Regioselective Acylation of Ginsenosides by *Novozyme 435* to Generate Molecular Diversity

by **Rongwei Teng***[a]), **Chingseng Ang**[a]), **David McManus**[b]), **David Armstrong**[b]), **Shaiolim Mau**[a]), and **Antony Bacic***[a])

[a]) CRC for Bioproducts, School of Botany, The University of Melbourne, VIC 3010 Australia (phone: +61-3-8344 5072; fax: +61-3-9347-1071; e-mail: tengrongwei@hotmail.com and abacic@unimelb.edu.au)

[b]) CRC for Bioproducts, Tridan-Albright & Wilson (Aust) Ltd. Partnership, VIC 3013 Australia

Ginsenosides are major bioactive constituents of ginseng (*Panax* spp.; Araliaceae), a traditional Chinese medicinal herb. In order to increase the molecular diversity and broaden the potential usage of ginsenosides, ginsenosides Rd (**1**), Rg3 (**2**), (20*R*)-Rg3 (**3**), Rh2 (**4**), Re (**5**), Rh1 (**8**), Rg2 (**9**), gypenoside XVII (**6**), and pseudoginsenoside F11 (**7**) were regioselectively acylated with vinyl acetate, catalyzed by *Novozyme 435* (lipase B from *Candida antarctica*), in organic solvents to afford different mono-acetyl ginsenosides. Ginsenoside Rd (**1**) was also acylated with vinyl decanoate or vinyl cinnamate to generate **1b** and **1c**, respectively. Acylation of glucosylated ginsenosides (**1**–**4**, **6**, **8**) occurred at the primary 6-OH function of the terminal glucose (Glc) moiety of the sugar at C(3) or C(20) of the dammarane-type aglycone. In contrast, ginsenosides **5**, **7**, and **9**, containing mixed sugar moieties, resulted in acylation of both the rhamnose (Rha) and the glucose (Glc) moieties. In the case of ginsenoside Re (**5**) and pseudoginsenoside F11 (**7**), acylation at the secondary 4-OH function of the terminal Rha moiety, attached at C(3) of the aglycone, is preferred. The structures of all acylated products were determined by extensive MALDI-TOF-MS and NMR analyses.

Introduction. – Ginsenosides are triterpenoid saponins with a dammarane-type skeleton. They are isolated from ginseng (*Panax* spp.; Araliaceae) and are considered to be its major bioactive components. These natural products exert pharmacological effects on the central nervous, cardiovascular, endocrine, and immune systems, and also have anticancer properties [1–6]. Although more than 40 ginsenosides have been identified, it is a formidable task to search for novel ginsenosides due to their low abundance and the tedious chromatographic procedures required for their purification. Modification of existing ginsenosides, thus, provides an alternative of generating molecular diversity, as performed by either chemical, enzymatic, or microbial transformations [7–17].

Although chemical methods are often applied to modify the structures of molecules in order to modulate their pharmaceutical activity and/or bioavailability, they are difficult to perform on natural products and their derivatives, especially when the molecules are labile or possess multiple functional groups, *e.g.*, OH functions, as in the case of glycosides [14]. However, it has been shown that biocatalysts offer a number of key advantages over chemical syntheses when working on complex molecules. These advantages are based on the chemo-, regio-, and stereoselectivity of enzymes and the possibility to carry out such reactions under mild conditions [18].

Acylation of natural products could be important, since acyl groups increase the structural diversity of natural compounds and may also be important for their

bioactivity [13–22]. For example, the level of micronuclei induced by rutin ester in mammalian cells was *ca.* two- to three-times that induced by rutin, probably due to a higher degree of penetration of the esterified rutin through cell membranes [20]. Similarly, acylation of ginsenosides increases their lipophilicity, which could enhance their uptake into cells [14][17].

Lipase B from *Candida antarctica* (*Novozyme 435*) has been used for the regioselective acylation of plant glycosides such as ginsenosides Rg_1, Rb_1, and some steroid saponins in the presence of vinyl acetate in organic solvents [13–15]. In a previous publication [23], we generated and partially characterized a series of acetylated derivatives of ginsenosides Rd (**1**), Rg3 (**2**), (20*R*)-Rg3 (**3**), Rh2 (**4**), Re (**5**), gypenoside XVII (**6**), and pseudoginsenoside F11 (**7**), using vinyl acetate and *Novozyme 435*. In the present report, we report on further studies on the acetylation of ginsenosides Rh1 (**8**) and Rg2 (**9**) with vinyl acetate, and acylation of ginsenoside Rd (**1**) with vinyl decanoate and vinyl cinnamate, respectively, and the characterization of these acylated ginsenoside derivatives.

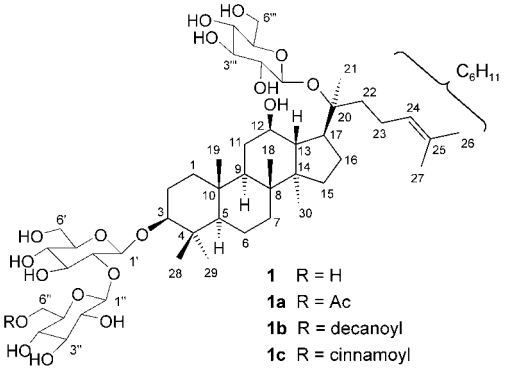
Results and Discussion. – Ginsenosides were dissolved in organic solvents in the presence of both *Novozyme 435* and an acyl donor (vinyl acetate, vinyl decanoate, or vinyl cinnamate). The reactions were terminated at the times when highest yields were achieved [23]. The acylated products were purified by column chromatography (CC) on silica gel and/or by preparative reverse-phase high-performance liquid chromatography (RP-HPLC), and their structures were determined by MALDI-TOF-MS and NMR (^{1}H, ^{13}C, HMBC, HMQC, TOCSY, ^{1}H,^{1}H-COSY), as well as by spectral comparison with the parent ginsenosides.

Acetylation of ginsenosides Rd (**1**), Rg3 (**2**), (20*R*)-Rg3 (**3**), Rh2 (**4**), Rh1 (**8**), and gypenoside XVII (**6**) afforded only a single product in each case, identified as 6″-*O*-acetylginsenoside Rd (**1a**), 6″-*O*-acetylginsenoside Rg3 (**2a**), (20*R*)-6″-*O*-acetylginsenoside Rg3 (**3a**), 6′-*O*-acetylginsenoside Rh2 (**4a**), 6′-*O*-acetylginsenoside Rh1 (**8a**), and 6‴-*O*-acetylgypenoside XVII (**6a**), respectively[1]).

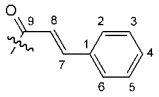
The MALDI-TOF mass spectrum of **1a** showed quasi-molecular ions at *m*/*z* 1027.5 ($[M+K]^+$) and 1011.6 ($[M+Na]^+$), 42 mass units higher than the corresponding signals of ginsenoside Rd (**1**). In comparison with ginsenoside Rd (**1**) [24], the ^{13}C-NMR spectrum of **1a** showed two additional signals at δ(C) 171.0 and 21.0 for the Ac group, and a downfield-shifted oxymethylene signal at δ(C) 64.8 for the acetylated oxymethylene C-atom of one glucose (Glc) unit. Moreover, the ^{1}H-NMR spectrum showed, among other signals, a *singlet* at δ(H) 2.03 for the Ac group, and the *AB* portion of an *ABX* system at low field, δ(H) 4.92 and 4.78, for the acetylated oxymethylene resonances of one Glc unit. Detailed 1D- and 2D-NMR spectra, along with the complete assignments of the NMR spectra of **1** [24], allowed us to completely assign the signals of the Glc moieties. For example, based on a TOCSY spectrum, the ^{1}H-NMR signals of the terminal Glc unit at C(3) of the aglycone were observed at δ(H) 5.31 (*d*, $J = 7.6$ Hz), 4.92 (br. *d*, $J = 12.0$ Hz), 4.78 (*dd*, $J = 4.8, 12.0$ Hz), 4.30 (*m*), 4.20 (*m*), 4.12 (*m*), and 4.01 (*m*), which were assigned to H–C(1″), H_a–C(6″), H_b–C(6″),

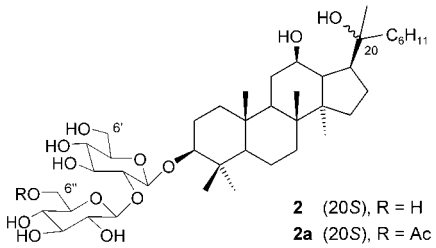
---

[1]) For systematic names, see the *Exper. Part.*

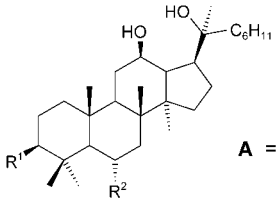


1 R = H
1a R = Ac
1b R = decanoyl
1c R = cinnamoyl

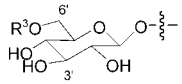




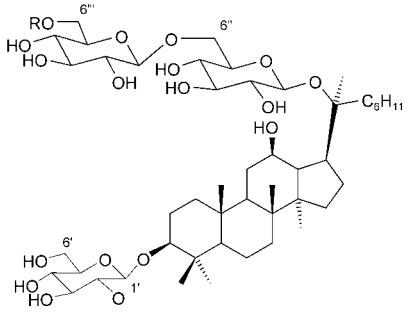
2 (20*S*), R = H
2a (20*S*), R = Ac
3 (20*R*), R = H
3a (20*R*), R = Ac



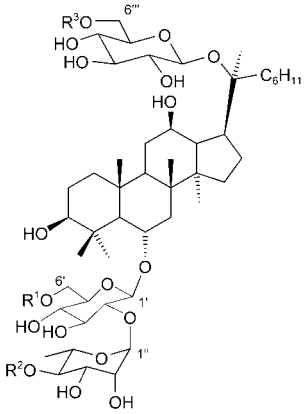
A =



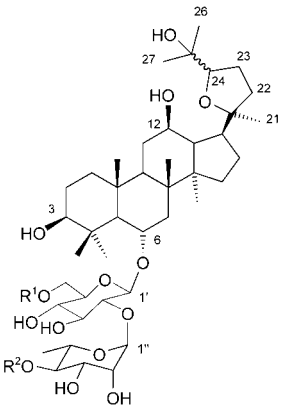
4 R^1 = **A**, R^2 = H, R^3 = H
4a R^1 = **A**, R^2 = H, R^3 = Ac
8 R^1 = H, R^2 = **A**, R^3 = H
8a R^1 = H, R^2 = **A**, R^3 = Ac



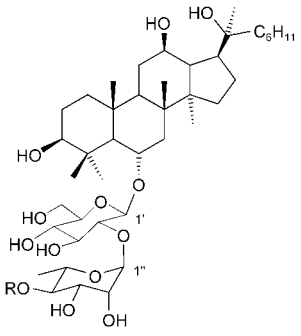
6 R = H
6a R = Ac



5 R^1 = R^2 = R^3 = H
5a R^1 = R^3 = H, R^2 = Ac
5b R^2 = R^3 = H, R^1 = Ac
5c R^1 = R^2 = H, R^3 = Ac



7 R^1 = R^2 = H
7a R^1 = H, R^2 = Ac
7b R^1 = Ac, R^2 = H



9 R = H
9a R = Ac

H–C(4″), H–C(3″), H–C(2″), and H–C(5″), respectively, by a combination of ^{1}H,^{1}H-COSY and HMQC spectra.

Comparing the ^{1}H-NMR data of **1a** with those of ginsenoside Rd (**1**) [24], CH_2(6″) was shifted downfield by *ca.* 0.47 ppm, characteristic of an Ac-induced shift (AIS) [12][23]. These data suggested that the Ac group was attached to the 6″-OH group (terminal Glc moiety), which was further confirmed by a HMBC spectrum showing a long-range correlation between CH_2(6″) at δ(H) 4.92 and 4.78 and the C=O C-atom at δ(C) 171.1 of the Ac group.

