We will begin momentarily at 2pm ET

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Including companies in the cosmetics industry.
We convene 40 companies from across the world to focus on the science of sustainable and green chemistry and its implementation.

“Cosmetic Chemistry: Novel Approaches using Natural and Renewable Ingredients”

Nidia Trejo
Research Intern, Ithaca Area Waste Water Treatment Facility

Richard Blackburn
Associate Professor, the University of Leeds and Founder of Keracol Limited

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Cosmetics industry and natural ingredients

- Cosmetics products include deodorants, hair dyes, hair styling products, make-up, sunscreens, nail colorants, skin & hair care products, and skin & hair cleansing products, amongst others.

- Global beauty care products industry forecast to reach around $265 billion in 2017 (Mintel).

- Interest in natural ingredients is significantly increasing among cosmetic consumers in general.

- Naturally-derived personal care market is expected to reach $16 billion by 2020 (Grand View Research).

- Potentially reduces reliance on petroleum-based products.

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Extraction of active ingredients from plant matter

Idealised extraction from plant material

- Target compound (active) exhaustively removed from source.
- Active is as free as possible from interfering or undesirable compounds extracted from the same source.

1) Mass transfer process: solvent is transferred into the solid phase.
2) Molecular diffusion: solvent penetrates the solid matrix.
3) Solvation of soluble material and return to the surface of the solid.
4) Transfer of solvated active to bulk solution via natural/coerced convection.

Complications

- Interactions of target active with other compounds within the chemical matrix.
- Enzymatic processes that may degrade target active before it is able to be extracted.

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Clean extraction

- Polar metabolites such as anthocyanins can be extracted using water, superheated water, ethanol, or solvent blends

  - Non-toxic solvents that allow efficient extractions in optimised conditions
  - Acceptable solvents for food or personal care and cosmetic applications
  - No-regulatory limitations
  - Non-selective solvents
  - Free sugars, proteins and low-polarity metabolites are extracted too

Solid-Phase Extraction (SPE): strategy for extract purification

- Anthocyanins interact with solid phase via H-bonding and hydrophobic interactions
- Resin allows for removal of interferents via preferential sorption of active
  - Free sugars removed with acidified water
- Anthocyanins subsequently eluted with acidified ethanol

  - Simple, safe and low cost
  - Allows high recovery of active
  - Reduces consumption of solvents

Source needs to be loaded in water

Scale-up limitation?

---

Extraction-Purification

Industrial-scale process

[Diagram of purification process]
Which is the most difficult color to obtain from nature for application in cosmetics, food and textiles?

- Red
- Yellow
- Blue
- Purple

Anthocyanins

- Found in fruits, vegetables, flowers

<table>
<thead>
<tr>
<th>Anthocyanin</th>
<th>R₁</th>
<th>R₂</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; @ pH3</th>
</tr>
</thead>
<tbody>
<tr>
<td>pelargonidin</td>
<td>– H</td>
<td>– H</td>
<td>503</td>
</tr>
<tr>
<td>cyanidin</td>
<td>– OH</td>
<td>– H</td>
<td>517</td>
</tr>
<tr>
<td>peonidin</td>
<td>– OCH₃</td>
<td>– H</td>
<td>517</td>
</tr>
<tr>
<td>delphinidin</td>
<td>– OH</td>
<td>– OH</td>
<td>526</td>
</tr>
<tr>
<td>petunidin</td>
<td>– OCH₃</td>
<td>– OH</td>
<td>526</td>
</tr>
<tr>
<td>malvidin</td>
<td>– OCH₃</td>
<td>– OCH₃</td>
<td>529</td>
</tr>
</tbody>
</table>

- Glycosylation typically at 3-O position
- In fruits, typically various mono- and disaccharides
- More complex glycosylation observed in other plants
• Need to work with fruits where there is a sustainable supply of waste material

**STRAWBERRY (Fragaria x ananassa)**
BLACKBERRY (Rubus fruticosus)
BLUEBERRY (Vaccinium corymbosum)
BLACK MULBERRY (Morus nigra)

**GRAPE (Vitis vinifera)**

1. Cyanidin-3-O-glucoside (5.84%)
2. Delphinidin-3-O-glucoside (7.27%)
3. Malvidin-3-O-glucoside (65.30%)
4. Peonidin-3-O-glucoside (5.95%)
5. Petunidin-3-O-glucoside (15.64%)

**ARONIA (Aronia melanocarpa)**

1. cyanidin-3-O-galactoside (68%)
2. cyanidin-3-O-arabinoside (30%)

**BLACKCURRANT (Ribes nigrum)**

1. delphinidin-3-O-glucoside (15.71%)
2. delphinidin-3-O-rutinoside (43.25%)
3. cyanidin-3-O-glucoside (7.03%)
4. cyanidin-3-O-rutinoside (34.00%)

**Case Study 1: Natural hair dyes**

**Extract from blackcurrants (Ribes nigrum)**

- grown in UK and sustainably sourced
- waste from blackcurrant juice process (Ribena)
- Extracted and purified using SPE to give high levels anthocyanins
- Formulated to give optimum hair dyeing performance

- Patented semi-permanent hair colorants and coloration process
- Range of shades, fast to 12+ washes

1. US8361167
Case Study 1: Natural hair dyes

Dyeing from acidic medium (pH 3-4)

• $\lambda_{\text{max}}$ in aqueous solution at pH 3.0: cyanidin 517 nm; delphinidin 526 nm
  – purple/violet colour consistent with flavylium cation

• $\lambda_{\text{max}}$ when adsorbed onto hair from aqueous medium:
  570-580 nm
  – Blue colour consistent with quinonoidal base
  – in situ neutralisation by basic sites on hair surface leading to formation of anhydrobase
  – Stable over 12+ washes, minimal colour loss, no colour change

