 4089–4098.

18 P. Fugedi, in *The Organic Chemistry of Sugars*, ed. D. E. Levy and P. Fugedi, CRC Press, Boca Raton, 2006, ch. 4.

19 H. C. Braga, A. D. Wouters, F. B. Zerillo and D. S. Lüdtke, *Carbohydr. Res.*, 2010, **345**, 2328–2333.

20 A. Krief, W. Dumont and C. Delmotte, *Angew. Chem., Int. Ed.*, 2000, **39**, 1669–1672.

21 (*a*) P. Dowd and P. Kennedy, *Synth. Commun.*, 1981, **11**, 935–641; (*b*) A. Krief, M. Trabelsi and W. Dumont, *Synthesis*, 1992, 933–935.

22 (*a*) B. G. Bag and S. S. Dash, *Nanoscale*, 2011, **3**, 4564–4566; (*b*) B. G. Bag and S. S. Dash, *Langmuir*, 2015, **31**, 13664–13672.

23 (*a*) K. Bock, I. Lundt and C. Pedersen, *Tetrahedron Lett.*, 1973, **14**, 1037–1040; (*b*) K. Bock and C. Pedersen, *J. Chem. Soc., Perkin Trans. II*, 1974, 293–297; (*c*) K. Bock and C. Pedersen, *Acta Chem. Scand., Ser. B*, 1975, **29**, 258–264; (*d*) I. Tvaroska, *Adv. Carbohydr. Chem. Biochem.*, 1995, **51**, 15–61.

24 H. B. Sinclair and R. T. Sleeter, *Tetrahedron Lett.*, 1970, 833–836.

25 *Agilent, CrysAlis PRO*, Agilent Technologies, Yarnton, England, 2011.

26 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112–122.

