



Canada 2016

Chemistry of Dyeing

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Content

- Chemistry of dyes and wool



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- Mordanting and binding of dyes to the wool



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- Transfer of dyes from the fungi to the dye bath and from the dye bath to the wool



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- Mordanting and binding of dyes to the wool
- Transfer of dyes from the fungi to the dye bath and from the dye bath to the wool
- pH aspects of mordanting and dyeing
- Time optimization of mordanting and dyeing
- Stability of colors in dyed wool

Variations in colors using natural dyes



Dyeing with various Cortinarius species at pH 3.5, 7, 10
Pre-mordanted in 60 min with tin (SnCl_2)

1-3 C.sanguineus 1.bath

4-6 C.sanguineus 2.bath

7-9 C.semisangiuneus

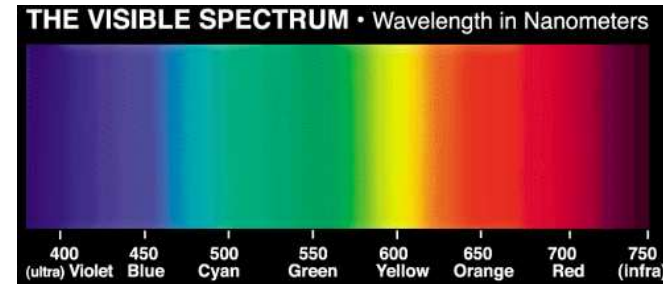
10-12 C.cinnamomeus

13-15 C.malicorius



Chemical aspects of dyes

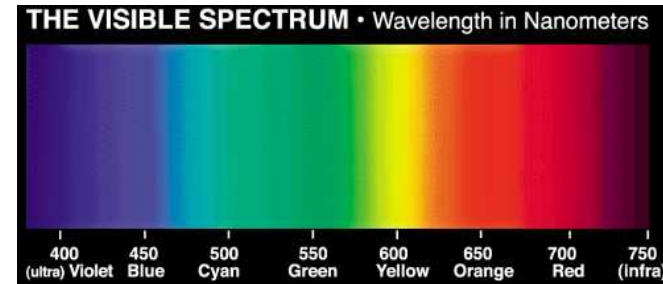
- Dyes are chemicals which absorb parts of visible light such that they appear brightly colored. or absorb UV light and emit visible light (fluorescence)





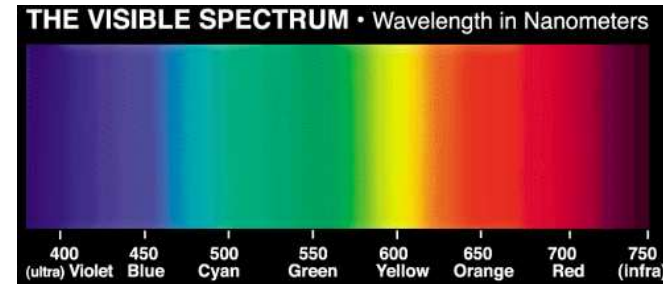
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- Natural dyes are produced in plants and fungi. They are byproducts of ordinary cell chemistry and are biodegradable and ecofriendly.



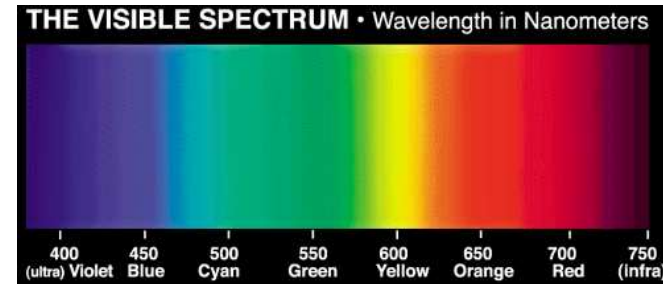
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- Natural dyes have important biological function such as protection against UV light or as insecticide.
- The colour of a dye depends mainly on its molecular structure and to some extent on how it is attached to the fabric.



