UNIVERSITY OF HELSINKI

https://helda.helsinki.fi

Biocolourants from onion crop side streams and forest mushroom for regenerated cellulose fibres

Räisänen, Riikka; Primetta, Anja; Toukola, Peppi Pauliina; Fager, Silja; Ylänen, Joanna

2023-08
Elsevier B.V.
http://hdl.handle.net/10138/357699
Räisänen, R, Primetta, A, Toukola, P P, Fager, S & Ylänen, J 2023, 'Biocolourants from onion crop side streams and forest mushroom for regenerated cellulose fibres', Industrial Crops and Products, Vuosikerta. 198. https://doi.org/10.1016/j.indcrop.2023.116748

Downloaded from Helda, University of Helsinki institutional repository. https://helda.helsinki.fi
This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.
Please cite the original version.

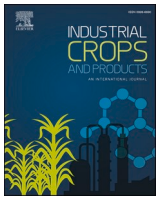
Industrial Crops & Products 198 (2023) 116748



Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop





Biocolourants from onion crop side streams and forest mushroom for regenerated cellulose fibres

Riikka Räisänen *, Anja Primetta, Peppi Toukola, Silja Fager, Joanna Ylänen

Craft Studies, University of Helsinki, Helsinki, Finland

ARTICLE INFO

Keywords:
Regenerated cellulose fibre
Ioncell
Viscose
Side stream
Natural dye
Biocolourant

ABSTRACT

Biocolourants and sustainable textile materials have gained growing interest. Traditionally natural dyes have been used for dyeing wool and silk, but demand for cotton and regenerated cellulose fibres increases because of their popularity especially in clothing. This study expands the natural dye research to one of the latest innovations among regenerated cellulosic fibres, i.e. Ioncell®. It explains for the first time the dyeability of Ioncell–F fibres with biocolourants and compares the results with three other regenerated cellulose fibres, i.e. viscose, bamboo viscose and lyocell, using protein fibre wool as a reference. The colourants from the food side stream, the yellow onion (*Allium cepa* cv. Settonia) and the forest mushroom *Cortinarius semisanguineus* were used as dyes. The composition of colourants in each dye sources was analyzed in detail. Methods of exhaust dyeing (80 °C, 1 h), with alum, $FeSO_4$ and tannin as mordants, and the high temperature high pressure dyeing (130 °C, 1 h) were applied. The colour of the dyed materials was studied as CIE L*, a*, b*, C^*_{ab}, h_{ab} and the K/S ($\lambda_{420/480\ nm}$) values. The colourfastness to washing and light was examined according to the ISO standards. The results showed that for regenerated cellulose fibres the strongest colour was obtained with polyphenols in acidic conditions, whereas with the anthraquinones the dyeing results remained light revealing hindering forces between the dye and the fibre. The colourfastness values were at highest for iron and aluminium mordanted samples, which indicate the metal ions' ability to stabilize the organic compound's structure and form strong coordination bonding between the fibre and the dye. The colourfastness varied from poor to moderate. The exhaustion levels between different regenerated cellulose fibres varied very little. The search for sustainable colourants, fibres and their applications in long lifetime artefacts is strongly supported by the sustainability goals, and colourant production in connection with forest and agricultural industries support this emerging field.

1. Introduction

In this study, two types of natural compounds, polyphenols and anthraquinones, were applied as dyes for regenerated cellulose fibres. The yellow onion (*Allium cepa* L.) skins, abundantly available as a side stream from agriculture and food production, are a rich source of polyphenols (Sharma et al., 2016), whereas anthraquinones are one of the most stable compound groups among natural colorants, and obtainable from several sources for example in plant and fungal kingdoms. The forest mushroom *Cortinarius semisanguineus* (Fr.) Gillet was selected as a source of anthraquinones, as we had previous knowledge of its properties in textile colouration (Räisänen et al., 2021; Räisänen, 2019; Räisänen, 2002). Also, as ectomycorrhizal fungi *Cortinarius* species have growth increasing effects for their host trees, which give interesting perspectives for forest economy (Itoo and Reshi, 2014).

Recently, a growing amount of research has been carried out to map potential side streams and sources for natural dye production, as sustainability drives companies to search for environmentally sound and ecological alternatives for current oil based derivatives in the dyeing industry. In addition to colouring properties, natural compounds have other functional characteristics, such as antimicrobial and UV radiation protective properties, which give them multi-functionality and added value as colourants. Especially flavonoids have shown remarkable antioxidant activity and ability to protect human skin against UV radiation (Pucciarini et al., 2019; Verma et al., 2021).

In addition to colourants, also fibre materials are under increasing sustainability evaluation. Cotton is the second most important fibre, after polyester, in terms of the production volume, with ca. 26 Mt and a market share of 23% of the global fibre production in 2020 (TextileExchange, 2020; OECD, FAO, 2021). The environmental load that

* Corresponding author.
E-mail address: riikka.raisanen@helsinki.fi (R. Räisänen).

https://doi.org/10.1016/j.indcrop.2023.116748
Received 22 October 2022; Received in revised form 12 March 2023; Accepted 16 April 2023
Available online 21 April 2023
0926-6690/© 2023 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

cotton production causes for the landscapes and soils has led to development and expansion of other cellulose based textile fibres, as cellulose fibre properties, such as moisture absorbency, breathability, softness and biodegradability, are highly favoured in textile use. The production share of regenerated cellulose fibres was 6% of the total fibre production in 2020. The production grew between 2010 and 2018 slightly over 6%, the estimation of its yearly growth being over 2% (TextileExchange, 2020; The Fibre Year, 2020). In the course of time, the methods for viscose production have been developed towards more environmentally sound solvents and their recycling procedures (Räisänen et al., 2017; Sharma et al., 2019; Jiang et al., 2020). The development of lyocell process at the end of 1970′s was one of the first to recycle the solvent, i.e. NMMO (N–methylmorpholine N–oxide) (Jiang et al., 2020; Michud et al., 2016). Later, in 2015, the closed loop Ioncell–F technology was introduced, in which non-toxic ionic liquids are used in polymer dissolving and fibre spinning stages (Michud et al., 2016; Parviainen et al., 2015; Sixta et al., 2015). Ioncell technology is not yet at industrial production stage, but plans to start commercializing are set in 2025 (Ioncell, 2022). Because of the new production technology, which very currently received a significant recognition (MWP, 2022), most studies on Ioncell have concentrated on fibre physical characteristics (Michud et al., 2016; Guizani et al., 2020; Elsayed et al., 2021; Ma et al., 2021). So far, only two works have been published about Ioncell colouration: one with natural compounds from *Salix* sp. (Lothander et al., 2020) and the other coating with silver and gold nanoparticles (Haslinger et al., 2020).

In this study the regenerated cellulose fibres, Ioncell, lyocell, viscose and bamboo viscose, were used as material into which natural polyphenol (*A. cepa*) and anthraquinone (*C. semisanguineus*) type colourants were applied. Merino wool was used as a reference fibre because it is known to absorb natural dyes well, even though its fibre characteristics, being protein, differ from the cellulose.

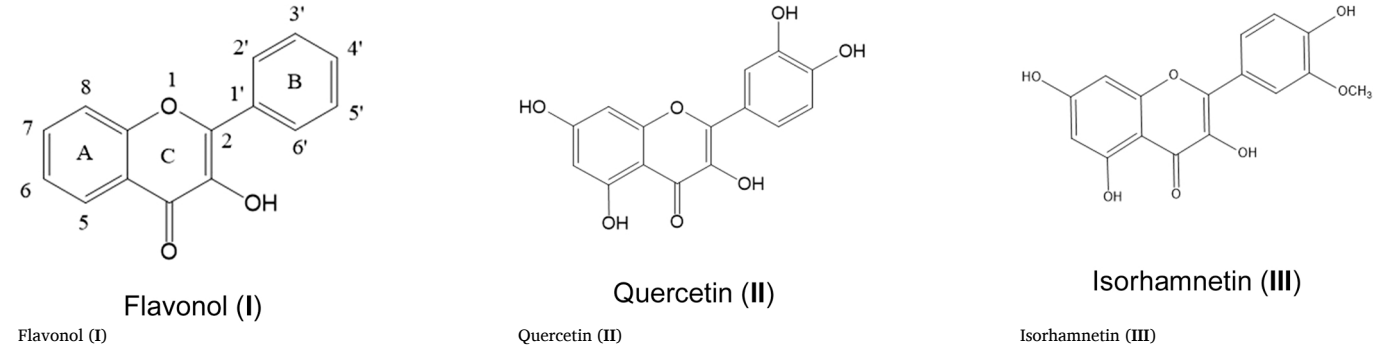
1.1. *Allium cepa*

The common onion, *Allium cepa* L., has been farmed for 4700 years. It is the economically most important member of the genus *Allium* and cultivated around the world. There is a huge variety of cultivars and landraces within the species, which differ in their adaptation to photoperiod and temperature, bulb storage life, dry matter content, flavour and skin colour (Gurushidze et al., 2007; Slimestad et al., 2007; Brewster, 2008). The onions are classified in different day type varieties, and in northern Europe long–day cultivars are grown (Brewster, 2008; Morgen, 2006). The leftover side streams of skins are considered as valuable raw material, as it has been shown that especially onions grown in the Nordic hemisphere contain high levels of flavonoids (Okamoto et al., 2006; Rodrigues et al., 2017). World onion production (including all forms of edible *Allium* species) was nearly 125 million tonnes in 2020, making it one of the most important horticultural crops in the world (FAOStat, 2020).

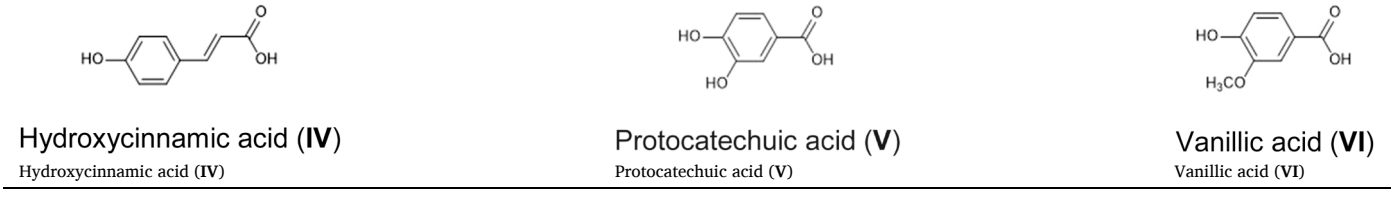
The dry outer skins of onions are rich in antioxidant compounds (Morgen, 2006; Suh et al., 1999; Lee et al., 2008), such as phenolics (Lee et al., 2008), of which the content is affected by various factors such as light and temperature (Dixon and Paiva, 1995). For a polyphenol to be defined as an antioxidant, there are two basic conditions. Firstly, when it is present in low concentration relative to the substrate to be oxidized, it is capable of delaying, retarding, or preventing the autoxidation or free radical–mediated oxidation. Secondly, the resulting radical formed after scavenging must be stable through intramolecular hydrogen bonding on further oxidation (Rice-Evans et al., 1996).

