Grape marc as a source of high-value products including antioxidant biopolymers

+ Waste to Treasure MBIE programme

38th Australasian Polymer Symposium
Feb 2024

Paul Kilmartin

A. Etxabide, Y. Yang, J.I. Mate, K. de la Caba and P.A. Kilmartin, “Developing active and intelligent films through the incorporation of grape skin and seed tannin extracts into gelatin”, *Food Packaging and Shelf Life* **33** (2022) 100896.

Dr Alaitz Etxabide

State Research Agency of Spain within the Juan de la Cierva - Incorporation action (IJC2019-039697I) and the New Zealand Ministry of Business, Innovation and Employment (Biocide Toolbox programme) for funding.

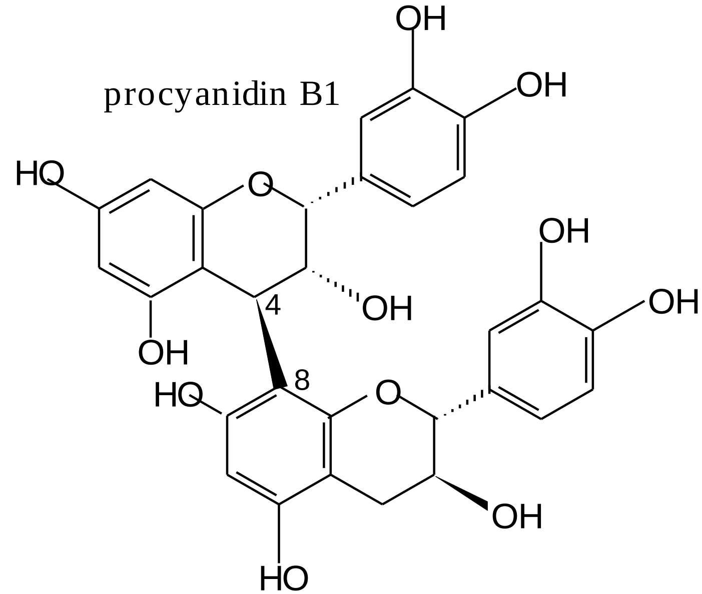
Agro-wastes represent an abundant and economical source of antioxidant compounds

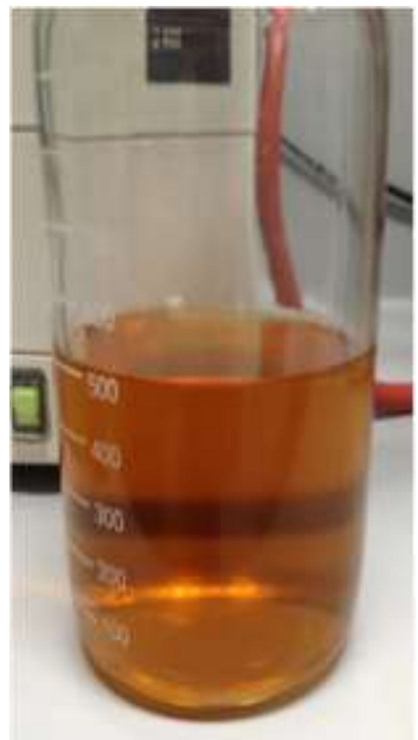
Grape tannins can be extracted from grape marc, produced in large quantities in regions such as Marlborough and the Hawkes Bay

Extraction and Purification

Grape tannins were sourced from commercial suppliers, and also prepared directly from Sauvignon blanc and Chardonnay grape marc in a water-only process. Purification was performed with Amberlite FPX-66 resin.

