Enantiospecific Total Synthesis of Valeriananoids A-C

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Supplementary Information

S2-S8 Characterization data

- S-9 ^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$) spectrum of the compound **9**.
- S-10 ^{13}C NMR (75 MHz, CDCl_3) spectrum of the compound **10**.
- S-11 ^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$) spectrum of the compound **11**.
- S-12 ^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$) spectrum of the compound **12**.
- S-13 ^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$) spectrum of the compound **13**.
- S-14 ^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$) spectrum of the compound **14**.
- S-15 ^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$) spectrum of the compound **15**.
- S-16 ^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$) spectrum of the compound **16A**.
- S-17 ^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$) spectrum of the compound **16B**.
- S-18 ^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$) spectrum of the compound **17**.
- S-19 ^{13}C NMR (75 MHz, CDCl_3) spectrum of the compound **1**.
- S-20 ^{13}C NMR (75 MHz, CDCl_3) spectrum of the compound **18**.
- S-21 ^{13}C NMR (75 MHz, CDCl_3) spectrum of the compound **2**.
- S-22 ^{13}C NMR (75 MHz, CD_3OD) spectrum of the compound **2**.
- S-23 ^{13}C NMR (75 MHz, CDCl_3) spectrum of the compound **3**.

(–)-(1*S*,2*R*,4*S*,8*S*)-8-Isopropenyl-4,6,6-trimethyl-5-oxobicyclo[2.2.2]octane-2-carboxylic acid methyl ester (9):

$[\alpha]_D^{23}$: –96.6 (c 3.0, CHCl₃).

IR (neat): $\nu_{\max}/\text{cm}^{-1}$ 3073, 2952, 2875, 1731, 1715, 1642, 1463 1436, 1385, 1236, 1214, 1181, 1092, 1018, 895, 848, 827, 768.

¹H NMR (300 MHz, CDCl₃+CCl₄): δ 4.71 (1 H, s) and 4.65 (1 H, s) [C=CH₂], 3.69 (3 H, s, OMe), 2.78 (1 H, t, J=9.9 Hz), 2.46 (1 H, t, J=9.6 Hz), 2.40 (1 H, brs), 2.14 (1 H, dd, J=14.6 and 9.0 Hz), 2.00-1.75 (3 H, m), 1.49 (3 H, s, olefinic CH₃), 1.16 (3 H, s), 0.98 (3 H, s) and 0.90 (3 H, s) [3 x *tert* CH₃].

¹³C NMR (75 MHz, CDCl₃+CCl₄): δ 219.8 (C, C=O), 174.9 (C, O-C=O), 145.9 (C) and 114.1 (CH₂) [C=CH₂], 51.8 (CH₃, OMe), 51.0 (CH), 46.5 (C), 46.0 (C), 41.0 (CH), 40.9 (CH), 35.4 (CH₂), 30.4 (CH₂), 25.8 (CH₃), 23.7 (CH₃), 19.6 (CH₃), 18.2 (CH₃).

Mass: 265 (M+1, 4%), 264 (50), 177 (28), 163 (70), 133 (88), 121 (75), 109 (75), 107 (100).

HRMS: m/z Calcd. for C₁₆H₂₄O₃Na (M+Na): 287.1623; Found: 287.1622.

(–)-(1*S*,4*S*,5*R*,7*S*)-5-(2-Hydroxypropan-2-yl)-7-isopropenyl-1,3,3-trimethylbicyclo[2.2.2]octan-2-one (10):

Mp: 151-153 °C.

$[\alpha]_D^{25}$: –85.7 (c 1.9, CHCl₃).

IR (neat): $\nu_{\max}/\text{cm}^{-1}$ 3493, 3074, 2964, 2929, 1702, 1638, 1462, 1377, 1346, 1180, 1162, 1133, 1029, 968, 891.