The structures of the acetylated ginsenosides **2a**–**4a** and **8a** were determined in a similar manner. The ^{1}H-NMR spectrum of **2a** showed a *singlet* at δ(H) 2.04, and low-field signals of the *AB* portion of an *ABX* system at δ(H) 4.92 and 4.78. The ^{13}C-NMR spectrum showed signals at δ(C) 171.2 and 21.1 for the Ac group, and a downfield-shifted oxymethylene resonance at δ(C) 64.9 of one Glc moiety. Similar to **2a**, the ^{1}H-NMR spectrum of **3a** showed a *singlet* at δ(H) 2.04 and the *AB* portion of an *ABX* system at low field (δ(H) 4.80 and 4.58). The ^{13}C-NMR spectrum of **3a** showed two Ac signals at δ(C) 171.2 and 21.0, and a downfield-shifted oxymethylene at δ(C) 64.9. The low-field *AB* H-atoms and the oxymethylene C-atom were assigned to CH_2(6″) and C(6″) of the terminal Glc unit of **2a** and **3a**, respectively, as derived by 2D-NMR, mainly TOCSY and HMQC, which established the locations of the Ac groups at 6″-OH in both **2a** and **3a**.

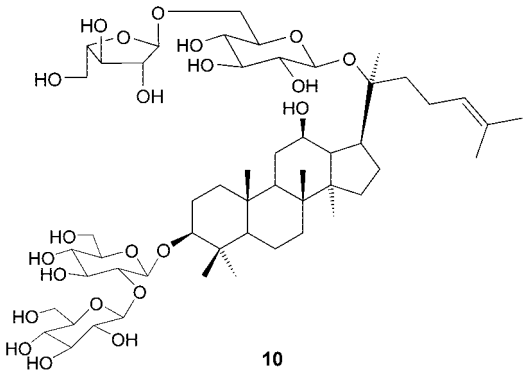
In comparison with the NMR spectra of ginsenoside Rh2 (**4**) and Rh1 (**8**) [25], the ^{1}H-NMR spectra of **4a** and **8a** showed, among other signals, the oxymethylene signals of a Glc unit at low field (δ(H) 4.93 and 4.82 *vs.* δ(H) 5.06 and 4.62). The Ac groups were found to be located at the 6′-OH positions, as confirmed by HMBC.

The acetylated products **1a**–**4a** and **8a** all bear the Ac groups at the OCH_2 function of the corresponding terminal 'lower' Glc unit connected to C(3) or C(6) of the aglycone. In contrast, gypenoside XVII (**6**) was acylated at the terminal Glc unit of the 'upper' gentiobiose moiety, linked at C(20), giving rise to **6a**, whose structure was elucidated spectroscopically as 6‴-*O*-acetylgypenoside XVII.

Compound **6a** showed quasi-molecular-ion peaks at *m*/*z* 1027.8 ($[M+K]^+$) and 1011.9 ($[M+Na]^+$) in its MALDI-TOF mass spectrum. Compared with **6** [24], the ^{13}C-NMR spectrum of **6a** showed, among other signals, two additional resonance at δ(C) 171.1 and 21.0, diagnostic for the Ac group, and a downfield-shifted oxymethylene signal at δ(C) 64.9 of one Glc unit. Moreover, ^{1}H-NMR spectroscopy showed a *singlet* at δ(H) 2.03, and the *AB* portion of an *ABX* system at low field (δ(H) 4.90, 4.72). A detailed NMR study allowed us to establish the direct, vicinal, and long-range H,H and H,C connectivity of the Glc moieties, which led to the conclusion that the *AB* portion at δ(H) 4.90 and 4.72 was due to CH_2(6‴) of the terminal Glc unit at C(20) of the aglycone. The HMBC spectrum of **6a** also showed a long-range correlation between the *AB* portion of H-atoms (δ(H) 4.90 and 4.72) and the Ac C=O group (δ(C) 171.1).

Unlike ginsenosides **1**–**6**, the carbohydrate moieties of ginsenoside Re (**5**), ginsenoside Rg2 (**9**), pseudoginsenoside F11 (**7**), and ginsenoside Rc (**10**) comprise not only Glc units, but rhamnopyranosyl (**5**, **7**, **9**) and arabinofuranosyl (**10**) units, respectively. The results of the acetylation experiments on these compounds were more complicated. One major product was detected by TLC and HPLC after a reaction time of 3 d for ginsenoside Rg2 (**9**), but two products were found after 2 d for

pseudoginsenoside F11 (**7**). In the case of the acetylation of ginsenosides Re (**5**) and Rc (**10**), a mixture of products were detected, with at least six compounds detected by HPLC for **10** after only 6 h reaction time. Three major products were detected for **5** after 2 d, and even more (six major and more than six minor products) with longer reaction times. Therefore, these reactions were terminated after 2 d for **5** and **7**, and after 3 d for **9**. The acetylated products were then purified by CC and/or preparative RP-HPLC, except for the reaction mixture of **10**, which could not be separated.



10

The structures of the acetylated products of **5a**–**c**, **7a**,**b**, and **9a** were determined on the basis of spectroscopic evidence and by comparing the NMR data with those of the parent compounds. Compounds **5**, **7**, and **9** were found to be acylated preferentially at the secondary HO–C(4) group of the terminal rhamnose (Rha) unit, in yields of *ca.* 12%. Lower yields (*ca.* 4%) were obtained for acylation at HO–C(6) of the Glc unit at C(3) and/or C(20) of the aglycone.

The MALDI-TOF mass spectrum of **5a** showed a quasi-molecular ion at *m*/*z* 1011.8 ($[M+Na]^+$), 42 mass units higher than the parent compound **5** (*m*/*z* 969.8 ($[M+Na]^+$)). In comparison with **5** [25], the ^{13}C-NMR spectrum of **5a** showed two additional signals at δ(C) 171.0 and 21.2 (Ac group). Further, a downfield shift of C(4″) of the Rha moiety from δ(C) 74.2 to 76.2 with a corresponding upfield shift of the neighboring C(3″)- and C(5″)-atoms from δ(C) 72.6 to 69.9 and from 69.6 to 67.1, respectively, were in accordance with an Ac-induced chemical shift (AIS) [15][23]. The ^{1}H-NMR spectrum of **5a** showed a *triplet* at low field (δ(H) 5.83), which was assigned to H–C(4″) of Rha from the TOCSY and ^{1}H,^{1}H-COSY spectra. Comparing the ^{1}H-NMR data with those of ginsenoside Re (**5**) [25], H–C(4″) of Rha was shifted downfield by *ca.* 1.5 ppm. These data suggested that the Ac group was attached to HO–C(4″), as further confirmed by HMBC, showing a long-range correlation between H–C(4″) (δ(H) 5.83 (t, J = 10.0 Hz)) of the Rha moiety and the Ac C=O group (δ(C) 171.0). The structure of compound **5a** was, therefore, established as 4″-*O*-acetylginsenoside Re.

The MS and ^{13}C-NMR data of compounds **5b** and **5c** were similar to those of **5a**, with quasi-molecular ions at *m*/*z* 1011.8 ($[M+Na]^+$) and 1011.7 ($[M+Na]^+$), respectively, and additional NMR signals at δ(C) 170.8/20.8 and at 170.8/20.9. The ^{1}H-NMR spectra of **5b** and **5c** showed, among other signals, the low-field *AB* portion of an *ABX* system at δ(H) 4.98, 4.62 (CH_2(6′) of Glc) and at 4.96, 4.60 (CH_2(6‴) of Glc),

respectively, by a TOCSY experiment. The structures of **5b** and **5c** were, therefore, deduced as 6′-*O*-acetylginsenoside Re and 6‴-*O*-acetylginsenoside Re, respectively.

Similar to compound **5a**, the ^{1}H-NMR-spectrum of **9a** also showed a *triplet* at low field (δ(H) 5.83 ($J = 10.0$ Hz)), which was assigned by means of TOCSY and ^{1}H,^{1}H-COSY spectra to H−C(4″) of the Rha unit. Therefore, **9a** was identified as 4″-*O*-acetylginsenoside Rg2.

Similar to **5a** and **9a**, a *triplet* at low field (δ(H) 5.83 ($J = 10.0$ Hz) was observed in the ^{1}H-NMR-spectrum of **7a**. A combination of TOCSY and ^{1}H,^{1}H COSY experiments allowed us to assign this signal to H−C(4″) of Rha, which established the structure of **7a** as 4″-*O*-acetylpseudoginsenoside F11. The structure of compound **7b** was deduced as 6′-*O*-acetylpseudoginsenoside F11, since the *AB* portion of an *ABX* system was found at low field (δ(H) 5.01, 4.69), assigned to CH_2(6′) of the 'inner' Glc unit at C(3) of the aglycone.

To investigate the reactivity of ginsienosides towards long-chain and bulky acylation reagents, vinyl decanoate and vinyl cinnamate were reacted with ginsenoside Rd (**1**), respectively. The solvent was changed from pyridine and *tert*-amylalcohol (=2-methylbutan-2-ol) to THF/DMF 4:1 for solubility reasons. In a small-scale reaction, 1 mg of ginsenoside Rd (**1**) was reacted with vinyl decanoate and vinyl cinnamate, respectively, in the presence of *Novozyme 435*, and was completely converted to a single product each (**1b** or **1c**) after 6 h and 1 d, respectively. On a larger scale (20 mg of **1**), complete conversion was observed after 24 and 30 h, respectively.

In the ^{1}H-NMR spectrum of **1b**, one *AB* portion of an *ABX* system was observed at δ(H) 4.95 and 4.85, and assigned by a TOCSY experiment to CH_2(6″) of the terminal Glc unit at C(3) of the aglycone. This was confirmed by an HMBC experiment showing a long-range correlation between CH_2(6″) (δ(C) 4.95, 4.85) and the C=O resonance at δ(C) 174.0 of the decanoyl group. Similarly, the long-range HMBC correlation between CH_2(6″) (δ(H) 4.49, 4.29) and the C=O signal at δ(C) 169.5 of the cinnamoyl (Cin) group confirmed the structure of **1c**.

Based on the isolated yields[2]) and the qualitatively observed differential reaction rates (for times of reaction, see *Exper. Part*) with different reagents (vinyl acetate, decanoate, and cinnamate), it seems that both the structure of the ginsenosides and the solvents have a major effect on the acylation rate.

Conclusions. – Ginsenosides **1**–**9** were regioselectively acylated with *Novozyme 435* in the presence of different acylating reagents to afford different mono-acyl ginsenosides. The acylation was found to take place preferentially at the terminal glycosyl moieties. Acylation of glucosylated ginsenosides (compounds **1**–**4**, **6**, and **8**) occurred at the primary 6-OH sugar function. In contrast, ginsenosides **5**, **7**, and **9**, which contain both glucose (Glc) and rhamnose (Rha) units, were acylated both at the Glc and Rha residues. Thereby, acylation of the Rha moiety took place at the secondary 4-OH function (12%), and, to a lesser degree, also at the primary 6-OH group of the 'inner' Glc attached to C(6) of the aglycone, or of the terminal Glc attached at C(20) of the aglycone.

---

[2]) The following yields were found as a function of reaction time: **1a** (65%), **1b** (80%), **1c** (72%), **2a** (59%), **3a** (66%), **4a** (72%), **5a** (11%), **5b** (4%), **5c** (4%), **6a** (78%), **7a** (12%), **7b** (2.5%), **8a** (30%), **9a** (14%).

This work was funded by a grant from the Australian Government to the *CRC for Bioproducts*. We wish to thank Dr. *T. K. Lim* and Dr. *Frances Separovic*, School of Chemistry, The University of Melbourne, for access to the NMR spectrometer, and *Novozymes Australia Pty, Ltd* for providing *Novozyme 435*.

Experimental Part

1. *General*. Vinyl acetate, vinyl decanoate, vinyl cinnamate, *tert*-amyl alcohol (=2-methylbut-2-enoate), and *t*-BuOH were purchased from *Sigma*. Lipase B from *Candida antarctica* (commercial name: *Novozyme 435*), immobilized on acrylic resin, was a gift from *Novozymes Australia Pty, Ltd*. Ginsenosides **4**, **8**, and **9** were purchased from *Si-Chuan Medical & Pharmaceutical Co.*, China. Ginsenosides **1**, **5**–**7**, and **10** were obtained from the root extract of American ginseng (*P. quinquefolium*), and ginsenosides **2** and **3** from the mild-acid hydrolysate of ginsenoside Rb1 (also obtained from the root of *P. quinquefolium*). The ginsenosides and acylated products were detected on TLC by spraying with H_2SO_4/EtOH 1:9 followed by heating on a hot plate. Precoated TLC plates (silica gel *60* F_{254}, 0.25 mm) and silica gel (200–400 mesh) for column chromatography (CC) were obtained from *Merck* and *Sigma*, respectively. Prep. HPLC: *Beckman Gold-126* (*Beckman Coulter, Inc.*, USA), with UV monitor. Anal. HPLC: *Luna C18(2)* column (5 μm/250 × 4.6 mm or 10 μm/250 × 10.0 mm; *Phenomenex Australia Pty., Ltd.*). M.p.: electrothermal melting-point apparatus; uncorrected. Optical rotation: *Jasco DIP-1000* digital polorimeter, Na lamp. ^{1}H- and ^{13}C-NMR: *Varian Unity Plus-400*, at 400 and 100 MHz, resp.; δ in ppm rel. to solvent signals of (D_5)pyridine (δ(H) 8.71, δ(C) 149.9) or of CD_3OD (δ(H) 3.31, δ(C) 49.0) at room temp. 2D-NMR: *Varian Inova-400* spectrometer (400 MHz), at 25°. ^{1}H,^{1}H-COSY and HMQC Experiments were performed under standard conditions. HMBC: spin-lock delay time of 60 ms for ^{1}H,^{13}C long-range correlations. TOCSY: spin-lock period of 100 ms. MS: *Voyager-DE STR* biospectrometry workstation (*Perspective Biosystems*); matrix: α-cyano-4-hydroxycinnamic acid.

