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Supplementary material

SUPPLEMENTARY MATERIAL TO

Synthesis and bioactivity of *erythro*-nordihydroguaiaretic acid, *threo*-(–)-saururenin and their analogues

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SPECTROSCOPIC DATA OF THE SYNTHESIZED COMPOUNDS

*Diethyl 2-(3,4-methylenedioxybenzylidene)succinate (**2a**)*. ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 1.22 (3H, *t*, *J* = 7.3 Hz), 1.29 (3H, *t*, *J* = 7.3 Hz,), 3.51 (2H, *s*), 4.16 (2H, *q*, *J* = 7.3 Hz), 4.27 (2H, *q*, *J* = 7.3 Hz), 5.96 (2H, *s*), 6.76−6.87 (3H, *m*), 7.76 (1H, *s*). EI-MS (*m*/*z*, %): 306 (M^+, 70), 261 (20), 232 (34), 203 (52), 175 (59), 159 (100).

*Diethyl 2-(3,4-dimethoxybenzylidene)succinate (**2b**)*. ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 1.33 (3H, *t*, *J* = 7.3 Hz), 1.26 (3H, *t*, *J* = 7.2 Hz), 3.58 (2H, *s*), 3.87 (3H, *s*), 3.90 (3H, *s*), 4.21 (2H, *q*, *J* = 7.3 Hz), 4.27 (2H, *q*, *J* = 7.3 Hz), 6.86−7.00 (3H, *m*), 7.84 (1H, *s*). EI-MS (*m*/*z*, %): 322 (M^+, 42), 276 (14), 249 (16), 175 (100).

*Diethyl 2-(3,4-methylenedioxybenzyl)-3-(3,4-methylenedioxybenzylidene)succinate (**3a**)*. m.p. 58–59 °C. ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 1.26 (3H, *t*, *J* = 7.2 Hz, CH_3), 1.34 (3H, *t*, *J* = 7.2 Hz, CH_3), 2.85 (1H, *dd*, *J* = 10.0, 14.2 Hz, H-7"α), 3.34 (1H, *dd*, *J* = 5.0, 14.2 Hz, H-7"β), 3.98 (1H, *dd*, *J* = 5.0, 10.0 Hz, H-3), 4.15−4.32 (4H, *m*, 2×C**H**$_2$CH$_3$), 5.88 (2H, *s*, OCH_2O), 5.97 (2H, *s*, OCH_2O), 6.35−6.73 (6H, *m*, ArH), 7.66 (1H, *s*, H-7'). ^{13}C-NMR (50 MHz, $CDCl_3$, δ / / ppm): 14.4 (2×CH_2**C**H_3), 36.0 (C-3), 45.8 (C-7"), 61.2 (2×O**C**H_2CH_3), 100.9 (OCH_2O), 101.4 (OCH_2O), 108.1 (C-5'), 108.4 (C-5"), 108.7 (C-2'), 109.7 (C--2"), 122.4 (C-6'), 122.7 (C-6"), 129.3 (C-1'), 130.1 (C-1"), 133.2 (C-2), 142.5 (C-7'), 146.1(C-4'), 147.5 (C-4'), 147.8 (C-3', C-3''), 166.9 (C=O), 172.9 (C=O). EI-MS (*m*/*z*, %): 440 (M^+, 4), 395 (1), 306 (5), 231 (40), 137 (100); HRMS Calcd. for $C_{24}H_{25}O_8$ ($M+H^+$): 441.1544. Found: 441.1538.