¹H NMR (300 MHz, CDCl₃+CCl₄): δ 4.72 (1 H, s) and 4.65 (1 H, s) [C=CH₂], 2.55 (1 H, dd, J=10.5 and 8.7 Hz), 2.10-1.60 (7 H, m), 1.53 (3 H, s, olefinic-CH₃), 1.33 (3 H, s), 1.32 (3 H, s), 1.28 (3 H, s), 1.18 (3 H, s), 0.92 (3 H, s) [5 x *tert* CH₃].

¹³C NMR (75 MHz, CDCl₃+CCl₄): δ 222.6 (C, C=O), 146.6 (C) and 113.4 (CH₂) [C=CH₂], 70.3 (C, C-OH), 50.0 (CH), 47.7 (CH), 46.7 (C), 45.6 (C), 40.1 (CH), 34.5 (CH₂), 33.8 (CH₂), 31.7 (CH₃), 29.6 (CH₃), 28.4 (CH₃), 25.6 (CH₃), 20.1 (CH₃), 18.5 (CH₃).

Mass: 264 (M, 14%), 206 (64), 191 (16), 177 (38), 163 (42), 137 (46), 135 (100), 133 (46), 123 (67), 121 (70), 107 (85).

HRMS: m/z Calcd. for C₁₇H₂₈O₂Na: 287.1987; Found: 287.2002.

(–)-(1*S*,4*S*,5*R*,7*R*)-7-Acetyl-5-(2-hydroxypropan-2-yl)-1,3,3-trimethylbicyclo[2.2.2]octan-2-one (11):

Mp: 127-130 °C.

$[\alpha]_D^{23}$: –84 (c 1.0, CHCl₃).

IR (neat): $\nu_{\max}/\text{cm}^{-1}$ 3503, 2972, 2928, 1723, 1714, 1464, 1360, 1172, 1035, 918, 736.

^1H NMR (300 MHz, $\text{CDCl}_3+\text{CCl}_4$): δ 3.03 (1 H, dd, $J=10.5$ and 7.2 Hz), 2.13 (3 H, s, $\text{CH}_3\text{C}=\text{O}$), 2.10-1.65 (7 H, m), 1.32 (3 H, s), 1.30 (3 H, s), 1.25 (3 H, s), 1.16 (3 H, s), 0.95 (3 H, s) [5 x *tert* CH_3]

^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$): δ 218.4 (C, $\text{C}=\text{O}$), 210.2 (C, $\text{CH}_3\text{C}=\text{O}$), 69.8 (C, $\text{C}-\text{OH}$), 53.6 (CH), 48.5 (CH), 45.5 (C), 45.2 (C), 40.2 (CH), 33.3 (CH_2), 31.9 (2 C, CH_3 and CH_2), 31.3 (CH_3), 29.4 (CH_3), 27.7 (CH_3), 26.2 (CH_3), 18.8 (CH_3).

Mass: 266 (M, 5%), 208 (16), 177 (18), 165 (33), 142 (42), 135 (48), 126 (80), 125 (70), 107 (60), 93 (100).

HRMS: m/z Calcd. for $\text{C}_{16}\text{H}_{26}\text{O}_3\text{Na}$ (M+Na): 289.1780; Found: 289.1790.

(–)-(1S,4S,7R)-7-Acetyl-5-isopropylidene-1,3,3-trimethylbicyclo[2.2.2]octan-2-one (12):

Mp: 174-176 °C.

$[\alpha]_D^{23}$: –40.0 (c 3.0, CHCl_3).

IR (neat): $\nu_{\max}/\text{cm}^{-1}$ 2988, 2960, 2921, 2872, 2834, 1722, 1704, 1449, 1427, 1370, 1356, 1262, 1179, 1152, 1035, 999, 958, 732.