The major polyphenolic compounds in yellow onions (*Allium* spp.) include phenolic acids and flavonoids, such as flavonols (Slimestad et al., 2007). Flavonols (**I**) contain a 3–hydroxyflavone backbone and their diversity arises from the various positions of the phenolic OH–groups. The antioxidant activity of flavonol compounds is connected to their phenolic OH–group via donation of hydrogen atoms to free radicals. In general, flavonol glycosides have remarkably lower antioxidant capacity than their respective aglycones. The OH–groups in B–ring (4′–position) and C–ring (3–position) have higher hydrogen donation ability than the A–ring OH–groups (Heim et al., 2002), and for example dihydroxy B–ring–substituted flavonoids have great potential to perform antioxidant functions (Agati et al., 2012). In colourants, a high antioxidant capacity is connected to a photostability as it prevents the compound from degradation (Nuutila et al., 2003). The high antioxidant capacity improves material's colourfastness towards light, a property that is crucial for long lifetime artefacts.

The major flavonols in the outer skins of yellow onion (*A. cepa*) include quercetin 4′–glucoside and quercetin (**II**), the minor ones being quercetin 7,4′–diglucoside, quercetin 3,4′–diglucoside, quercetin 3–glucoside, isorhamnetin 4′–glucoside and isorhamnetin (**III**) (Pucciarini et al., 2019).



Flavonol (**I**) Quercetin (**II**) Isorhamnetin (**III**)

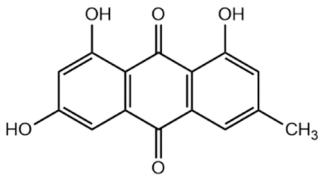


Hydroxycinnamic acid (**IV**) Protocatechuic acid (**V**) Vanillic acid (**VI**)

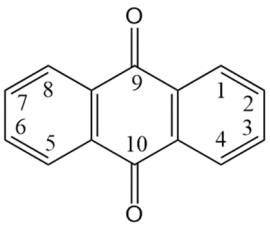
Of the phenolic acids, particularly hydroxycinnamic acid (**IV**) derivatives contribute to the cell wall formation through esterification with complex carbohydrates (Agati et al., 2012). The main phenolic acids in yellow onion (*A. cepa*) skins have been found to be protocatechuic acid glucoside, protocatechuic acid (**V**) and vanillic acid (**VI**) (Nuutila et al., 2003).

1.2. *Cortinarius semisanguineus*

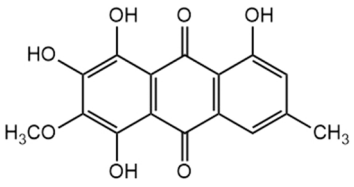
Anthraquinones are among the most stable natural secondary metabolites and natural dye structures, and they produce bright colours. Important is that for natural dyes their tinctorial strength is high. In disperse dyeing experiments the K/S value for emodin (**VII**) was observed to be comparable to its synthetic equivalents, i.e. synthetic anthraquinone dyes with related structures, in similar concentrations (Räisänen et al., 2021). The number and quality of donor groups and their positions in the anthraquinone ring system (**VIII**) affect the wide variety of achieved colours. In natural compounds, tetra–substituted (1,4,5,8−) anthraquinones are more bathochromic, e.g. dermocybin (**IX**), than di– (1,4−) or trisubstituted (1,2,4−), as with the greater number of substituents the circuit of electrons expands causing bathochromic shift in absorption towards longer wavelengths (Hunger, 2003).



Emodin (**VII**)



Anthraquinone (**VIII**)



Dermocybin (**IX**)

Emodin (**VII**) Anthraquinone (**VIII**) Dermocybin (**IX**)

In nature, anthraquinones can be found in plants, insects, fungi, lichen and bacteria. In the forest mushroom *Cortinarius* species, subgroup *Dermocybe*, the amount of anthraquinones can be as high as 6% (in dry weight, dw) whereas for plant sources, e.g. madder root (*Rubia* sp.), the amounts of colourants are typically 1.5–4% (dw) and require 2–3 years of growth period (Räisänen, 2019; Mussak and Bechtold, 2009). Colourants can be obtained from mushrooms yearly when in nature, and some fungi can also be cultivated in bioreactors (Suthar et al., 2021). Previously, we have studied anthraquinones from forest mushrooms especially *Cortinarius* species, and found them potential biocolourant sources even for long lifetime commodities (Räisänen et al., 2021; Räisänen, 2019; Räisänen, 2002). Also, *Cortinarius* species have been found beneficial for the growth of their host trees, and thus interesting from the forest economy point of view (Itoo and Reshi, 2014). Therefore, they were selected as one type of dye source for this study.

C. semisanguineus is a forest mushroom, which grows abundantly in the Northern hemisphere, and has been largely used for dyeing purposes by craft enthusiasts. The fruiting bodies are not especially big, being less than 10 cm tall and the diameters of the caps varying from 3 to 9 cm, but mycorrhiza produces numerous mushrooms which are dry and easy to pick. *Cortinarius* spp. are mycorrhizal fungi and form fungus roots mainly with coniferous trees (Liimatainen, 2013; Räisänen et al., 2016). Ectomycorrhizal fungi have gained increasing interest, as it has been recognized that they have the ability to promote the growth of their host symbionts. This opens up new prospects to develop techniques to culture such beneficial fungi, and benefit from their plant growth increasing properties in forest industry (Itoo and Reshi, 2014). In this picture, various *Cortinarius* species have been under investigation (Itoo and Reshi, 2014), and this brings up interesting foresight for combining beneficial forest economy with biocolorant production.

Currently, natural anthraquinones produced by fungi are not commercially available as biocolourants. There is discussion about anthraquinones characteristics, for example that some of the structures, if occurring in high concentrations, may have harmful effects such as mutagenicity and carcinogenicity (Suthar et al., 2021; Dufossé, 2014). This sets requirements for further research about the characteristics of these compounds, their safe dosage and applications (Herrala et al., 2022).

2. Materials and methods

2.1. Chemicals

Commercial standards of quercetin–3–O–glucopyranoside, quercetin dihydrate (aglycone) and cyanidin-3-O-glucoside chloride (kuromanin chloride) were purchased from Extrasynthese (Genay, France). HPLC grade MeOH and MeCN were obtained from Honeywell Riedel–de Haën (Charlotte, NC, USA) and formic acid ($\geq$ 99%) from VWR international (Radnor, PA, USA). Filtered deionized Milli–Q water (Merck KGaA, Darmstadt, Germany) was used for chemical analysis.

For the dyeing experiments, technical grade $KAl(SO_4)_2$ * 12 H_2O (J. T. Baker, Deventer, the Netherlands), $FeSO_4$ * 7 H_2O and tannin (tannic acid, $C_{14}H_{10}O_9$) (Tetri Design, Helsinki, Finland) were used as mordants. Water was regular tap water (pH~7.8, Helsinki Region Environmental Services Authority HSY, Helsinki, Finland). HCl and NaOH of analytical grade (VWR Chemicals, Czech Republic) were used in concentrations of 10 mass-% aqueous solutions to adjust the pH of the dye liquor to pH 4 and 8, respectively.

Commercial detergent, without optical brightener, Serto Silkkivilla (Kiilto, Turku, Finland) contained anionic 5–15%, nonionic 5–15% and amphoteric < 5% surface active substances, and was used to wash impurities from textile samples before dyeing.

Table 1
The HPLC protocol used in the analysis of *Allium cepa* (cv. Settonia).

Time / min	Eluent / % B (1% HCOOH aq)	Flow rate / mL/min
0–8	88–87	0.7
8–15	87–69	0.7–0.6
15–22	69–67	0.6
22–28	67–64	0.6
28–36	64–60	0.6
36–42	60–58	0.6
42–50	58–54	0.6
50–57	54–48	0.6–0.7
57–60	48–20	0.7
60–62	20	0.7
62–65	20–88	0.7
65–70	88	0.7

2.2. Plant and fungal material

The dry skins of yellow onion [*A. cepa*, cultivar (cv.) Settonia], cultivated in Siilinjärvi, Finland, were obtained from Kesko (Helsinki, Finland). The forest mushrooms (*C. semisanguineus*), collected from the southwestern Finland near Turku, were dried at 60 °C for 6 h and then stored in a dry, dark place at room temperature (RT).

2.3. Sample preparation for characterisation of plant and fungal colourants

The onion skins were ground using a blender (Bodum, Switzerland). The sample was extracted with a modified method from Primetta and coworkers (Lätti et al., 2008). The sample (1.67 g) and 10 mL of extraction solution (10% MeCN:MeOH, 85:15, v/v + 90% aqueous HCOOH 8.5%, v/v) was vortexed 2 min, ultrasonicated 20 min at 50 °C, vortexed again and centrifuged at 3000 rpm for 5 min at ambient temperature (without temperature control). The extraction was repeated twice with 5 mL. The supernatants were combined and the volume adjusted to 20 mL. Before HPLC analysis the extract was filtered using Chromafil® GF/RC–45/25 0.45 μm glass fibre/regenerated cellulose syringe filter (Magherey–Nagel GmbH & CO, Germany).

The main colourants in the forest mushroom *C. semisanguineus* were identified previously by Räisänen and coworkers (Räisänen, 2019; Räisänen et al., 2020) using the 2D–TLC and HPLC–UV/Vis–MS protocols.

2.4. HPLC–DAD–ESI–MS/MS

HPLC-analyses of the yellow onion samples were performed with HP Agilent 1100 HPLC system (Agilent Technologies, Santa Clara, CA, USA) equipped with degasser, binary pump, autosampler and DAD detector. The column was Gemini C18 15 mm × 4.6 mm, 3 μm (Phenomenex, Torrance, CA, USA) fitted with SecurityGuard C18 precolumn. Data acquisition and analysis for HPLC–DAD were done with Chemstation for LC 3D software (rev A 10.02). The ESI–MS detector was Bruker Esquire 3000 plus (Bruker, Billerica, MA, USA) quadrupole ion trap mass spectrometer. The HPLC program was modified from Primetta and coworkers (Lätti et al., 2008, 2010, 2011) (Table 1). Eluent A was MeCN: MeOH 85:15 (v/v) and eluent B 1% HCOOH in water (v/v).

