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# Transformation of 9α,14α-epoxy-14-deoxy-20-hydroxyecdysone diacetonide into 25-hydroxydachryhainansterone

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9α,14α-Epoxy-14-deoxy-20-hydroxyecdysone diacetonide on treatment with $NaBH_4$ undergoes reduction of 6-keto group and cleavage of allylic oxetane ring, the 6-keto reduction is accompanied by β→α epimerization of the adjacent $HC^5$ centre. Subsequent re-oxidation of the 6-CHOH fragment into ketone with pyridinium chlorochromate and acidic deprotection affords 25-hydroxydachryhainansterone possessing β-$HC^5$ configuration due to the re-epimerisation at this centre.

Previously[1] we have prepared the oxetane-containing 9α,14α-epoxy-14-deoxy-20-hydroxyecdysone diacetonide **1** from 20-hydroxyecdysone, the plant (*Serratula coronata*) ecdysteroid (content 2%).[2] Compound **1** represents a challenge for the further transformations on the 6-keto group and the allylic oxetane ring. Here, compound **1** was transformed into 25-hydroxydachryhainansterone **7**, which was earlier[3,4] obtained by the dehydration of turkesterone (minor ecdysteroid of the *Ajuga turkestanica*,[5] content 0.14%). Note that 7,9-diene ecdysteroids exhibit high biological activity in the *Drosophila melanogaster* $B_{II}$ bioassay and can serve as photoaffinity analogues for ecdysteroid binding proteins on irradiation.[3]

Treatment of compound **1** with $NaBH_4$ in MeOH–THF (Scheme 1) followed by aqueous work-up gives the mixture of 6α,14α-dihydroxy-7,9-diene- **2** and 6α,9α-dihydroxy-7,14-diene- **3** derivatives and 6β-epimer **4** of the latter. Compounds **2**–**4** were separated by column chromatography and their structures were established by 1D and 2D $^1$H NMR and $^{13}$C NMR.†

The $^{13}$C NMR spectrum of **2** contains the signals of the $C^7$=$C^8$ bond at δ 123.3 ($C^7$, correlation with the $HC^6$ doublet) and 138.0 ($C^8$, two cross-peaks with $HC^6$ and $HC^{11}$ protons). In addition, the signals of other $sp^2$-hybridised C-atoms (δ 122.6 and 133.5) were observed, which were assigned to $C^{11}$ and $C^9$ atoms, respectively, on the basis of HMBC experiment: the signal at δ 133.5 correlates with $HC^7$ (δ 5.49) and $H_2C^{12}$ (δ 2.19 and 2.48), whereas the signal at δ 122.6 correlates with $H_2C^{12}$ group signal. The HSQC spectrum showed the absence of cross-peaks for $C^8$ and $C^9$ atoms, but signals of $C^7$ and $C^{11}$ atoms correlate with their protons (δ 5.49 and 5.62).

The chemical shift of $C^6$ atom signal at δ 66.6 of compound **2** confirms the α-configuration of its OH group.[6,7] $HOC^6$ group of compound **3** (δ 66.5) has α-configuration too, whereas the chemical shift of $C^6$ of compound **4** at δ 70.37 is characteristic of β-orientation of its OH group. The $C^5$ signals of alcohols **2** and **3** at δ 41.1 are in accordance with upfield shift of $\Delta^7$- and $\Delta^{7,14}$-6α-alcohols, since such carbon atoms of 6β-epimers resonate at δ 43.3.[7,8]

As previously reported[7] the epimerization at $C^5$ atom took place during the hydride reduction of 6-keto ecdysteroids, therefore one may expect that compounds **2**–**4** possess *trans*-junction. This is confirmed by the absence of correlations between $H_3C^{19}$ and $HC^5$ signals in NOESY experiments for **2**–**4**, by the presence of COSY-correlations between $HC^5$ and $HC^6$ signals in **2** and **3**, whereas for compound **4** such a COSY-correlation is absent.