^1H NMR (300 MHz, $\text{CDCl}_3+\text{CCl}_4$): δ 2.81 (1 H, dd, $J=1.4$ and 6.9 Hz), 2.51 (1 H, t, $J=3.0$ Hz), 2.20 (1 H, d, $J=16.8$ Hz), 2.05 (3 H, s, $\text{CH}_3\text{C}=\text{O}$), 2.03 (1 H, d, $J=16.8$ Hz), 1.95-1.70 (2 H, m), 1.60 (3 H, s) and 1.52 (3 H, s) [2 x olefinic CH_3], 1.09 (3 H, s), 0.90 (3 H, s) and 0.87 (3 H, s) [3 x *tert*- CH_3].

^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$): δ 217.6 (C, $\text{C}=\text{O}$), 209.4 (C, $\text{CH}_3\text{C}=\text{O}$), 128.7 (C), 123.8 (C), 55.0 (CH), 46.3 (C), 45.9 (C), 43.2 (CH), 39.7 (CH_2), 31.2 (CH_3), 26.0 (CH_2), 25.8 (CH_3), 23.0 (CH_3), 19.8 (CH_3), 19.6 (CH_3), 18.7 (CH_3).

Mass: 248 (M^+ , 18%), 163 (12), 149 (12), 135 (35), 134 (100), 119 (78), 93 (30).

HRMS: m/z Calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_2\text{Na}$ (M+Na): 271.1674; Found: 271.1664.

(–)-(1S,4S,7R)-7-(2-Hydroxybut-3-en-2-yl)-5-isopropylidene-1,3,3-trimethylbicyclo[2.2.2]octan-2-one (13):

$[\alpha]_D^{23}$: –73.8 (c 1.8 CHCl_3).

IR (neat): $\nu_{\max}/\text{cm}^{-1}$ 3493, 2928, 1713, 1455, 1381, 1102, 1030, 920.

^1H NMR (300 MHz, $\text{CDCl}_3+\text{CCl}_4$, 1:2 mixture of epimers): δ 5.94 (dd, $J=17.7$ and 11.1 Hz) and 5.81 (dd, $J=17.4$ and 10.8 Hz) [1 H, $\text{CH}=\text{CH}_2$], 5.20 and 5.17 (1 H, d, $J=17.4$ Hz), 5.06 (d, $J=11.1$ Hz) and 4.99 (d, $J=10.8$ Hz) [1 H], 2.65-2.20 (2 H, m), 2.15-1.55 (5 H, m), 1.68 (3 H, s) and 1.59 (3 H, s) [2 x olefinic CH_3], 1.24 and 1.15 (3 H, s), 1.18 (3 H, s), 1.12 and 1.10 (3 H, s), 0.91 and 0.90 (3 H, s) [4 x *tert*- CH_3].

^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$, 1:2 mixture of epimers): δ 222.5 and 221.4 (C, C=O), 147.0 and 142.8 (CH), 129.4 and 129.3 (C), 123.2 and 123.1 (C), 113.7 and 111.1 (CH_2), 76.5 and 76.2 (C, C-OH), 52.5 and 52.2 (CH), 48.8 and 48.6 (C), 46.2 and 46.0 (C), 43.4 and 43.3 (CH), 43.0 and 42.6 (CH_2), 27.1 (CH_3), 26.9 (CH_2), 26.5 and 26.2 (CH_3), 22.9 (CH_3), 21.7 and 21.0 (CH_3), 19.8 (CH_3), 19.6 (CH_3).

Mass: 276 (M, 4%), 249 (5), 206 (97), 191 (24), 177 (16), 163 (34), 135 (100), 121 (46), 107 (64), 93 (43).

HRMS: m/z Calcd. for $\text{C}_{18}\text{H}_{28}\text{O}_2\text{Na}$ (M+Na): 299.1987; Found: 299.1967.

(–)-(1*S*,4*S*,7*R*)-7-[2-(Methoxymethoxy)but-3-en-2-yl]-5-isopropylidene-1,3,3-trimethyl-bicyclo[2.2.2]octan-2-one (14):

$[\alpha]_D^{24}$: –62.2 (c 1.8, CHCl_3).

IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 3083, 2930, 1714, 1639, 1454, 1414, 1381, 1219, 1176, 1144, 1101, 1082, 1023, 922.