The wavelengths of 280, 360 and 520 nm were monitored, and the positive and negative modes in ESI-MS/MS employed. The ESI conditions for the positive ionisation included capillary voltage 4.2 kV and temperature 300 °C, and for the negative ionisation 3.7 kV and 340 °C, respectively. Nitrogen was the nebulizer and drying gas. Full scan mass spectra were measured over the range 100–1000 *m/z*. Data acquisition and analysis was conducted with Bruker Daltonics Esquire 5.3 software (Bruker, Billerica, MA, USA).

Table 2
Properties of the fabrics used in the dyeing experiments.

Material	Square weight [g/m^2]	Knit type	Composition	Crystallinity (ref)
Viscose	158	1 × 1 ribbing	100%	50–58% (Rocky, Thompson, 2021)
Bamboo viscose	220	2 yarn reinforced single	100%	35–40% (Rocky, Thompson, 2021)
Lyocell	215	single	98% CLY, 2% EA	54–56% (Singh and Murthy, 2017)
Ioncell–F	160	interlock	100%	46–52% (Lothander et al., 2020)
Merino wool	220	interlock	100%	46% (Yu et al., 2021)

CLY: lyocell, EA: elastane

2.5. Textile materials

The aim was to study the dyeability of regenerated cellulose fibres, and wool was used as a reference material for its known good dyeability with natural dyes. Ioncell–F was obtained from Aalto University (Espoo, Finland) as fibres and knitted fabric. Viscose, bamboo viscose and lyocell were knitted fabrics from Orneule (Orivesi, Finland). Merino wool fibres were from Hoppy Point (Helsinki, Finland) and knitted fabric from Orneule (Orivesi, Finland). The detailed information of the materials is in Table 2.

2.6. Dyeing experiments

The dyeing experiments were performed using Original Hanau Linitest equipment (Hanau, Germany) following two types of exhaust dyeing procedures: A) mordant dyeing at 80 °C for 1 h, and B) high temperature high pressure (HTHP) dyeing at 130 °C for 1 h.

Before dyeing knitted fabrics and fibres were washed at 40 °C for 10 min to remove potential impurities. Commercial detergent Serto Silkkivilla was used in concentration 5 mL/L. After washing samples were rinsed twice with water and dried at RT.

To prepare the dye liquor, the amount of dry onion skins [33% on weight of fibre (owf)] or mushrooms [100% (owf)] was weighed, chopped or crushed, and treated in water with liquor ratio 1:20 in 80 °C for 1 h, where after the extract was drained through 60 mesh polyester filter. Organic material was discarded and the filtrate used in dyeing, where the fabric to liquor ratio was 1:20 or 1:50. If needed water was added to obtain the required liquor ratio. Table 3 summarizes the dyeing conditions in procedures A and B. Method A applied meta mordanting, which means that the mordant and the dye were at the same time in the dye liquor. This procedure saves water and energy because the mordanting and dyeing step are combined. 10% alum, 3% ferrous sulphate and 5% tannin (owf) were used as mordants, one at a time (Method A). Also, a sample without any mordant was dyed. HCl and NaOH were used to adjust the pH of the dye liquor to pH 4 and 8, respectively.

2.7. Dye content determination in the dye liquor

The dye (solid) content in dye liquor was determined by extracting the amount of 10 g of finely powdered yellow onion skins in 1:10 liquor ratio H_2O at 80 °C for 1 h, where after the dye liquor was filtered twice through a 140 mesh filter. A sample size of 20.0 g of dye liquor was evaporated to dryness at 50 °C for 36 h and dry content in the sample was calculated (m (solid dye): m (dye liquor) x 100%). Further, the dye content in onion skins was calculated according to the onion skin amount that was used to prepare the dye liquor. To proof the concept, extraction was repeated twice with 4 parallel samples (20.0 g) evaporated to dryness of each extraction. For the yellow onion the dye (solid) content was 1.25% of dw of the skins. The amount of the yellow onion dye in the dye liquor was 0.4% owf. According to Räisänen (2019) the anthraquinone content in *C. semisanguineus* is 4% of dw, which makes the dye amount in the dye liquor 4% owf.

2.8. Determining characteristics of the coloured fabrics

The colour of the dyed samples was measured as CIE L* , a* and b* and reflectance values (Smith, 1997) using a Konica Minolta (Tokyo, Japan) CM–2600d spectrophotometer (illuminant D65, CIE 10° observer). SCI (Specular Component Included) values were recorded, as this type of colour evaluation measures the total appearance independent of the surface conditions. The K/S value was calculated by the Kubelka–Munk equation [1]:

$$K / S = (1- R)^2 / 2 R \quad (1)$$

where K is the absorption coefficient and S the scattering coefficient of

Table 3
Conditions and parameters in the dyeing experiments.

Procedure	Dye (owf)	Temp [°C]	LR	pH	Mordants (owf)	Sample
Method A: Mordant dyeing	0.4% *A. cepa*	80	1:50	4 or 8	0, $KAl(SO_4)_2$ 10%, $FeSO_4$ 3%, tannin 5%	á 3 g fibres: Ioncell–F, merino wool
	4% *C. semisanguineus*	80	1:50	4 or 8	0, $KAl(SO_4)_2$ 10%, $FeSO_4$ 3%, tannin 5%	á 3 g fibres: Ioncell–F, merino wool
Method B: HTHP dyeing	0.4% *A. cepa*	130	1:50	8	0, tannin 5%	á 10 g knitted fabric: viscose, bamboo viscose, lyocell, Ioncell–F
	"	"	"	4	"	á 10 g knitted fabric: merino wool
	4% *C. semisanguineus*	130	1:20	8	0, tannin 5%	á 10 g knitted fabric: viscose, bamboo viscose, lyocell, Ioncell–F
	"	"	"	4	"	á 10 g knitted fabric: merino wool

owf: on weight of fibre, LR: liquor ratio, HTHP: high temperature high pressure.

the fabric to be tested, and R is the reflectance at the maximum absorption wavelengths. The wavelengths of 420 nm (*A. cepa*) and 460 nm (*C. semisanguineus*) were used for the R values.

The measured CIE L* , a* , b* values were converted to RGB values with Corel PaintShop Pro 2023 25.1.0.32 × 64 software. The corresponding RGB values were used to colour cells in Tables 5 and 6.

The colourfastness for domestic and commercial laundering was tested according to the (ISO 105–C06:2010) standard using AATCC detergent (WOB), A1S method and DW multi–fibre test fabric. The colour change after the washing fastness test was measured with the CIE Lab spectrophotometer and converted into the grey scale rating 1–5 according to the (ISO 105–A05:1996) standard. The values for staining were measured as CIELab values, and converted to the 1–5 scale according to the (ISO 105–A04:2000) standard. The (ISO 105–B02:2014) standard, Method 2, was followed to test the light fastness using James Heal TruFade 200 equipment (James Heal, Halifax, UK) with a xenon arc lamp.

3. Results

3.1. Colourants in yellow onion (A. cepa cv. Settonia)

The main colourants from the yellow onion skins were tentatively identified, and the results can be seen in the HPLC-DAD chromatogram (Fig. 1) and Table 4. The results are in accordance with the previously published works (Pucciarini et al., 2019; Ly et al., 2005). Most flavonols (**I**) exhibit two major characteristic absorption bands in the UV/Vis region: Band II (A ring) absorption occurs at 250–285 nm, and the Band I (B ring) at 320–385 nm (Markham, 1989).

The tentative identification of flavonoids from the MS data revealed the presence of quercetin (**II**) and its derivatives. The most prominent peaks were identified as quercetin hexoside (**3**) and quercetin aglycone (**4**).

The first eluted peak was the most polar compound of the separated quercetin derivatives, quercetin dihexoside (**1**), which is typical when using RP-column, and finding is consistent with the literature (Lee et al., 2008; Lee et al., 2011). The fragmentation of the compound is in accordance with (Lee et al., 2011) (Table 4).

Second peak was tentatively identified as benzofuranone derivative (**2**). A benzofuranone derivative 2–(3,4–dihydroxybenzoyl)–2,4,6–trihydroxybenzofuran–3(2 H)–one has previously been identified in *A. cepa* skins by Ly et al. (2005) and has been identified as an oxidation product of quercetin (Gülşen et al., 2007).

The third peak was tentatively identified as quercetin hexoside (**3**), and is most probably quercetin glucoside (e.g. Lee and Mitchell, 2011). Compound **4** was tentatively identified as quercetin aglycone (**4**) presenting UV/Vis and MS characteristics typical for quercetin (Ma et al., 1997; Fabre et al., 2001; Bonaccorsi et al., 2005). Compounds **5**, **6** and **7** were all tentatively identified as quercetin dimer hexosides (Ly et al., 2005; Campone et al., 2018). Compounds **5** and **6** eluted close together at 35.0 and 35.3 min and presented very similar MS characteristics. Compound **7** detected at 40.8 min and tentatively identified as quercetin dimer hexoside presented a slightly different fragmentation pattern to the previous two compounds. The differences in the MS fragmentation patterns as well as UV/Vis spectral characteristics suggest a difference in molecular structures for compounds **5** and **6** versus **7**, as reported also earlier by Ly and coworkers (2005). More detailed analysis based on the MS-MS fragmentation of the compounds is presented in the supplementary material, S1.

3.2. Colourants in the forest mushroom C. semisanguineus

The main anthraquinones in the *C. semisanguineus* were previously identified and reported by Räisänen and coworkers (Räisänen, 2019; Räisänen et al., 2020) as dermolutein, physcion, dermocybin glycoside, dermorubin, 5–chlorodermolutein, emodin glycoside and 5–chloroemodin (Table 5 S in supplementary material). In fresh mushrooms the majority of emodin and dermocybin are as glucosides, i.e. 1–*β*–D–glucopyranosides, which can turn into aglycones by enzymatic hydrolysis occurring endogenously in the fungus by the β–glucosidase enzyme. Endogenous hydrolysis is possible in old mushrooms, and during drying, when the cell walls are disrupted enabling reactions.