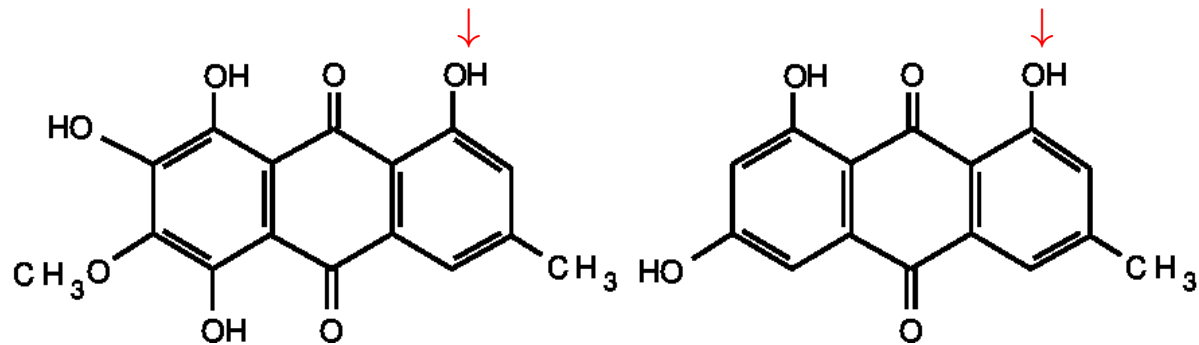


Chemical aspects of dyes

- Anthraquinones are examples of natural dyes from fungi

Chemical aspects of dyes

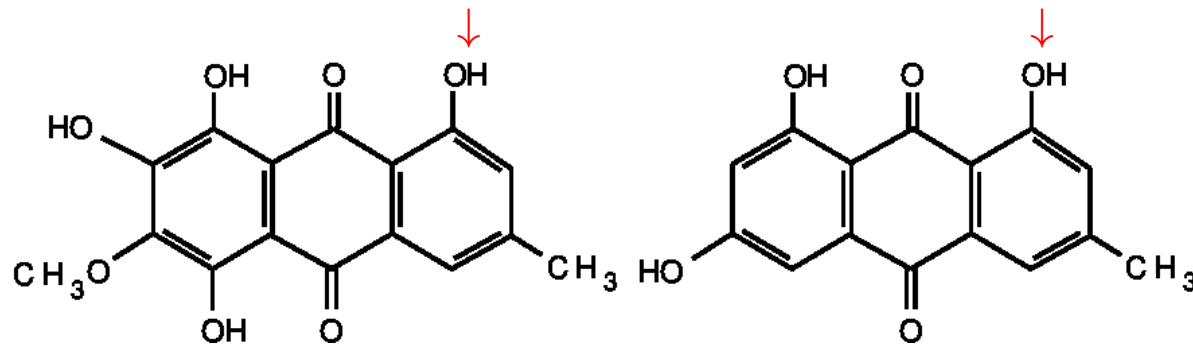
- Anthraquinones are examples of natural dyes from fungi
- Two anthraquinones were isolated from *C.sanguineus* in 1925



Dermocybin (red) and Emodin (yellow)

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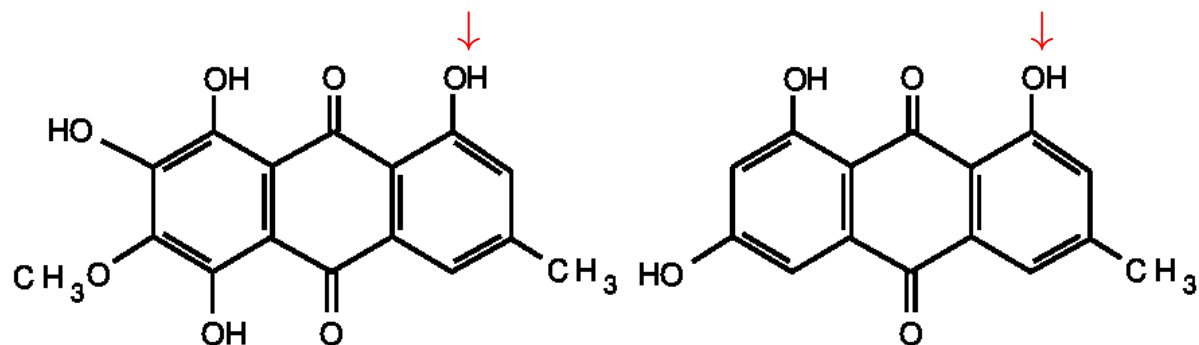


Dermocybin (red) and Emodin (yellow)

- Many other anthraquinones have been found later in *C.sanguineus* and in other *Cortinarius* species.