2. *Enzymatic Acylation of Ginsenosides with* Novozyme 435. 2.1. *Small-Scale Acetylation*. The ginsenoside (1–2 mg) was dissolved in 2-methylbutan-2-ol (100 μl; for **1**) or 2-methylbutan-2-ol/pyridine 10:1 (100 μl; for **2**–**7**, **9**, **10**) and treated with both *Novozyme 435* (3–5 mg) and vinyl acetate (50 μl). The reaction was monitored by TLC and HPLC [23].

2.2. *Medium-Scale Acetylation*. Ginsenoside **1** (100 mg) was dissolved in 2-methylbutan-2-ol/pyridine 10:1 (4.4 ml), **2** (86 mg) and **4** (78 mg) were dissolved in plain 2-methylbutan-2-ol (4 ml), **5** (360 mg), **7** (400 mg), and **9** (200 mg) were dissolved in 20, 18, and 8 ml of *t*-BuOH, respectively, and **3** (88 mg), **6** (35 mg), and **8** (95 mg), were dissolved in 10, 2, and 5 ml each of THF/DMF 4:1. Then, to each of these separate solns. were added *Novozyme 435* (*ca*. two- to three-times the weight of ginsenoside) and vinyl acetate (*ca*. 25 vol.-% of the soln.), and the resulting mixtures were then incubated at 37° on a gyratory shaker at 250 r.p.m. The reactions were terminated after a given time[2]) by filtering off the enzyme, followed by evaporation to dryness under reduced pressure at 45°.

2.3. *Medium-Scale Acylations*. Two solns. of ginsenoside Rd (**1**; 20 mg) in THF/DMF 4:1 (1.2 ml) were prepared in separate vessels and treated each with both *Novozyme 435* (95 and 65 mg, resp.) and either vinyl decanoate (0.5 ml) or vinyl cinnamate (0.5 ml), respectively. Workup and purification was performed as described in *Sect. 2.2* and *2.4*, resp.

2.4. *Isolation of Acylation Products*. The dry residues were dissolved in $CHCl_3$/MeOH and subjected to CC (SiO_2) using variable mixtures of $CHCl_3$, MeOH, and H_2O as the eluent. The yields of acylated products, as a function of reaction time, were: **1a** (1 d, 65%), **1b** (1 d, 80%), **1c** (30 h, 72%), **2a** (3 d, 59%), **3a** (3 d, 66%), **4a** (3 d, 72%), **5a** (2 d, 11%), **5b** (2 d, 4%), **5c** (2 d, 4%), **6a** (6 h, 78%), **7a** (2 d, 12%), **7b** (2 d, 2.5%), **8a** (4 d, 30%), and **9a** (3 d, 14%). Compounds **7b** (14 mg) and **7c** (14 mg) were purified by prep. HPLC using binary mixtures of *Milli-Q* H_2O (*A*) and MeCN (*B*). The following gradient was applied: 0–13 min 30–40% *B*, then 13–18 min 40–50% *B*, at a flow rate of 4.7 ml/min (UV detection at 203 nm and 220 nm).

*(3β,12β,20S,24E)-20-[(β-*D*-Glucopyranosyl)oxy]-3-[(β-*D*-glucopyranosyl-(1→2)-β-*D*-glucopyranosyl)oxy]-dammar-24-en-12-ol* (=*Ginsenoside Rd*; **1**) [24]. Amorphous solid. ^{1}H-NMR (400 MHz, C_5D_5N): 5.37 (*d*, *J*= 7.6, H–C(1″)); 5.24 (*t*, *J* = 6.9; H–C(24)); 5.18 (*d*, *J* = 7.7, H–C(1‴)); 4.90 (*d*, *J* = 7.6, H–C(1′)); 4.45 (H_a–C(6″)); 4.31 (H_b–C(6″)); 4.11 (H–C(12)); 3.26 (*dd*, *J* = 3.9, 11.6, H–C(3)); 1.61 (*s*, Me(21)); 1.59 (*s*, Me(26), Me(27)); 1.28 (*s*, Me(28)); 1.10 (*s*, Me(29)); 0.96 (*s*, Me(18)); 0.94 (*s*, Me(30)); 0.78 (*s*, Me(19)). ^{13}C-NMR (100 MHz, C_5D_5N): 131.0 (C(25)); 126.0 (C(24)); 106.1 (C(1″)); 105.2 (C(1′)); 98.4 (C(1‴)); 89.1 (C(3)); 83.5 (C(2′)); 83.4 (C(20)); 79.3 (C(3″)); 78.4 (C(5″)); 78.3 (C(5′), C(3‴)); 78.2 (C(5‴)); 78.0 (C(3′)); 77.2 (C(2′)); 75.3 (C(2‴)); 71.8 (C(4‴)); 71.7 (C(4′), C(4″)); 70.3 (C(12)); 62.8 (C(6″), C(6″), C(6‴)); 56.4 (C(5)); 51.8 (C(17)); 51.5 (C(14)); 50.2 (C(9)); 49.5 (C(13)); 40.1 (C(8)); 39.8 (C(4)); 39.2 (C(1)); 36.9 (C(10));

36.1 (C(22)); 35.2 (C(7)); 30.9 (C(11)); 30.8 (C(15)); 28.2 (C(28)); 26.8 (C(16)); 26.7 (C(2)); 25.9 (C(26)); 23.4 (C(23)); 22.5 (C(21)); 18.5 (C(6)); 17.9 (C(27)); 17.4 (C(30)); 16.7 (C(29)); 16.4 (C(19)); 16.0 (C(18)). MALDI-TOF-MS ($C_{48}H_{82}O_{18}$; 947.15): 970.1 ($[M+Na]^+$).

*(3β,12β,20*S*,24*E*)-3-[(6-*O*-Acetyl-β-*D*-glucopyranosyl-(1→2)-β-*D*-glucopyranosyl)oxy]-20-[(β-*D*-glucopyranosyl)oxy]dammar-24-en-12-ol* (=*6″-O-Acetylginsenoside Rd*; **1a**). Amorphous solid. M.p. 180–184°. ^{1}H-NMR (400 MHz, C_5D_5N): 5.31 (*d*, *J* = 7.6, H–C(1″)); 5.24 (*t*, *J* = 6.9, H–C(24)); 5.18 (*d*, *J* = 7.6, H–C(1‴)); 4.92 (br. *d*, *J* = 12.0, H_a–C(6″)); 4.90 (*d*, *J* = 8.0, H–C(1′)); 4.78 (*dd*, *J* = 4.8, 12.0, H_b–C(6″)); 4.55 (br. *d*, *J* = 11.2, H_a–C(6′)); 4.48 (br. *d*, *J* = 10.4, H_a–C(6‴)); 4.31 (H_b–C(6‴)); 4.31 (H_b–C(6′)); 4.30 (H–C(4″)); 4.29 (H–C(3′)); 4.22 (H–C(3‴)); 4.22 (H–C(2′)); 4.20 (H–C(3″)); 4.18 (H–C(4‴)); 4.12 (H–C(2″)); 4.11 (H–C(4′)); 4.11 (H–C(12)); 4.01 (H–C(5″)); 3.99 (H–C(2‴)); 3.91 (H–C(5′)); 3.90 (H–C(5‴)); 3.25 (*dd*, *J* = 4.0, 11.2, H–C(3)); 2.55 (H–C(17)); 2.22, 2.48 (CH_2(23)); 2.19, 1.83 (CH_2(2)); 2.03 (*s*, Ac); 1.96 (H–C(13)); 1.94, 1.43 (CH_2(11)); 1.83, 2.39 (CH_2(22)); 1.83, 1.34 (CH_2(16)); 1.61 (*s*, Me(21)); 1.58 (*s*, Me(26), Me(27)); 1.52, 0.98 (CH_2(15)); 1.52, 0.72 (CH_2(1)); 1.50, 1.33 (CH_2(6)); 1.49, 1.19 (CH_2(7)); 1.35 (H–C(9)); 1.31 (*s*, Me(28)); 1.11 (*s*, Me(29)); 0.94 (*s*, Me(30)); 0.93 (*s*, Me(18)); 0.80 (*s*, Me(19)); 0.66 (br. *d*, *J* = 11.3, H–C(5)). ^{13}C-NMR (100 MHz, C_5D_5N): 170.1 (Me*C*OO); 131.0 (C(25)); 126.0 (C(24)); 106.2 (C(1″)); 105.2 (C(1′)); 98.4 (C(1‴)); 89.3 (C(3)); 84.4 (C(2′)); 83.4 (C(20)); 79.3 (C(3″)); 78.6 (C(5′)); 78.4 (C(3‴)); 78.2 (C(5‴)); 78.0 (C(3′)); 76.8 (C(2″)); 75.4 (C(5″)); 75.2 (C(2‴)); 71.6 (C(4″)); 71.4 (C(4‴)); 71.1 (C(4′)); 70.3 (C(12)); 64.8 (C(6″)); 62.9 (C(6‴)); 62.8 (C(6′)); 56.5 (C(5)); 51.8 (C(17)); 51.5 (C(14)); 50.2 (C(9)); 49.5 (C(13)); 40.1 (C(8)); 39.8 (C(4)); 39.2 (C(1)); 37.0 (C(10)); 36.1 (C(22)); 35.2 (C(7)); 31.0 (C(11)); 30.8 (C(15)); 28.1 (C(28)); 26.9 (C(16)); 26.7 (C(2)); 25.8 (C(26)); 23.3 (C(23)); 22.5 (C(21)); 21.0 (*Me*COO); 18.5 (C(6)); 17.8 (C(27)); 17.4 (C(30)); 16.5 (C(29)); 16.3 (C(19)); 16.0 (C(18)). MALDI-TOF-MS ($C_{50}H_{84}O_{19}$, 989.19): 1027.5 ($[M+K]^+$), 1011.6 ($[M+Na]^+$).