3.3. Colour and colour fastness of the dyed materials

The CIELab colour codes of the dyed samples are shown in Table 5 (*A. cepa*) and 7 (*C. semisanguineus*). The polyphenolic compounds create yellowish colours indicated from the high positive values of b* . The aluminium mordant produce with the polyphenolic dyes metal complexes creating a clearly yellow colour, while the result without a mordant or with tannin is light brown. Iron's metal complex with the polyphenolic dyes create green, indicated from a low positive value of a* (near 0) and relatively low positive value of b* (ca. 10). The K/S values (Table 5, Fig. 2) show that the highest colour uptake is obtained with polyphenolic dyes in acidic, pH 4, environment, and there is a surprisingly big difference compared to the result with the basic environment, pH 8. Normally, cellulose fibres are dyed in basic environment because the fibres are then at the most reactive stage as cellulose's hydroxyl groups are ionized, and this opens up the fibre structure (Burkinshaw and Filarowski, 2016). However, as our results show with

Table 4
The results of the HPLC–DAD–MS/MS data of yellow onion (*A. cepa* cv. Settonia). The numbers refer to the peaks in Fig. 1.

			Positive ions		Negative ions				
Peak	**RT (min)**	**UV/Vis (nm)**	**MS (*m/z*)**	**MS–MS (*m/z*) (precursor in bold)**	**MS (*m/z*)**	**MS–MS (*m/z*) (precursor in bold)**	**Tentative identification**	**Molecular formula (mass)**	**Literature**
1	16.3	NA	627 $[M+H]^+$	**627:** 465 $[M+H–Hx]^+$, 303 $[Aglc+H]^+$ (100), 257 $[Aglc+H–H_2O–CO]^+$, 247 $[Aglc+H–2CO]^+$, 229 $[Aglc+H–H_2O–2CO]^+$	625 $[M–H]^-$	**625:** 463 $[M–H–Hx]^-$ (100), 301 $[Aglc–H]^-$, 343 [M–H–Hx–150 (hx cleavage)]$^-$	Quercetin dihexoside	$C_{27}H_{30}O_{17}$ (626.1483)	(Lee and Mitchell, 2011)
2	16.7	234, 294, 320sh	341 $[M+H+Na]^+$, 319 $[M+H]^+$, 301 $[M+H–H_2O]^+$ (100)	NA	635 $[2\ M–H]^-$ (100), 317 $[M–H]^-$	**317:** 299 $[M–H–H_2O]^-$, 273 $[M–H–CO_2]^-$, 271 $[M–H–H_2O–CO]^-$, 208 $[M–H–B–ring]^-$, 207 $[M–H–B–ring –H]^-$, 255 $[M–H–H_2O–CO_2]^-$, 191 $[M–H–B–ring–OH]^-$ (100), 163 $[M–H–B–ring–OH–CO]^-$ **635:** 317 $[M–H]^-$	Benzofuranone derivative		(Ly et al., 2005; Gülşen et al., 2007; Jungbluth and Ternes, 2000; Jørgensen et al., 1998)
3	21.5	254, 265sh, ~310sh, 366	465 $[M+H]^+$	**465:** 303 $[Aglc+H]^+$ (100), 285 $[Aglc–H_2O]^+$, 257 $[Aglc–H_2O–CO]^+$, 229 $[Aglc–H_2O–2CO]^+$, 165 ($^{0,2}A^+$ aglc fragment), 155, 145	463 $[M–H]^-$	**436:** 301 $[Aglc–H]^-$, 179 [^{1,2}A–H (aglc fragment)]$^-$ (100), 151 [^{1,2}A–H–CO]$^-$	Quercetin hexoside	$C_{21}H_{20}O_{12}$ (464.0955)	(Lee et al., 2008; Lätti et al., 2010; Lee et al., 2011; Bonaccorsi et al., 2005)
4	30.0	256, 298, 372	303 $[M+H]^+$	**303:** 283 $[M+H–H_2O–2\ H]^+$, 276, 275 $[M+H–CO]^+$, 273 $[M+H–CH_2O]^+$, 257 $[M+H–H_2O–CO]^+$ (100), 229 $[M+H–H_2O–2CO]^+$, 201 $[M+H–H_2O–3CO]^+$, 121	617 (100), 301 $[M–H]^-$	**301:** 273 $[M–H–CO]^-$, 272, 271 $[M–H–CH_2O]^-$, 257 $[M–H–CO_2]^-$, 229 $[M–H–CO_2–CO]–$, 193 $[M–H–B–ring]^-$, 179 [^{1,2}A–H]$^-$ (100), 151 [^{1,2}A–H–CO]$^-$, 107 [^{1,2}A–H–CO–CO_2]$^-$	Quercetin aglycone	$C_{15}H_{10}O_7$ (302.2380)	(Lee et al., 2008; Bonaccorsi et al., 2005)
5	35.0	256, 273, 304, 370	765 $[M+H]^+$	**765:** 613 $[M+H–152]^+$, 603 $[M+H–Hx]^+$ (100), 585 $[M+H–Hx–H_2O]^+$, 543 $[M+H–Hx–C_2H_2O]^+$, 467, 451 [M+H–Hx–152 (C–ring cleavage)]$^+$, 423, 341, 303 $[Monom+H]^+$	763 $[M–H]^-$	**763:** 611 $[M–H–152]^-$ (100), 599, 593, 583 $[M–H–Hx–H_2O]^-$, 449 [M–H–Hx–152 (C–ring cleavage)]$^-$, 421, 299 $[Monom–3\ H]^-$	Quercetin dimer hexoside	$C_{36}H_{28}O_{19}$ (764.1225)	(Ly et al., 2005; Campone et al., 2018)
6	35.3	256, 274, 303, ~368	765 $[M+H]^+$	**765:** 603 $[M+H–Hx]^+$ (100), 585 $[M+H–Hx–H_2O]^+$, 559, 493, 467, 451 [M+H–Hx–152 (C–ring cleavage]$^+$, 433, 423, 341, 303 $[Monom+H]^+$	763 $[M–H]^-$	**763**: 611 $[M–H–152]^-$ (100), 583 $[M–H–Hx–H_2O]^-$, 449 [M–H–Hx–152 (C–ring cleavage)]$^-$, 431	Quercetin dimer hexoside	$C_{36}H_{28}O_{19}$ (764.1225)	(Ly et al., 2005; Campone et al., 2018)
7	40.8	250, 272, 304, 364	765 $[M+H]^+$	**765:** 603 $[M+H–Hx]^+$ (100), 585 $[M+H–Hx–H_2O]^+$, 567 $[M+H–Hx–2\ H_2O]^+$ (4), 557 $[M+H–Hx–H_2O–CO]^+$, 405, 313, 303 $[Monom+H]^+$, 273 $[Monom–2\ H–CO]^+$	763 $[M–H]^-$	**763:** 601 $[M–H–Hx]^-$, 571, 300, 299 $[Monom–3\ H]^-$ (100), 271 [Monom–3 H–CO]$^-$, 227, 215	Quercetin dimer hexoside	$C_{36}H_{28}O_{19}$ (764.1225)	(Ly et al., 2005; Campone et al., 2018)

sh: shoulder, Aglc: aglycone, Hx: hexoside, Monom: monomer.

natural dyes this is not the optimal condition: the cellulose fibre creates a negative charge, and repelling forces push likely charged dyes away from the fibre surface.

The HTHP dyeing (Method B, Table 5) increase the dye uptake of wool greatly, compared to the conventional dyeing, indicated by the remarkably higher K/S values, but for cellulose fibres the dye uptake remain at the same level as in the conventional dyeing revealed by the faint colour and the low K/S values. Moreover, the conventional dyeing in pH 4 results the highest K/S values for the regenerated cellulose fibres, and thus shows the most favourable dyeing environment for the polyphenolic yellow onion dyes. At pH 4 conditions hydrogen bonding between cellulose OH-groups and colourants is possible, and this creates more favourable environment for dye uptake. When comparing the different regenerated cellulose fibres it can be observed, that the dyeing result is nearly the same under the identical conditions.

Dyeing experiments with the yellow onion dye show that if the clear yellow colour is desired, aluminium is needed as the mordant, because the natural mordants (being phenols) themselves give a beige (light brown) background tone. Tannins are complex polyphenols and therefore, it is logic that the colour with tannin mordant is nearly the same than that without any mordant. In this research we wanted to use as environmentally sound mordants as possible, and according to the current knowledge aluminium and iron are the most appropriate from the metal salts. Important is to use mordants in small amounts where the majority attaches to the fibres.

The anthraquinone structure is flat and it has delocalized π electrons, which create a negative electron cloud around the molecule. Electro negativity is even stronger when the attached hydroxyl groups are

Table 5
The CIELab values of the samples dyed with *A. cepa*. (printing with colour).

Sample*/Method A	pH	Colour	L*	a*	b*	C^*_{ab}	h_{ab}	K/S λ 420 nm
Ac-0-WO-f	4		63.02	7.58	31.28	32.19	1.33	7.1
Ac-Al-WO-f	4		71.97	4.84	51.53	51.76	1.48	6.1
Ac-Tann-WO-f	4		66.96	8.72	31.23	32.42	1.30	7.0
Ac-Fe-WO-f	4		50.14	1.39	11.12	11.21	1.45	3.4
Ac-0-Ioncell-f	4		70.94	5.14	31.03	31.45	1.41	3.6
	8		69.03	5.23	15.29	16.17	1.24	1.4
Ac-Al-Ioncell-f	4		67.26	10.41	65.73	66.56	1.41	14.9
	8		82.37	0.74	19.43	19.47	-0.03	0.6
Ac-Tann-Ioncell-f	4		74.88	5.02	14.32	15.18	1.23	1.0
	8		72.55	5.80	23.41	24.13	1.33	2.8
Ac-Fe-Ioncell-f	4		56.60	0.47	16.27	16.27	1.54	3.0
	8		74.26	0.64	9.73	9.77	0.72	0.7
Ac-Tann-WO	4		53.23	20.95	37.39	42.86	1.59	19.0
Ac-Tann-Viscose	8		69.91	7.33	21.84	23.04	2.87	3.0
Ac-Tann-Bviscose	8		65.77	7.83	19.22	20.75	2.32	2.7
Ac-Tann-Lyocell	8		71.22	5.88	19.91	20.76	3.29	2.1
Sample*/Method B								
Ac-0-WO	4		37.60	21.95	34.00	40.47	1.33	48.5
Ac-Tann-WO	4		37.86	22.59	29.67	37.29	1.05	37.5
Ac-0-Viscose	4		60.97	7.76	27.07	28.16	3.39	6.7
	8		69.48	5.91	23.70	24.43	3.93	2.5
Ac-Tann-Viscose	8		68.94	6.27	23.02	23.86	3.58	3.0
Ac-0-Bviscose	4		59.05	6.47	25.95	26.74	3.93	7.4
	8		61.07	6.29	22.73	23.58	3.52	3.7
Ac-Tann-Bviscose	8		63.16	6.37	19.59	20.60	2.97	3.3
Ac-0-Lyocell	4		62.08	6.06	25.40	26.11	4.11	6.7
	8		70.58	4.94	22.18	22.72	4.42	2.4
Ac-Tann-Lyocell	8		68.88	4.37	22.06	22.49	4.98	3.1
Ac-0-Ioncell	8		60.65	6.97	18.69	19.95	2.56	3.0
Ac-Tann-Ioncell	8		63.83	6.11	18.16	19.16	2.86	2.5

Ac: *A. cepa*, f: fibre, Bviscose: bamboo viscose, Tann: tannin, Al: alum.

ionized. As the cellulose fibres are equally negatively charged in aqueous environment (Reischl et al., 2006), repulsive electrochemical forces appear, and dyeing result remains light. Even the aluminium and iron mordants are not able to improve the situation, as indicated from the alike low K/S values.