The allylic oxetane ring-opening of compound **1** in aqueous alcohol occurs in an ordinary way,[9] however, this transformation definitely takes place after the completion of the reduction of 6-keto group and aqueous work up. It should be noted that oxetane fragment in compound **1** is resistant towards KOH in methanol for 48 h (TLC control).

The oxidation of dienol **2** gave the corresponding previously unknown ketone **5** (25-hydroxydachryhainansterone diacetonide),‡ the structure of which was proved by the 1D and 2D NMR. Carbon signals at δ 202.3 ($C^6$), 119.1 ($C^7$), 153.1 ($C^8$), 135.6 ($C^9$) and 131.2 ($C^{11}$) correspond to a 7(8),9(11)-dien-6-one system. In the HMBC spectrum of **5** the correlations were observed as follows: for the $C^7$ atom signal – with the $HC^5$ signal, for $C^8$ – with the $HC^{11}$, for $C^9$ – with $HC^7$ and $H_2C^{12}$ and for $C^{11}$ – with $H_2C^{12}$ signals. In the HMBC spectrum, two singlets at δ 39.3 and 46.7 were assigned to $C^{10}$ and $C^{13}$ atoms: the signal at δ 39.3 correlates with $H_3C^{19}$ and $HC^{11}$ signals, and the signal at δ 46.7 – with $HC^{11}$, $H_2C^{12}$, $HC^{17}$ and $H_3C^{18}$. The interaction of the $HC^5$ proton with the $H_3C^{19}$ group protons in NOESY spectrum is a result of *cis*-junction of A and B rings ($HC^5$ proton β-configuration). *cis*-Junction of A/B rings in compound **5** is assigned based on the chemical shift of $HC^5$ proton being 2.45 ppm. Previously this parameter was found typical of brassinosteroids[10] and ecdysteroids:[11] in the case of

† Compound **1** was obtained according to a published procedure,[1] mp 232–233 °C.