^1H NMR (300 MHz, $\text{CDCl}_3+\text{CCl}_4$, 1:2 mixture of epimers): δ 5.71 (dd, $J=17.4$ and 10.8 Hz) and 5.69 (dd, $J=17.7$ and 11.1 Hz) [1 H, $\text{CH}=\text{CH}_2$], 5.25 (dd, $J=10.8$ and 1.5 Hz) and 5.14 (dd, $J=10.8$ and 0.9 Hz) [1 H], 5.15 (dd, $J=17.7$ and 1.5 Hz) and 5.05 (dd, $J=17.7$ and 1.2 Hz) [1 H], 4.62 and 4.44 (1 H, 2 x d, $J=6.9$ Hz) and 4.60 and 4.46 (1 H, 2 x d, $J=6.9$ Hz) [1 H], $[\text{OCH}_2\text{OMe}]$, 3.34 and 3.15 (3 H, s, OMe), 2.50 (1 H, brs), 2.30 (1 H, d, $J=17.4$ Hz), 2.10-1.95 (1 H, m), 1.93 (1 H, dd, $J=12.6$ and 10.5 Hz), 1.73-1.49 (2 H, m), 1.67 (3 H, s) and 1.59 (3 H, s) [2 x olefinic CH_3], 1.25 and 1.23 (3 H, s), 1.15 (3 H, s), 1.13 and 1.09 (3 H, s), 0.92 and 0.89 (3 H, s) [4 x *tert*- CH_3].

^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$): δ 221.4 and 221.1 (C, C=O), 143.0 and 140.3 (CH, $\text{CH}=\text{CH}_2$), 129.4 (C), 123.2 and 123.1 (C), 117.8 and 115.1 (CH_2 , $\text{CH}=\text{CH}_2$), 91.7 and 91.4 (CH_2 , OCH_2OCH_3), 82.6 and 82.2 (C, OCH_2OCH_3), 56.0 and 55.5 (CH_3 , OCH_3), 52.6 and 52.0 (CH), 48.9 and 48.8 (C), 46.0 and 45.9 (C), 43.3 (CH), 43.2 and 43.1 (CH_2), 26.9 and 26.4 (CH_2), 26.6 (CH_3), 23.0 and 22.9 (CH_3), 21.3 and 21.1 (CH_3), 19.8 (CH_3), 19.6 (CH_3), 18.1 (CH_3).

Mass: 259 (M - OCH_2OCH_3 , 3%), 250 (28), 205 (43), 177 (34), 135 (100), 133 (37), 115 (77), 107 (30).

HRMS: m/z Calcd. for $\text{C}_{20}\text{H}_{32}\text{O}_3\text{Na}$ (M+Na): 343.2249; Found: 343.2261.

(–)-(1*S*,3*S*,7*S*,8*S*)-10-Isopropylidene-2,2,6,8-tetramethyltricyclo[5.3.1.0^{3,8}]undecan-5-en-3-ol (15):

$[\alpha]_D^{22}$: –12.0 (c 1.0, CHCl_3).

IR (neat): $\nu_{\max}/\text{cm}^{-1}$ 3505, 2928, 2870, 1560, 1454, 1435, 1385, 1371, 1150, 1059, 1040, 997, 963, 826, 812.

^1H NMR (300 MHz, $\text{CDCl}_3+\text{CCl}_4$): δ 5.15 (1 H, brs), 2.42 (1 H, d, $J=17.7$ Hz), 2.30 (1 H, dd, $J=17.7$ and 4.5 Hz), 2.06 (1 H, t, $J=2.8$ Hz), 1.87 (1 H, t of d, $J=15.0$ and 2.1 Hz), 1.80-1.45 (5 H, m), 1.67 (3 H, s) and 1.59 (6 H, s) [3 x olefinic CH_3], 1.11 (3 H, s), 0.91 (3 H, s) and 0.86 (3 H, s) [3 x *tert*- CH_3].