The lightfastness results for all regenerated cellulose fibres are about the same, varying from poor to moderate (Tables 7 and 8). For phenolic compounds the lightfastness values are slightly better for samples that were dyed in the acidic environment. Even that anthraquinones generally are more lightfast than phenolic compounds, were the colourfastness results for *C. semisanguineus* dyed cellulose samples very low, attributed to the low amount of dye attached to the fibres (low K/S value), and it fading away (Table 8). The morphological structures and the degree of crystallinity (Table 2) of fibres may have an effect to the dyeing result, as dye particles penetrate the amorphous areas, and thus the lower the crystallinity the more room for dyes in fibres (Räisänen et al., 2017; Guizani et al., 2020). Table 2 shows that differences in crystallinity between the different regenerated fibres is small. Bamboo viscose and Ioncell have slightly lower rate of crystallinity, but it does not result significant differences in dyeing rate, i.e. the K/S values (Table 6, Fig. 2) compared to viscose and lyocell.

Washing fastness results for staining vary for all samples between moderate to good (Tables 7 and 8), whereas colour change receives partly low values. This shows one of the challenges of natural colourants – the washing. From delicate colours like yellow, the change in hue is easily observable: the basic environment of detergent liquor often induces colour change in natural dyed textile, attributed to the ionization of dye molecules and thus bathochromic shift in light absorption. Washing with neutral or slightly acidic environment is highly recommended to decrease the phenomenon.

Phan and coworkers (2021) reviewed several agricultural sidestreams, and propose that agricultural and food processing waste streams are adequate sources for natural dye production, especially when applied in niche scale. Through the life cycle analysis they showed that there is environmental competitiveness of certain natural dyes compared with synthetic dyes, when applied as crude liquid form extracts (Phan et al., 2021), obviously because the evaporation of the solvent requires energy. The comparisons also showed that the dye extraction phase (solvent and energy use) and the dyeing phase (liquor ratio) have the largest environmental impact on the entire process when estimating the processes sustainability (Phan et al., 2021). When designing valorisation routes for natural dyes it is good to keep in mind that by–products may contain other added–value substances. To remain competitive in processing costs, the EU RESFOOD (2016) project advises the co–production of multiple compounds. This means that by–products should be valorised toward a major bulk compound (e.g., protein, fat, carbohydrate, or fibre), while the minor compounds can be separated from the crude extract afterwards (RESFOOD, 2016). Even though dyeing with the crude liquid extract is in all cases the most competitive and environmentally sound approach, this is recommended only when the extract is depleted of the main valuable substances or their extraction is not economically viable. Otherwise, purification is justified; the purified dye extract can be processed into a concentrate, even a powder, via vacuum evaporation or spray drying (Phan et al., 2021).

Table 6
The CIELab values of the samples dyed with *C. semisanguineus*. (printing with colour).

Sample*/Method A	pH	Colour	L*	a*	b*	C^*_{ab}	h_{ab}	K/S λ 480 nm
Cs-0-WO-f	4		41.77	26.54	24.04	35.81	0.74	8.8
Cs-Al-WO-f	4		54.69	29.67	30.51	42.56	0.80	4.3
Cs-Tann-WO-f	4		45.43	29.25	26.66	39.57	0.74	7.4
Cs-Fe-WO-f	4		47.60	20.98	25.25	32.82	0.88	5.7
Cs-0-Ioncell-f	4		80.24	4.68	4.96	6.82	0.81	0.5
	8		76.88	6.94	1.41	7.09	0.20	0.5
Cs-Al-Ioncell-f	4		77.83	7.16	6.37	9.59	0.73	0.7
	8		83.93	6.21	3.85	7.31	0.56	0.3
Cs-Tann-Ioncell-f	4		79.47	5.12	9.23	10.56	1.06	0.9
	8		74.22	6.09	7.57	9.72	0.89	1.2
Cs-Fe-Ioncell-f	4		71.45	2.33	4.65	5.26	1.09	1.1
	8		77.48	2.02	2.37	3.12	0.86	0.6
Cs-Tann-WO	4		35.47	25.30	26.45	36.60	0.71	15.1
Cs-Tann-Viscose	8		77.27	6.95	6.85	9.76	0.62	0.4
Cs-Tann-Bviscose	8		70.81	9.73	8.80	13.12	0.50	0.5
Cs-Tann-Lyocell	8		75.07	5.48	5.88	8.04	0.74	0.3
Sample*/Method B								
Cs-0-WO	4		24.73	17.09	21.22	27.25	0.96	29.9
Cs-Tann-WO	4		23.99	17.64	22.24	28.39	0.99	34.5
Cs-0-Viscose	8		73.67	8.89	1.85	9.08	-0.09	1.1
Cs-Tann-Viscose	8		73.56	7.18	6.31	9.56	0.46	0.4
Cs-0-Bviscose	8		67.61	12.06	4.57	12.90	-1.82	0.6
Cs-Tann-Bviscose	8		68.41	8.23	8.26	11.66	0.65	0.6
Cs-0-Lyocell	8		73.45	7.76	2.53	8.16	-13.42	0.4
Cs-Tann-Lyocell	8		74.85	7.17	5.38	8.97	0.24	0.3
Cs-0-Ioncell	8		75.06	8.39	4.01	9.30	-0.85	0.4
Cs-Tann-Ioncell	8		59.86	8.25	8.74	12.02	0.72	0.9

Cs: *C. semisanguineus*, f: fibre, Bviscose: bamboo viscose, Tann: tannin, Al: alum.

We showed that agricultural streams and ectomychorrizal fungi, like *Cortinarius* species, possess potential as biocolourants: very well for protein fibres like wool, and also for regenerated cellulose materials in certain conditions. Ectomychorrizal fungi are important for growth of trees and they should be examined from the point of view of beneficial forest economy (Itoo and Reshi, 2014), which could be combed with biocolourant production. Further research is needed of these less known mushroom species and their symbiotic relationships in forest ecosystems. As well as the dyeability of cellulose regenerated fibres with different types of biocolourants.

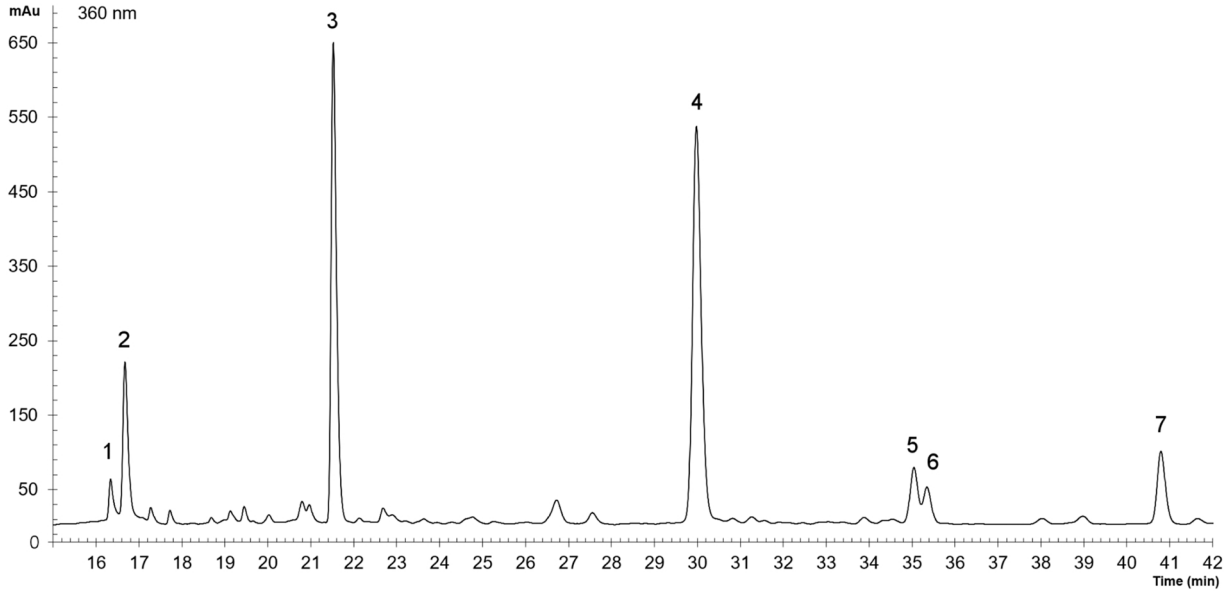


Fig. 1. The HPLC–DAD profile of the *A. cepa* (cv. Settonia) sample monitored at 360 nm. The numbered peaks of the tentatively identified compounds are presented in Table 4.