*(3β,12β,20*S*,24*E*)-3-[(6-*O*-Decanoyl-β-*D*-glucopyranosyl-(1→2)-β-*D*-glucopyranosyl)oxy]-20-[(β-*D*-glucopyranosyl)oxy]dammar-24-en-12-ol* (=*6″-O-Decanoylginsenoside Rd*; **1b**). Amorphous solid. ^{1}H-NMR (400 MHz, C_5D_5N): 5.32 (*d*, *J* = 7.6, H–C(1″)); 5.24 (H–C(24)); 5.19 (H–C(1‴)); 4.95 (br. *d*, *J* = 10.4, H_a–C(6″)); 4.91 (*d*, *J* = 7.6, H–C(1′)); 4.78 (*dd*, *J* = 4.0, 11.6, H_b–C(6″)); 3.28 (*dd*, *J* = 3.2, 11.6, H–C(3)); 1.61 (*s*, Me(21)); 1.58 (*s*, Me(26), Me(27)); 1.34 (*s*, Me(28)); 1.14 (*s*, Me(29)); 0.96 (*s*, Me(18), Me(30)); 0.86 (*s*, *J* = 6.4, *Me*$(CH_2)_8$COO); 0.84 (*s*, Me(19)). ^{13}C-NMR (100 MHz, C_5D_5N): 174.0 (Me$(CH_2)_8$*COO*); 131.0 (C(25)); 126.0 (C(24)); 106.4 (C(1″)); 105.2 (C(1′)); 98.4 (C(1‴)); 89.3 (C(3)); 84.5 (C(2′)); 83.4 (C(20)); 79.3 (C(3″)); 78.6 (C(5′)); 78.4 (C(3‴)); 78.2 (C(5‴)); 78.0 (C(3′)); 76.8 (C(2″)); 75.5 (C(5″)); 75.3 (C(2‴)); 71.6 (C(4″)); 71.4 (C(4‴)); 71.1 (C(4′)); 70.4 (C(12)); 64.8 (C(6″)); 62.9 (C(6‴)); 62.8 (C(6′)); 56.5 (C(5)); 51.8 (C(17)); 51.5 (C(14)); 50.3 (C(9)); 49.5 (C(13)); 40.1 (C(8)); 39.9 (C(4)); 39.3 (C(1)); 37.0 (C(10)); 36.1 (C(22)); 35.3 (C(7)); 34.5 (Me$(CH_2)_7C\mathit{H}_2$COO); 32.2 (Me $(CH_2)_6C\mathit{H}_2CH_2$COO); 30.9 (C(11), C(15)); 30.1–29.7 (Me$CH_2(C\mathit{H}_2)_5(CH_2)_2$COO); 28.1 (C(28)); 26.9 (C(16)); 26.7 (C(2)); 25.9 (C(26)); 25.4 (Me$C\mathit{H}_2(CH_2)_7$COO); 23.4 (C(23)); 22.5 (C(21)); 18.6 (C(6)); 17.9 (C(27)); 17.4 (C(30)); 16.6 (C(29)); 16.4 (C(19)); 16.1 (C(18)); 14.4 (*Me*$(CH_2)_8$COO). MALDI-TOF-MS ($C_{58}H_{100}O_{19}$, 1101.40): 1100.2 (M^+) 1124.3 ($[M+Na]^+$), 1140.4 ($[M+K]^+$).

*(3β,12β,20*S*,24*E*)-20-[(β-*D*-glucopyranosyl)oxy]-3-[[6-*O*-((*E*)-3-phenylprop-2-enoyl)-β-*D*-glucopyranosyl-(1→2)-β-*D*-glucopyranosyl]oxy]dammar-24-en-12-ol* (=*6″-O-Cinnamoylginsenoside Rd*; **1c**). Amorphous solid. ^{1}H-NMR (400 MHz, CD_3OD): 7.72 (*d*, *J* = 16.0, Cin H–C(7)); 7.63–7.27 (Cin H–C(2) to H–C(6)); 6.57 (*d*, *J* = 16.0, Cin H–C(8)); 5.11 (*t*, *J* = 6.4, H–C(24)); 4.68 (*d*, *J* = 8.0, H–C(1″)); 4.60 (*d*, *J* = 8.0, H–C(1‴)); 4.49 (br. *d*, *J* = 10.4, H_a–C(6″)); 4.41 (*d*, *J* = 7.6, H–C(1′)); 4.29 (*dd*, *J* = 4.8, 12.0, H_b–C(6″)); 3.08 (H–C(3)); 1.69 (*s*, Me(21)); 1.62 (*s*, Me(26)); 1.30 (*s*, Me(27)); 1.02 (*s*, Me(28)); 0.87 (*s*, Me(29)); 0.86 (*s*, Me(30)); 0.78 (*s*, Me(18)); 0.75 (*s*, Me(19)). ^{13}C-NMR (100 MHz, CD_3OD): 169.5 (C=O); 147.3 (Cin C(7)); 141.8 (Cin C(1)); 138.2 (Cin C(4)); 132.5 (C(25)); 130.6 (Cin C(2,6)); 129.4 (Cin C(3,5)); 126.7 (C(24)); 119.9 (Cin C(8)); 106.2 (C(1″)); 106.1 (C(1′)); 99.2 (C(1‴)); 91.8 (C(3)); 85.8 (C(20)); 84.0 (C(2′)); 79.4 (C(3″)); 79.1 (C(5′)); 78.8 (C(3‴)); 78.6 (C(3′)); 78.4 (C(5‴)); 77.3 (C(2″)); 76.4 (C(5″)); 76.3 (C(2‴)); 74.4 (C(12)); 72.8 (C(4″)); 72.3 (C(4‴)); 72.1 (C(4′)); 65.9 (C(6″)); 63.6 (C(6′)); 62.9 (C(6‴)); 58.3 (C(5)); 54.0 (C(17)); 53.3 (C(14)); 51.8 (C(9)); 50.5 (C(13)); 41.8 (C(8)); 41.4 (C(4)); 41.0 (C(1)); 38.7 (C(10)); 37.5 (C(22)); 36.6 (C(7)); 32.5 (C(11)); 31.8 (C(15)); 29.3 (C(28)); 28.2 (C(16)); 28.1 (C(2)); 26.8 (C(26)); 25.1 (C(23)); 23.7 (C(21)); 20.3 (C(6)); 18.9 (C(27)); 18.1 (C(30)); 17.9 (C(29)); 17.6 (C(19)); 17.1 (C(18)). MALDI-TOF-MS ($C_{57}H_{88}O_{19}$, 1077.30): 1100.2 ($[M+Na]^+$).

*(3β,12β,20*S*,24*E*)-3-[(β-*D*-Glucopyranosyl-(1→2)-β-*D*-glucopyranosyl)oxy]dammar-24-ene-12,20-diol* (=*Ginsenoside Rg3*; **2**) [26]. Amorphous solid. ^{1}H-NMR (400 MHz, C_5D_5N): 5.34 (*d*, *J* = 7.5, H–C(1″)); 5.31 (*t*, *J* = 7.2, H–C(24)); 4.90 (*d*, *J* = 7.3, H–C(1′)); 4.53 (*dd*, *J* = 2.6, 11.8, H_a–C(6′)); 4.47 (*dd*, *J* = 2.9, 11.5, H_a–C(6″)); 4.43 (*dd*, *J* = 3.7, 11.5, H_b–C(6″)); 4.33 (H_b–C(6′)); 4.30 (H–C(4″)); 4.28 (H–C(3‴)); 4.22

(H–C(2′)); 4.19 (H–C(3′)); 4.11 (*t*, *J* = 7.5, H–C(4′)); 4.11 (H–C(2″)); 3.91 (H–C(5″)); 3.90 (H–C(12)); 3.89 (H–C(5′)); 3.26 (*dd*, *J* = 4.3, 11.5, H–C(3)); 2.35 (H–C(17)); 2.27, 2.56 (CH_2(23)); 2.01 (H–C(13)); 1.82, 2.18 (CH_2(2)); 1.69, 2.02 (CH_2(22)); 1.65 (*s*, Me(26)); 1.62 (*s*, Me(27)); 1.51, 1.99 (CH_2(11)); 1.42 (*s*, Me(21)); 1.41, 1.89 (CH_2(16)); 1.40 (H–C(9)); 1.36, 1.50 (CH_2(6)); 1.28 (*s*, Me(28)); 1.20, 1.45 (CH_2(7)); 1.09 (*s*, Me(29)); 1.05, 1.57 (CH_2(15)); 0.96 (*s*, Me(18)); 0.95 (*s*, Me(30)); 0.80 (*s*, Me(19)); 0.76, 1.50 (CH_2(1)); 0.68 (br. *d*, *J* = 11.2, H–C(5)). ^{13}C-NMR (100 MHz, C_5D_5N): 130.8 (C(25)); 126.4 (C(24)); 106.1 (C(1″)); 105.2 (C(1′)); 89.0 (C(3)); 83.4 (C(2′)); 78.4 (C(3″)); 78.2 (C(5′), C(5″)); 78.0 (C(3′)); 77.2 (C(2″)); 73.1 (C(20)); 71.7 (C(4′), C(4″)); 71.1 (C(12)); 62.9 (C(6′)); 62.8 (C(6″)); 56.4 (C(5)); 54.9 (C(17)); 51.8 (C(14)); 50.4 (C(9)); 48.6 (C(13)); 40.0 (C(8)); 39.8 (C(4)); 39.2 (C(1)); 37.0 (C(10)); 35.9 (C(22)); 35.2 (C(7)); 32.1 (C(11)); 31.4 (C(15)); 28.2 (C(21), C(28)); 26.9 (C(16)); 26.8 (C(2)); 25.9 (C(26)); 23.1 (C(23)); 18.5 (C(6)); 17.8 (C(30)); 17.1 (C(27)); 16.7 (C(29)); 16.4 (C(19)); 15.9 (C(18)). MALDI-TOF-MS ($C_{42}H_{72}O_{13}$, 785.01): 807.6 ($[M+Na]^+$).

*(3β,12β,20*S*,24*E*)-3-[(6-*O*-Acetyl-β-*D*-glucopyranosyl-(1 → 2)-β-*D*-glucopyranosyl)oxy]dammar-24-ene-12,20-diol* (=*6″-*O*-Acetylginsenoside Rg3*; **2a**). Amorphous solid. M.p. 154–157°. ^{1}H-NMR (400 MHz, C_5D_5N): 5.34 (*d*, *J* = 7.5, H–C(1″)); 4.92 (br. *d*, *J* = 11.6, H_a–C(6″)); 4.90 (*d*, *J* = 7.2, H–C(1′)); 4.78 (*dd*, *J* = 3.7, 11.6, H_b–C(6″)); 3.27 (br. *d*, *J* = 11.2, H–C(3)); 2.04 (*s*, Ac); 1.64 (*s*, Me(26)); 1.61 (*s*, Me(27)); 1.43 (*s*, Me(21)); 1.36 (*s*, Me(28)); 1.10 (*s*, Me(29)); 0.95 (*s*, Me(30)); 0.95 (*s*, Me(18)); 0.79 (*s*, Me(19)). ^{13}C-NMR (100 MHz, C_5D_5N): 171.2 (Me*C*OO); 130.9 (C(25)); 126.4 (C(24)); 106.2 (C(1″)); 105.0 (C(1′)); 89.3 (C(3)); 84.4 (C(2′)); 78.6 (C(3″)); 78.2 (C(5′)); 78.0 (C(3′)); 76.8 (C(5″)); 75.4 (C(2″)); 73.2 (C(20)); 71.4 (C(4′)); 71.1 (C(12), C(4″)); 64.9 (C(6″)); 62.9 (C(6′)); 56.5 (C(5)); 54.9 (C(17)); 51.8 (C(14)); 50.5 (C(9)); 48.6 (C(13)); 40.1 (C(8)); 39.9 (C(4)); 39.2 (C(1)); 37.0 (C(10)); 36.0 (C(22)); 35.3 (C(7)); 32.1 (C(11)); 31.5 (C(15)); 28.1 (C(21), C(28)); 27.0 (C(16)); 26.9 (C(2)); 26.0 (C(26)); 23.1 (C(23)); 21.1 (*Me*COO); 18.6 (C(6)); 17.9 (C(30)); 17.1 (C(27)); 16.6 (C(29)); 16.5 (C(19)); 16.0 (C(18)). MALDI-TOF-MS ($C_{44}H_{74}O_{14}$, 827.05): 865.8 ($[M+K]^+$), 849.9 ($[M+Na]^+$).