^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$): δ 138.9 (C), 132.4 (C), 119.9 (C), 118.6 (CH), 74.9 (C, COH), 44.6 (CH), 44.3 (CH), 41.2 (C), 37.9 (C), 35.7 (2 C, CH_2), 29.0 (CH_2), 26.3 (CH_3), 26.0 (CH_3), 22.4 (CH_3), 21.1 (CH_3), 19.7 (CH_3), 19.4 (CH_3).

Mass: 260 (M, 33), 242 (100), 227 (19), 217 (45), 199 (23), 157 (35), 149 (96), 148 (88), 137 (98), 123 (75), 105 (40).

HRMS: m/z Calcd. for $\text{C}_{18}\text{H}_{27}$ (M-OH): 243.2113; Found: 243.2106.

(–)-(1*S*,3*R*,4*R*,6*R*,7*S*)-9-Isopropylidene-5-(methoxymethoxy)-2,2,4,5,7-pentamethyl-tricyclo[4.3.1.0^{3,7}]decan-3-ol (16A):

Mp: 54-56 °C.

$[\alpha]_D^{23}$: –51.3 (c 1.5, CHCl_3).

IR (neat): $\nu_{\max}/\text{cm}^{-1}$ 3626, 3530, 2930, 2875, 1456, 1375, 1155, 1089, 1035, 918.

^1H NMR (300 MHz, $\text{CDCl}_3+\text{CCl}_4$): δ 4.73 and 4.48 (2 H, 2 x d, $J=6.9$ Hz, OC H_2 -OMe), 3.32 (3 H, s, OMe), 2.37 (1 H, q, $J=7.5$ Hz), 2.14 and 2.01 (2 H, 2 x d, $J=18.3$ Hz), 1.97 (1 H, m), 1.77 (1 H, dd, $J=18.3$ Hz), 1.73-1.60 (1 H, m), 1.57 (3 H, s) and 1.53 (3 H, s) [2 x Olefinic- CH_3], 1.60–1.40 (1 H, m), 1.35 (3 H, s), 1.35-1.10 (1 H, m), 1.08 (3 H, s), 1.01 (3 H, d, $J=7.5$ Hz, *sec*- CH_3), 0.95 (3 H, s), 0.80 (3 H, s).

^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$): δ 133.2 (C), 117.7 (C), 91.5 (CH_2 , OCH_2O), 83.9 (C, OCH_2OCH_3), 82.0 (C, C-OH), 55.4 (CH_3 , OCH_3), 49.6 (CH), 47.1 (C), 47.0 (CH), 43.2 (CH), 42.6 (C), 36.1 (CH_2), 26.6 (CH_2), 26.5 (CH_3), 25.8 (CH_3), 23.5 (CH_3), 23.0 (CH_3), 19.4 (CH_3), 19.1 (CH_3), 11.8 (CH_3).

Mass: 262 [(M+1)- OCH_2OCH_3 , 16%], 261 (100), 217 (14), 205 (12), 177 (20), 163 (17), 149 (15), 135 (43), 121 (18), 107 (19).

HRMS: m/z Calcd. for $\text{C}_{20}\text{H}_{34}\text{O}_3\text{Na}$ (M+Na): 345.2406; Found: 345.2387.

(–)-(1*S*,3*R*,4*R*,6*R*,7*S*)-9-Isopropylidene-5-(methoxymethoxy)-2,2,4,5,7-pentamethyl-tricyclo[4.3.1.0^{3,7}]decan-3-ol (16B):

$[\alpha]_D^{23}$: –135.2 (c 1.7, CHCl_3).

IR (neat): $\nu_{\max}/\text{cm}^{-1}$ 3516, 2929, 1456, 1386, 1145, 1088, 1030, 916.