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*Diethyl 2-(3,4-dimethoxybenzylidene)-3-(3,4-methylenedioxybenzyl)succinate (**3b**)*. ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 1.26 (3H, *t*, *J* = 7.2 Hz, CH_3), 1.35 (3H, *t*, *J* = 7.2 Hz, CH_3), 2.91 (1H, *dd*, *J* = 9.8, 14.2 Hz, H-7''α), 3.34 (1H, *dd*, *J* = 5.0, 14.2 Hz, H-7''β), 3.78 (3H, *s*, OCH_3), 3.88 (3H, *s*, OCH_3), 4.10 (1H, *dd*, *J* = 5.0, 9.8 Hz, H-3), 4.18 (2H, *q*, *J* = 7.2 Hz, C**H**$_2$CH$_3$), 4.30 (2H, *q*, *J* = 7.2 Hz, C**H**$_2$CH$_3$), 5.85 (2H, *s*, OCH_2O), 6.35–6.80 (6H, *m*, ArH), 7.71 (1H, *s*, H-7'). ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 14.1 (CH$_2$**C**H$_3$), 14.2 (CH$_2$**C**H$_3$), 35.7 (C--3), 45.5 (C-7''), 55.7 (OCH_3), 55.8 (OCH_3), 60.9 (2 × **C**H$_2$CH$_3$), 100.7 (OCH_2O), 107.7 (C-5'), 109.4 (C-5''), 110.7 (C-2'), 111.4 (C-2''), 121.1 (C-6'), 122.0 (C-6''), 127.9 (C-1'), 129.5 (C-1''), 132.9 (C-2), 142.3 (C-7'), 145.7 (C-4'), 147.2 (C-4''), 148.6 (C-3'), 149.1 (C-3''), 166.7 (C=O), 172.7 (C=O). EI-MS (*m*/*z*, %): 456 (M^+, 3), 411 (1), 382 (1), 322 (4), 247 (51), 137 (100). HRMS Calcd. for $C_{25}H_{29}O_8$ ($M+H^+$): 457.1857. Found: 457.1856.

*(–)-2-(3,4-Methylenedioxybenzyl)-3-(3,4-methylenedioxybenzylidene)succinic acid (**4a**)*. M.p. 98–99 °C. ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.85 (1H, *dd*, *J* = 10.2, 13.8 Hz, H-7''α), 3.25 (1H, *dd*, *J* = 4.4, 13.8 Hz, H-7''β), 3.93 (1H, *dd*, *J* = 4.4, 10.2 Hz, H-3), 5.92 (2H, *s*, OCH_2O), 6.04 (2H, *s*, OCH_2O), 6.37−6.90 (6H, *m* , ArH), 7.53 (1H, *s*, H-7'). EI-MS (*m*/*z*, %): 384 (M^+, 1), 366 (1), 244 (1), 203 (3), 159 (2), 135 (100). $[\alpha]_D^{16}$ = –95.3 (*c* 1.0, EtOH).

*(+)-2-(3,4-Methylenedioxybenzyl)-3-(3,4-methylenedioxybenzylidene)succinic acid (**4a'**)*. M.p. 96–97 °C. $[\alpha]_D^{16}$ = +94.8 (*c* 0.8, EtOH). The ^{1}H-NMR, IR and MS data of **4a'** were in agreement with those of **4a**.

*(–)-2-(3,4-Dimethoxybenzylidene)-3-(3,4-methylenedioxybenzyl)succinic acid (**4b**)*. M.p. 159−160 °C. ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.83 (1H, *dd*, *J* = 10.2, 14.0 Hz, H-7''α), 3.18 (1H, *dd*, *J* = 4.8, 14.0 Hz, H-7''β), 3.64 (3H, *s*, OCH_3), 3.73 (3H, *s*, OCH_3), 3.95 (1H, *dd*, *J* = 4.8, 10.2 Hz, H-3), 5.87 (2H, *d*, *J* = 8.2 Hz, OCH_2O), 6.35−6.89 (6H, *m*, ArH), 7.52 (1H, *s*, H-7'). EI-MS (*m*/*z*, %): 400 (M^+, 1), 382 (17), 260 (5), 219 (12), 175 (26), 135 (100); HRMS Calcd. for $C_{21}H_{21}O_8$ ($M+H^+$): 401.1231. Found: 401.1239. $[\alpha]_D^{16}$ = –143.2 (*c* 0.7, EtOH).

*(+)-2-(3,4-Dimethoxybenzylidene)-3-(3,4-methylenedioxybenzyl)succinic acid (**4b'**)*. M.p. 89–91 °C; $[\alpha]_D^{16}$ = +142.6 (*c* 0.6, EtOH). The ^{1}H-NMR, IR and MS of **4b'** were in agreement with those of **4b**.