*(3β,12β,20*R*,24*E*)-3-[(β-*D*-Glucopyranosyl-(1 → 2)-β-*D*-glucopyranosyl)oxy]dammar-24-ene-12,20-diol* (=*(20*R*)-Ginsenoside Rg3*; **3**) [26]. Amorphous solid. ^{1}H-NMR (400 MHz, C_5D_5N): 5.37 (*d*, *J* = 7.7, H–C(1″)); 5.23 (*t*, *J* = 7.2, H–C(24)); 4.92 (*d*, *J* = 7.5, H–C(1′)); 4.55 (*dd*, *J* = 2.5, 11.6, H_a–C(6′)); 4.49 (*dd*, *J* = 3.3, 11.6, H_a–C(6″)); 4.45 (*dd*, *J* = 4.2, 11.6, H_b–C(6″)); 4.33 (H_b–C(6′)); 4.31 (H–C(4″)); 4.28 (H–C(3″)); 4.22 (H–C(2′)); 4.20 (H–C(3′)); 4.14 (*t*, *J* = 7.5, H–C(4′)); 4.12 (*t*, *J* = 7.5, H–C(2″)); 3.93 (H–C(5″)); 3.91 (H–C(12)); 3.89 (H–C(5′)); 3.29 (*dd*, *J* = 4.2, 11.6, H–C(3)); 2.47, 2.55 (CH_2(23)); 2.40 (*dd*, *J* = 6.9, 10.2, H–C(17)); 2.01 (H–C(13)); 1.81, 2.19 (CH_2(2)); 1.71, 1.75 (CH_2(22)); 1.70 (*s*, Me(26)); 1.66 (*s*, Me(27)); 1.51, 1.98 (CH_2(11)); 1.41 (H–C(9)); 1.40 (*s*, Me(21)); 1.37, 1.94 (CH_2(16)); 1.37, 1.50 (CH_2(6)); 1.30 (*s*, Me(28)); 1.23, 1.49 (CH_2(7)); 1.11 (*s*, Me(29)); 1.05, 1.57 (CH_2(15)); 1.02 (*s*, Me(18)); 0.99 (*s*, Me(30)); 0.82 (*s*, Me(19)); 0.76, 1.50 (CH_2(1)); 0.69 (br. *d*, *J* = 11.2, H–C(5)). ^{13}C-NMR (100 MHz, C_5D_5N): 130.9 (C(25)); 126.1 (C(24)); 106.1 (C(1″)); 105.2 (C(1′)); 89.0 (C(3)); 83.4 (C(2′)); 78.4 (C(5″)); 78.3 (C(3″)); 78.2 (C(5′)); 78.0 (C(3′)); 77.2 (C(2″)); 73.1 (C(20)); 71.7 (C(4′), C(4″)); 70.9 (C(12)); 62.9 (C(6′)); 62.7 (C(6″)); 56.4 (C(5)); 51.8 (C(14)); 50.7 (C(17)); 50.4 (C(9)); 49.3 (C(13)); 43.3 (C(22)); 40.1 (C(8)); 39.8 (C(4)); 39.2 (C(1)); 37.0 (C(10)); 35.2 (C(7)); 32.2 (C(11)); 31.5 (C(15)); 28.2 (C(28)); 26.8 (C(16)); 26.7 (C(2)); 25.9 (C(26)); 22.8 (C(21)); 22.7 (C(23)); 18.5 (C(6)); 17.8 (C(27)); 17.4 (C(30)); 16.7 (C(29)); 16.4 (C(19)); 15.9 (C(18)). MALDI-TOF-MS ($C_{42}H_{72}O_{13}$, 785.01): 807.6 ($[M+Na]^+$).

*(3β,12β,20*R*,24*E*)-3-[(6-*O*-Acetyl-β-*D*-glucopyranosyl-(1 → 2)-β-*D*-glucopyranosyl)oxy]dammar-24-ene-12,20-diol* (=*(20*R*)-6″-*O*-Acetylginsenoside Rg3*; **3a**). Amorphous solid. M.p. 252–255°. ^{1}H-NMR (400 MHz, C_5D_5N): 5.33 (*d*, *J* = 7.6, H–C(1″)); 4.92 (*d*, *J* = 7.6, H–C(1′)); 4.80 (*dd*, *J* = 5.2, 12.0, H_a–C(6″)); 4.78 (br. *d*, *J* = 12.0, H_b–C(6″)); 3.28 (*dd*, *J* = 4.4, 11.2, H–C(3)); 2.04 (*s*, Ac); 1.69 (*s*, Me(26)); 1.65 (*s*, Me(27)); 1.40 (*s*, Me(21)); 1.33 (*s*, Me(28)); 1.12 (*s*, Me(29)); 1.01 (*s*, Me(30)); 0.95 (*s*, Me(18)); 0.82 (*s*, Me(19)). ^{13}C-NMR (100 MHz, C_5D_5N): 171.2 (Me*C*OO); 130.9 (C(25)); 126.1 (C(24)); 106.2 (C(1″)); 105.0 (C(1′)); 89.2 (C(3)); 84.4 (C(2′)); 78.6 (C(3″)); 78.3 (C(5′)); 78.0 (C(3′)); 76.8 (C(5″)); 75.4 (C(2″)); 73.1 (C(20)); 71.4 (C(4′)); 71.1 (C(12), C(4″)); 64.9 (C(6″)); 62.9 (C(6′)); 56.5 (C(5)); 51.9 (C(14)); 50.9 (C(17)); 50.5 (C(9)); 49.3 (C(13)); 43.3 (C(22)); 40.1 (C(8)); 39.8 (C(4)); 39.2 (C(1)); 37.0 (C(10)); 35.3 (C(7)); 32.2 (C(11)); 31.5 (C(15)); 28.1 (C(28)); 26.9 (C(16)); 26.7 (C(2)); 26.0 (C(26)); 22.9 (C(21)); 22.7 (C(23)); 21.0 (*Me*COO); 18.6 (C(6)); 17.8 (C(27), C(30)); 16.6 (C(29)); 16.5 (C(19)); 15.9 (C(18)). MALDI-TOF-MS ($C_{44}H_{74}O_{14}$, 827.05): 865.8 ($[M+K]^+$), 849.8 ($[M+Na]^+$).

*(3β,12β,20*S*,24*E*)-3-[(6-*O*-Acetyl-β-*D*-glucopyranosyl)oxy]dammar-24-ene-12,20-diol* (=*6′-*O*-Acetylginsenoside Rh2*; **4a**). Amorphous solid. M.p. 155–157°. ^{1}H-NMR (400 MHz, C_5D_5N): 5.32 (*t*, *J* = 7.2, H–C(24)); 4.93 (br. *d*, *J* = 12.0, H_a–C(6′)); 4.88 (*d*, *J* = 7.6, H–C(1′)); 4.82 (*dd*, *J* = 5.2, 12.0, H_b–C(6′)); 3.92 (H–C(12)); 3.34 (*dd*, *J* = 4.0, 11.6, H–C(3)); 2.00 (*s*, Ac); 1.65 (*s*, Me(26)); 1.63 (*s*, Me(27)); 1.43 (*s*, Me(21)); 1.31 (*s*, Me(28)); 1.26 (*s*, Me(29)); 0.97 (*s*, Me(18), Me(30)); 0.82 (*s*, Me(19)). ^{13}C-NMR (100 MHz, C_5D_5N): 170.9

(Me*C*OO); 130.8 (C(25)); 126.4 (C(24)); 107.1 (C(1′)); 89.3 (C(3)); 78.6 (C(3′)); 75.6 (C(5′)); 75.0 (C(2′)); 73.0 (C(20)); 71.8 (C(4′)); 71.1 (C(12)); 64.9 (C(6′)); 56.5 (C(5)); 54.9 (C(17)); 51.8 (C(14)); 50.5 (C(9)); 48.6 (C(13)); 40.1 (C(8)); 39.7 (C(4)); 39.3 (C(1)); 37.1 (C(10)); 36.0 (C(22)); 35.2 (C(7)); 32.1 (C(11)); 31.4 (C(15)); 28.2 (C(28)); 28.2 (C(21)); 26.9 (C(16)); 26.8 (C(2)); 25.9 (C(26)); 23.1 (C(23)); 20.9 (*Me*COO); 18.6 (C(6)); 17.8 (C(30)); 17.1 (C(27)); 16.8 (C(29)); 16.4 (C(19)); 15.9 (C(18)). MALDI-TOF-MS ($C_{38}H_{64}O_9$, 664.91): 687.7 ($[M+Na]^+$).

*(3β,6α,12β,20*S*,24*E*)-20-[(β-*D*-Glucopyranosyl)oxy]-6-[(α-*L*-rhamnopyranosyl-(1 → 2)-β-*D*-glucopyranosyl)-oxy]dammar-24-ene-3,12-diol* (= *Ginsenoside Re*; **5**) [25]. Amorphous solid. ^{1}H-NMR (400 MHz, C_5D_5N): 6.44 (br. *d*, H−C(1″)); 5.24 (H−C(24)); 5.20 (*d*, *J* = 7.0, H−C(1′)); 5.14 (*d*, *J* = 7.5, H−C(1‴)); 4.68 (H−C(6)); 4.09 (H−C(12)); 3.44 (H−C(3)); 2.07 (*s*, Me(28)); 1.78 (*d*, *J* = 6.0, Me(6″)); 1.59 (*s*, Me(21), Me(26)); 1.56 (*s*, Me(27)); 1.34 (*s*, Me(29)); 1.14 (*s*, Me(18)); 0.94 (*s*, Me(19)); 0.92 (*s*, Me(30)). ^{13}C-NMR (100 MHz, C_5D_5N): 131.1 (C(25)); 126.0 (C(24)); 102.0 (C(1′)); 101.9 (C(1″)); 98.4 (C(1‴)); 83.4 (C(20)); 79.5 (C(2′)); 79.2 (C(3‴)); 78.6 (C(3′)); 78.5 (C(5′)); 78.4 (C(3), C(5‴)); 75.2 (C(2″)); 74.2 (C(4″), C(6)); 72.6 (C(3″)); 72.5 (C(2″)); 71.5 (C(4′), C(4‴)); 70.4 (C(12)); 69.6 (C(5″)); 63.2 (C(6′), C(6‴)); 60.9 (C(5)); 51.9 (C(14)); 51.5 (C(17)); 49.6 (C(9)); 49.1 (C(13)); 46.0 (C(7)); 41.3 (C(8)); 40.1 (C(4)); 39.7 (C(1), C(10)); 36.1 (C(22)); 32.3 (C(28)); 31.0 (C(15)); 30.8 (C(11)); 27.8 (C(2)); 26.7 (C(16)); 25.9 (C(26)); 23.4 (C(23)); 22.5 (C(21)); 18.9 (C(6″)); 17.9 (C(19)); 17.7 (C(27)); 17.6 (C(18)); 17.3 (C(29), C(30)). MALDI-TOF-MS ($C_{48}H_{82}O_{18}$, 947.15): 969.8 ($[M+Na]^+$).

*(3β,6α,12β,20*S*,24*E*)-6-[(4-*O*-Acetyl-α-*L*-rhamnopyranosyl-(1 → 2)-β-*D*-glucopyranosyl)oxy]-20-[(β-*D*-glu-copyranosyl)oxy]dammar-24-ene-3,12-diol* (= *4″-O-Acetylginsenoside Re*; **5a**). Amorphous solid. M.p. 175–178°. $[\alpha]_D^{18} = -15.94$ (*c* = 0.5, MeOH). ^{1}H-NMR (400 MHz, C_5D_5N): 6.51 (br. *d*, H−C(1″)); 5.83 (*t*, *J* = 10.0, H−C(4″)); 5.23 (*d*, *J* = 6.8, H−C(1′)); 5.22 (H−C(24)); 5.16 (*d*, *J* = 8.0, H−C(1‴)); 4.97 (*dq*, *J* = 6.4, 10.0, H−C(5″)); 4.78 (br. *d*, H−C(2″)); 4.68 (H−C(6)); 4.65 (H−C(3″)); 4.49 (br. *d*, *J* = 11.2, H_a−C(6′)); 4.46 (br. *d*, *J* = 12.4, H_a−C(6‴)); 4.34 (H_b−C(6′)); 4.32 (H−C(2′)); 4.30 (H_b−C(6‴)); 4.28 (H−C(3′)); 4.20 (H−C(3‴)); 4.16 (H−C(4‴)); 4.07 (H−C(12)); 3.98 (*t*, *J* = 7.5, H−C(4′)); 3.97 (H−C(2‴)); 3.94 (H−C(5′)); 3.90 (H−C(5‴)); 3.55 (H−C(3)); 2.46 (H−C(17)); 2.27, 2.46 (CH_2(23)); 2.08 (*s*, Me(28)); 2.02, 1.93 (CH_2(7)); 2.02, 1.48 (CH_2(11)); 1.98 (*s*, Ac); 1.92 (H−C(13)); 1.86, 1.65 (CH_2(2)); 1.78, 2.36 (CH_2(22)); 1.74, 1.24 (CH_2(16)); 1.60 (*s*, Me(26)); 1.60 (*s*, Me(21)); 1.58 (*s*, Me(27)); 1.52 (*d*, *J* = 6.0, Me(6″)); 1.48, 0.85 (CH_2(15)); 1.48 (H−C(9)); 1.38 (H−C(5)); 1.36 (*s*, Me(29)); 1.25 (*s*, Me(18)); 0.96, 1.80 (CH_2(1)); 0.96 (*s*, Me(19)); 0.89 (*s*, Me(30)). ^{13}C-NMR (100 MHz, C_5D_5N): 171.0 (Me*C*OO); 131.1 (C(25)); 126.0 (C(24)); 101.8 (C(1′)); 101.7 (C(1″)); 98.4 (C(1‴)); 83.4 (C(20)); 79.5 (C(2′)); 79.2 (C(3‴)); 78.8 (C(5‴)); 78.6 (C(3′)); 78.5 (C(5′)); 78.4 (C(3)); 76.2 (C(4″)); 75.3 (C(2‴)); 74.8 (C(6)); 72.6 (C(4′)); 72.4 (C(2″)); 71.5 (C(4‴)); 70.4 (C(12)); 69.9 (C(3″)); 67.1 (C(5″)); 63.0 (C(6′)); 62.8 (C(6‴)); 61.1 (C(5)); 51.9 (C(14)); 51.5 (C(17)); 49.7 (C(9)); 49.1 (C(13)); 46.1 (C(7)); 41.3 (C(8)); 40.1 (C(4)); 39.8 (C(10)); 39.4 (C(1)); 36.0 (C(22)); 32.2 (C(28)); 30.9 (C(11), C(15)); 27.9 (C(2)); 26.7 (C(16)); 25.9 (C(26)); 23.4 (C(23)); 22.5 (C(21)); 21.2 (*Me*COO); 18.2 (C(6″)); 17.9 (C(19)); 17.7 (C(27)); 17.5 (C(18)); 17.3 (C(30)); 17.2 (C(29)). MALDI-TOF-MS ($C_{50}H_{84}O_{19}$, 989.19): 1011.8 ($[M+Na]^+$).