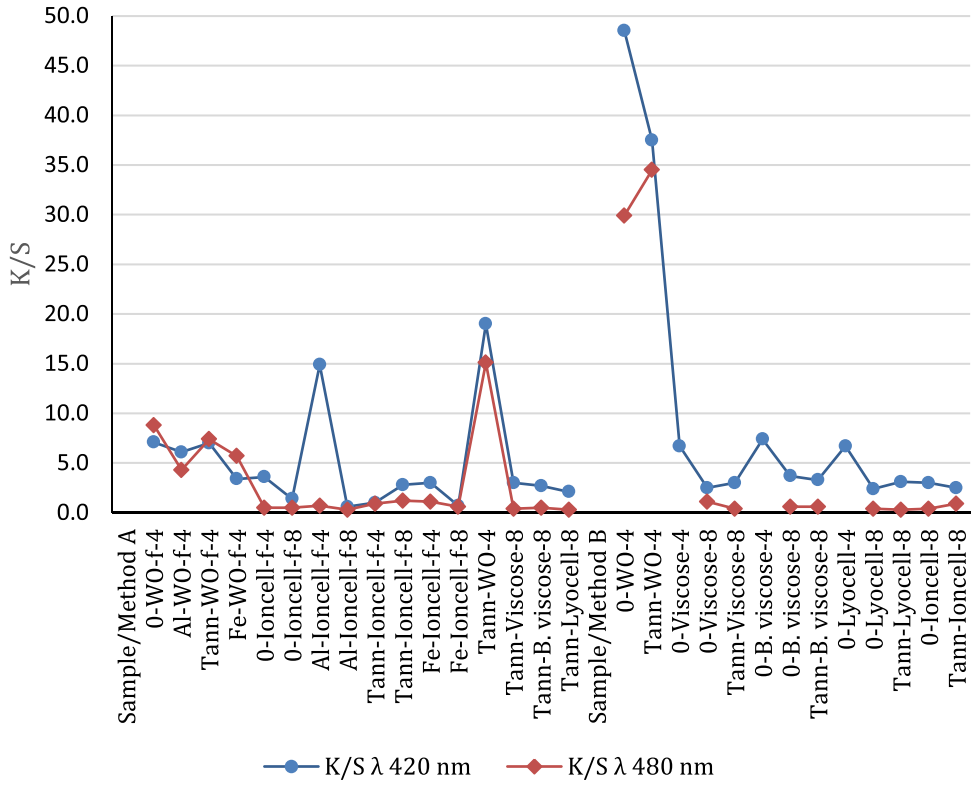


Fig. 2. The K/S values of the samples dyed with *A. cepa* (at λ 420 nm, blue) and *C. semisanguineus* (at λ 480 nm, orange). Method A refers to the mordant dyeing and Method B to the HTHP dyeing. (printing with colour).

Table 7
Colourfastness of the textile materials dyed with *A. cepa* in pH 4 and 8.

Sample[#]	Dyeing		WF	WF, staining					
Method A	**pH**	**LF**	**CC**	**CA**	**CO**	**PA**	**PES**	**PAN**	**WO**
Ac-0-WO-f	4	3	4	4–5	3	4	3–4	5	5
Ac-Al-WO-f	4	3	2	5	5	5	5	5	5
Ac-Tann-WO-f	4	3	3–4	5	4–5	4–5	5	5	4–5
Ac-Fe-WO-f	4	4	1	4–5	4–5	4	5	5	5
Ac-0-Ioncell-f	4	2	1	5	4–5	5	5	5	4–5
	8	2	2	5	4–5	5	5	4–5	4–5
Ac-Al-Ioncell-f	4	4	1	5	4–5	5	5	5	4–5
	8	1	1	5	5	5	5	5	4–5
Ac-Tann-Ioncell-f	4	2	2	4–5	4–5	5	5	5	4–5
	8	3	1	5	4–5	5	5	5	4–5
Ac-Fe-Ioncell-f	4	4	1	4–5	4–5	5	5	5	5
	8	2	1–2	5	5	5	5	4–5	4–5
Ac-Tann-WO	4	4	1	3	2–3	4–5	4–5	5	5
Ac-Tann-Viscose	8	2	1–2	5	4	5	5	5	5
Ac-Tann-Bviscose	8	2	2–3	4	4	5	5	5	5
Ac-Tann-Lyocell	8	2	3	4–5	3–4	5	5	5	5
Method B									
Ac-0-WO	4	4	2	3–4	3	4–5	5	5	5
Ac-Tann-WO	4	4	1	3–4	3	4–5	5	5	5
Ac-0-Viscose	4	3	2	4–5	3–4	3–4	1	5	5
	8	2	1–2	4–5	3	5	5	5	5
Ac-Tann-Viscose	8	2	1–2	5	4	5	5	5	5
Ac-0-Bviscose	4	4	2	5	3–4	5	4	5	4
	8	2	1–2	3–4	2–3	5	5	5	5
Ac-Tann-Bviscose	8	2	3	4–5	4	5	5	5	5
Ac-0-Lyocell	4	3	3	4	3	5	5	5	5
	8	2	1	3–4	2–3	5	5	5	5
Ac-Tann-Lyocell	8	2	1–2	3–4	3–4	5	5	5	5
Ac-0-Ioncell	8	2	2	4	4	5	5	5	5
Ac-Tann-Ioncell	8	2	3–4	4	3–4	5	5	5	5

Ac: *A. cepa*, f: fibre, Bviscose: bamboo viscose, Tann: tannin, Al: alum, LF: light fastness, WF: washing fastness, CC: colour change, CA: cellulose acetate, CO: cotton PA: polyamide, PES: polyester, PAN: polyacrylonitrile, WO: wool.

Table 8
Colourfastness of the textile materials dyed with *C. semisanguineus* in pH 4 and 8.

Sample[#]	Dyeing		WF	WF, staining					
Method A	**pH**	**LF**	**CC**	**CA**	**CO**	**PA**	**PES**	**PAN**	**WO**
Cs-0-WO-f	4	3	1	4–5	2	4–5	4–5	5	5
Cs-Al-WO-f	4	3	1	4–5	3	3	3–4	4–5	4–5
Cs-Tann-WO-f	4	3	1	3–4	2	4–5	4–5	5	3
Cs-Fe-WO-f	4	3	1	4–5	2	3	3–4	4–5	4–5
Cs-0-Ioncell-f	4	1	1–2	5	5	4	5	4–5	4–5
	8	3	1	4–5	4–5	4	4–5	5	4–5
Cs-Al-Ioncell-f	4	1	1–2	4–5	4–5	5	4	4–5	4–5
	8	1	2	5	5	4–5	5	5	5
Cs-Tann-Ioncell-f	4	2	1	4–5	4–5	4	4–5	5	5
	8	3	1–2	4	4–5	4–5	4–5	5	4–5
Cs-Fe-Ioncell-f	4	3	1–2	5	4–5	5	5	5	4–5
	8	2	2	5	5	4–5	5	5	5
Cs-Tann-WO	4	3	1	2–3	3	4	5	5	4–5
Cs-Tann-Viscose	8	1	1–2	4–5	4–5	5	5	5	5
Cs-Tann-B. viscose	8	2	1	4	4–5	4–5	5	5	5
Cs-Tann-Lyocell	8	2	2–3	4	4–5	4–5	5	5	5
Method B									
Cs-0-WO	4	4	1–2	3	2–3	2–3	4	4–5	3–4
Cs-Tann-WO	4	6	1–2	2–3	3	2–3	4–5	4–5	3
Cs-0-Viscose	8	1	1–2	4–5	4–5	4–5	5	5	5
Cs-Tann-Viscose	8	1	1–2	4–5	4–5	5	5	5	5
Cs-0-B. viscose	8	2	1–2	4	4	4	5	5	5
Cs-Tann-B. viscose	8	2	3	4	4–5	4–5	5	5	5
Cs-0-Lyocell	8	1	1	4	4	4	5	5	5
Cs-Tann-Lyocell	8	2	1–2	4–5	4	4–5	5	5	5
Cs-0-Ioncell	8	1	1–2	4–5	5	5	5	5	5
Cs-Tann-Ioncell	8	2	1–2	4–5	4–5	4–5	5	5	5

Cs: *C. semisanguineus*, for other abbreviations see Table 7.

4. Conclusions

The main phenolic colourants of yellow onion (*A. cepa*) were successfully analysed and characterized as quercetin aglycone and quercetin glycosides. The antraquinones from the forest mushroom (*C. semisanguineus*) were previously analysed and characterized (Räisänen, 2019; Räisänen et al., 2020; Räisänen et al., 2000). Extracted crude mixtures of onion and mushroom were applied as dyes for regenerated cellulose fibres. Different regenerated fibre types did not show significant differences between the dye uptake, but the phenolic compounds received higher uptake (K/S 0.7–14.9) than the anthraquinones (K/S 0.3–1.2). HTHP dyeing didn't enhance dye uptake for cellulose fibres compared to conventional dyeing nor were the colour fastness values increased. The HTHP dyeing was applied because we knew from our previous experience that cellulose is a difficult material to dye with natural dyes, and temperature is one of the focal parameters in dyeing. Water in gas phase (130 °C) has more energy to open the fibres and carry the dissolved dye molecules. From the results (Fig. 2) we see that the higher temperature gave considerable advantage and increase in dye uptake for wool, but not for regenerated cellulose fibres.

Colourfastness properties for dyed regenerated cellulose materials were low (1–4, 8 being maximum) for long lifespan consumables, which sets questions for further research on colouration practises. Iron mordant resulted the best light fastness values revealing strong stabilization ability for the dye. Free phenolic compounds, such as quercetin, have high antioxidant capacity and activity (Nuutila et al., 2003), and this may lead to higher photostability of the colourant increasing the colourfastness of the dyed textile. Related to this, Willemen and coworkers have noticed that colour change after UV exposure was less for crude extracts compared to purified flavonoids. However, when they compared colour change, ΔE, values of flavonoid aglycones to mono- and di-glycosides, they noticed that aglycones had slightly lower values indicating better colour fastness (Willemen et al., 2019). On the other hand, Ford and coworkers noticed when studying anthraquinones from madder that anthraquinone glycosides were absorbed to a greater extend by the fibre compared to aglycones (Ford et al., 2018). Both Willemen's and Ford's groups dyed wool. In plants, as revealed by our analysis of yellow onion, flavonoids are often connected to glucosides, having lower antioxidant capacity than aglycones (Nuutila et al., 2003). Therefore, our next step is to develop natural dyes as aglycones through enzymatic hydrolysis, and study the properties of obtained compounds to find out whether improvement in the dyed textile's colourfastness can be received especially for cellulose fibres. For Ioncell at pH 4 the flavonoids dye uptake and colourfastness values were tiny bit higher than those of the other studied cellulose fibres, and would need further research for confirmation.

Funding

This work was supported by the Strategic Research Council at the Academy of Finland [funding decision no. 327178].