*(–)-Diethyl 2-(3,4-methylenedioxybenzyl)-3-(3,4-methylenedioxybenzylidene)succinate (**5a**)*. $[\alpha]_D^{16}$ = –68.4 (*c* 1.0, $CHCl_3$). The ^{1}H-NMR, IR, MS and HRMS data of **5a** were in agreement with those of **3a**.

*(–)-Diethyl 2-(3,4-methylenedioxybenzyl)-3-(3,4-dimethoxybenzylidene)succinate (**5b**)*. $[\alpha]_D^{16}$ = –170.1 (*c* 1.0, $CHCl_3$). The ^{1}H-NMR, IR, MS and HRMS data of **5b** were in agreement with those of **3b**.

*(–)-Dihydrocubebin (**6a**)*. M.p. 112–113 °C. ^{1}H-NMR (200 MHz, $CDCl_3$, δ / / ppm): 1.80−1.84 (2H, *m*, H-2, H-3), 2.55−2.81 (4H, *m*, 2×ArCH$_2$), 3.48 (2H, *d*,

J = 11.2 Hz, C**H**$_2$OH), 3.72 (2H, *s*, 2×OH), 3.74 (2H, *d*, *J* = 11.2 Hz, C**H**$_2$OH), 5.91 (4H, *s*, 2×OCH$_2$O), 6.58−6.73 (6H, *m*, ArH). ^{13}C-NMR (100 MHz, CDCl$_3$, *δ* / ppm): 35.8 (C-2, C-3), 44.2 (C-7', C-7''), 59.9 (C-1, C-4), 100.7 (2×OCH$_2$O), 108.1 (C-5', C-5''), 109.2 (C-2', C-2''), 121.8 (C-6', C-6''), 134.3 (C-1', C-1''), 145.6 (C-4', C-4''), 147.5 (C-3', C-3''). EI-MS (*m*/*z*, %): 358 (M$^+$, 2), 340 (0.1), 204 (0.3), 161 (3), 135 (100); HRMS Calcd. for $C_{20}H_{26}NO_6$ (M+NH$_4^+$): 376.1755. Found: 376.1760. $[\alpha]_D^{16}$ = –41.9 (*c* 0.8, CHCl$_3$). The spectral data are in agreement with the literature.[22]

*(2*R*,3*R*)-2-(3,4-Dimethoxybenzyl)-3-(3,4-methylenedioxybenzyl)-1,4-butanediol (**6b**)*. ^{1}H-NMR (200 MHz, CDCl$_3$, *δ* / ppm): 1.85−1.87 (2H, *m*, H-2, H-3), 2.60−2.80 (4H, *m*, 2×H-7', 2×H-7''), 3.50 (2H, *d*, *J* = 11.6 Hz, C**H**$_2$OH), 3.56 (2H, *s*, 2×OH), 3.80 (2H, *d*, *J* = 11.6 Hz, C**H**$_2$OH), 3.82 (3H, *s*, OCH$_3$), 3.84 (3H, *s*, OCH$_3$), 5.90 (2H, *s*, OCH$_2$O), 6.57−6.80 (6H, *m*, ArH). ^{13}C-NMR (100 MHz, CDCl$_3$, *δ* / ppm): 35.7 (C-2), 35.9 (C-3), 43.9 (C-7'), 44.1 (C-7''), 55.8 (OCH$_3$), 55.9 (OCH$_3$), 60.2 (C-1), 60.3 (C-4), 100.7 (OCH$_2$O), 108.0 (C-5'), 109.3 (C-5''), 111.2 (C-2'), 112.1 (C-2''), 121.0 (C-6'), 121.8 (C-6''), 133.1 (C-1'), 134.3 (C-1''), 145.7 (C-4'), 147.3 (C-4''), 147.5 (C-3'), 148.8 (C-3''). EI--MS (*m*/*z*, %): 374 (M$^+$, 4), 356 (0.4), 220 (3), 203 (3), 151 (100). HRMS Calcd. for $C_{21}H_{30}NO_6$ (M+NH$_4^+$): 392.2068. Found: 392.2063. $[\alpha]_D^{16}$ = –36.8 (*c* 0.5, CHCl$_3$). The spectral data are in agreement with the literature.[23]