Case Study 1: Natural hair dyes

Blackcurrant glycoside sorption

• HPLC study revealed apparent preferential adsorption in favour of monosaccharides (glucosides): two-fold over disaccharides (rutinosides)

• Isotherm study: cyanidin-3-O-glucoside higher adsorption energy in comparison with cyanidin-3-O-rutinoside

• Superior H-bonding through primary hydroxyl? Steric effects?
Case Study 1: Natural hair dyes

Grape glucoside sorption

- Isotherm study: Glucosides show consistent sorption properties
- Anthocyanin parent structure does not have significant effect on sorption – glycosylation more important

\[
\ln q_e = \frac{\Delta \mu_0}{R} \ln C_e
\]

French was the official language of England from 1066 to 1362

Despite a diet of cheese, croissants, and crème brûlée, the French have low levels of CVD

French toast isn’t French and was actually invented by a man called Joseph French

The croissant was actually invented in Austria
Antioxidants for skin care

- Radicals cause skin damage and skin ageing, originating from:
  - our own metabolism
  - external factors: UV radiation, tobacco smoke, pollution, etc...
- Antioxidants provide cell protection so they can regenerate and repair themselves
- Reduces skin damage and ageing

Naturally occurring antioxidants
plant phenolics: carotenoids & flavonoids

Vitamin E (tocopherol)

Case Study 2: Pure Super Grape

- Expanding portfolio of M&S cosmetic products
- Want a range of skincare products that fit in with Plan A
- Extraction of antioxidants from M&S waste
Case Study 2: Pure Super Grape

- Opportunity with Pinot noir pressed for champagne and sparkling wine
- Waste pomace rich in polyphenols

World's largest fruit crop
>60 million tonnes/year

>250 billion litres of wine

Resveratrol

- Phytoalexin - a protective compound produced by plants in response to environmental stresses (dehydration, nutrient deprivation, attack by pathogenic organisms)
- Present in nuts and berries, in particular in grape (skin and seeds) wine
- Discovered in 1940
- 1992 - credited with a key role in the cardiovascular health benefits of red wine: the French Paradox
- Biological properties: antioxidant, anti-inflammatory, antithrombotic, anticancer
Case Study 2: Pure Super Grape

Pinot Noir grape pomace harvested in October 2012 stored at -20°C

1) Optimization of the extraction procedure
   optimum extraction time for highest extract yield and activity
   optimum solvent-feed ratio for highest extract yield and activity

2) Quantification of actives
   
   Total phenolic content

   High Pressure Liquid Chromatography
   trans-resveratrol content in grape extract

3) Process scale-up

Case Study 2: Pure Super Grape

4) Range of products developed
   Face serum, Day Cream, Night Cream, Eye Cream, Overnight oil treatment, Clay mask

   • Formulations developed to maximise antioxidant activity
   • Full formulation based on sustainable and naturally-derived ingredients as much as possible

Radical Scavenging Activity of formulations

Launched in July 2014
What are some fastest growing organisms on the planet, which come in several colors, rich in trace elements, have vitamins, carotenoids and other antioxidants, and contain polymers that are gelling and emulsifying?

- Berries
- Cruciferous Vegetables
- Whole Grains
- Seaweeds
Case Study 3: Haircare Naturally

- Hair sprays and hair gels typically utilise film-forming polymers (e.g. polyvinyl pyrrolidone) to provide hold
- Industry desire to move to natural polymers to provide this activity
- Some natural polymer systems have been developed, but mainly aqueous systems
- Need to use ethanol-water mixtures for effective delivery and rapid drying of styling product
- Natural polymers incompatible with significant levels of ethanol

Case Study 3: Haircare Naturally

- KeraStyle natural styling polymers
- Extracted from seaweed or waste fruit skins
- Patented formulation combining alginic acid or pectin with an amine to make amine salt
- Soluble in up to 80% ethanol
- Performance as good as (if not better than) current PVP/VA copolymer systems
  - Strong hold
  - Natural feel
  - High shine
  - Good sprayability
  - Excellent film forming
  - High curl retention in both dry and humid conditions

2. WO2014102545
Case Study 3: Haircare Naturally

**Hair Gels**
- Citrus fruit peel – converted waste from food and drink industry
- Pectin amine derivative – gives both hold and gels the system
- Pectin much more viscous than alginate

**Hair Sprays**
- Seaweed – produced from sustainable seaweed sources growing naturally on British coastline
- Alginic acid derivative – gives both hold and gels the system
- Less viscous, so can be delivered in a spray

The future of our research…
- Semi-permanent hair colorant products to be launched commercially in 2017
- Applications of anthocyanins in make-up and other skin applications being developed
- New actives for both skin care and hair care from waste food/plant material being developed
- Interested in working with large companies, SMEs and other academic groups to work collaboratively on novel approaches in using natural and renewable ingredients in cosmetics
Things to consider...

- Does the use of naturally-derived ingredients represent true sustainability or marketing greenwash?
- Does the use of natural extracts and the perception of their inherent safety, present toxicity concerns?
- Plant-based materials often produced either by cultivation or from wild harvesting - should this land be used to grow food?
- Cosmetics industry needs to consider alternative sources of green materials such as marine ingredients, microalgae, bacteria, and food waste
- Extraction of naturally-derived extracts must involve green chemical processes
- Can we use biotechnology to make even better naturally-derived ingredients
- Majority of cosmetic formulation is a vehicle to deliver an active ingredient (typically present at levels of under 5% by weight)
- Use of green chemistry to produce more sustainable cosmetic formulations, including green surfactants, emulsifiers, conditioning agents, emollients, etc.

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