¹H NMR (300 MHz, CDCl₃+CCl₄): δ 4.61 and 4.56 (2 H, 2 x d, J=6.6 Hz, CH₂OMe), 3.36 (3 H, s, OMe), 2.55 (1 H, q, J=7.8 Hz), 2.37 (1 H, br d, J=12.6 Hz), 2.12 and 2.03 (2 H, 2 x d, J=18.3 Hz), 2.00 (1 H, brs), 1.67 (1 H, dd, J=10.2 and 1.8 Hz), 1.59 (3 H, s) and 1.53 (3 H, s) [2 x olefinic CH₃], 1.42 (3 H, s), 1.30-1.20 (1 H, m), 1.11 (1 H, brs), 1.03 (3 H, d, J=7.8 Hz, sec CH₃), 1.02 (3 H, s), 0.97 (3 H, s), 0.82 (3 H, s).

¹³C NMR (75 MHz, CDCl₃+CCl₄): δ 133.4 (C), 117.4 (C), 92.2 (CH₂, OCH₂OMe), 83.8 (C, COMOM), 81.8 (C, COH), 55.7 (CH₃, OMe), 51.4 (CH), 47.2 (CH), 46.0 (C), 43.2 (C), 42.9 (CH), 36.2 (CH₂), 26.6 (CH₃), 25.9 (CH₃), 24.7 (CH₃), 24.6 (CH₂), 24.1 (CH₃), 19.4 (CH₃), 19.1 (CH₃), 14.5 (CH₃).

Mass: 322 (M, 2%), 307 (30), 261 (70), 260 (38), 217 (100), 203 (18), 189 (18), 177 (30), 161 (28), 149 (28), 135 (65), 119 (40), 105 (34).

HRMS: m/z Calcd. for C₂₀H₃₄O₃Na (M+Na): 345.2406; Found: 345.2391.

(+)-(1S,3S,6S,7S,8S)-10-Isopropylidene-2,2,6,8-tetramethyltricyclo[5.3.1.0^{3,8}]undecan-3-ol (17):

[α]_D²³: +124.0 (c 2.0, CHCl₃).

IR (neat): ν_{max}/cm⁻¹ 3620, 3499, 2954, 2928, 2870, 1459, 1386, 1375, 1277, 1185, 1150, 1092, 1058, 1043, 982.

¹H NMR (300 MHz, CDCl₃+CCl₄): δ 2.35 (1 H, d, J=17.4 Hz), 2.08 (1 H, brs), 2.05-1.85 (1 H, m), 1.80-1.65 (2 H, m), 1.59 (3 H, s) and 1.55 (3 H, s) [2 x olefinic CH₃], 1.60-1.20 (7 H, m), 1.13 (3 H, s), 0.93 (3 H, s), 0.83 (3 H, s), 0.78 (3 H, d, J=6.6 Hz).

¹³C NMR (75 MHz, CDCl₃+CCl₄): δ 133.1 (C), 119.3 (C), 75.3 (C, GOH), 44.6 (CH), 44.3 (CH), 41.1 (C), 40.1 (C), 37.7 (CH₂), 32.8 (CH₂), 28.8 (CH₂), 28.2 (CH), 27.7 (CH₃), 23.9 (CH₃), 23.2 (CH₂), 20.7 (CH₃), 19.5 (CH₃), 19.2 (CH₃), 18.8 (CH₃).

Mass: 262 (M, 16%), 244 (58), 229 (33), 219 (41), 201 (41), 161 (25), 149 (84), 133 (100), 125 (65), 107 (75).

HRMS: m/z Calcd. for C₁₈H₂₉ (M-OH): 245.2269; Found: 245.2276.

(-)-(1R,3S,6S,7S,8S,10S)-2,2,6,8,3',3'-Hexamethyl[5.3.1.0^{3,8}]undecanespiro[10.2]oxiran-3-ol (18):

Mp: 132-134 °C.

[α]_D²⁵: -74.5 (c 0.55, CHCl₃).

IR (neat): ν_{max}/cm⁻¹ 3446, 2950, 2924, 2865, 1466, 1376, 1210, 1161, 1093, 1065, 954, 837.