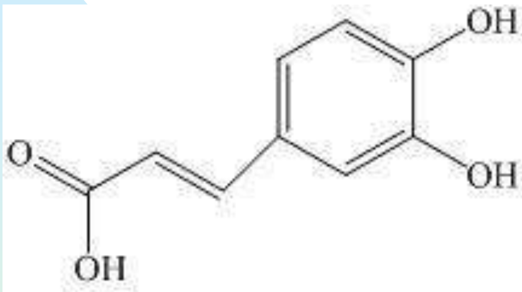
procyanidin B1



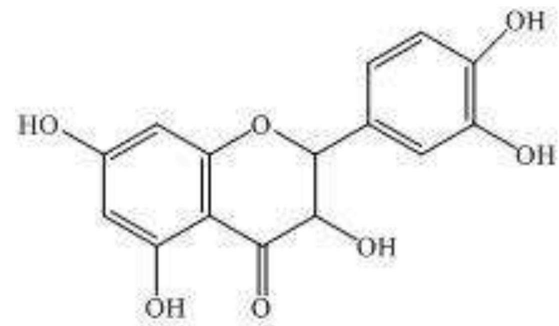


Polyphenol classes in wine grapes

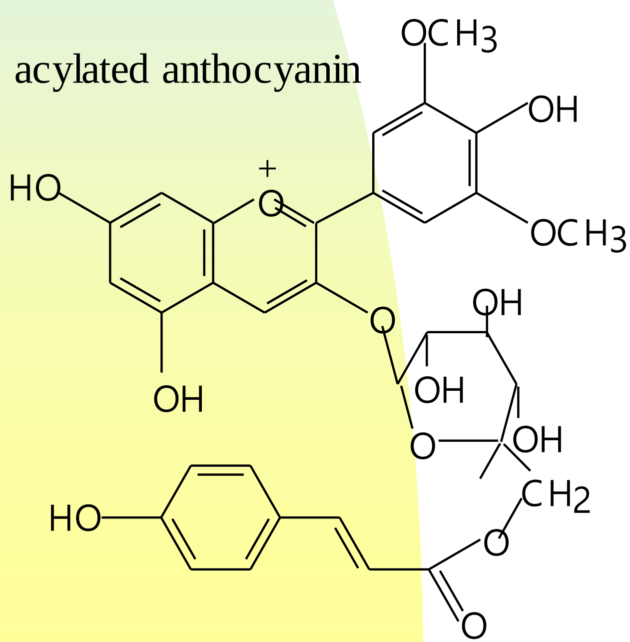
Hydroxycinnamic acids: caffeic acid



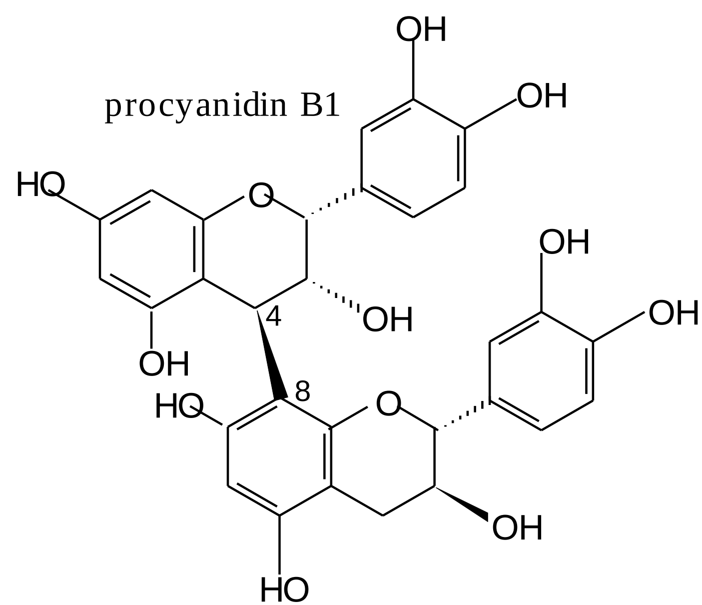
Flavonols: quercetin



Coloured Anthocyanins

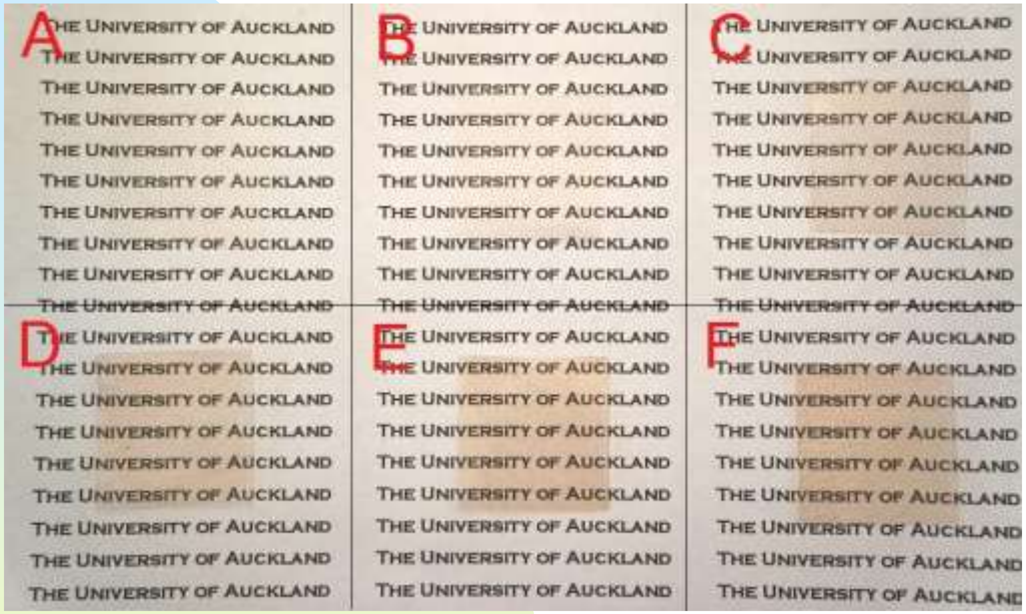


Astringent tannins – catechins



Mechanical testing of films formed by solution blending

EC is ethyl cellulose and GT is a grape tannin



A: pristine ethyl cellulose
B: 0.25% grape tannin
C: 0.5% grape tannin
D: 1.0% grape tannin
E: 2.0% grape tannin
F: 3.0% grape tannin

