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PHENOLIC COMPOUNDS FROM *Plantago major* AND *P. lanceolata*

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We studied the polyphenol compositions of the plantains *Plantago major* L. and *P. lanceolata* L. in order to find new sources of drug raw material. For this, the total polyphenols were isolated from the aerial parts of the plants (yields of 4.6% and 5.4, respectively, of the air-dried raw material mass).

Paper chromatography using system 1 (*n*-BuOH:AcOH:H_2O, 40:12:28) found that polyphenols from *P. major* contained 11 compounds. Column chromatography over hide powder using Et_2O (1), H_2O (2), and aqueous acetone (60%) (3) separated the total polyphenols into three fractions [1].

The first fraction contained a single compound (compound **1**), R_f 0.51 (system 2, *n*-BuOH:AcOH:H_2O, 4:1:5, upper phase). The second fraction had five compounds with R_f 0.45, 0.58, 0.53, 0.35, and 0.64 (system 3, *n*-BuOH:AcOH:H_2O, 4:1:2). Rechromatography of it over a column of polyamide with elution by aqueous EtOH of various concentrations separated the pure compounds (compounds **2**–**6**). The third fraction was rechromatographed over a column of silica gel with elution by a gradient of Et_2O:EtOAc with increasing EtOAc content to isolate five pure compounds with R_f 0.68, 0.36, 0.31, 0.22, and 0.14 (system 1) that were tannins (compounds **7**–**11**).

Compounds **1**–**9** were identified from the physicochemical properties as gallic acid (**1**), quercetin-3-rutinoside (rutin) (**2**), 5,7,3′,4′-tetrahydroxyflavone (luteolin) (**3**), 3,5,7,4′-tetrahydroxy-3′-methoxyflavone (isorhamnetin) (**4**), quercetin-3-*O*-*β*-D-galactopyranoside (hyperoside) (**5**), 3,5,7,3′,4′-pentahydroxyflavone (quercetin) (**6**) [2, 3], 1,2,3,4,6-penta-*O*-galloyl-*β*-D-glucose (**7**), 1,2,3-tri-*O*-galloyl-*β*-D-glucose (**8**), and 1,3,4,6-tetra-*O*-galloyl-*β*-D-glucose (**9**) [2, 3].

Hexahydroxydiphenoyl-1-(*O*-2-*O*-galloyl-*β*-D-glucopyranoside)-1-(*O*-*β*-D-xylopyranoside) Diester (10). $C_{32}H_{32}O_{23}$, white amorphous powder, R_f 0.22 (system 1). The acid hydrolysis products (HCl, 5%) were xylose, glucose, gallic and ellagic acids. UV spectrum (EtOH, λ_{max}, nm): 265, 283. IR spectrum (KBr, ν, cm^{-1}): 3350-3345 (OH), 1730-1710 (ester), 1620-1510 (Ar), 1020-1010 (sugar). PMR spectrum (200 MHz, acetone-d_6, δ, ppm, J/Hz): 4.24 (1H, d, J = 7.7, xyl-1), 3.03 (1H, m, J = 9.3, xyl-2), 3.11 (1H, m, J = 6.2, xyl-3), 3.26 (1H, m, J = 9.3, xyl-4), 3.63 (1H, m, J = 8.5, xyl-5), 4.01 (1H, t, J = 8, Glu-2), 4.20 (1H, d, J = 12, Glu-6), 4.43 (1H, t, J = 8, Glu-4), 4.64 (1H, m, J = 12, Glu-5), 4.60 (1H, t, J = 8, Glu-3), 6.01 (1H, d, J = 8, Glu-1), 7.00, 7.03, 7.08, 7.12, 7.16 (H, galloyl), 6.62, 6.63, 6.70, 6.71 (H, hexahydroxydiphenoyl). ^{13}C NMR spectrum (50 MHz, acetone-d_6, δ, ppm): xylose: 97.6 (C-1), 70.07 (C-2), 68.6 (C-3), 73.0 (C-4), 64.6 (C-5), 14.6 (C-6); hexahydroxydiphenoyl: 115.5 (C-1), 125.8 (C-2), 107.08 (C-3), 145.8 (C-4), 136.6 (C-5), 144.4 (C-6), 167.6 (C-7), 115.6 (C-1′), 126.4 (C-2′), 108.2 (C-3′), 145.3 (C-4′), 136.5 (C-5′), 144.5 (C-6′), 168.00 (C-7′); glucose: 93.6 (C-1), 71.05 (C-2), 73.00 (C-3), 70.6 (C-4), 73.00 (C-5), 63.0 (C-6); galloyl: 120.4 (C-1), 110.1 (C-2), 145.8 (C-3), 139.1 (C-4), 145.8 (C-5), 110.1 (C-6), 165.3 (C-7).