¹H NMR (300 MHz, CDCl₃+CCl₄): δ 2.30 (1 H, d, J=15.6 Hz), 2.10-1.90 (1 H, m), 1.85-1.35 (10 H, m), 1.27 (3 H, s), 1.25 (3 H, s), 1.14 (3 H, s), 1.00 (3 H, s), 0.93 (3 H, s), 0.83 (3 H, d, J=6.6 Hz, sec. CH₃).

^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$): δ 74.4 (C, C-OH), 67.8 (C), 63.7 (C), 42.9 (CH), 42.7 (CH), 40.5 (C), 39.6 (C), 38.3 (CH_2), 33.0 (CH_2), 28.5 (CH_2), 28.0 (CH_3), 26.7 (CH_3), 24.0 (CH_3), 21.0 (CH_3), 20.9 (CH_3), 20.2 (CH_3), 19.2 (CH_2), 18.6 (CH_3).

Mass: 278 (M, 17%), 236 (8), 235 (6), 205 (8), 179 (13), 152 (14), 137 (46), 125 (100), 121 (35), 110 (28), 107 (44), 91 (30).

**(–)(1*R*,3*S*,6*S*,7*S*,8*S*)-3-Hydroxy-2,2,6,8-tetramethyltricyclo[5.3.1.0^{3,8}]undecan-10-one
(Valeriananoid-A 1):**

Mp: 117-118 °C (Lit.¹ 122-124 °C).

$[\alpha]_D^{24}$: –33.3 (c 0.3, CHCl_3) {Lit.¹ –34.6 (c 0.231, CHCl_3)}.

IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 3474, 2953, 2928, 1715, 1467, 1387, 1331, 1225, 1094, 1065, 1045, 998, 912.

^1H NMR (300 MHz, $\text{CDCl}_3+\text{CCl}_4$): δ 2.64 (1 H, d, $J=19.2$ Hz), 2.15-1.95 (1 H, m), 1.92-1.80 (2 H, m), 1.78 (1 H, d, $J=19.2$ Hz), 1.65-1.36 (7 H, m), 1.18 (3 H, s), 1.02 (3 H, s), 0.98 (3 H, s), 0.85 (3 H, d, $J=6.6$ Hz, sec. CH_3).

^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$): δ 216.1 (C, C=O), 74.3 (C, C-OH), 57.7 (CH), 46.5 (CH_2), 43.6 (CH), 42.4 (C), 40.5 (C), 33.1 (CH_2), 28.3 (CH_2), 27.9 (CH), 27.7 (CH_3), 23.0 (CH_3), 20.9 (CH_2), 19.5 (CH_3), 18.7 (CH_3).

Mass: 236 (M, 55%), 221 (40), 153 (47), 138 (38), 137 (40), 135 (59), 125 (100), 109 (40), 107 (40).

**(–)(1*R*,3*S*,6*S*,7*S*,8*S*,10*R*)-2,2,6,8-Tetramethyltricyclo[5.3.1.0^{3,8}]undecane-3,10-diol
(Valeriananoid-B 2):**

Mp: 185-187 °C (Lit.¹ 200-202 °C; Lit.² 133-135 °C; Lit.³ 179-181 °C).

$[\alpha]_D^{24}$: –90.0 (c 1.0, CHCl_3) {Lit.¹ –57.87 (c 0.197, CHCl_3); Lit.² –115.8 (c 0.41, CHCl_3); Lit.³ –75.4 (c 1.1, CHCl_3)}.

IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 3354, 2912, 1463, 1376, 1331, 1109, 1046, 1012, 914.

^1H NMR (300 MHz, $\text{CDCl}_3+\text{CCl}_4$): δ 3.92 (1 H, dd, $J=9.0$ and 8.4 Hz, CHOH), 2.00-1.84 (1 H, m), 1.88 (1 H, dd, $J=13.8$ and 7.8 Hz), 1.75 (1 H, dd, $J=13.8$ and 6.6 Hz), 1.70-1.40 (6 H, m), 1.40-1.20 (4 H, m), 1.24 (3H, s), 1.12 (3 H, s) and 0.89 (3 H, s) [3 x *tert*- CH_3], 0.80 (3 H, d, $J=6.6$ Hz, sec- CH_3).