Sample	Tensile strength (MPa)	Tensile strain at break (%)
EC	34 ± 2	1.8 ± 0.1
0.25% GT	35 ± 1	1.9 ± 0.1
0.5% GT	32 ± 3	2.1 ± 0.5
1.0% GT	31.4 ± 0.5	2.0 ± 0.3
2.0% GT	32 ± 3	2.1 ± 0.4
3.0% GT	28 ± 1	1.5 ± 0.1

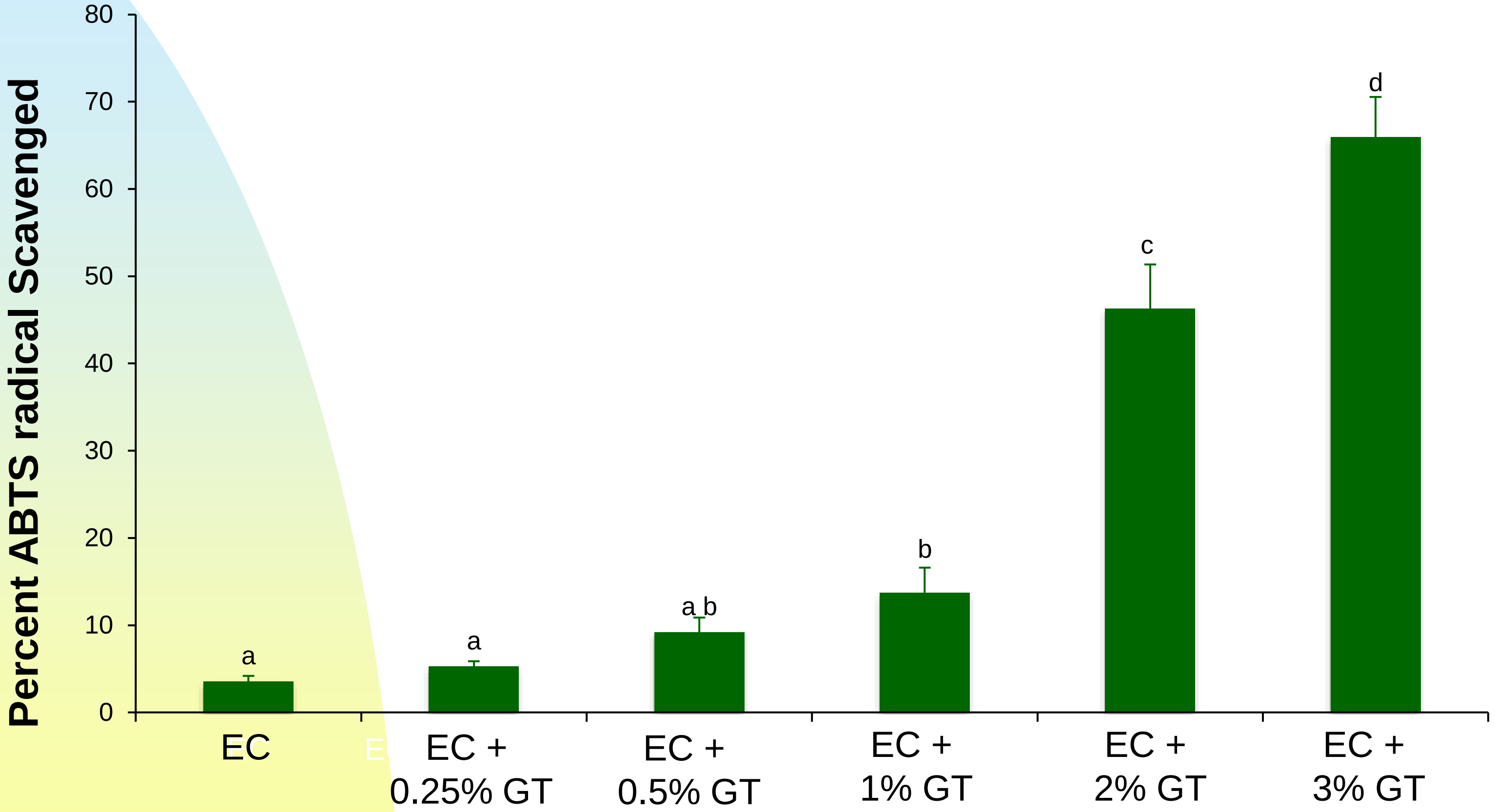
Slight decrease in the tensile properties was noted due the plasticizing affect of grape tannins

Good contact clarity, even with 3% grape tannin included

K.J. Olejar, S. Ray, A. Ricci and P.A. Kilmartin, "Superior antioxidant polymer films created through the incorporation of grape tannins in ethyl cellulose", *Cellulose* **21** (2014) 4545-4556