CRediT authorship contribution statement

Riikka Räisänen, Anja Primetta: Conceptualization, Writing – review & editing. **Riikka Räisänen, Anja Primetta, Peppi Toukola, Silja Fager, Joanna Ylänen**: Methodology, Investigation, Data curation, Formal analysis. **Riikka Räisänen, Anja Primetta, Peppi Toukola**: Software, Validation, Writing – original draft preparation. **Riikka Räisänen, Anja Primetta:** Supervision. **Riikka Räisänen:** Resources, Project admistration, Funding acquisition. **Riikka Räisänen, Peppi Toukola**: Visualization. All authors have read and agreed to the published version of the manuscript.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Riikka Raisanen reports financial support was provided by Academy of Finland.

Data availability

Data will be made available on request.

Acknowledgements

We express our gratitude to laboratory engineer Matti Jussila, University of Helsinki, for assistance with the HPLC–DAD–MS studies, staff scientist Marja Rissanen, Aalto University, for providing Ioncell–F material and associate professor Muriel Rigout, University of Leeds, School of Textiles, for performing the lightfastness tests.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2023.116748.

References

Agati, G., Azzarello, E., Pollastri, S., Tattini, M., 2012. A review. Flavonoids as antioxidants in plants: Location and functional significance, 67–6 Plant Sci. 196. https://doi.org/10.1016/j.plantsci.2012.07.014.

Bonaccorsi, P., Caristi, C., Gargiulli, C., Leuzzi, U., 2005. Flavonol glucoside profile of southern Italian red onion (*Allium cepa* L.). J. Agric. Food Chem. 53 (7), 2733–2740. https://doi.org/10.1021/jf048152r.

Brewster, J.L., 2008. Onions and Other Vegetable Alliums, 2nd ed.,. CAB International, Wallingford.

Burkinshaw, S.M., Filarowski, A., 2016. Physico-Chemical Aspects of Textile Coloration. John Wiley & Sons, Chichester.

Campone, L., Celano, R., Piccinelli, A.L., Pagano, I., Carabetta, S., Di Sanzo, R., Russo, M., Ibañez, E., Cifuentes, A., Rastrelli, L., 2018. Response surface methodology to optimize supercritical carbon dioxide/co-solvent extraction of brown onion skin by-product as source of nutraceutical compounds. Food Chem. 269, 495–502. https://doi.org/10.1016/j.foodchem.2018.07.042.

Dixon, R.A., Paiva, N.L., 1995. Stress–induced phenylpropanoid metabolism. Plant Cell 7, 1085–1097. https://doi.org/10.1105/tpc.7.7.1085.

Dufossé, L., 2014. Anthraquinones, the Dr Jekyll and Mr Hyde of the food pigment family. Food Res. Int. 65, 132–136. https://doi.org/10.1016/j.foodres.2014.09.012.

Elsayed, S., Hummel, M., Sawada, D., Guizani, C., Rissanen, M., Sixta, H., 2021. Superbase–based protic ionic liquids for cellulose filament spinning. Cellulose 28, 533–547. https://doi.org/10.1007/s10570–020–03505–y.

Fabre, N., Rustan, I., de Hoffmann, E., Quetin-Leclercq, J., 2001. Determination of flavone, flavonol, and flavanone aglycones by negative ion liquid chromatography electrospray ion trap mass spectrometry. J. Am. Soc. Mass Spectrom. 12 (6), 707–715. https://doi.org/10.1016/S1044-0305(01)00226-4.

FAOStat, 2020, Crops. Food and Agriculture Organization of the United Nations. ⟨http://www.fao.org/faostat/en/#data/QC⟩ (accessed 1 May 2022).

Ford, L., Rayner, C.M., Blackburn, R.S., 2018. Comparative sorption isotherms for colorants present in Dyers' madder (*Rubia tinctorum* L.) provide new insights into historical dyeing. Color. Technol. 134 (1), 3–12. https://doi.org/10.1111/cote.12327.

Guizani, C., Nieminen, K., Rissanen, M., Larkiala, S., Hummel, M., Sixta, H., 2020. New insights into the air gap conditioning effects during the dry–jet wet spinning of an ionic liquid-. cellulose solution. Cellul. 27, 4931–4948. https://doi.org/10.1007/s10570–020–03115–8.

Gülşen, A., Turan, B., Makris, D.P., Kefalas, P., 2007. Copper(II)-mediated biomimetic oxidation of quercetin: generation of a naturally occurring oxidation product and evaluation of its in vitro antioxidant properties. Eur. Food Res. Technol. 225, 435–441. https://doi.org/10.1007/s13197-010-0201-3.

Gurushidze, M., Mashayekhi, S., Blattner, F., Friesen, N., Fritschl, R.M., 2007. Phylogenetic relationships of wild and cultivated species of *Allium* section *Cepa* inferred by nuclear rDNA ITS sequence analysis. Plant. Syst. Evol. 269, 259–269. https://doi.org/10.1007/s00606–007–0596–0.

Haslinger, S., Ye, Y., Rissanen, M., Hummel, M., Sixta, H., 2020. Cellulose fibers for high–performance textiles functionalized with incorporated gold and silver nanoparticles. ACS Sustain. Chem. Eng. 8, 649–658. https://doi.org/10.1021/acssuschemeng.9b06385.

Heim, K.E., Tagliaferro, A.R., Bobilya, D.J., 2002. Flavonoid antioxidants: chemistry, metabolism and structure-activity relationships. J. Nutr. Biochem. 13 (10), 572–584. https://doi.org/10.1016/S0955–2863(02)00208–5.

Herrala, M., Yli-Öyrä, J., Fernandes de Albuquerque, A., Oliveira de Farias, N., Alexandre Morales, D., Räisänen, R., Freeman, H.S., de Aragão Umbuzeiro, G., Rysä, J., 2022. Waterless dyeing and in vitro toxicological properties of biocolorants from *Cortinarius sanguineus*. In: J. Fungi, 8, p. 1129. https://doi.org/10.3390/jof8111129.

Hunger, K. (Ed.), 2003. Industrial Dyes: Chemistry, Properties, Applications. Wiley, Weinheim.

Ioncell, 2022, Commercialization. ⟨https://ioncell.fi⟩ (accessed 1 June 2022).

ISO, 1996. Textiles — Tests for colour fastness — Part A05: Instrumental assessment of change in colour for determination of grey scale rating, 105–A05 Last reviewed and confirmed in 2019. International Organization for Standardization, Geneva.

ISO, 2000. Textiles. Test for colour fastness, 105–A04 Part A04: Method for the instrumental assessment of the degree of staining of adjacent fabrics. International Organization for Standardization, Geneva.

ISO, 2010. Textiles — Tests for colour fastness — Part C06, 105–C06 Colour fastness to domestic and commercial laundering. International Organization for Standardization, Geneva.

ISO, 2014. Textiles—Tests for colour fastness—Part B02, 105–B02 Colour fastness to artificial light: Xenon Arc Fading Lamp Test. International Organization for Standardization, Geneva.

Itoo, Z.A., Reshi, Z.A., 2014. Effect of different nitrogen and carbon sources and concentrations on the mycelial growth of ectomycorrhizal fungi under in-vitro conditions. Scand. J. For. Res 29 (7), 619–628. https://doi.org/10.1080/02827581.2014.96475.

Jiang, X., Bai, Y., Chen, X., Liu, W., 2020. A review on raw materials, commercial production and properties of lyocell fiber. J. Biores. Bioprod. 5 (1), 16–25. https://doi.org/10.1016/j.jobab.2020.03.002.

Jørgensen, L.V., Cornett, C., Justesen, U., Skibsted, L.H., Dragsted, L.O., 1998. Two-electron electrochemical oxidation of quercetin and kaempferol changes only the flavonoid C-ring. Free Radic. Res. 29, 339–350. https://doi.org/10.1080/10715769800300381.

Jungbluth, G., Ternes, W., 2000. HPLC separation of flavonols, flavones and oxidized flavonols with UV-, DAD-, electrochemical and ESI-ion trap MS detection. Fresenius J. Anal. Chem. 367, 661–666. https://doi.org/10.1007/s002160000434.

Lätti, A.K., Riihinen, K.R., Kainulainen, P.S., 2008. Analysis of anthocyanin variation in wild populations of bilberry (*Vaccinium myrtillus* L.) in Finland. J. Agric. Food Chem. 56, 190–196. https://doi.org/10.1021/jf072857m.

Lätti, A.K., Jaakola, L., Riihinen, K.R., Kainulainen, P.S., 2010. Anthocyanin and flavonol variation in bog bilberries (*Vaccinium uliginosum* L.) in Finland. J. Agric. Food Chem. 58, 427–433. https://doi.org/10.1021/jf903033m.

Lätti, A.K., Riihinen, K.R., Jaakola, L., 2011. Phenolic compounds in berries and flowers of a natural hybrid between bilberry and lingonberry (*Vaccinium* × intermedium Ruthe). Phytochem 72, 810–815. https://doi.org/10.1016/j.phytochem.2011.02.015.

Lee, J., Mitchell, A.E., 2011. Quercetin and isorhamnetin glycosides in onion (*Allium cepa* L.): varietal comparison, physical distribution, coproduct evaluation, and long–term storage stability. J. Agric. Food Chem. 59, 857–863. https://doi.org/10.1021/jf1033587.

Lee, S.U., Lee, J.H., Choi, S.H., Lee, J.S., Ohnisi–Kameyama, M., Kozukue, N., Levin, C.E., Friedman, M., 2008. Flavonoid content in fresh, home–processed, and light–exposed onions and in dehydrated commercial onion products. J. Agric. Food Chem. 56, 8541–8548. https://doi.org/10.1021/jf801009p.

Liimatainen, K., 2013, Towards a better understanding of the systematics and diversity of Cortinarius, with an emphasis on species growing in boreal and temperate zones of Europe and North America. PhD thesis. University of Helsinki, Helsinki, 2013. Available at http://urn.fi/URN:ISBN:978–952-10–9450-7 (accessed 1 Dec 2021).

Lothander, T., Arola, S., Laaksonen, P., 2020. Biomordanting willow bark dye on cellulosic materials. Color. Technol. 136 (1), 3–14. https://doi.org/10.1111/cote.12442.

Ly, T.N., Hazama, C., Shimoyamada, M., Ando, H., Kato, K., Yamauchi, R., 2005. Antioxidative compounds from the outer scales of onion. J. Agric. Food Chem. 53, 8183–8189. https://doi.org/10.1021/jf051264d.