^{13}C NMR (75 MHz, $\text{CDCl}_3+\text{CCl}_4$): δ 75.2 (C, C-OH), 72.5 (CH, CH-OH), 46.7 (CH), 42.4 (CH), 40.4 (C), 39.4 (CH_2), 39.3 (C), 32.5 (CH_2), 28.5 (CH_2), 28.1 (CH), 27.7 (CH_3), 25.4 (CH_3), 24.1 (CH_2), 20.1 (CH_3), 18.9 (CH_3).

Mass: 220 (M – H_2O , 5%), 205 (3), 177 (7), 159 (5), 149 (6), 126 (7), 125 (100), 107 (16), 96 (58).

Valeriananoid-B 2 in CD₃OD:

¹H NMR (300 MHz, CD₃OD): δ 3.88 (1 H, t, J=9.0 Hz, CH-OH), 1.97 (1 H, dd, J=13.5 and 7.5 Hz), 2.10-1.90 (1 H, m), 1.73 (1 H, dd, J=14.1 and 5.1 Hz), 1.65-1.20 (10 H, m), 1.18 (3 H, s), 1.10 (3 H, s) and 0.88 (3 H, s) [3 x *tert* CH₃], 0.81 (3 H, d, J=6.9 Hz, sec. CH₃).

¹³C NMR (75 MHz, CD₃OD): δ 76.5 (C, GOH), 73.1 (CH, CHOH), 47.7 (CH), 44.2 (CH), 41.7 (C), 40.2 (CH₂), 39.9 (C), 33.0 (CH₂), 29.7 (CH₂), 29.1 (2 C, CH, CH₃), 26.0 (CH₃), 25.2 (CH₂), 21.1 (CH₃), 19.4 (CH₃).

(–)-(1*R*,3*S*,6*S*,7*S*,8*S*,10*R*)-10-Acetoxy-2,2,6,8-tetramethyltricyclo[5.3.1.0^{3,8}]undecan-3-ol (Valeriananoid-C 3):

Mp: 74-76 °C (Lit.¹ 79-80 °C; Lit.² 85-86 °C).

$[\alpha]_D^{22}$: –116.0 (c 1.0, CHCl₃) {Lit.¹ –56.88 (c 0.16, CHCl₃); Lit.² –114.8 (c 3.3, CHCl₃)}.

IR (neat): $\nu_{\max}/\text{cm}^{-1}$ 3516, 2930, 1738, 1724, 1715, 1456, 1367, 1249, 1087, 1030, 954.

¹H NMR (300 MHz, CDCl₃+CCl₄): δ 4.79 (1 H, t, J=9.0 Hz, CHOAc), 2.02 (3 H, s, CH₃C=O), 2.01 (1 H, dd, J=15.9 and 7.8 Hz), 1.94 (1 H, d, J=7.5 Hz), 1.80-1.20 (10 H, m), 1.15 (3 H, s) and 1.11 (3 H, s) and 0.90 (3 H, s) [3 x *tert*-CH₃], 0.80 (3 H, d, J=7.2 Hz, sec. CH₃).

¹³C NMR (75 MHz, CDCl₃+CCl₄): δ 170.8 (C, O-C=O), 75.0 (C, GOH), 74.5 (CH, CH-OAc), 43.3 (CH), 42.4 (CH), 40.1 (C), 39.1 (C), 35.9 (CH₂), 32.6 (CH₂), 28.5 (CH₂), 27.8 (CH), 27.6 (CH₃), 25.0 (CH₃), 23.4 (CH₂), 21.6 (CH₃), 20.0 (CH₃), 18.8 (CH₃).

Mass: 220 (M- AcOH, 4%), 177 (3), 126 (3), 125 (100), 107 (7), 96 (59).