Antioxidant activity of the blended polymers expressed as percent ABTS radical scavenging

EC is ethyl cellulose and GT is grape tannin



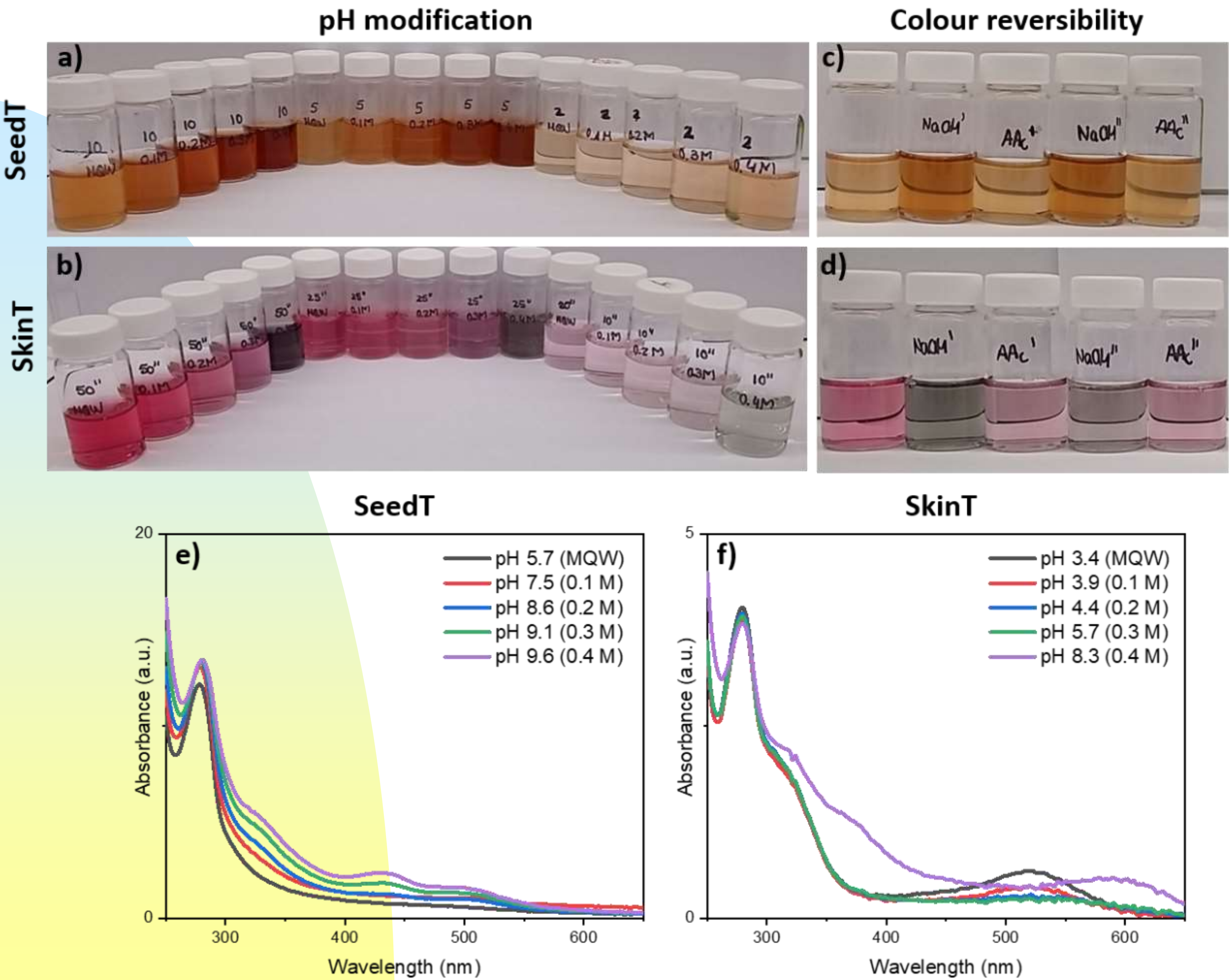
Grape tannins display high antioxidant activity in the ethyl cellulose blend – a promising start!