*(3β,6α,12β,20*S*,24*E*)-20-[(β-*D*-Glucopyranosyl)oxy]-6-[(α-*L*-rhamnopyranosyl-(1 → 2)-6-*O*-acetyl-β-*D*-glu-copyranosyl)oxy]dammar-24-ene-3,12-diol* (= *6′-O-Acetylginsenoside Re*; **5b**). Amorphous solid. M.p. 186–189°. ^{1}H-NMR (400 MHz, C_5D_5N): 6.46 (br. *d*, H−C(1″)); 5.23 (H−C(1′)); 5.22 (H−C(24)); 5.17 (*d*, *J* = 7.5, H−C(1‴)); 4.98 (br. *d*, *J* = 12.1, H_a−C(6′)); 4.92 (H−C(5″)); 4.76 (br. *d*, H−C(2″)); 4.70 (H−C(6)); 4.62 (H−C(3″)); 4.62 (H_b−C(6′)); 4.46 (br. *d*, *J* = 12.4, H_a−C(6‴)); 4.31 (H−C(2′)); 4.30 (H−C(4″)); 4.30 (H_b−C(6‴)); 4.28 (H−C(3′)); 4.20 (H−C(3‴)); 4.16 (H−C(4‴)); 4.09 (H−C(12)); 4.02 (*t*, *J* = 7.5, H−C(4′)); 3.99 (H−C(2‴)); 3.92 (H−C(5‴)); 3.92 (H−C(5′)); 3.44 (H−C(3)); 2.52, 2.27 (CH_2(23)); 2.46 (H−C(17)); 2.33, 1.78 (CH_2(22)); 2.22, 1.95 (CH_2(7)); 2.11 (*s*, Me(28)); 2.05 (*s*, Ac); 2.02, 1.48 (CH_2(11)); 1.93 (H−C(13)); 1.80, 1.62 (CH_2(2)); 1.76, 0.95 (CH_2(1)); 1.76 (*d*, *J* = 6.0, Me(6″)); 1.74, 1.24 (CH_2(16)); 1.64 (*s*, Me(26)); 1.62 (*s*, Me(21)); 1.54 (*s*, Me(27)); 1.54 (H−C(9)); 1.50, 0.89 (CH_2(15)); 1.37 (H−C(5)); 1.35 (*s*, Me(29)); 1.17 (*s*, Me(18)); 0.95 (*s*, Me(19)); 0.94 (*s*, Me(30)). ^{13}C-NMR (100 MHz, C_5D_5N): 170.8 (Me*C*OO); 131.1 (C(25)); 126.0 (C(24)); 102.0 (C(1′), C(1″)); 98.0 (C(1‴)); 83.4 (C(20)); 79.5 (C(2′)); 79.2 (C(3‴)); 78.5 (C(3′)); 78.4 (C(3), C(5‴)); 75.0 (C(5′)); 74.8 (C(2‴)); 74.6 (C(6)); 74.2 (C(4″)); 72.5 (C(3″)); 72.3 (C(2″), C(4′)); 71.6 (C(4‴)); 70.1 (C(12)); 69.4 (C(5″)); 64.8 (C(6′); 63.0 (C(6‴)); 60.8 (C(5)); 51.8 (C(14)); 51.4 (C(17)); 49.6 (C(9)); 49.1 (C(13)); 46.0 (C(7)); 41.2 (C(8)); 40.0 (C(4)); 39.4 (C(1), C(10)); 36.0 (C(22)); 32.2 (C(28)); 31.0 (C(15)); 30.9 (C(11)); 27.8 (C(2)); 26.7 (C(16)); 25.8 (C(26)); 23.1 (C(23)); 22.5 (C(21)); 20.8 (*Me*COO); 18.8 (C(6″)); 17.8 (C(19)); 17.6 (C(18)); 17.5 (C(27)); 17.4 (C(30)); 17.3 (C(29)). MALDI-TOF-MS ($C_{50}H_{84}O_{19}$, 989.19): 1027.8 ($[M+K]^+$), 1011.8 ($[M+Na]^+$).

*(3β,6α,12β,20*S*,24*E*)-20-[(6-*O*-Acetyl-β-*D*-glucopyranosyl)oxy]-6-[(α-*L*-rhamnopyranosyl-(1 → 2)-β-*D*-glucopyranosyl)oxy]dammar-24-ene-3,12-diol* (=6‴-O-*Acetylginsenoside Re*; **5c**). Amorphous solid. M.p. 180–183°. ^{1}H-NMR (400 MHz, C_5D_5N): 6.51 (br. *d*, H−C(1″)); 5.24 (H−C(1′)); 5.23 (H−C(24)); 5.08 (*d*, *J* = 7.6, H−C(1‴)); 4.96 (br. *d*, *J* = 12.1, H_a−C(6‴)); 4.92 (H−C(5″)); 4.81 (br. *d*, H−C(2″)); 4.70 (H−C(6)); 4.66 (H−C(3″)); 4.60 (H_b−C(6‴)); 4.50 (H_a−C(6′)); 4.36 (H−C(2′)); 4.34 (H_b−C(6′)); 4.32 (H−C(3′)); 4.30 (H−C(4″)); 4.18 (*t*, *J* = 7.5, H−C(4′)); 4.17 (H−C(3‴)); 4.14 (H−C(4‴)); 4.10 (H−C(12)); 3.97 (H−C(2‴)); 3.95 (H−C(5‴)); 3.95 (H−C(5′)); 3.46 (*dd*, *J* = 5.2, 11.6, H−C(3)); 2.49, 2.22 (CH_2(23)); 2.48 (H−C(17)); 2.38, 1.82 (CH_2(22)); 2.08 (*s*, Me(28)); 2.02, 1.49 (CH_2(11)); 2.02 (*s*, Ac); 2.00, 2.16 (CH_2(7)); 1.92 (H−C(13)); 1.87, 1.69 (CH_2(2)); 1.78, 0.97 (CH_2(1)); 1.76 (*d*, *J* = 6.0, Me(6″)); 1.73, 1.26 (CH_2(16)); 1.59 (*s*, Me(21), Me(26); 1.55 (*s*, Me(27)); 1.54 (H−C(9)); 1.50, 0.92 (CH_2(15)); 1.38 (H−C(5)); 1.32 (*s*, Me(29)); 1.24 (*s*, Me(18)); 1.03 (*s*, Me(19)); 1.01 (*s*, Me(30)). ^{13}C-NMR (100 MHz, C_5D_5N): 170.8 (Me*C*OO); 131.0 (C(25)); 126.0 (C(24)); 102.1 (C(1′)); 101.4 (C(1″)); 98.3 (C(1‴)); 83.3 (C(20)); 79.5 (C(2′)); 79.3 (C(3‴)); 78.3 (C(3), C(3′), C(5′)); 75.3 (C(5‴)); 75.2 (C(2‴)); 74.6 (C(6)); 74.2 (C(4″)); 72.5 (C(3″)); 72.3 (C(2″), C(4′)); 71.6 (C(4‴)); 70.3 (C(12)); 69.4 (C(5″)); 65.0 (C(6‴)); 63.2 (C(6′)); 60.7 (C(5)); 51.7 (C(17)); 51.5 (C(14)); 49.6 (C(9)); 49.2 (C(13)); 46.1 (C(7)); 41.3 (C(8)); 39.9 (C(4), C(10)); 39.4 (C(1)); 36.1 (C(22)); 32.2 (C(28)); 30.9 (C(11), C(15)); 27.8 (C(2)); 26.6 (C(16)); 25.8 (C(26)); 23.3 (C(23)); 22.4 (C(21)); 20.9 (*Me*COO); 18.7 (C(6″)); 17.7 (C(18), C(19)); 17.5 (C(27)); 17.3 (C(29), C(30)). MALDI-TOF-MS ($C_{50}H_{84}O_{19}$, 989.19): 1027.6 ($[M+K]^+$), 1011.7 ($[M+Na]^+$).

*(3β,12β,20*S*,24*E*)-3-[(β-*D*-Glucopyranosyl)oxy]-20-[(β-*D*-glucopyranosyl-(1 → 6)-β-*D*-glucopyranosyl)oxy]-dammar-24-en-12-ol (=Gypenoside XVII*; **6**) [24]. Amorphous solid. ^{1}H-NMR (400 MHz, C_5D_5N): 5.31 (*t*, *J* = 6.9, H−C(24)); 5.10 (*d*, *J* = 7.6, H−C(1″)); 5.08 (*d*, *J* = 7.6, H−C(1‴)); 4.95 (*d*, *J* = 8.0, H−C(1′)); 4.17 (H−C(12)); 3.36 (*dd*, *J* = 3.9, 11.6, H−C(3)); 1.90 (*s*, Me(26)); 1.65 (*s*, Me(21), Me(27)); 1.30 (*s*, Me(28)); 0.99 (*s*, Me(29)); 0.97 (*s*, Me(30)); 0.93 (*s*, Me(18)); 0.78 (*s*, Me(19)). ^{13}C-NMR (100 MHz, C_5D_5N): 131.1 (C(25)); 126.0 (C(24)); 107.0 (C(1′)); 105.4 (C(1‴)); 98.2 (C(1″)); 88.9 (C(3)); 83.5 (C(20)); 79.3 (C(3‴)); 78.8 (C(3′)); 78.4 (C(3‴), C(5′), C(5‴)); 77.1 (C(5″)); 75.8 (C(2′)); 75.3 (C(2‴)); 74.9 (C(2″)); 72.0 (C(4′)); 71.8 (C(4‴)); 71.6 (C(4″)); 70.2 (C(6″), C(12)); 63.2 (C(6′)); 62.9 (C(6‴)); 56.5 (C(5)); 51.7 (C(17)); 51.5 (C(14)); 50.3 (C(9)); 49.6 (C(13)); 40.1 (C(8)); 39.7 (C(4)); 39.3 (C(1)); 37.0 (C(10)); 36.3 (C(22)); 35.2 (C(7)); 30.9 (C(11)); 30.8 (C(15)); 28.2 (C(28)); 26.8 (C(16)); 26.7 (C(2)); 25.8 (C(26)); 23.3 (C(23)); 22.5 (C(21)); 18.5 (C(6)); 18.0 (C(30)); 18.0 (C(27)); 16.8 (C(29)); 16.3 (C(19)); 16.1 (C(18)). MALDI-TOF-MS ($C_{48}H_{82}O_{18}$; 947.15): 970.1 ($[M+Na]^+$).