Hexahydroxydiphenoyl-1-(*O*-*β*-D-glucopyranoside)-2-(*O*-4-*O*-galloyl-*β*-D-glucopyranoside) Diester (11). $C_{33}H_{34}O_{24}$, white amorphous powder, R_f 0.14 (system 1). The acid hydrolysis products (HCl, 5%) were glucose, gallic and ellagic acids. UV spectrum (EtOH, λ_{max}, nm): 218-220. IR spectrum (KBr, ν, cm^{-1}): 3350–3345 (OH), 1730–1710 (ester), 1620-1510 (Ar), 1020–1010 (sugar). PMR spectrum (200 MHz, acetone-d_6, δ, ppm, J/Hz): 3.80, 3.87 (2H, dd, J = 8, 12, Glc-6), 5.14 (1H, d, J = 6, Glc-1), 5.57 (1H, m, J = 4, Glc-3), 4.07 (1H, d, J = 4, Glc-2), 5.49 (1H, m, J = 4, Glc-4), 4.89 (1H, m, J = 11, Glc-5), 7.07, 7.10, 7.15, 7.21 (H, galloyl), 6.46, 6.64 (H, hexahydroxydiphenoyl). ^{13}C NMR spectrum (50 MHz, acetone-d_6, δ, ppm): hexahydroxydiphenoyl: 115.5 (C-1), 125.8 (C-2), 107.08 (C-3), 145.8 (C-4), 136.6 (C-5), 144.4 (C-6), 167.6 (C-7), 115.6 (C-1′), 126.4 (C-2′), 108.2 (C-3′), 145.3 (C-4′), 136.5 (C-5′), 144.5 (C-6′), 168.00 (C-7′); glucose-1: 92.34 (C-1), 76.77 (C-2), 76.98 (C-3), 69.61 (C-4), 73.37 (C-5), 63.37 (C-6); glucose-2: 92.34 (C-1′), 75.38 (C-2′), 78.07 (C-3′), 66.89 (C-4′), 73.92 (C-5′), 63.57 (C-6′); galloyl: 120.4 (C-1), 110.1 (C-2), 145.8 (C-3), 139.1 (C-4), 145.8 (C-5), 110.1 (C-6), 165.3 (C-7).

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Compounds **10** and **11** were new and not previously described in the literature.

In a similar manner 10 pure compounds were isolated from total polyphenols from the aerial part of *P. lanceolata* L. The structures of compounds **1**–**9** were identified from the physicochemical properties as gallic acid (**1**), quercetin-3-rutinoside (rutin) (**2**), quercetin-3-*O*-*β*-D-galactopyranoside (hyperoside) (**5**), 3,5,7,4′-tetrahydroxyflavonol (kaempferol) (**12**), 3,5,7,3′,4′-pentahydroxyflavone (quercetin) (**6**), 3,5,3′,4′-tetrahydroxy-7-methoxyflavonol (rhamnetin) (**13**) [1, 4], 3-*O*-galloyl-4,6-hexahydroxydiphenoyl-*β*-D-glucose (**14**), 2,3-di-*O*-galloyl-*β*-D-glucose (**15**), and 1,2,3-tri-*O*-galloyl-*β*-D-glucose (**8**) [2, 5].

Compound 16. $C_{41}H_{30}O_{27}$, amorphous yellow powder, R_f 0.14 (system 3), $[\alpha]_D$ +35.5° (*c* 0.6, acetone). UV spectrum (MeOH, λ_{max}, nm): 221, 267. PMR spectrum (200 MHz, acetone-d_6, δ, ppm, J/Hz): 6.39 (1H, d, J = 4, Glc-1), 5.66 (1H, dd, J = 4, 10, Glc-2), 6.06 (1H, t, J = 10, Glc-3), 5.70 (1H, t, J = 10, Glc-4), 4.60 (1H, m, J = 7, Glc-5), 4.60 (2H, dd, J = 7, 14, Glc-6), 7.03, 6.84, 6.54 (valoneyl), 6.84, 6.87, 7.10, 7.11, 7.16, 7.17 (galloyl). ^{13}C NMR spectrum (50 MHz, acetone-d_6, δ, ppm): glucose: 92.34 (C-1), 76.77 (C-2), 76.98 (C-3), 69.61 (C-4), 73.37 (C-5), 63.37 (C-6); valoneyl: 114.42 (C-1), 126.56 (C-2), 106.61 (C-3), 144.99 (C-4), 136.13 (C-5), 144.58 (C-6), 169.57 (C-7), 116.63 (C-1′), 126.06 (C-2′), 102.64 (C-3′), 146.70 (C-4′), 135.36 (C-5′), 145.07 (C-6′), 168.33 (C-7′), 111.51 (C-1″), 135.50 (C-2″), 140.65 (C-3″), 139.90 (C-4″), 143.04 (C-5″), 110.29 (C-6″), 164.14 (C-7″); digalloyl: 124.9 (C-1), 116.6 (C-2), 141.6 (C-3), 141.7 (C-4), 144.8 (C-5), 115.1 (C-6), 167.0 (C-7), 126.0 (C-1′), 111.3 (C-2′), 145.8 C-3′), 136.9 (C-4′), 145.8 (C-5′), 111.3 (C-6′), 164.1 (C-7′). The acid hydrolysis products were glucose, gallic and valoneic acid in a 1:2:1 ratio. The structure of the compound was established as 2-*O*-*bis*-digalloyl-4,6-valoneyl-*β*-D-glucose (**16**) based on the results. This was a new compound that was not described previously in the literature.

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