Supporting Information

Design and Characterization of Chitosan-Graphene Oxide Nanocomposites for the Delivery of Proanthocyanidins

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Phloroglucinolysis: A solution of 0.1 moleq./HCl in methanol containing 50 g L-1 of phloroglucinol was reacted with the seed and skin extracts (5 g L-1) at 50°C for 20 min. Then, the mixture was combined with 5 volumes of aqueous sodium acetate 40 mM, to stop the reaction. The procedure was performed in duplicate for all tested samples. The compounds were detected with an HPLC Merck-Hitachi chromatograph LaChrom L7000 Series, with a gradient pump L-7100, Autosampler L-7200, UV detector L-4250 (wavelength 280 nm) and two Chromolith Performance Series RP-18e columns (Merck, Darmstadt, Germany). The mobile phase consisted of Milli-Q water with 1% v/v aqueous acetic acid (mobile phase A) and acetonitrile with 1% v/v acetic acid (mobile phase B) and elution was performed with 3% B for 4 min. The linear gradients used were 3–18% B for 14 min and 80% B for 2 min at a flow rate of 3 mL min-1 and 30°C. The column was washed with 3% B for 2 min before the next injection was performed. To quantify the samples, an external standard of catechin (100 mg of C L-1) was used. The extract characterization gave values of mean degree of polymerization (mDP), average molecular weight (aMW), the proportion of their components ((+)-catechin (C), (-)-epicatechin (EC), (-)-epigallocatechin (EGC), (-)- epicatechingallate (ECG), (-)-epicatechin-phloroglucinol (EC-P), (d)- epicatechingallatephloroglucinol (ECG-P), (d) epigallocatechin-phloroglucinol (EGC-P)), yield (>80 g/100 g), and concentration.

Table S1: Structure composition, mean degree of polymerization (mDP), average molecular weight (aMW) and concentration of the grape extract.

Compound[a]	Extract
C	166 ± 13
EC	88 ± 3
ECG	445 ± 18
C-P	459 ± 18
EC-P	2937 ± 46
ECG-P	1604 ± 19
EGC-P	nd
mDP[b]	9.2 ± 0.3
aMW[c]	3019 ± 87
PA content[d]	329.5 ± 6.7

nd: not detected. (C) (+)-catechin. (EC) (-)-epicatechin. (EGC) epigallocatechin. (C-P) (+)-catechin-phloroglucinol. (EC-P) (-)-epicatechin-phloroglucinol. (ECG-P) epicatechin gallate-phlorogucinol. (EGC-P) epigallocatechin-phloroglucinol. Values are mean±standard deviation (n=2)

[a] Flavan-3-ol subunit expressed as micromolar (μм) of (+)-catechin equivalents.

[b]Mean degree of polymerization dimensionless.

[c]Average molecular weight of PA.

[d]Total Proanthocyanidin concentration in the extract (mg CE/g extract).

Gel permeation chromatography (GPC). Samples (50 mg) were acetylated with pyridine and acetic anhydride (2 mL, 1:1, v/v) overnight at room temperature. The solvents were evaporated and the acetylated extracts were dissolved in tetrahydrofuran THF (10–15 mg mL-1), and the molecular weight distribution of the extracts was determined with the HPLC (ACME 9000, Young Lin Instrument Co. Ltd., Anyang, Korea) which was equipped with a UV/VIS detector and two PSS SDV gel columns (5 µm, 100 and 500 Å) of 30 cm and a PSS SDV gel precolumn (5 µm) equilibrated at 23°C. Analytes were detected at 254 nm at a flow rate of 1 mL/min of the mobile phase (THF) and with an injection volume of 20 µL. Ten standards of polystyrenes with different molecular weights were used, Mw 162–19,950 Da.

Table S2: Molecular weight distribution of grape seed extract

Molecules percentage (%)	Molecular weight range (g/mol)
15.9	21928-13944
25.1	13944-9263
58.9	9263-800

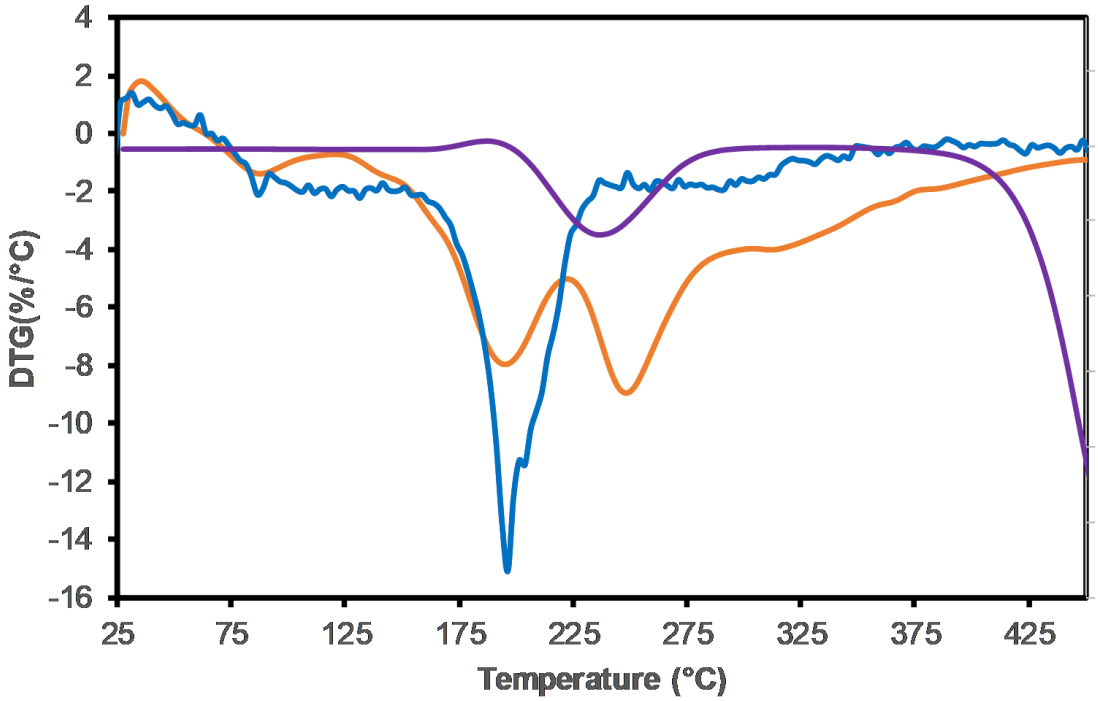

Figure 1S. DTG curves of GO (blue), CS (purple) and GO-CS (orange).