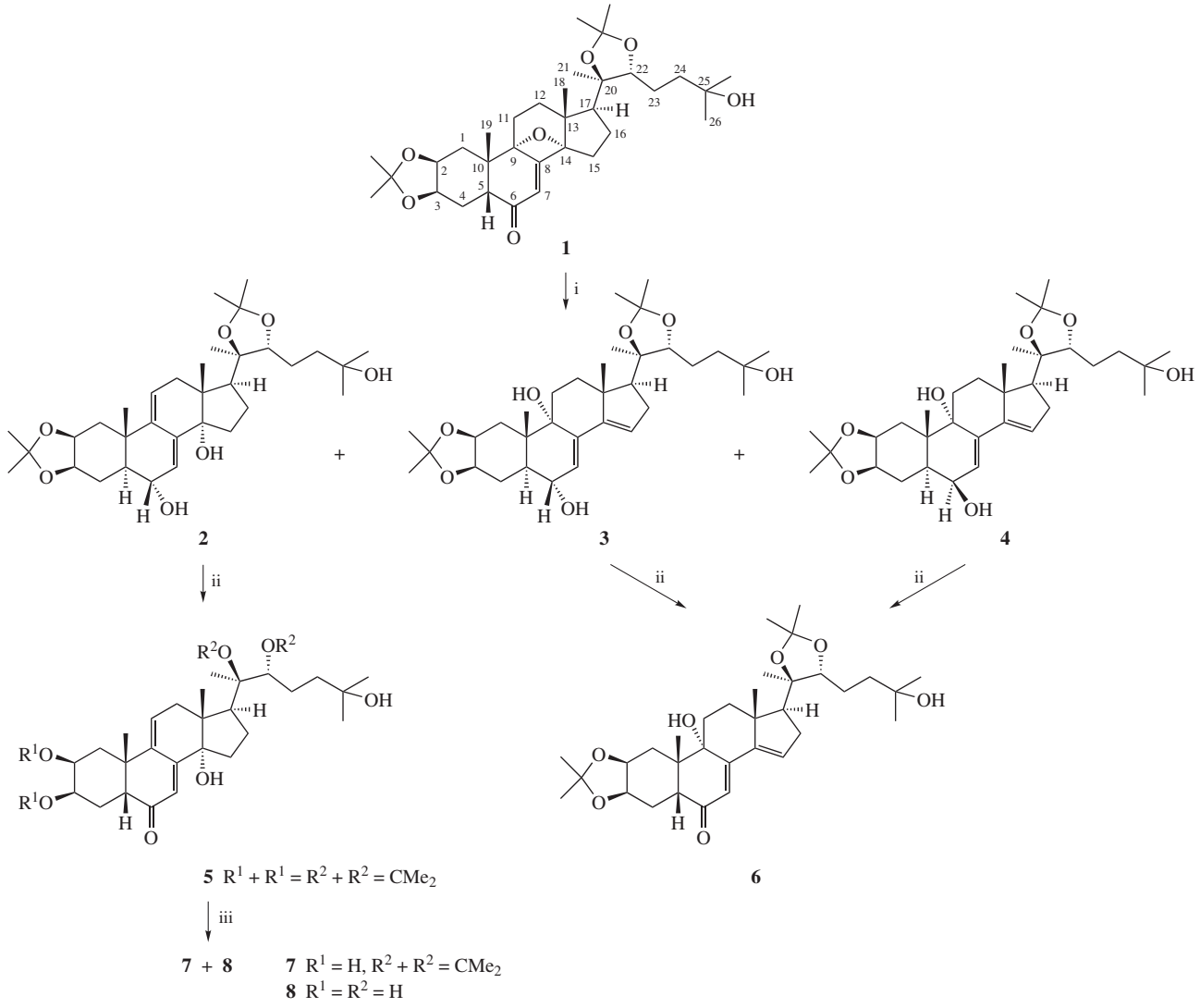
*Synthesis of (20*R*,22*R*)-6α,14α,25-trihydroxy-2β,3β:20,22-bis[(dimethylmethylene)dioxy]-5α-cholest-7,9-diene* **2**, *(20*R*,22*R*)-6α,9α,25-trihydroxy-2β,3β:20,22-bis[(dimethylmethylene)dioxy]-5α-cholest-7,14-diene* **3** *and (20*R*,22*R*)-6β,9α,25-trihydroxy-2β,3β:20,22-bis[(dimethylmethylene)dioxy]-5α-cholest-7,14-diene* **4**. $NaBH_4$ (0.16 g, 3.55 mmol) was added to a solution of compound **1** (0.4 g, 0.71 mmol) in 10 ml of anhydrous THF at –5 °C, then MeOH (~1 ml) was dropped and the mixture was stirred for 2 h. Reaction mixture was filtered and concentrated to 5 ml, 5 ml of water was added with further extraction with EtOAc (3×30 ml). The organic layers were concentrated and crude product (400 mg) was chromatographed on a column (8 g $SiO_2$, eluting with $CHCl_3$) to give compound **2** [0.1 g, 25%, $R_f$ 0.36 ($CHCl_3$–MeOH, 10:1)], compound **3** [0.14 g, 35%, $R_f$ 0.54 ($CHCl_3$–MeOH, 10:1)] and compound **4** [0.12 g, 30%, $R_f$ 0.59 ($CHCl_3$–MeOH, 10:1)].

For **2**: mp 126–128 °C, $[\alpha]_D^{18}$ 21.97 (*c* 0.72, $CHCl_3$).

For **3**: mp 116–118 °C, $[\alpha]_D^{18}$ –65.30 (*c* 1.01, $CHCl_3$).

For **4**: mp 98–100 °C, $[\alpha]_D^{20}$ –94.50 (*c* 0.42, $CHCl_3$).

For spectral characteristics of compounds **2**–**4**, see Online Supplementary Materials.




**Scheme 1** *Reagents and conditions*: i, $NaBH_4$, THF–MeOH (10:1, v/v); ii, PCC, $CHCl_3$; iii, 10% $HClO_4$, MeOH (3.5:1, v/v).

*cis*-junction $HC^5$ proton resonated at $\delta$ ~ 2.4 ppm, whereas in the case of *trans*-junction this value was ~2.2 ppm.