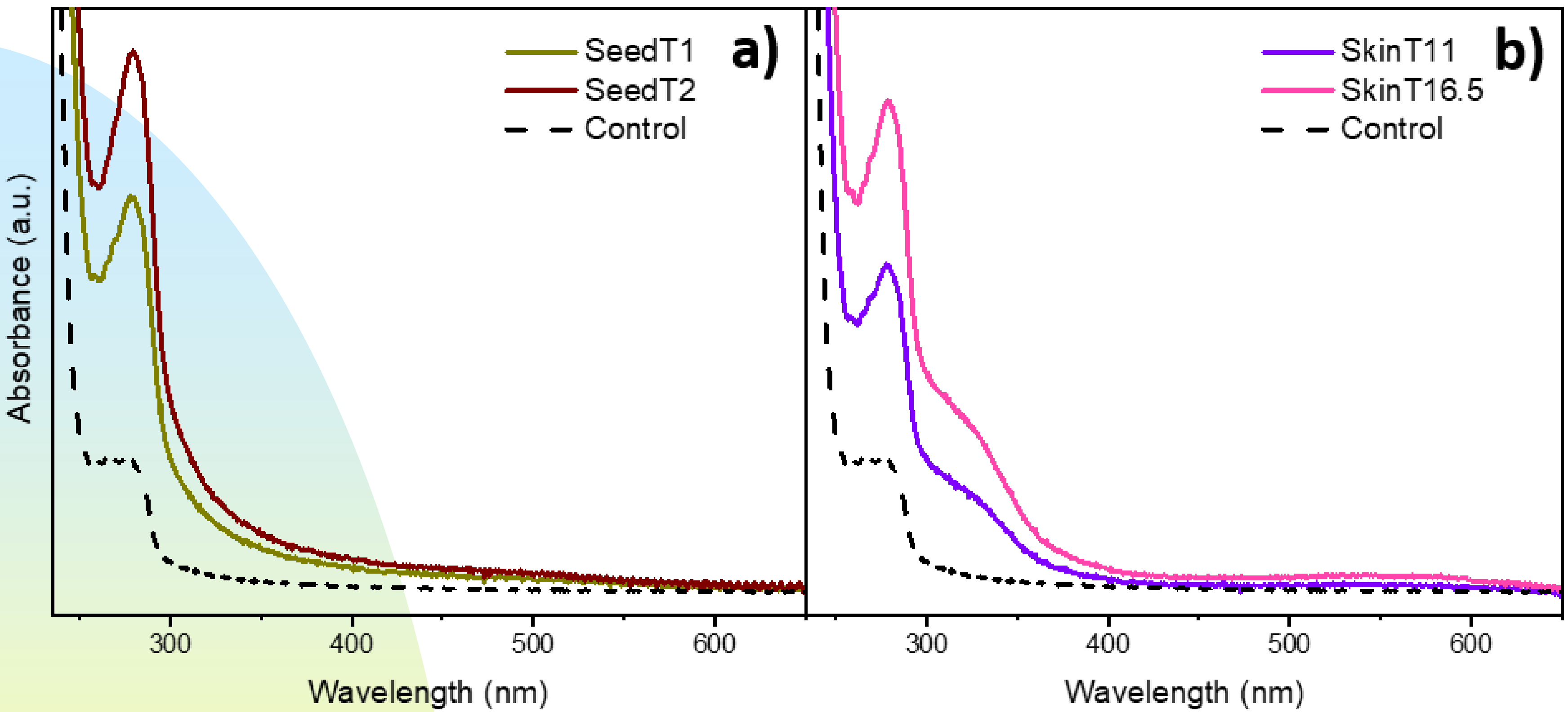
An edible (1999/724/CE) codfish gelatin type A with a bloom value of 200 (Weishardt International, Slovakia).

Edible tannin extracts from (*Vitis vinifera* sp) grape skins (SkinT) – liquid (14 mg/g phenolics) and grape seeds (SeedT) – powder (437 mg/g phenolics) were kindly supplied by Tarac technologies (Australia).

Water contact angle, ultimate tensile strength and elongation at break for gelatin films with 1 or 2% added grape seed (SeedT) or 11 or 16.5% grape skin (SkinT) tannin.

Film	Water contact angle (°)	Ultimate tensile strength (MPa)	Elongation at break (%)
Control	79.8 ± 2.7	65.2 ± 6.0	4.5 ± 0.2
SeedT1	85.4 ± 1.7	65.8 ± 2.2	4.3 ± 0.3
SeedT2	92.4 ± 2.5	68.0 ± 6.1	4.5 ± 0.3
SkinT11	86.8 ± 1.9	68.5 ± 5.0	4.2 ± 0.6
SkinT16.5	86.2 ± 1.2	67.0 ± 8.0	5.0 ± 0.4


pH modification
Colour reversibility
a)
b)
c)
d)
SeedT
SkinT
SeedT
SkinT
e)
pH 5.7 (MQW)
pH 7.5 (0.1 M)
pH 8.6 (0.2 M)
pH 9.1 (0.3 M)
pH 9.6 (0.4 M)
Absorbance (a.u.)
Wavelength (nm)
20
0
300
400
500
600
f)
pH 3.4 (MQW)
pH 3.9 (0.1 M)
pH 4.4 (0.2 M)
pH 5.7 (0.3 M)
pH 8.3 (0.4 M)
Absorbance (a.u.)
Wavelength (nm)
5
0
300
400
500
600

