Supplementary Information

New sources of genipin-rich substances for crosslinking future manufactured bio-based materials

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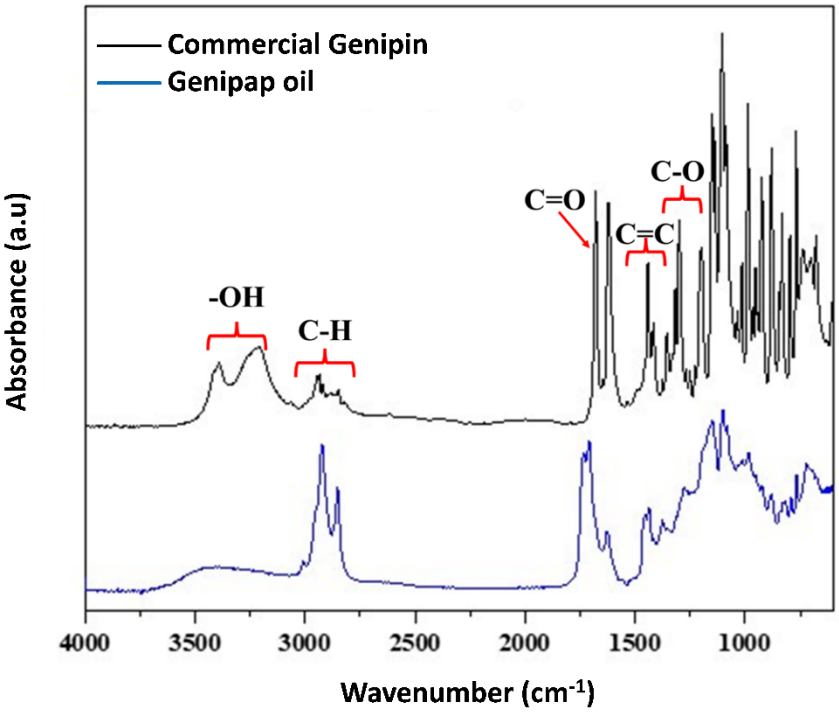

Figure S1. FTIR spectrum of the caruto oil from the Venezuelan caruto compared with the commercial genipin in the region of 4000-500 cm^{-1}.

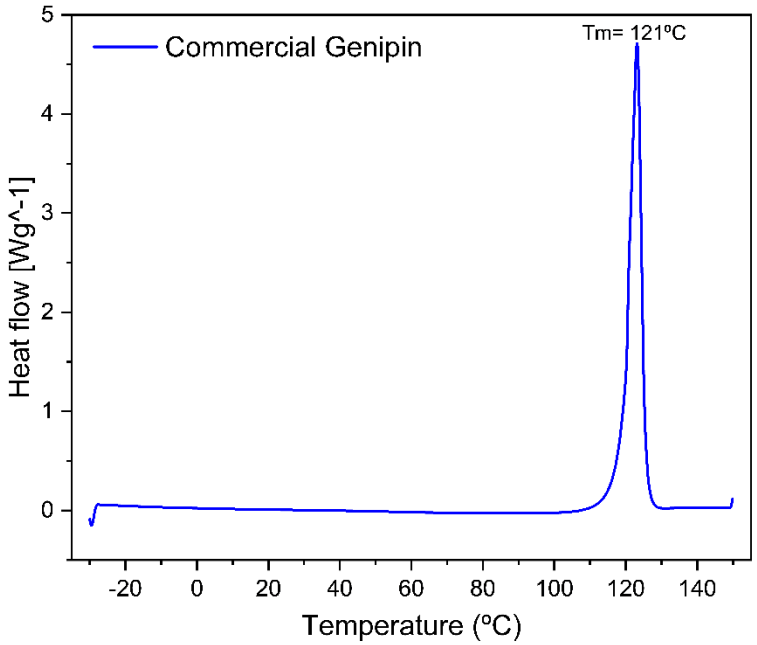

Figure S2. DSC of commercial genipin.