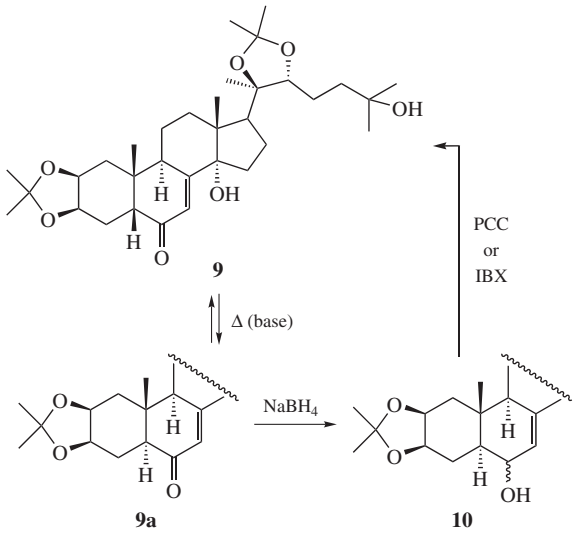
The oxidation of epimeric alcohols **3** and **4** led to the same ketone **6**[§] which was identical in mp, UV, $^1H$ and $^{13}C$ NMR spectra to the known[9] 9α-hydroxystachysterone B diacetonide. It is worth noting an easier oxidation of the 6β-alcohol **4** compared to its 6α-epimer **3**, which can be explained by the deactivating effect of spatially close 9α-OH group to αH-6 of the latter.

Removal of acetonide protections from compound **5** gives a mixture of monoacetonide **7** and 25-hydroxydachryhainansterone **8**. $^{13}C$ NMR spectrum of this mixture[¶] contains singlets at 35.8 (for 20,22-acetonide **6**) and 37.7 ppm (for 25-hydroxydachryhainansterone) which are related to $C^{10}$ atom, while singlets at $\delta$ 47.5 (for **7**) and 46.6 ppm (for **8**) belong to $C^{13}$ atom (published[3] data for 25-hydroxydachryhainansterone show the presence of $C^{10}$ signal at $\delta$ 46.6 ppm and the absence of signal at $\delta$ ~ 37.7 ppm). Other spectral data for compounds **7** and **8** are in agreement with the literature,[3,4] whereas our data on melting point of **8** (151–153 °C) are drastically different from those previously reported[4] (243–244 °C).

The well known[12–14] $C^5$-epimerisation of 6-keto group goes through enol form. The possibility of this epimerization at hydride