meso-*2,3-Bis(3,4-methylenedioxybenzyl)butane-1,4-diol (**7a**)*. ^{1}H-NMR (200 MHz, CDCl$_3$, *δ* / ppm): 1.99−2.05 (2H, *m*, H-2, H-3), 2.49−2.63 (4H, *m*, 2×ArCH$_2$), 3.45−3.61 (4H, *m*, 2×C**H**$_2$OH), 3.71 (2H, *s*, 2×OH), 5.92 (4H, *s*, 2×OCH$_2$O), 6.61−6.76 (6H, *m*, ArH). ^{13}C-NMR (50 MHz, CDCl$_3$, *δ* / ppm): 33.4 (C-2, C-3), 45.2 (C-7', C-7''), 62.9 (C-1, C-4), 100.8 (2×OCH$_2$O), 108.1 (C-5', C-5''), 109.2 (C-2', C-2''), 121.8 (C-6', C-6''), 134.1 (C-1', C-1''), 145.8 (C-4', C-4''), 147.6 (C-3', C-3''). EI-MS (*m*/*z*, %): 358 (M$^+$, 3), 340 (0.3), 204 (0.8), 161 (4), 135 (100); HRMS Calcd. for $C_{20}H_{26}NO_6$ (M+NH$_4^+$): 376.1755. Found: 376.1760.

*(2*R*,3*S*)-2-(3,4-Dimethoxybenzyl)-3-(3,4-methylenedioxybenzyl)-1,4-butanediol (**7b**)*. ^{1}H-NMR (200 MHz, CDCl$_3$, *δ* / ppm): 1.84−1.86 (2H, *m*, H-2, H-3), 2.56−2.82 (4H, *m*, 2×H-7', 2×H-7''), 3.50 (2H, *d*, *J* = 11.0 Hz, C**H**$_2$OH), 3.75 (2H, *d*, *J* = 11.0 Hz, C**H**$_2$OH), 3.81 (3H, *s*, OCH$_3$), 3.83 (3H, *s*, OCH$_3$), 3.95 (2H, *s*, 2×OH), 5.89 (2H, *s*, OCH$_2$O), 6.56–6.78 (6H, *m*, ArH). ^{13}C-NMR (100 MHz, CDCl$_3$, *δ* / ppm): 33.1 (C-2), 33.4 (C-3), 45.0 (C-7'), 45.2 (C-7''), 55.8 (OCH$_3$), 55.9 (OCH$_3$), 62.9 (C-1), 63.0 (C-4), 100.8 (OCH$_2$O), 108.1 (C-5'), 109.3 (C-5''), 111.2 (C-2'), 112.1 (C-2''), 121.0 (C-6'), 121.8 (C-6''), 133.0 (C--1'), 134.2 (C-1''), 145.8 (C-4'), 147.3 (C-4''), 147.6 (C-3'), 148.8 (C-3''). EI--MS (*m*/*z*, %): 374 (M$^+$, 4.7), 356 (0.23), 220 (1.8), 203 (2.5), 151 (100). HRMS Calcd. for $C_{21}H_{30}NO_6$ (M+NH$_4^+$): 392.2068. Found: 392.2063. $[\alpha]_D^{16}$ = –1.7 (*c* 0.3, CHCl$_3$). The spectral data were in agreement with the literature.[24]

*(–)-Dehydroxycubebin (**8a**)*. ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 2.07––2.18 (2H, *m*, H-3, H-4), 2.42–2.59 (4H, *m*, 2×$ArCH_2$), 3.49 (2H, *dd*, *J* = 5.8, 8.6 Hz, 2×H-2), 3.89 (2H, *dd*, *J* = 6.8, 8.8 Hz, 2×H-5), 5.91 (4H, *s*, 2×OCH_2O), 6.51–6.75 (6H, *m*, ArH). ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 39.1 (C-3, C-4), 46.4 (C-7', C-7''), 73.2 (C-2, C-5), 100.7 (2×OCH_2O), 107.9 (C-5', C-5''), 108.9 (C-2', C-2''), 121.4 (C-6', C-6''), 134.0 (C-1', C-1''), 145.7 (C-4', C-4''), 147.5 (C-3', C-3''). EI-MS (*m*/*z*, %): 340 (M^+, 11), 204 (2), 187 (3), 161 (2), 136 (100). $[\alpha]_D^{16}$ = –54.2 (*c* 0.8, $CHCl_3$).