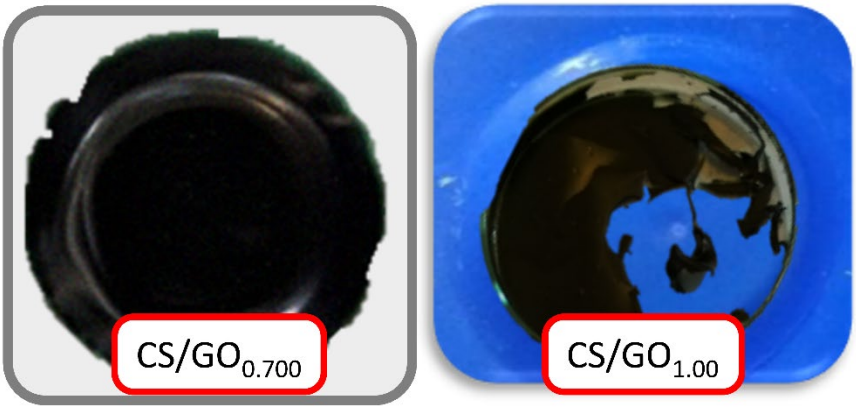

Figure S3. Appearance of the chitosan film obtained by solvent casting.

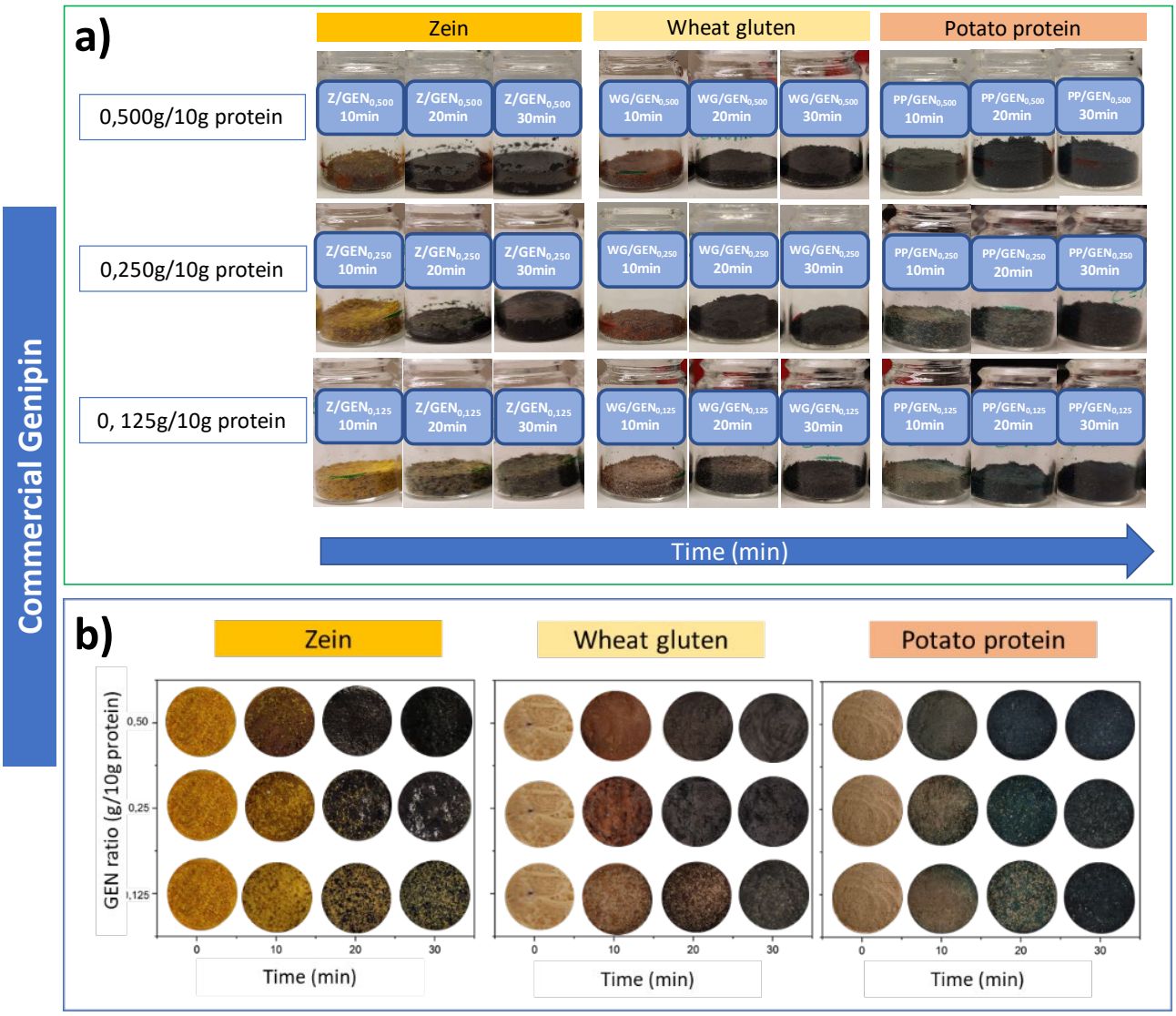

Figure S4. a) Appearance of protein foams prepared at 110°C over the time in the oven and their b) color change.

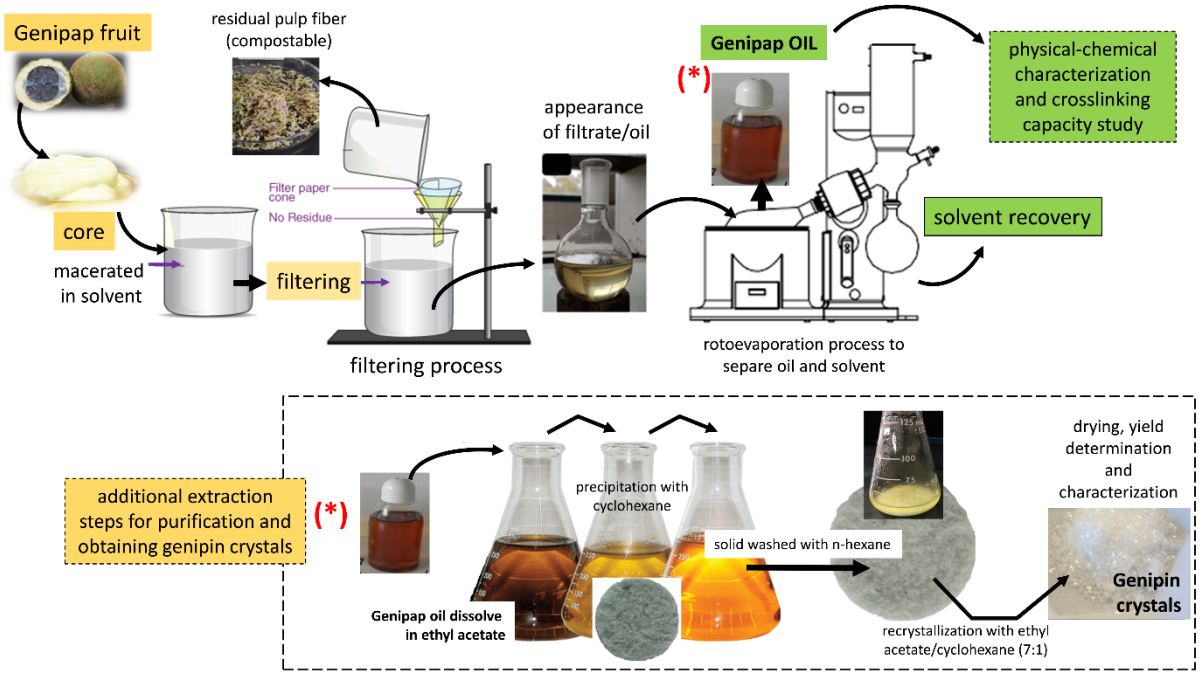

Figure S5. Diagram of the oil extraction and purification of genipin.

Table S1. The monosaccharide analysis results from TFA (trifluoracetic acid) hydrolysis, tested on the extracted genipap oil, core. and peel of the genipap fruit. ND: not detected

Monosaccharides	Peel	Core	Oil
Fucose	0.07 ± 0.12	ND	ND
Arabinose	35.31 ± 2.28	30.52 ± 2.65	0.33 ± 0.37
Rhamnose	5.61 ± 0.36	4.24 ± 0.43	0.16 ± 0.28
Galactose	39.11 ± 2.18	33.46 ± 2.79	0.40 ± 0.25
Glucose	66.25 ± 2.58	207.12 ± 21.06	2.90 ± 0.56
Xylose	99.46 ± 7.27	36.07 ± 5.05	ND
Mannose	4.51 ± 0.54	4.21 ± 1.01	ND
Glucoronic acid	33.73 ± 2.17	21.35 ± 2.10	4.15 ± 3.93
Galactronic acid	1.86 ± 0.08	2.27 ± 0.14	0.61 ± 0.27