‡ *Synthesis of 25-hydroxydachryhainansterone diacetonide, or (20*R*,22*R*)-14α,25-dihydroxy-2β,3β:20,22-bis[(dimethylmethylene)dioxy]-5α-cholest-7,9-dien-6-one* **5**. PCC (80 mg, 0.45 mmol) on $Al_2O_3$ (0.45 g) was added to a solution of compound **2** (0.1 g, 0.18 mmol) in 3 ml of dry chloroform at 40 °C with stirring. The mixture was stirred for 2 h, then chromatographed on a column (2 g $SiO_2$, eluting with $CHCl_3$) to give compound **5** [0.08 g, 80%, $R_f$ 0.49 ($CHCl_3$–MeOH, 10:1)], mp 116–118 °C, $[\alpha]_D^{20}$ 53.6 (*c* 0.5, $CHCl_3$). IR (KBr, $\nu$/cm$^{-1}$): 3444, 2981, 2935, 1658, 1456, 1367. UV (EtOH, $\lambda_{max}$/nm): 297. $^1H$ NMR ($CDCl_3$) $\delta$: 0.81 (s, 3H, $H_3C^{18}$), 1.17 (s, 3H, $H_3C^{21}$), 1.248 (s, 6H, $H_3C^{26}$, $H_3C^{27}$), 1.253 (s, 3H, $H_3C^{19}$), 1.32, 1.33, 1.43 and 1.53 (4s, 12H, $2Me_2C$), 1.50 and 1.60 (2m, 2H, $H_2C^{23}$), 1.56 and 2.16 (2m, 2H, $H_2C^1$), 1.56 and 1.72 (2m, 2H, $H_2C^{24}$), 1.72 and 2.03 (2m, 2H, $H_2C^{15}$), 1.91 and 2.04 (2m, 2H, $H_2C^{16}$), 1.92 and 2.06 (2m, 2H, $H_2C^4$), 2.39 and 2.64 (2m, 2H, $H_2C^{12}$), 2.31 (m, 1H, $HC^{17}$), 2.45 (m, 1H, $HC^5$), 3.67 (m, 1H, $HC^{22}$, $\omega_{1/2}$ 8.4 Hz), 4.14 (m, 2H, $HC^2$, $HC^3$, $\omega_{1/2}$ 11.6 Hz), 5.82 (s, 1H, $HC^7$), 6.11 (br. s, 1H, $HC^{11}$, $\omega_{1/2}$ 4.4 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 17.4 ($C^{18}$), 21.5 ($C^{16}$), 21.6 ($C^{21}$), 23.6 ($C^{23}$), 26.4, 26.8, 28.6 and 29.0 ($2Me_2CO_2$), 28.1 ($C^4$), 29.2 and 29.4 ($C^{26}$, $C^{27}$), 29.7 ($C^{19}$), 30.6 ($C^{15}$), 36.9 ($C^1$), 37.7 ($C^{12}$), 39.3 ($C^{10}$), 41.4 ($C^{24}$), 46.7 ($C^{13}$), 49.1 ($C^{17}$), 50.7 ($C^5$), 70.3 ($C^{25}$), 71.2 ($C^2$), 72.1 ($C^3$), 81.9 ($C^{22}$), 84.07 ($C^{20}$), 84.14 ($C^{14}$), 107.0 (20,22-$Me_2CO_2$), 108.4 (2,3-$Me_2CO_2$), 119.1 ($C^7$), 131.2 ($C^{11}$), 135.6 ($C^9$), 153.1 ($C^8$), 202.3 ($C^6$). HRMS, *m*/*z*: 581.762 $[M + Na]^+$ (calc. for $C_{33}H_{50}O_7Na$, 581.746).

§ *Synthesis of 9α-hydroxystachysterone B 2,3:20,22-diacetonide* **6**. PCC (50 mg, 0.275 mmol) on $Al_2O_3$ (0.28 g) was added to a solution of compound **3** (0.06 g, 0.11 mmol) or compound **4** (0.06 g, 0.11 mmol) in 10 ml of dry chloroform at room temperature with stirring. The mixture was stirred at 40 °C for 14 h (for **3**) or 4 h (for **4**), then chromatographed on a column (1.2 g $SiO_2$, eluting with $CHCl_3$) to give compound **6** (0.02 g, 33% in the case of **3** or 0.05 g, 83% in the case of **4**), $R_f$ 0.52 ($CHCl_3$–MeOH, 10:1), mp 228–230 °C, $[\alpha]_D^{18}$ –222 (*c* 1.0, $CHCl_3$). IR, UV, $^1H$ and $^{13}C$ NMR spectra are identical to published data.[9]




**Scheme 2**

reduction is confirmed by us by the transformation of 20-hydroxyecdysone diacetonide **9** to its 5α-epimer **9a** in MeOH–MeONa solution or MeOH–MeONa–THF solution (Scheme 2). Purified by column chromatography the 5α-epimer **9a** contains ~15% of 5β-epimer **9** [$R_f$ 0.52 ($CHCl_3$–MeOH, 10:1) for each]. The signals of **9a** in $^{13}C$ NMR spectrum†† are close to those of **9** but are slightly shifted.[15] In $CDCl_3$ solution **9a** slowly (for 3 months) transforms into more stable natural epimer **9**. It is possible that previously[7] described hydride reduction of compound **9** into 6-hydroxy derivative **10** takes place after its epimerization into **9a**. The oxidation of alcohols **10** with pyridinium chlorochromate (PCC) or 2-iodoxybenzoic acid (IBX)[16] leads to the starting 5β-epimer **9** only.