*(3β,12β,20*S*,24*E*)-20-[(6-*O*-Acetyl-β-*D*-glucopyranosyl-(1 → 6)-β-*D*-glucopyranosyl)oxy]-3-[(β-*D*-glucopyranosyl)oxy]dammar-24-en-12-ol* (=6‴-O-*Acetylgypenoside XVII*; **6a**). Amorphous solid. M.p. 145–148°. ^{1}H-NMR (400 MHz, C_5D_5N): 5.30 (*t*, *J* = 7.4, H−C(24)); 5.12 (*d*, *J* = 7.6, H−C(1″)); 5.04 (*d*, *J* = 7.6, H−C(1‴)); 4.93 (*d*, *J* = 8.0, H−C(1′)); 4.90 (br. *d*, *J* = 11.2, H_a−C(6‴)); 4.72 (H_b−(6‴)); 4.72 (br. *d*, *J* = 11.6, H_a−C(6″)); 4.59 (br. *d*, *J* = 11.6, H_a−C(6′)); 4.38 (*dd*, *J* = 5.6, 11.6, H_b−C(6′)); 4.32 (H_b−C(6″)); 4.24 (H−C(4′)); 4.23 (H−C(3′)); 4.20 (H−C(4‴)); 4.18 (H−C(3‴)); 4.15 (H−C(12)); 4.14 (H−C(3″)); 4.10 (H−C(2‴)); 4.05 (H−C(4″)); 4.02 (H−C(5″); 4.02 (H−C(2′)); 4.00 (H−C(5′)); 3.98 (H−C(5‴)); 3.92 (H−C(2″)); 3.35 (*dd*, *J* = 4.4, 12.0, H−C(3)); 2.58, 2.37 (CH_2(23)); 2.58 (H−C(17)); 2.20, 1.80 (CH_2(2)); 1.98 (*s*, Ac); 1.98 (H−C(13)); 1.96, 1.48 (CH_2(11)); 1.82, 1.36 (CH_2(16)); 1.81, 2.38 (CH_2(22)); 1.65 (*s*, Me(21)); 1.63 (*s*, Me(27)); 1.60 (*s*, Me(26)); 1.52, 0.77 (CH_2(1)); 1.50, 1.36 (CH_2(6)); 1.48, 1.20 (CH_2(7)); 1.37 (H−C(9)); 1.33 (*s*, Me(28)); 0.99, 1.56 (CH_2(15)); 0.98 (*s*, Me(29)); 0.97 (*s*, Me(30)); 0.93 (*s*, Me(18)); 0.78 (*s*, Me(19)); 0.72 (H−C(5)). ^{13}C-NMR (100 MHz, C_5D_5N): 171.1 (Me*C*OO); 131.1 (C(25)); 126.1 (C(24)); 107.0 (C(1′)); 105.7 (C(1‴)); 98.2 (C(1″)); 89.0 (C(3)); 83.6 (C(20)); 79.4 (C(3″)); 78.8 (C(3′)); 78.5 (C(5′)); 78.2 (C(3‴)); 77.0 (C(5″)); 75.9 (C(2′)); 75.2 (C(2‴), C(5‴)); 75.0 (C(2″)); 72.0 (C(4′)); 71.6 (C(4″), C(4‴)); 70.8 (C(6″)); 70.2 (C(12)); 64.9 (C(6‴)); 63.2 (C(6′)); 56.5 (C(5)); 51.7 (C(17)); 51.5 (C(14)); 50.3 (C(9)); 49.6 (C(13)); 40.1 (C(8)); 39.8 (C(4)); 39.3 (C(1)); 37.0 (C(10)); 36.3 (C(22)); 35.2 (C(7)); 30.9 (C(15)); 30.9 (C(11)); 28.2 (C(28)); 26.8 (C(2)); 26.8 (C(16)); 26.0 (C(26)); 23.3 (C(23)); 22.4 (C(21)); 21.0 (*Me*COO); 18.5 (C(6)); 18.1 (C(27)); 17.5 (C(30)); 16.9 (C(29)); 16.4 (C(19)); 16.1 (C(18)). MALDI-TOF-MS ($C_{50}H_{83}O_{19}$; 988.18): 1027.8 ($[M+K]^+$), 1011.9 ($[M+Na]^+$).

*(3β,5α,6α,8β,9α,10β,12β,13β,14α,17*S*)-4,4,8,10,14-pentamethyl-6-[(α-*L*-rhamnopyranosyl-(1 → 2)-β-*D*-glucopyranosyl)oxy]-17-[2,3,4,5-tetrahydro-5-(1-hydroxy-1-methylethyl)-2-methylfuran-2-yl]gonan-3,12-diol* (=*Pseudoginsenoside F11*; **7**)[3]) [27][28]. Amorphous solid. ^{1}H-NMR (400 MHz, C_5D_5N): 6.49 (br. *d*, H−C(1″)); 5.25 (*d*, *J* = 6.8, H−C(1′)); 4.68 (H−C(6)); 4.07 (*dt*, *J* = 4.8, 10.4, H−C(12)); 3.94 (*t*, *J* = 7.6, H−C(24)); 3.46 (*dd*, *J* = 10.8, 4.8, H−C(3)); 2.10 (*s*, Me(28)); 1.78 (*d*, *J* = 6.0, Me(6″)); 1.60 (*s*, Me(21)); 1.45

[3]) Atom numbering according to dammarane with a cyclized side chain (see chemical formulae).

(*s*, Me(26)); 1.32 (*s*, Me(29)); 1.23 (*s*, Me(18)); 1.19 (*s*, Me(27)); 0.93 (*s*, Me(19)); 0.88 (*s*, Me(30)). ^{13}C-NMR (100 MHz, C_5D_5N): 102.1 (C(1″)); 101.8 (C(1′)); 86.8 (C(20)); 85.7 (C(24)); 79.5 (C(2′)); 78.6 (C(3)); 78.5 (C(3′)); 78.4 (C(5′)); 74.3 (C(4″)); 74.2 (C(6)); 72.7 (C(3″)); 72.5 (C(4′)); 72.3 (C(2″)); 71.2 (C(12)); 70.4 (C(5″)); 69.5 (C(25)); 63.1 (C(6′)); 61.0 (C(5)); 52.2 (C(14)); 50.2 (C(9)); 49.4 (C(17)); 48.3 (C(13)); 46.1 (C(7)); 41.2 (C(8)); 40.1 (C(4)); 39.6 (C(10)); 39.6 (C(1)); 32.8 (C(22)); 32.5 (C(15)); 32.2 (C(11)); 31.7 (C(28)); 28.8 (C(23)); 27.8 (C(27)); 27.6 (C(2)); 27.2 (C(21)); 27.1 (C(26)); 25.5 (C(16)); 18.8 (C(6")); 18.3 (C(30)); 17.9 (C(18)); 17.7 (C(19)); 17.0 (C(29)). Maldi-TOF-MS ($C_{42}H_{72}O_{14}$, 801.01): 823.5 ($[M+Na]^+$).

*(3β,5α,6α,8β,9α,10β,12β,13β,14α,17*S*)-6-[(4-*O*-Acetyl-α-*L*-rhamnopyranosyl-(1 → 2)-β-*D*-glucopyranosyl)-oxy]-4,4,8,10,14-pentamethyl-17-[2,3,4,5-tetrahydro-5-(1-hydroxy-1-methylethyl)-2-methylfuran-2-yl]gonan-3,12-diol* (=*4″-*O*-Acetylpseudoginsenoside F11*; **7a**). Amorphous solid. M.p. 170–173°. $[\alpha]_D^{19} = -25.47$ ($c = 0.1$, MeOH). ^{1}H-NMR (400 MHz, C_5D_5N): 6.51 (br. *d*, H–C(1″)); 5.83 (*t*, *J* = 10.0, H–C(4″)); 5.22 (*d*, *J* = 7.6, H–C(1′)); 4.99 (*dq*, *J* = 6.4, 10.0, H–C(5″)); 4.77 (br. *d*, H–C(2″)); 4.72 (H–C(3″)); 4.70 (H–C(6)); 4.53 (br. *d*, *J* = 9.6, H_a–C(6′)); 4.35 (H_b–C(6′)); 4.32 (H–C(2′)); 4.28 (H–C(3′)); 4.18 (*t*, *J* = 8.8, H–C(4′)); 3.95 (*t*, *J* = 7.6, H–C(5′)); 3.94 (H–C(24)); 3.68 (*dt*, *J* = 4.4, 10.4, H–C(12)); 3.58 (*dd*, *J* = 6.4, 11.2, H–C(3)); 2.25, 1.84 (CH_2(7)); 2.15 (H–C(17)); 2.12, 1.84 (CH_2(23)); 2.10 (H–C(13)); 2.08 (*s*, Ac); 2.07 (*s*, Me(28)); 1.87, 1.64 (CH_2(2)); 1.78, 1.40 (CH_2(16)); 1.78, 1.27 (CH_2(11)); 1.76, 0.99 (CH_2(1)); 1.57, 1.23 (CH_2(22)); 1.57, 1.12 (CH_2(15)); 1.54 (H–C(9)); 1.53 (*d*, *J* = 6.4, Me(6″)); 1.46 (*s*, Me(26)); 1.40 (H–C(5)); 1.33 (*s*, Me(29)); 1.27 (*s*, Me(21)); 1.24 (*s*, Me(18)); 1.21 (*s*, Me(27)); 0.95 (*s*, Me(19)); 0.85 (*s*, Me(30)). ^{13}C-NMR (100 MHz, C_5D_5N): 171.1 (Me*C*OO); 101.8 (C(1′), C(1″)); 86.8 (C(20)); 85.7 (C(24)); 79.5 (C(2′)); 78.8 (C(3′)); 78.6 (C(3), C(5′)); 76.2 (C(4″)); 74.4 (C(6)); 72.6 (C(4′)); 72.4 (C(2″)); 71.2 (C(12)); 70.5 (C(3″)); 69.8 (C(25)); 67.1 (C(5″)); 63.0 (C(6′)); 61.2 (C(5)); 52.2 (C(14)); 50.3 (C(9)); 49.4 (C(17)); 48.3 (C(13)); 46.2 (C(7)); 41.2 (C(8)); 40.1 (C(4)); 39.7 (C(1), C(10)); 32.9 (C(22)); 32.6 (C(15)); 32.2 (C(11)); 31.8 (C(28)); 28.9 (C(23)); 27.9 (C(27)); 27.6 (C(2)); 27.2 (C(21)); 27.1 (C(26)); 25.6 (C(16)); 21.3 (*Me*COO); 18.3 (C(6″)); 18.2 (C(30)); 17.9 (C(18)); 17.6 (C(19)); 17.0 (C(29). MALDI-TOF-MS ($C_{44}H_{74}O_{15}$, 843.05): 865.6 ($[M+Na]^+$).

*(3β,5α,6α,8β,9α,10β,12β,13β,14α,17*S*)-4,4,8,10,14-Pentamethyl-6-[(α-*L*-rhamnopyranosyl-(1 → 2)-6-*O*-acetyl-β-*D*-glucopyranosyl)oxy]-17-[2,3,4,5-tetrahydro-5-(1-hydroxy-1-methylethyl)-2-methylfuran-2-yl]gonan-3,12-diol* (=*6′-*O*-Acetylpseudoginsenoside F11*; **7b**). Amorphous solid. M.p. 155–158°. $[\alpha]_D^{18} = -10.91$ ($c = 0.3$, MeOH). ^{1}H-NMR (400 MHz, C_5D_5N): 6.46 (br. *d*, H–C(1″)); 5.22 (*d*, *J* = 6.4, H–C(1′)); 5.01 (br. *d*, *J* = 11.2, H_a–C(6′)); 4.95 (*dq*, *J* = 6.4, 9.6, H–C(5″)); 4.76 (br. *d*, H–C(2″)); 4.69 (*dd*, *J* = 4.0, 11.2, H_b–C(6′)); 4.66 (H–C(6)); 4.64 (H–C(3″)); 4.34 (*t*, *J* = 9.6, H–C(4″)); 4.30 (H–C(2′)); 4.28 (H–C(3′)); 4.03 (*t*, *J* = 7.2, H–C(4′)); 3.94 (*t*, *J* = 7.2, H–C(5′)); 3.94 (H–C(24)); 3.73 (*dt*, *J* = 5.6, 9.6, H–C(12)); 3.47 (*dd*, *J* = 4.8, 11.2, H–C(3)); 2.22 (H–C(17)); 2.15, 1.90 (CH_2(7)); 2.14, 1.84 (CH_2(23)); 2.10 (H–C(13)); 2.08 (*s*, Ac); 2.07 (*s*, Me(28)); 1.85, 1.62 (CH_2(2)); 1.84, 1.32 (CH_2(11)); 1.80, 1.28 (CH_2(16)); 1.77 (*d*, *J* = 6.4, Me(6″)); 1.72, 0.96 (CH_2(1)); 1.60 (H–C(9)); 1.57, 1.02 (CH_2(15)); 1.56, 1.25 (CH_2(22)); 1.46 (*s*, Me(26)); 1.38 (H–C(5)); 1.29 (*s*, Me(29)); 1.25 (*s*, Me(18), Me(21), Me(27)); 0.98 (*s*, Me(19)); 0.95 (*s*, Me(30)). ^{13}C-NMR (100 MHz, C_5D_5N): 171.0 (Me*C*OO); 102.2 (C(1″)); 101.4 (C(1′)); 86.8 (C(20)); 85.7 (C(24)); 79.1 (C(2′)); 78.5 (C(3)); 78.4 (C(3′)); 75.5 (C(5′)); 74.4 (C(6)); 74.2 (C(4″)); 72.5 (C(3″)); 72.4 (C(2″), C(4′)); 71.3 (C(12)); 70.5 (C(5″)); 69.5 (C(25)); 65.0 (C(6′)); 60.8 (C(5)); 52.3 (C(14)); 50.1 (C(9)); 49.5 (C(17)); 48.4 (C(13)); 46.2 (C(7)); 41.2 (C(8)); 40.0 (C(4)); 39.7 (C(1)); 39.5 (C(10)); 32.9 (C(22)); 32.5 (C(15)); 32.2 (C(11)); 31.7 (C(28)); 28.9 (C(23)); 27.8 (C(27)); 27.6 (C(2)); 27.2 (C(21)); 27.1 (C(26)); 25.6 (C(16)); 21.0 (*Me*COO); 18.8 (C(6″)); 18.3 (C(30)); 17.8 (C(18)); 17.6 (C(19)); 16.9 (C(29). MALDI-TOF-MS ($C_{44}H_{74}O_{15}$, 843.05): 865.6 ($[M+Na]^+$).

