**First report of flavonoids from leaves of *Machaerium acutifolium* by DI-ESI-MS/MS**

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**Supplementary material**

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**A**





**B**

**Fig. S1** Mass spectra of compound **1** (quercetin-3-O-rhamnosyl-(1→6)-hexoside): MS2 (**A**) and MS3 (**B**)





**Fig. S2** Mass spectra of compound **2** (quercetin-3-O-rhamnosyl-(1→6)-hexosyl-7-O-rhamnoside)



**Fig. S3** Mass spectra of compound **3** (quercetin-3-O-rhamnosyl-(1→2)-[rhamnosyl-(1→6)]-hexosyl-7-O-rhamnoside)



**A**



**B**



**C**

**Fig. S4** Mass spectra of compound **4** (kaempferol-3-O-rhamnosyl-(1→3)-rhamnosyl-(1→2)-[rhamnosyl-(1→6)]-hexosyl-7-O-rhamnoside): MS2 (**A**), MS3 (**B**) and MS4 (**C**)



**A**



**B**

**Fig. S5** Mass spectra of compound **5** (kaempferol-3-O-rhamnosyl-(1→2)-[rhamnosyl-(1→6)]-galactosyl-7-O-rhamnoside): MS2 (**A**) and MS3 (**B**)

**kaempferol-3-O-rhamnosyl-(1→2)-[rhamnosyl-(1→6)]-galactosyl-7-O-rhamnoside:** yellow amorphous solid; HPLC-UV λmax/nm: 264 and 347; tR=15.44 min. HRMS (ESI) *m/z*, calcd. for C33H40O19 [M-H]-: 740.6593, found: 740.2120. DI-ESI-MS/MS: *m/z* 739 [M-H]-, MS2: 593, 285; MS3: 285, 255, 211; MS4: 411, 327, 285, 151. NMR data: 1H NMR (DMSO-d6, 600 MHz): δ 6.41 (d, *J=*2.0 Hz, H-6); 6.77 (d, *J=*2.0 Hz, H-8); 8.05 (d, *J=*8.8 Hz, H-2’ and 6’); 6.83 (d, *J=*8.8 Hz, H-3’ and 5’); 5.50 (sl, 7-O-Rha-1); 4.35 (sl, 6”-O-Rha-2); 5.31 (d, *J=*7.7 Hz, 3-O-Gal-1); 1.01 (d, *J=*6.2 Hz, C-6-Rha-1); 1.07 (d, *J=*6.1 Hz, C-6-Rha-2); 13C NMR (DMSO-d6, 150 MHz): δ 156.0 (C-2), 133.5 (C-3), 177.6 (C-4), 160.9 (C-5), 99.4 (C-6), 161.6 (C-7), 94.7 (C-8), 157.1 (C-9), 105.6 (C-10), 120.7 (C-1’), 131.1 (C-2’ and 6’), 115.1 (C-3’ and 5’), 160.2 (C-4’), 98.4 (7-O-Rha-C-1’’), 70.3 (C-2’’), 70.6 (C-3’’), 71.6 (C-4’’), 69.8 (C-5’’), 17.9 (7-O-Rha-CH3); 101.8 (3-O-Gal-C-1”’), 71.1 (C-2”’), 72.9 (C-3”’), 68.0 (C-4”’), 73.6 (C-5”’), 65.1 (3-O-Gal-CH2), 100.0 (6-O-Rha-C-1””), 70.4 (C-2””), 70.1 (C-3””), 71.9 (C-4””), 68.3 (C-5””), 17.9 (6-O-Rha-CH3).



**A**





**B**

**Fig. S6** Mass spectra of compound **6** (kaempferol-3-O-rhamnosyl-(1→6)-galactosyl-7-O-rhamnoside): MS2 (**A**) and MS3 (**B**)

**kaempferol-3-O-rhamnosyl-(1→6)-galactosyl-7-O-rhamnoside:** yellow amorphous solid; HPLC-UV λmax/nm: 265 and 349; tR=9.99 min, 66.7 mg. HRMS (ESI) *m/z*, calcd. for C39H50O23 [M- H]-: 886.7863, found: 885.2670. DI-ESI-MS/MS: *m/z* 885 [M-H]-, MS2: 739, 285; MS3: 593, 575, 447, 285; MS4: 447, 429, 327, 285, 255. NMR data: 1H NMR (DMSO-d6, 600 MHz): δ 6.36 (d, *J*=2.0 Hz, H-6); 6.72 (d, *J*=2.0 Hz, H-8); 8.01 (d, *J*=8.8 Hz, H-2’ and 6’); 6.79 (d, *J*=8.8 Hz, H-3’ and 5’); 5.46 (sl, 7-O-Rha-1); 4.96 (sl, 6”’-O-Rha-2); 4.27 (sl, 2”’-O-Rha-3); 5.49 (d, *J*=7.7 Hz, 3-O-Gal-1); 0.69 (d, *J*=6.1 Hz, C-6-Rha-1); 0.96 (d, *J*=6.1 Hz, C-6-Rha-2); 1.04 (d, *J*=6.1 Hz, C-6-Rha-3); 13C NMR (DMSO-d6, 150 MHz): δ 156.4 (C-2), 133.4 (C-3), 177.9 (C-4), 161.3 (C-5), 99.4 (C-6), 162.0 (C-7), 95.1 (C-8), 157.3 (C-9), 106.0 (C-10), 121.1 (C-1’), 131.4 (C-2’ and 6’), 115.6 (C-3’ and 5’), 160.5 (C-4’), 98.8 (7-O-Rha-C-1”), 70.8 (C-2”), 71.1 (C-3”), 72.3 (C-4”), 70.5 (C-5”), 18.4 (7-O-Rha-CH3), 99.8 (3-O-Gal-C-1”’), 75.3 (C-2”’), 74.2 (C-3”’), 69.3 (C-4”’), 73.8 (C-5”’), 65.4 (6-O-Gal-CH2), 101.0 (2-O-Rha-C-1””), 70.5 (C-2””), 71.0 (C-3””), 72.0 (C-4””), 68.9 (C-5””), 17.7 (2-O-Rha-CH3), 100.4 (6-O-Rha-C-1””’), 70.7 (C-2””’), 71.0 (C-3””’), 72.3 (C-4””’), 69.1 (C-5””’), 18.4 (6-O-Rha-CH3).



**A**



**B**

**Fig. S7** Mass spectra of compound **7** (kaempferol-3-O-rhamnosyl-(1→6)-hexoside): MS2 (**A**) and MS3 (**B**)



**A**



**B**

**Fig. S8** Mass spectra of compound **8** (kaempferol-3-O-hexoside): MS2 (**A**) and MS3 (**B**)





**Fig. S9** Mass spectra of compound **9** (genistein)





**Fig. S10** Mass spectra of compound **10** (daidzein-8-*C*-glucoside)



**A**



**B**

**Fig. S11** Mass spectra of compound **11** (morelloflavone): MS2 (**A**) and MS3 (**B**)