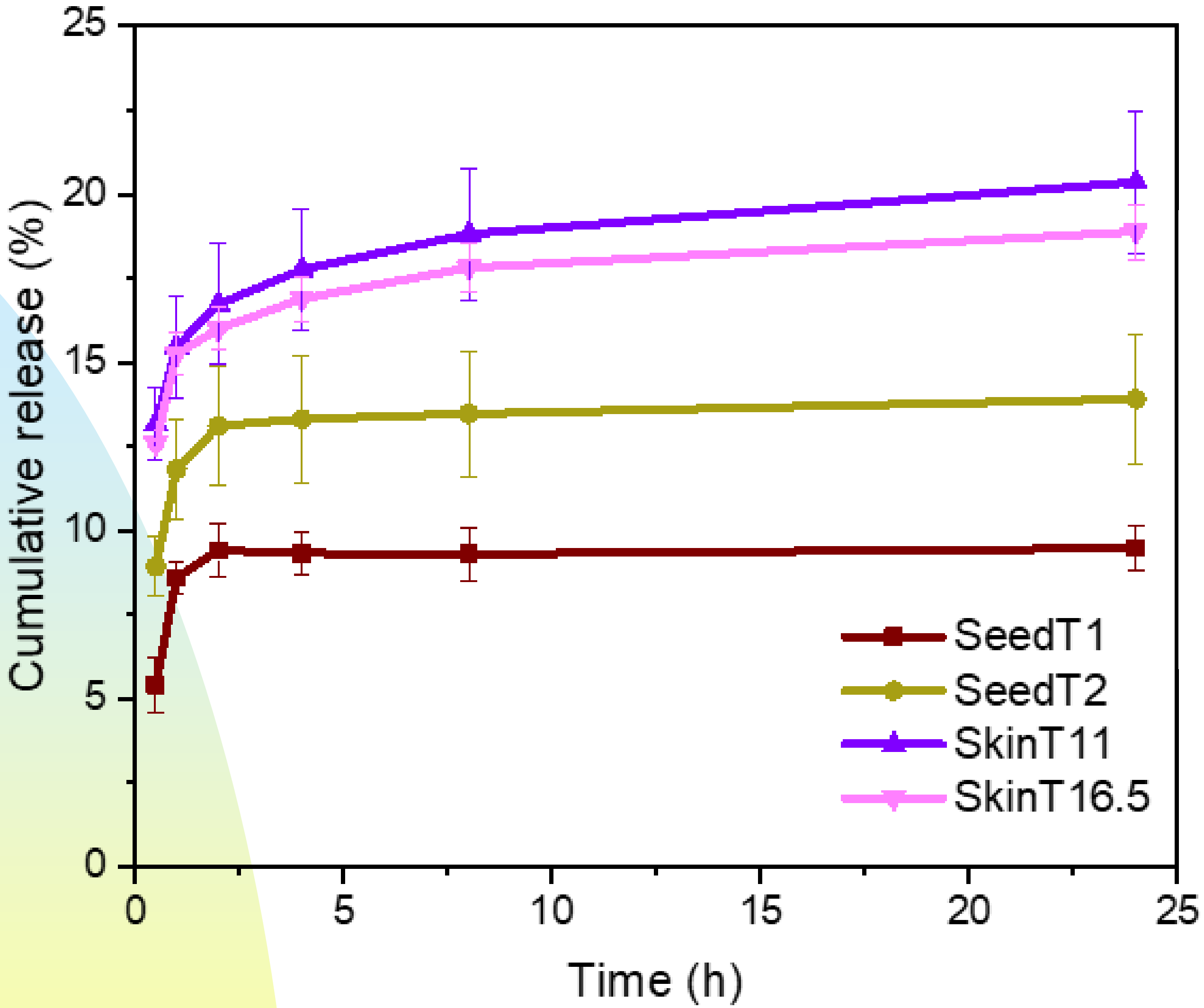


UV-Vis spectra for gelatin films with:

a) 1 and 2% seed tannin extract (SeedT1 and SeedT2), and

b) 11 and 16.5% skin tannin extract (SkinT11 and SkinT16.5) (on a gelatin dry weight basis).

Films without tannins were used as controls.



Release of seed tannin (SeedT at 1 & 2%) and skin tannin (SkinT at 11 and 16.5%) extracts from gelatin films, after immersion in 50% ethanol solution at 4 ◦C for 24 h.

Tannin release into 50% ethanol at 4 °C as a percentage of the tannin added, and DPPH antioxidant inhibition (I), for gelatin films with 1 or 2% added grape seed (SeedT) or 11 or 16.5% grape skin (SkinT) tannin.

Film	Tannin addition (%)	Release (%)	I (%)
Control	-	-	-
SeedT1	1	9.5 ± 0.6	6.0 ± 1.1
SeedT2	2	13.9 ± 1.9	13.3 ± 1.6
SkinT11	11	20.4 ± 2.1	3.5 ± 0.5
SkinT16.5	16.5	18.9 ± 0.8	5.4 ± 0.6

Gelatin-based active and intelligent packaging incorporating grape skin and seed tannins

Conclusions

The addition of tannin extracts into gelatin resulted in coloured and transparent films with better barrier properties: lower wettability (water contact angle up to 92°) and higher UV light absorbance (a secondary antioxidant function).