Table S2. Quantitative measurements of phenolic compounds through saponification of the samples and identification through HPLC-UV-Vis. The data is reported in µg/mg biomass units. ND: not detected

Sample	Caffeic acid	Coumaric acid	Ferulic acid	Sinapic acid	Cinnamic acid	Total
Peel	0.11 ± 0.00	0.17 ± 0.01	0.31 ± 0.01	ND	0.05 ± 0.00	0.63 ± 0.03
Core	0.10 ± 0.01	0.03 ± 0.00	0.23 ± 0.01	ND	0.09 ± 0.01	0.44 ± 0.03
Oil	0.24 ± 0.01	0.05 ± 0.01	0.87 ± 0.07	ND	0.11 ± 0.01	1.27 ± 0.09

Table S3. Characteristics of crosslinked structures with Genipap oil at different processing conditions.

Sample[a]	Polymer	GO xg/10g polymer	Type of processing	Temperature (°C)	Color change	Structure formation	Retains the shape of the mold
CS	Chitosan	0	Solvent casting	25	No	Yes	Partial
$CS/GO_{0.100}$		0.100		25	Yes	Yes	Partial
$CS/GO_{0.500}$		0.500		25	Yes	Yes	Complete
Z	Zein	0	Dry	100	No	Yes	Partial
				110	No	Yes	Partial
$Z/GO_{0.125}$		0.125		100	Yes	Yes	Complete
				110	Yes	Yes	Complete
$Z/GO_{0.250}$		0.250		100	Yes	Yes	Complete
				110	Yes	Yes	Complete
$Z/GO_{0.500}$		0.500		100	Yes	Yes	Complete
				110	Yes	Yes	Complete
WG	Wheat gluten	0	Dry	100	No	Yes	Partial
				110	No	Yes	Partial
$WG/GO_{0.125}$		0.125		100	Yes	Yes	Complete
				110	Yes	Yes	Complete
$WG/GO_{0.250}$		0.250		100	Yes	Yes	Complete
				110	Yes	Yes	Complete
$WG/GO_{0.500}$		0.500		100	Yes	Yes	No
				110	Yes	Yes	No
PP	Potato protein	0	Dry	100	No	No	No
				110	No	No	No
$PP/GO_{0.125}$		0.125		100	Yes	No	No
				110	Yes	No	No
$PP/GO_{0.250}$		0.250		100	Yes	No	No
				110	Yes	No	No
$PP/GO_{0.500}$		0.500		100	Yes	No	No
				110	Yes	No	No
75Z/25WG	Z+WG	0	Hot press	110	No	Yes	Complete
$75Z/25WG_{GO}$		0.250			Yes	Yes	Complete
60Z/25WG/15PP	Z+WG+PP	0			No	Yes	Complete
$60Z/25WG/15PP_{GO}$		0.250			Yes	Yes	Complete
25Z/25WG/50PP		0			No	Yes	Complete
$25Z/25WG/50PP_{GO}$		0.250			Yes	Yes	Complete

[a] All samples with commercial genipin showed color change and retained the shape of the mold except the samples with single proteins.

Table S4. Solvents used in the extraction of the caruto oil and the purification of genipin from the oil, according to the Greem Chemistry principles.[1]

Solvent	Safety score	Health score	Environment score	Ranking for default	Raking after discussion	Use
Chloroform	2	7	5	Problematic	Highly Hazardous	oil extraction
Acetone	5	3	5	Problematic	Recommended	GEN extraction
Ethyl acetate	5	3	3	Recommended	Recommended	GEN extraction
Cyclohexane	6	3	7	Problematic	Problematic	GEN extraction
Hexane	8	7	7	Hazardous	Hazardous	GEN extraction
Acetic acid	3	7	3	Problematic	Problematic	Chitosan films preparation

Classification	Score
Recommended	1-3
Problematic	4-6
Hazardous	7-10

Reference:

1. *Green Chem.*, 2015, **17**, 4848-4848.