*(3β,12β,20*S*,24*E*)-6-[(6-*O*-Acetyl-β-*D*-glucopyranosyl)oxy]dammar-24-ene-12,20-diol* (=*6′-*O*-Acetylginsenoside Rh1*; **8a**) [25]. Amorphous solid. M.p. 153–157°. ^{1}H-NMR (400 MHz, C_5D_5N): 5.32 (*t*, *J* = 6.8, H–C(24)); 5.06 (br. *d*, *J* = 12.0, H_a–C(6′)); 5.01 (*d*, *J* = 7.6, H–C(1′)); 4.62 (*dd*, *J* = 4.8, 12.0, H_b–C(6′)); 4.40 (*dt*, *J* = 2.8, 10.4, H–C(6)); 4.22 (*t*, *J* = 8.4, H–C(3′)); 4.06 (H–C(2′)); 3.98 (H–C(4′), H–C(5′)); 3.92 (H–C(12)); 3.50 (*dd*, *J* = 4.4, 11.2, H–C(3)); 2.58, 2.28 (CH_2(23)); 2.28 (H–C(17)); 2.15, 1.57 (CH_2(11)); 2.08 (*s*, Ac); 2.07 (*s*, Me(28)); 2.05, 1.70 (CH_2(22)); 2.04 (H–C(13)); 1.95, 2.48 (CH_2(7)); 1.85, 1.92 (CH_2(2)); 1.85, 1.40 (CH_2(16)); 1.72, 1.20 (CH_2(15)); 1.64 (*s*, Me(26)); 1.62 (*s*, Me(27)); 1.57 (H–C(9)); 1.54 (*s*, Me(29)); 1.42 (*s*, Me(21)); 1.42 (H–C(5)); 1.23 (*s*, Me(18)); 1.03 (*s*, Me(19)); 1.02, 1.68 (CH_2(1)); 0.93 (*s*, Me(30)). ^{13}C-NMR (100 MHz, C_5D_5N): 171.0 (Me*C*OO); 130.9 (C(25)); 126.4 (C(24)); 105.9 (C(1′)); 79.8 (C(6)); 79.2 (C(3′)); 78.6 (C(3)); 75.4 (C(2′)); 75.1 (C(5′)); 73.1 (C(20)); 71.5 (C(4′)); 71.1 (C(12)); 65.2 (C(6′)); 61.5 (C(5)); 54.8 (C(17)); 51.8 (C(14)); 50.2 (C(9)); 48.4 (C(13)); 45.5 (C(7)); 41.3 (C(8)); 40.4 (C(4)); 39.8 (C(10)); 39.5 (C(1)); 35.9 (C(22)); 32.2 (C(11)); 32.1(C(28)); 31.5 (C(15)); 27.9 (C(2)); 27.1 (C(26)); 26.8 (C(16)); 25.9 (C(21)); 23.1 (C(23)); 21.0 (*Me*COO); 17.8 (C(27)); 17.7 (C(19)); 17.5 (C(18)); 17.1 (C(30)); 16.6 (C(29)). MALDI-TOF-MS ($C_{38}H_{64}O_9$, 664.91): 703.9 ($[M+K]^+$).

(3β,6α,12β,20S,24E)-6-[(4-O-Acetyl-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyl)oxy]dammar-24-ene-3,12,20-triol (=*4″-O-Acetylginsenoside Rg2*; **9a**) [25]. Amorphous solid. ^{1}H-NMR (400 MHz, C_5D_5N): 6.52 (br. *d*, H−C(1″)); 5.83 (*t*, *J* = 10.0, H−C(4″)); 5.33 (*t*, *J* = 6.8, H−C(24)); 5.23 (*d*, *J* = 6.4, H−C(1′)); 4.99 (*dq*, *J* = 6.4, 10.0, H−C(5″)); 4.77 (br. *d*, H−C(2″)); 4.71 (*dd*, *J* = 3.2, 10.0, H−C(3″)); 4.66 (H−C(6)); 4.52 (br. *d*, *J* = 11.6, H_a−C(6′)); 4.38 (*dd*, *J* = 4.8, 11.6, H_b−C(6′)); 4.32 (H−C(2′), H−C(3′)); 4.20 (*t*, *J* = 7.6, H−C(4′)); 3.97 (H−C(5′)); 3.86 (br. *t*, *J* = 9.2, H−C(12)); 3.58 (*dd*, *J* = 4.8, 11.0, H−C(3)); 2.28, 2.58 (CH_2(23)); 2.26, 1.98 (CH_2(7)); 2.25 (H−C(17)); 2.10 (H−C(13)); 2.09 (*s*, Me(28)); 1.98, 1.50 (CH_2(11)); 1.97 (*s*, Ac); 1.88 (CH_2(2)); 1.66, 0.98 (CH_2(1)); 1.66 (*s*, Me(26)); 1.65, 2.00 (CH_2(22)); 1.62 (*s*, Me(27)); 1.54 (*d*, *J* = 6.4, Me(6″)); 1.50, 0.84 (CH_2(15)); 1.50 (H−C(9)); 1.39 (H−C(5)); 1.38 (*s*, Me(21)); 1.36 (*s*, Me(29)); 1.24, 1.76 (CH_2(16)); 1.19 (*s*, Me(18)); 0.97 (*s*, Me(19)); 0.88 (*s*, Me(30)). ^{13}C-NMR (100 MHz, C_5D_5N): 170.9 (Me*C*OO); 130.9 (C(25)); 126.4 (C(24)); 101.8 (C(1′)); 101.7 (C(1″)); 79.5 (C(2′)); 78.7 (C(3′)); 78.5 (C83), C(5′)); 76.2 (C(4″)); 74.5 (C(6)); 73.0 (C(20)); 72.6 (C(4′)); 72.3 (C(2″)); 71.0 (C(12)); 69.8 (C(3″)); 67.0 (C(5″)); 63.0 (C(6′)); 61.0 (C(5)); 54.8 (C(17)); 51.7 (C(14)); 49.9 (C(9)); 48.2 (C(13)); 46.2 (C(7)); 41.2 (C(8)); 40.1 (C(4)); 39.8 (C(10)); 39.5 (C(1)); 35.8 (C(22)); 32.4 (C(11)); 32.1 (C(28)); 31.3 (C(15)); 27.9 (C(2)); 27.1 (C(26)); 26.9 (C(16)); 25.9 (C(21)); 23.0 (C(23)); 21.2 (*Me*COO); 18.2 (C(6″)); 17.8 (C(19)); 17.7 (C(18), C(27)); 17.2 (C(30)); 16.9 (C(29)). MALDI-TOF-MS: 849.9 ($[M + Na]^+$).

REFERENCES

[1] J. Park, K. Lee, Y. Oh, K. Kim, S. Lee, *Cancer Lett.* **1997**, *21*, 73.
[2] A. Attele, J. Wu, C. Yan, *Biochem. Pharm.* **1999**, *58*, 1685.
[3] K. Salim, B. McEwen, H. Chao, *Mol. Brain Res.* **1997**, *47*, 177.
[4] D. Shangguan, H. Han, Y. Zhao, S. Xiong, G. Liu, *J. Chromatogr., A* **2001**, *910*, 367.
[5] I. Kitagawa, T. Hayashi, M. Yoshikawa, *Chem. Pharm. Bull.* **1983**, *31*, 3353.
[6] A. Attele, Y. Zhou, J. Xie, J. Wu, L. Zhang, L. Dey, W. Pugh, P. Rue, K. Polonsky, C. Yuan, *Diabetes* **2002**, *51*, 1851.
[7] Z. Li, N. Xu, C. Wu, Y. Xiong, H. Fan, W. Zhang, Y. Sun, G. Pei, *Neuropharmacol. Neurotoxicol.* **2001**, *12*, 1453.
[8] Z. Li, C. Wu, Y. Guo, X. Li, *Pharm. Biochem. Behav.* **2000**, *66,* 595.
[9] M. Karikura, T. Miyase, H. Tanizawa, Y. Takino, T. Taniyama, T. Hayashi, *Chem. Pharm. Bull.* **1990**, *38*, 2859.
[10] M. Karikura, T. Miyase, H. Tanizawa, Y. Takino, *Chem. Pharm. Bull.* **1991**, *339*, 2357.
[11] R. Teng, H. Li, X. Zhang, X. Liu, D. Wang, C. Yang, *Chin. Chem. Lett.* **2001**, *12*, 239.
[12] B. Han, M. Park, Y. Han, L. Woo, U. Sankawa, S. Yahara, O. Tanaka, *Planta Med.* **1982**, *44*, 146.
[13] B. Danieli, M. Luisetti, S. Riva, A. Bertinotti, E. Ragg, L. Scaglioni, *J. Org. Chem.* **1995**, *60*, 3637.
[14] S. Gebhardt, S. Bihler, M. Schubert-Zsilavecz, S. Riva, D. Monti, F. Laura, B. Danieli, *Helv. Chim. Acta.* **2002**, *85*, 1943.
[15] B. Yu, G. Xing, Y. Hui, X. Han, *Tetrahedron Lett.* **2001**, *42,* 5513.
[16] B. Danieli, G. Lesma, M. Luisetti, S. Riva, *Tetrahedron* **1997**, *53*, 5855.
[17] S. Riva, D. Monti, M. Luisetti, B. Danieli, *Ann. N.Y. Acad. Sci*. **1998**, *864*, 70.
[18] C. Walsh, *Nature (London)* **2001**, *409,* 226, and refs. cit. therein.
[19] M. Oosterom, F. Rantwijk, R. Sheldon, *Biotechnol. Bioeng.* **1995**, *19*, 328.
[20] G. Kodelia, K. Athanasiou, F. Kolisis. *Appl. Biochem. Biotechnol.* **1994**, *44*, 205.
[21] Y. Mimaki, M. Kuroda, A. Kameyama, Y. Sashida, *Bioorg. Med. Chem. Lett.* **1997**, *5*, 633.
[22] M. Melzig, G. Bader, R. Loose, *Planta Med.* **2000**, *67,* 43.
[23] R. Teng, C. Ang, D. McManus, D. Armstrong, S. Mau, A. Bacic, *Tetrahedron Lett*. **2003**, *44*, 5661.
[24] R. Teng, H. Li, D. Wang, N. He, C. Yang, *Chin. J. Magn. Reson*. **2002**, *19*, 25.
[25] R. Teng, H. Li, J. Chen, D. Wang, Y. He, C. Yang, *Magn. Reson. Chem*. **2002**, *40*, 483.
[26] R. Teng, H. Li, D. Wang, N. He, C. Yang, *Chin. J. Magn. Reson*. **2000**, *17*, 461.
[27] Y. Hukla, R. Thakur, *Planta Med.* **1988**, *54,* 367.
[28] J. Wang, X. Li, *Zhongguo Yanwu Huaxue Zazhi* **1997**, *7*, 130.

Received February 7, 2004