The films released antioxidant tannins by up to 20% in a 50% ethanol simulant, with significant antioxidant inhibition versus the DPPH radical.

SkinT tannins within the films showed a variation in colour from reddish to blueish with an increase of pH, which provided a pH indicator ability (an intelligent function).

Waste to treasure: using novel chemistry to valorise residual plant materials

MBIE Endeavour Programme Oct 2023 to Sept 2028

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www.waste2treasure.co.nz

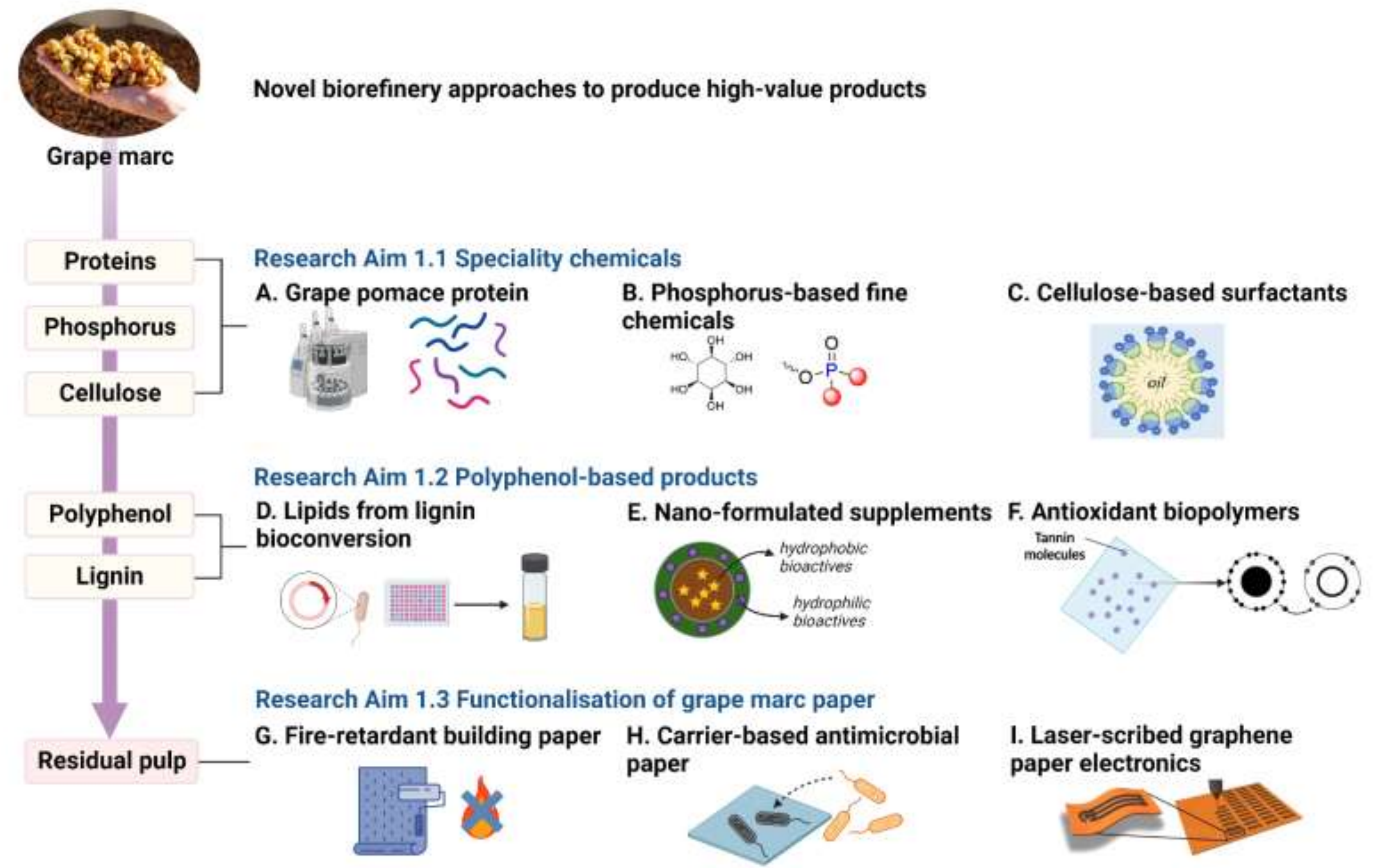
Context and challenge

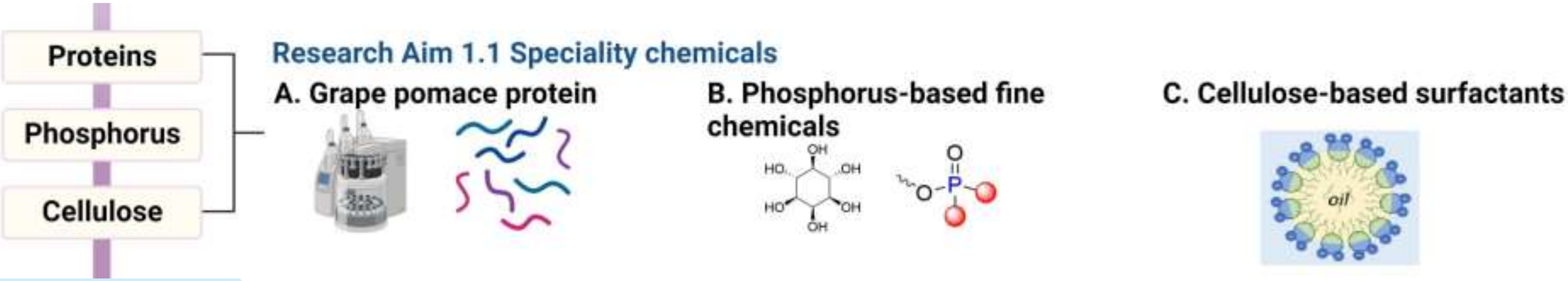
- Wineries produce ~50,000 tonnes of grape marc in New Zealand and 20 million tonnes globally, increasing 6% every year.
- This incurs costs for the wine growers and can become an environmental issue e.g. leachate, runoff, and odours
- Eliminating the whole grape marc waste stream will save money and improve the sustainability of NZ's $2.4B wine-producing industry.