*(–)-5-{[(3*R*,4*R*)-4-(3,4-Dimethoxybenzyl)-tetrahydro-3-furanyl]methyl}-1,3--benzodioxole (**8b**)*. ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 2.15−2.18 (2H, *m*, H-3, H-4), 2.45−2.59 (4H, *m*, 2 × $ArCH_2$), 3.46−3.54 (2H, *m*, 2 × H-2), 3.84 (3H, *s*, OCH_3), 3.85 (3H, *s*, OCH_3), 3.89−3.93 (2H, *m*, 2×H-5), 5.91 (2H, *s*, OCH_2O), 6.51–6.78 (6H, *m*, ArH). ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 39.0 (C-3), 39.1 (C-4), 46.5 (C-7'), 46.6 (C-7''), 55.7 (OCH_3), 55.8 (OCH_3), 73.2 (C-2), 73.3 (C--5), 100.8 (OCH_2O), 108.0 (C-5'), 108.9 (C-5''), 111.1 (C-2'), 111.8 (C-2'), 120.5 (C-6'), 121.4 (C-6''), 132.9 (C-1'), 134.1 (C-1''), 145.8 (C-4'), 147.4 (C-4''), 147.6 (C-3'), 148.8 (C-3''). EI-MS (*m*/*z*, %): 356 (M^+, 15), 220 (3), 177 (6), 151 (100). HRMS Calcd. for $C_{21}H_{25}O_5$ ($M+H^+$): 357.1697. Found: 357.1701. $[\alpha]_D^{16}$ = –104.7 (*c* 0.6, $CHCl_3$).

*(+)-5.5'-[(2*R*,3*R*)-2,3-Bis(methoxymethyl)-1,4-butanediyl]bis(1,3-dioxole) (**9a**)*. ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 2.00–2.03 (2H, *m*, H-2, H-3), 2.52−2.69 (4H, *m*, 2×$ArCH_2$), 3.28 (10H, *s*, 2×OCH_3, 2×H-1, 2×H-4), 5.92 (4H, *s*, 2×OCH_2O), 6.55−6.71 (6H, *m*, ArH). ^{13}C-NMR (75 MHz, $CDCl_3$, δ / / ppm): 35.1 (C-2, C-3), 41.2 (C-7', C-7''), 58.9 (C-7', C-7''), 72.7 (C-1, C--4), 100.9 (2×OCH_2O), 108.2 (C-5', C-5''), 109.7 (C-2', C-2''), 122.1 (C-6', C--6''), 135.1 (C-1', C-1''), 145.8 (C-4', C-4''), 147.7 (C-3', C-3''). EI-MS (*m*/*z*, %): 386 (M^+, 5), 354 (7), 218 (9), 187 (19), 161 (8), 135 (100). $[\alpha]_D^{16}$ +12.3 (*c* 0.5, $CHCl_3$).

*(+)-5-[(2-(2*R*,3*R*)-4-(3,4-Dimethoxybenzyl)-2,3-bis(methoxymethyl)-butyl]--1,3-benzodioxole (**9b**)*. ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 2.00–2.03 (2H, *m*, H-2, H-3), 2.61−2.64 (4H, *m*, 2×$ArCH_2$), 3.29 (10H, *s*, 2×OCH_3, 2×H-1, 2×H-4), 3.82 (3H, *s*, $ArOCH_3$), 3.86 (3H, *s*, $ArOCH_3$), 5.92 (2H, *s*, 2×OCH_2O), 6.55−6.78 (6H, *m*, ArH). ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 34.8 (C-2), 34.9 (C-3), 40.7 (C-7'), 40.9 (C-7''), 55.7 (OCH_3), 55.9 (OCH_3), 58.7 ($ArOCH_3$), 58.8 ($ArOCH_3$), 72.4 (C-1), 72.6 (C-4), 100.7 (OCH_2O), 107.9 (C-5'), 109.4 (C-5''), 110.9 (C-2'), 111.9 (C-2'), 121.1 (C-6'), 121.9 (C-6''), 133.5 (C-1'), 134.9 (C--1''), 145.5 (C-4'), 147.1 (C-4''), 147.4 (C-3'), 148.7 (C-3''). EI-MS (*m*/*z*, %): 402 (M^+, 21), 370 (6), 203 (17), 151 (100). $[\alpha]_D^{16}$ = +14.8 (*c* 0.6, $CHCl_3$).