Ma, Y., Rissanen, M., You, X., Moriam, K., Hummel, M., Sixta, H., 2021. New method for determining the degree of fibrillation of regenerated cellulose fibres. Cellulose 28, 31–44. https://doi.org/10.1007/s10570–020–03513–y.

Ma, Y.L., Li, Q.M., Van den Heuvel, H., Claeys, M., 1997. Characterization of flavone and flavonol aglycones by collision-induced dissociation tandem mass spectrometry. Rapid Commun. Mass Spectrom. 11 (12), 1357–1364. https://doi.org/10.1002/(SICI)1097-0231(199708)11:12<1357::AID-RCM983>3.0.CO;2-9.

Markham, K.R., 1989. 6. Flavones, flavonols and their glycosides. In: Dey, P.M., Harborne, J.B. (Eds.), Methods in Plant Biochemistry, Vol 1. Plant phenolics. Academic Press, Cambridge, MA, pp. 197–236.

Michud, A., Tanttu, M., Asaadi, S., Ma, Y., Netti, E., Kääriäinen, P., Persson, A., Berntsson, A., Hummel, M., Sixta, H., 2016. Ioncell–F: ionic liquid–based cellulosic textile fibers as an alternative to viscose and Lyocell. Text. Res. J. 86 (5), 543–552. https://doi.org/10.1177/0040517515591774.

Morgen, L., 2006, Quercetin content in yellow onion (*Allium cepa* L.). PhD thesis. Swedish University of Agricultural Sciences, Alnarp. https://www.researchgate.net/publication/30072855_Quercetin_content_in_yellow_onion_Allium_cepa_L (accessed 1 May 2022).

Mussak, R., Bechtold, T., 2009. Handbook of Natural Colorants. Wiley, Chichester.

MWP, 2022, The 2022 Marcus Wallengerg Prize. October 11, 2022. Available at https://www.mwp.org/professor-ilkka-kilpelainen-and-professor-herbert-sixta-receives-the-2022-marcus-wallenberg-prize/ (accessed 21 Oct 2022).

Nuutila, A.M., Puupponen–Pimiä, R., Aarni, M., Oksman–Caldentey, K., 2003. Comparison of antioxidant activities of onion and garlic extracts by inhibition of lipid peroxidation and radical scavenging activity. Food Chem. 81, 485–493. https://doi.org/10.1016/S0308–8146(02)00476–4.

OECD–FAO, 2021. OECD–FAO Agricultural Outlook 2021–2030. FAO, OECD Publishing, Cotton. Rome, Paris. https://doi.org/10.1787/1112c23b–en accessed 1 June 2022.

Okamoto, D., Noguchi, Y., Muro, T., Morishita, M., 2006. Genetic variation of quercetin glucoside content in onion (*Allium cepa* L.). J. Jpn Soc. Hortic. Sci. 75, 100–108. https://doi.org/10.2503/jjshs.75.100.

Parviainen, A., Wahlström, R., Liimatainen, U., Liitiä, T., Rovio, S., Helminen, J.K.J., Hyväkkö, U., King, A.W.T., Suurnäkki, A., Kilpeläinen, I., 2015. Sustainability of cellulose dissolution and regeneration in 1,5–diazabicyclo[4.3.0]non–5–enium

acetate: a batch simulation of the IONCELL–F process. RSC Adv. 5, 69728–69737. https://doi.org/10.1039/c5ra12386k.
Phan, K., Raes, K., Van Speybroeck, V., Roosen, M., De Clerck, K., De Meester, S., 2021. Non–food applications of natural dyes extracted from agro–food residues: A critical review. J. Clean. Prod. 301, 126920 https://doi.org/10.1016/j.jclepro.2021.126920.
Pucciarini, L., Ianni, F., Petesse, V., Pellati, F., Brighenti, V., Volpi, C., Gargaro, M., Natalini, B., Clementi, C., Sardella, R., 2019. Onion (*Allium cepa* L.) skin: A rich resource of biomolecules for the sustainable production of colored biofunctional textiles. Molecules 24 (3), 634. https://doi.org/10.3390/molecules24030634.
Räisänen, R., 2002, *Anthraquinones from the Fungus Dermocybe sanguinea as Textile Dyes*. PhD thesis. University of Helsinki, Helsinki. http://urn.fi/URN:ISBN:978–952–10–5928–5 (accessed 1 May 2022).
Räisänen, R., 2019. Fungal colourants in applications – focus on Cortinarius species. Color. Technol. 135, 22–31. https://doi.org/10.1111/cote.12376.
Räisänen, R., Björk, H., Hynninen, P.H., 2000. Two–dimensional TLC separation and mass spectrometric identification of anthraquinones isolated from the fungus *Dermocybe sanguinea*. Z. Naturforsch. C. J. Biosci. 55c, 195–202.
Räisänen, R., Primetta, A., Niinimäki, K., 2016. Dyes from Nature. Archetype Publications, London.
Räisänen, R., Rissanen, M., Parviainen, E., Suonsilta, H., 2017, Tekstiilien materiaalit [Textile materials]. Finn Lectura, Helsinki.
Räisänen, R., Primetta, A., Nikunen, S., Honkalampi, U., Nygren, H., Pihlava, J.M., Berghe, I.V., Wright, A.V., 2020. Examining safety of biocolourants from fungal and plant sources – examples from *Cortinarius* and *Tapinella*, *Salix* and *Tanacetum* spp. and dyed woollen fabrics. Antibiotics 9, 266. https://doi.org/10.3390/antibiotics9050266.
Räisänen, R., Montero, G.A., Freeman, H.S., 2021. A fungal-based anthraquinone emodin for polylactide and polyethylene terephthalate in supercritical carbon dioxide (SC-CO_2) dyeing. Color Res. Appl. 46 (3), 1–7. https://doi.org/10.1002/col.22627.
Reischl, M., Stana-Kleinschek, K., Ribitsch, V., 2006. Electrokinetic Investigations of Oriented Cellulose Polymers. Macromol. Symp. 244, 31–47. https://doi.org/10.1002/masy.200651203.
RESFOOD, 2016. Resource efficient and safe food production and processing. Final report. European Comission. https://cordis.europa.eu/project/id/308316/reporting (accessed 1 June 2022).
Rice–Evans, C.A., Miller, N.J., Paganga, G., 1996. Structure–antioxidant activity relationships of flavonoids and phenolic acids. Free Radic. Biol. Med. 20, 933–956. https://doi.org/10.1016/0891–5849(95)02227–9.
Rocky, B.P., Thompson, A.J., 2021. Characterization of the crystallographic properties of bamboo plants, natural and viscose fibers by X-ray diffraction method. J. Text. Inst. 112 (8), 1295–1303. https://doi.org/10.1080/00405000.2020.1813407.
Rodrigues, A.S., Almeida, D.P.F., Simal–Gándara, J., Pérez–Gregorio, M.R., 2017. Onions: A source of flavonoids – from biosynthesis to human health. Goncalo C. Justino. IntechOpen. https://doi.org/10.5772/intechopen.69896.
Sharma, A., Nagarkar, S., Thakre, S., Kumaraswamy, G., 2019. Structure–property relations in regenerated cellulose fibers: comparison of fibers manufactured using viscose and lyocell processes. Cellulose 26, 3655–3669. https://doi.org/10.1007/s10570–019–02352–w.
Sharma, K., Mahato, N., Nile, S.H., Lee, E.T., Lee, Y.R., 2016. Economical and environment friendly approaches for usage of onion (*Allium cepa* L.) wastes. Food Fund. 7, 3354–3369. https://doi.org/10.1039/C6FO00251J.
Singh, S.C., Murthy, Z.V.P., 2017. Study of cellulosic fibres morphological features and their modifications using hemicelluloses. Cellulose 24, 3119–3130. https://doi.org/10.1007/s10570-017-1353-3.
Sixta, H., Michud, A., Hauru, L., Asaadi, S., Ma, Y., King, A.W.T., Kilpeläinen, I., Hummel, M., 2015. Ioncell–F: A high–strength regenerated cellulose fibre. Nord. Pulp Pap. Res. J. 30 (1), 43–57. https://doi.org/10.3183/npprj–2015–30–01–p043–057.
Slimestad, R., Fossen, T., Vågen, I.M., 2007. Onions: a source of unique dietary flavonoids. A Rev. J. Agric. Food Chem. 55, 10067–10080. https://doi.org/10.1021/jf0712503.
Smith, K.J., 1997. Colour–order systems, colour spaces, colour difference and colour scales. In: McDonald, R. (Ed.), Colour Physics for Industry, 2nd ed.,. Society of Dyers and Colourists, Bradford.
Suh, H.J., Lee, J.M., Cho, J.S., Kim, Y.S., Chung, S.H., 1999. Radical scavenging compounds in onion skin. Food Res. Int. 32,, 659–664.
Suthar, M., Lagashetti, A.C., Räisänen, R., Singh, P.N., Dufossé, L., Robinson, S.C., Singh, S.K., 2021. Industrial application of pigments from macrofungi. In: Sridhar, K. R., Deshmukh, S.K. (Eds.), Advances in Macrofungi: Industrial Avenues and Prospects. CRC press, London, pp. 223–251.
TextileExchange, 2020, Preferred Fiber & Materials Market Report 2020. https://textileexchange.org/wp–content/uploads/2020/06/Textile–Exchange_Preferred–Fiber–Material–Market–Report_2020.pdf (accessed 1 May 2022).
The Fibre Year, 2020, World Survey on Textiles & Nonwovens. The Fiber Year, Speicher.
Verma, M., Gahlot, N., Singh, S.S.J., Rose, N.M., 2021. UV protection and antibacterial treatment of cellulosic fibre (cotton) using chitosan and onion skin dye. Carbohydr. Polym. 257, 117612 https://doi.org/10.1016/j.carbpol.2020.117612.
Willemen, H., van den Meijdenberg, G.J.P., van Beek, T.A., Derksen, G.C.H., 2019. Comparison of madder (*Rubia tinctorum* L.) and weld (*Reseda luteola* L.) total extracts and their individual dye compounds with regard to their dyeing behaviour, colour, and stability towards light. Color. Technol. 135, 40–47. https://doi.org/10.1111/cote.12384.
Yu, H., Hurren, C., Liu, X., Wang, X., 2021. Understanding the difference in softness of Australian Soft Rolling Skin wool and conventional Merino wool.Text. Res. J. 92 (17–18), 3130–3141. https://doi.org/10.1177/00405175211050524.