- Grape marc is more than waste. It provides a significant resource for new bio-based products, creating new export opportunities underpinning government and industry strategies to help New Zealand to transition to a circular economy.

Our approach

Develop total-use strategy for grape marc and an economically viable biorefinery concept.

This will be the cornerstone for a technology platform technology supporting NZ companies to produce high-value products from agricultural waste streams.





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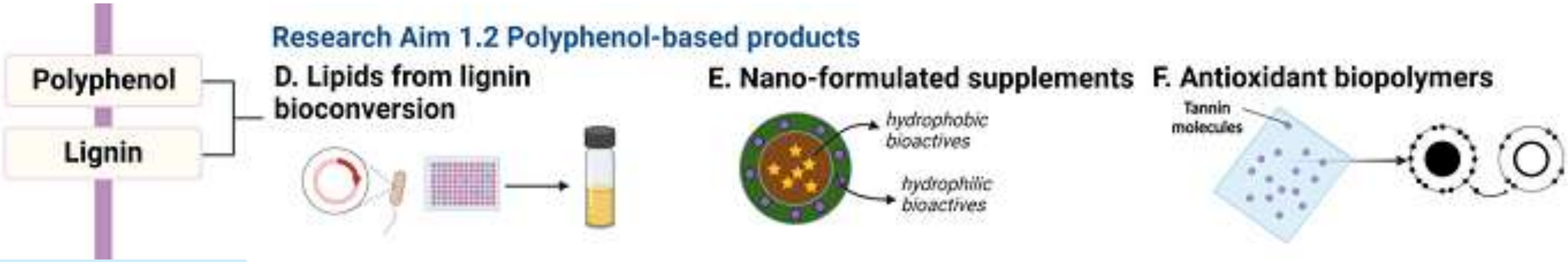
Green Chemistry Principles



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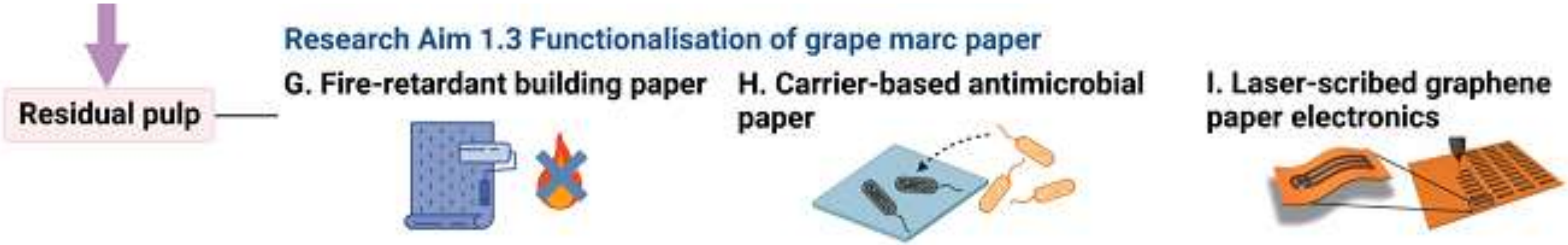

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1. Engage Stakeholders

Industry

Consumers

2. Understand stakeholder demands of products

Interviews

Ethnographic insight

Survey

3. Develop products with insights

RA1 (speciality chemicals)

RA2 (polyphenol based)

RA3 (paper based)

Stakeholder Advisory Group

Dr Joya Kemper
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