*(–)-Austrobailignan-5 (**10a**)*. M.p. 44–45 °C. ^{1}H-NMR (200 MHz, $CDCl_3$, δ / / ppm): 0.81 (6H, *d*, *J* = 6.8 Hz, 2×CH_3), 1.67−1.77 (2H, *m*, H-2, H-3), 2.33 (2H, *dd*, *J* = 8.2, 13.6 Hz, $ArCH_2$), 2.55 (2H, *dd*, *J* = 6.0, 13.6 Hz, $ArCH_2$), 5.92 (4H,

s, 2×OCH_2O), 6.52−6.75 (6H, *m*, ArH). ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 13.9 (C-1, C-4), 38.2 (C-2, C-3), 41.2 (C-7', C-7''), 100.7 (2×OCH_2O), 107.9 (C-5', C-5''), 109.3 (C-2', C-2''), 121.8 (C-6', C-6''), 135.5 (C-1', C-1''), 145.5 (C-4', C-4''), 147.4 (C-3', C-3''). EI-MS (*m*/*z*, %): 326 (M^+, 1), 135 (20), 123 (100). $[\alpha]_D^{16}$ = –36.3 (*c* 0.5, $CHCl_3$). The spectral data are in agreement with the literature.[25]

*(–)-Saururenin (**10b**)*. ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 0.82 (6H, *d*, *J* = 6.6 Hz, 2×CH_3), 1.71−1.77 (2H, *m*, H-2, H-3), 2.30–2.42 (2H, *m*, $ArCH_2$), 2.49−2.59 (2H, *m*, $ArCH_2$), 3.83 (3H, *s*, OCH_3), 3.85 (3H, *s*, OCH_3), 5.90 (2H, *s*, OCH_2O), 6.51−6.78 (6H, *m*, ArH). ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 13.7 (C-1), 13.8 (C-4), 37.7 (C-2), 37.9 (C-3), 40.9 (C-7'), 41.1 (C-7''), 55.7 (OCH_3), 55.8 (OCH_3), 100.6 (OCH_2O), 107.8 (C-5'), 109.2 (C-5''), 111.0 (C-2'), 112.0 (C-2''), 120.8 (C-6'), 121.7 (C-6''), 134.1 (C-1'), 135.4 (C-1''), 145.4 (C-4'), 147.0 (C-4''), 147.3 (C-3'), 148.7 (C-3''). EI-MS (*m*/*z*, %): 342 (M^+, 8), 206(2), 151 (100). $[\alpha]_D^{16}$ = –33.0 (*c* 0.8, $CHCl_3$). The spectral data were in agreement with the literature.[10]

meso-*5,5'-[(Tetrahydro-3,4-furandiyl)bis(methylene)]bis(1,3-benzodioxole) (**11a**)*. ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 2.49−2.53 (4H, *m*, H-3, H-4, $ArCH_2$), 2.75−2.84 (2H, *m*, $ArCH_2$), 3.62 (2H, *dd*, *J* = 5.6, 8.2 Hz, 2×H-2), 3.79 (2H, *dd*, *J* = 5.6, 8.2 Hz, 2×H-5), 5.95 (4H, *s*, 2×OCH_2O), 6.57−6.78 (6H, *m*, ArH). ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 33.2 (C-3, C-4), 43.6 (C-7', C-7''), 71.9 (C-2, C-5), 100.8 (2×OCH_2O), 108.2 (C-5', C-5''), 108.9 (C-2', C-2''), 121.5 (C-6', C-6''), 134.3 (C-1', C-1''), 145.8 (C-4', C-4''), 147.7 (C-3', C-3''). EI-MS (*m*/*z*, %): 340 (M^+, 9), 204 (5), 187(2), 161 (5), 136 (100). HRMS Calcd. for $C_{20}H_{24}NO_5$ ($M+NH_4^+$): 358.1649. Found: 358.1648. $[\alpha]_D^{16}$ = 0 (*c* 0.8, $CHCl_3$).