In conclusion, the developed double stage transformation involves the epimerization at $C^5$ atom on hydride reduction of 6-keto derivative **1**, while on re-oxidation of allylic alcohols **2–4** re-epimerisation at this centre occurs.

*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2010.09.019.

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¶ *Synthesis of 25-hydroxydachryhainansterone 20,22-monoacetonide, or (20*R,*22*R*)-2β,3β,14α,25-tetrahydroxy-20,22-(dimethylmethylene)dioxy-5α-cholest-7,9-dien-6-one* ***7*** *and 25-hydroxydachryhainansterone, or 2β,3β,14α,20,22,25-hexahydroxy-5β-cholest-7,9-dien-6-one* **8**. 10% $HClO_4$ (0.4 ml) was added to a stirring solution of compound **5** (0.08 g, 0.14 mmol) in 1.4 ml of dry MeOH at room temperature. The mixture was stirred at 40 °C for 16 h. After compound **5** reacted (TLC control), 1 ml of water and 3 ml of saturated $NaHCO_3$ solution were added with further extraction with EtOAc (6×5 ml). The organic layers were concentrated and the crude product was chromatographed on a column (1.6 g $SiO_2$, eluting with $CHCl_3$–MeOH, 7:1) to give compound **7** [0.04 g, 50%, $R_f$ 0.67 ($CHCl_3$–MeOH, 3:1)] and compound **8** [0.03 g, 38%, $R_f$ 0.40 ($CHCl_3$–MeOH, 3:1)].

For **7**: mp 136–138 °C, $[\alpha]_D^{20}$ 56.15 (*c* 0.52, $CHCl_3$). IR (KBr, $\nu$/cm$^{-1}$): 3444, 2981, 2935, 1658, 1456, 1367. UV (EtOH, $\lambda_{max}$/nm): 299. $^1H$ NMR ($CDCl_3$–$CD_3OD$) $\delta$: 0.89 (s, 3H, $H_3C^{18}$), 0.95 (s, 3H, $H_3C^{21}$), 0.986 and 0.993 (2s, 6H, $H_3C^{26}$, $H_3C^{27}$), 1.03 (s, 3H, $H_3C^{19}$), 1.10 and 1.19 (2s, 6H, 20,22-$Me_2$C), 1.30–2.00 (m, 12H, CH, $CH_2$), 2.12 (m, 1H, $HC^{17}$), 2.43 and 2.48 (2m, 2H, $H_2C^{12}$), 3.63 (br. s, 1H, $HC^{22}$, $\omega_{1/2}$ 11.6 Hz), 4.19 (br. s, 2H, $HC^2$, $HC^3$, $\omega_{1/2}$ 26.8 Hz), 5.55 (s, 1H, $HC^7$), 6.02 (d, 1H, $HC^{11}$, *J* 5.2 Hz). $^{13}C$ NMR ($CDCl_3$–$CD_3OD$) $\delta$: 16.7 ($C^{18}$), 21.0 ($C^{16}$), 21.1 ($C^{21}$), 23.0 ($C^{23}$), 26.2, 28.2 ($Me_2CO_2$), 28.3 ($C^{26}$, $C^{27}$), 29.2 ($C^4$), 29.9 ($C^{19}$), 30.5 ($C^{15}$), 35.8 ($C^{10}$), 37.1 ($C^1$), 39.3 ($C^{12}$), 40.6 ($C^{24}$), 41.1 ($C^{17}$), 47.5 ($C^{13}$), 49.6 ($C^5$), 66.5 ($C^2$), 67.1 ($C^3$), 69.8 ($C^{25}$), 81.5 ($C^{20}$), 83.0 ($C^{22}$), 83.9 ($C^{14}$), 106.6 (20,22-$Me_2CO_2$), 117.8 ($C^7$), 132.0 ($C^{11}$), 134.4 ($C^9$), 154.5 ($C^8$), 205.5 ($C^6$). HRMS, *m/z*: 541.738 $[M + Na]^+$ (calc. for $C_{30}H_{46}O_7Na$, 541.682).