*(+)-5-{[(3*S*,4*R*)-4-[(3,4-Dimethoxyphenyl)methyl]tetrahydro-3-furanyl]methyl}-1,3-benzodioxole (**11b**)*. ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 2.15−2.18 (2H, *m*, H-3, H-4), 2.45−2.59 (4H, *m*, 2×$ArCH_2$), 3.46−3.54 (2H, *m*, 2×H-2), 3.84 (3H, *s*, OCH_3), 3.85 (3H, *s*, OCH_3), 3.89−3.93 (2H, *m*, 2×H-5), 5.91 (2H, *s*, OCH_2O), 6.51−6.78 (6H, *m*, ArH). ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 39.0 (C-3), 39.1 (C-4), 46.5 (C-7'), 46.6 (C-7''), 55.7 (OCH_3), 55.8 (OCH_3), 73.2 (C--2), 73.3 (C-5), 100.8 (OCH_2O), 108.0 (C-5'), 108.9 (C-5''), 111.1 (C-2'), 111.8 (C-2'), 120.5 (C-6'), 121.4 (C-6''), 132.9 (C-1'), 134.1 (C-1''), 145.8 (C-4'), 147.4 (C-4''), 147.6 (C-3'), 148.8 (C-3''). EI-MS (*m*/*z*, %): 356 (M^+, 15), 220 (3), 177 (6), 151 (100); HRMS Calcd. for $C_{21}H_{25}O_5$ ($M+H^+$): 357.1697. Found: 357.1695. $[\alpha]_D^{16}$ = +2.5 (*c* 0.8, $CHCl_3$).

meso-*5,5'-[Bis(methoxymethyl)-1,4-butanediyl]bis(1,3-benzodioxole) (**12a**)*. ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 2.04−2.08 (2H, *m*, H-2, H-3), 2.51−2.69 (4H, *m*, 2×$ArCH_2$), 3.26 (6H, *s*, 2×OCH_3), 3.26−3.38 (4H, *m*, H-1, H-4), 5.92 (4H, *s*, 2×OCH_2O), 6.58−6.74 (6H, *m*, ArH). ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 34.4

(C-2, C-3), 40.9 (C-7', C-7''), 58.6 (C-7', C-7''), 72.7 (C-1, C-4), 100.7 (2×OCH_2O), 107.9 (C-5', C-5''), 109.3 (C-2', C-2''), 121.8 (C-6', C-6''), 134.9 (C-1', C-1''), 145.6 (C-4', C-4''), 147.5 (C-3', C-3''). EI-MS, (*m*/*z*, %): 386 (M^+, 5), 354 (5), 322 (3), 218 (11), 187 (21), 173 (12), 135 (100). HRMS Calcd. for $C_{22}H_{27}O_6$ ($M+H^+$): 387.1802. Found: 387.1812. $[\alpha]_D^{16}$ = 0 (*c* 0.4, $CHCl_3$).

*(+)-5-{[(3*S*,4*R*)-4-[(3,4-Dimethoxyphenyl)-2,3-bis(methoxymetyl)butyl]-1,3--benzodioxole (**12b**)*. ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 2.07−2.11 (2H, *m*, H--2, H-3), 2.58−2.66 (4H, *m*, 2×$ArCH_2$), 3.29 (6H, *s*, 2×OCH_3), 3.26−3.38 (4H, *m*, 2×$ArCH_2$), 3.85 (3H, *s*, $ArOCH_3$), 3.86 (3H, *s*, $ArOCH_3$), 5.92 (2H, *s*, 2×OCH_2O), 6.60−6.80 (6H, *m*, ArH). ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 34.8 (C-2), 34.9 (C-3), 40.7 (C-7'), 40.8 (C-7''), 55.6 (OCH_3), 55.8 (OCH_3), 58.7 ($ArOCH_3$), 58.8 ($ArOCH_3$), 72.4 (C-1), 72.6 (C-4), 100.7 (OCH_2O), 107.8 (C-5'), 109.4 (C-5''), 110.9 (C-2'), 120.0 (C-2'), 121.0 (C-6'), 121.9 (C-6''), 133.5 (C--1'), 134.8 (C-1''), 145.5 (C-4'), 147.1 (C-4''), 147.4 (C-3'), 148.7 (C-3''). HRMS Calcd. for $C_{23}H_{34}NO_6$ ($M+NH_4^+$): 420.2381. Found: 420.2384. $[\alpha]_D^{16}$ = = +2.7 (*c* 0.8, $CHCl_3$).

meso-*Machilin A (**13a**)*. M.p. 47–48 °C. ^{1}H-NMR (200 MHz, $CDCl_3$, δ / / ppm): 0.83 (6H, *d*, *J* = 6.6 Hz, 2×CH_3), 1.72−1.76 (2H, *m*, H-2, H-3), 2.26 (2H, *dd*, *J* = 9.4, 13.4 Hz, $ArCH_2$), 2.72 (2H, *dd*, *J* = 4.8, 13.4 Hz, $ArCH_2$), 5.93 (4H, *s*, 2×OCH_2O), 6.58−6.76 (6H, *m*, ArH). ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 16.1 (C-1, C-4), 39.0 (C-2, C-3), 39.3 (C-7', C-7''), 100.6 (2×OCH_2O), 107.9 (C-5', C-5''), 109.2 (C-2', C-2''), 121.8 (C-6', C-6''), 135.6 (C-1', C-1''), 145.4 (C-4', C-4''), 147.4 (C-3', C-3''). EI-MS (*m*/*z*, %): 326 (M^+, 3), 135(58), 123 (100). $[\alpha]_D^{16}$ = 0 (*c* 0.4, $CHCl_3$). The spectral data are in agreement with the literature.[26]

*(–)-Isosaururenin (**13b**)*. ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 0.82 (3H, *d*, *J* = 6.6 Hz, CH_3), 0.85 (3H, *d*, *J* = 6.6 Hz, CH_3), 1.62−1.79 (2H, *m*, H-2, H-3), 2.20−2.35 (2H, *m*, $ArCH_2$), 2.68−2.78 (2H, *m*, $ArCH_2$), 3.86 (6H, *s*, 2×OCH_3), 5.90 (2H, *s*, OCH_2O), 6.59−6.81 (6H, *m*, ArH). ^{13}C-NMR (50 MHz, $CDCl_3$, δ / / ppm): 16.0 (C-1), 16.2 (C-4), 38.7 (C-2), 39.0 (C-3), 39.1 (C-7'), 39.3 (C-7''), 55.7 (OCH_3), 55.9 (OCH_3), 100.6 (OCH_2O), 107.9 (C-5'), 109.3 (C-5''), 111.0 (C-2'), 112.2 (C-2''), 120.9 (C-6'), 121.7 (C-6''), 134.4 (C-1'), 135.6 (C-1''), 145.4 (C-4'), 147.0 (C-4''), 147.4 (C-3'), 148.7 (C-3''). EI-MS (*m*/*z*, %): 342 (M^+, 6), 206(10), 151 (100). $[\alpha]_D^{16}$ = –1.9 (*c* 0.8, $CHCl_3$).

meso-*Nordihydroguaiaretic acid (**14**)*. M.p. 184–185 °C. ^{1}H-NMR (300 MHz, acetone-d_6, δ / ppm): 0.86 (6H, *d*, *J* = 6.3 Hz, 2×CH_3), 1.80−1.85 (2H, *m*, H-2, H-3), 2.49 (2H, *dd*, *J* = 9.6, 12.9 Hz, $ArCH_2$), 2.96 (2H, *dd*, *J* = 5.4, 12.9 Hz, $ArCH_2$), 7.14−7.33 (6H, *m*, ArH). ^{13}C-NMR (75 MHz, acetone-d_6, δ / ppm): 16.1 (C-1, C-4), 39.5 (C-2, C-3), 40.3 (C-7', C-7''), 110.6 (C-5', C-5''), 111.5 (C-2', C-2''), 126.1 (C-6', C-6''), 140.2 (C-1', C-1''), 142.4 (C-4', C-4''), 144.3 (C-3', C-3''). EI–MS (*m*/*z*, %): 302 (M^+, 4), 178 (1), 151 (2), 137 (4), 123 (100).