For **8**: mp 151–153 °C, $[\alpha]_D^{20}$ 16.8 (*c* 0.196, EtOH). UV and $^1H$ NMR spectra are identical to published data.[3] $^{13}C$ NMR ($CD_3OD$) $\delta$ (*cf.* ref. 3): 17.0 ($C^{18}$), 19.6 ($C^{21}$), 20.4 ($C^{16}$), 25.9 ($C^{23}$), 28.5 ($C^{26}$, $C^{27}$), 29.4 ($C^{15}$), 30.1 ($C^{19}$), 34.2 ($C^4$), 36.1 ($C^1$), 37.7 ($C^{10}$), 39.5 ($C^{12}$), 40.8 ($C^{24}$), 46.6 ($C^{13}$), 49.1 ($C^{17}$), 50.0 ($C^5$), 66.9 ($C^2$), 67.1 ($C^3$), 70.2 ($C^{25}$), 76.5 ($C^{20}$), 76.9 ($C^{22}$), 83.2 ($C^{14}$), 118.0 ($C^7$), 132.6 ($C^{11}$), 134.5 ($C^9$), 155.1 ($C^8$), 206.0 ($C^6$). HRMS, *m/z*: 501.646 $[M + Na]^+$ (calc. for $C_{27}H_{42}O_7Na$, 501.618).

†† For **9a**: $^1H$ NMR ($CDCl_3$) $\delta$: 0.96 (s, 3H, $H_3C^{18}$), 1.09 (s, 3H, $H_3C^{19}$), 1.18 (s, 3H, $H_3C^{21}$), 1.22 and 1.24 (2s, 6H, $H_3C^{26}$, $H_3C^{27}$), 1.32, 1.41 and 1.49 (all s, 12H, 2$Me_2$C), 1.18 and 1.95 (2m, 2H, $H_2C^1$), 1.48 and 1.55 (2m, 2H, $H_2C^{16}$), 1.57 and 1.73 (2m, 2H, $H_2C^{24}$), 1.66 and 2.00 (2m, 2H, $H_2C^{12}$), 1.71 and 2.14 (2m, 2H, $H_2C^{15}$), 1.83 and 2.01 (2m, 2H, $H_2C^{11}$), 1.86 and 2.43 (2m, 2H, $H_2C^4$), 2.23 (m, 2H, $H_2C^{23}$), 2.25 (m, 1H, $HC^{17}$), 2.98 (d, 1H, $HC^5$, *J* 2.8 Hz), 3.65 (m, 1H, $HC^{22}$), 4.06 (m, 1H, $HC^2$), 4.25 (d, 1H, $HC^3$, *J* 11.6 Hz), 5.83 (s, 1H, $HC^7$). $^{13}C$ NMR ($CDCl_3$) $\delta$: 17.1 ($C^{18}$), 18.2 ($C^{19}$), 20.9 ($C^{11}$), 23.5 ($C^{16}$), 21.9 ($C^{21}$), 24.4 ($C^{23}$), 26.3, 26.8, 28.7 and 28.9 (2$Me_2CO_2$), 30.5 ($C^4$), 29.2 and 29.4 ($C^{26}$, $C^{27}$), 28.0 ($C^{15}$), 31.0 ($C^{12}$), 34.5 ($C^9$), 37.7 ($C^1$), 41.7 ($C^{10}$), 41.3 ($C^{24}$), 47.0 ($C^{13}$), 48.8 ($C^{17}$), 45.0 ($C^5$), 70.5 ($C^{25}$), 73.5 ($C^2$), 73.9 ($C^3$), 82.0 ($C^{22}$), 84.4 ($C^{20}$), 86.0 ($C^{14}$), 107.0 (20,22-$Me_2CO_2$), 108.2 (2,3-$Me_2CO_2$), 123.9 ($C^7$), 158.3 ($C^8$), 200.9 ($C^6$).