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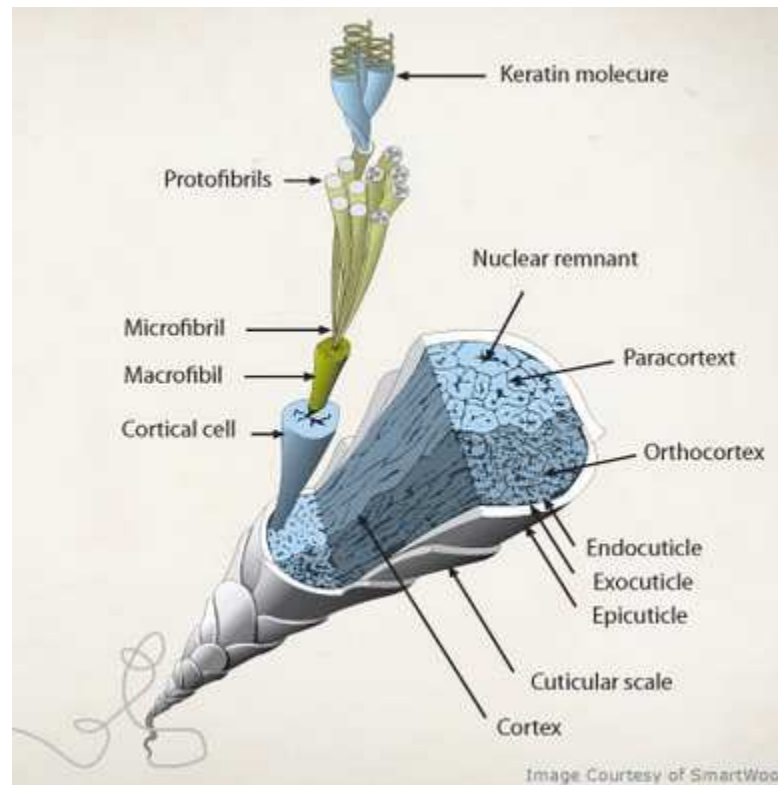


Dermocybin (red) and Emodin (yellow)

- Many other anthraquinones have been found later in *C.sanguineus* and in other *Cortinarius* species.
- In fresh fungi the anthraquinones are usually glycosylated by binding sugar molecules one of the OH sites marked with a red arrow.

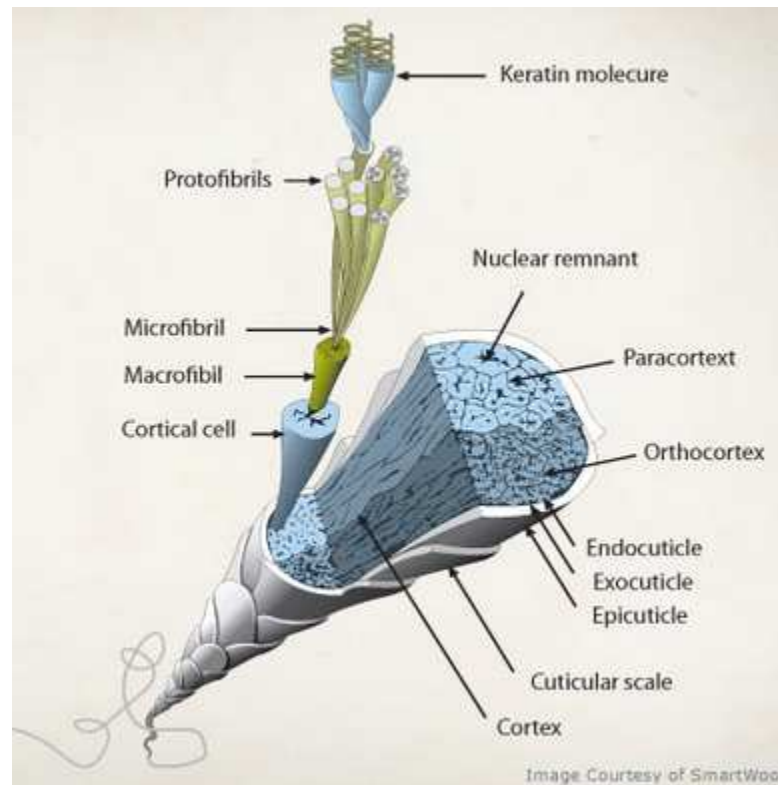
Chemistry of wool

- A wool fibre has a very complex structure with a surface area of appr. 100m^2 for 1g of wool.



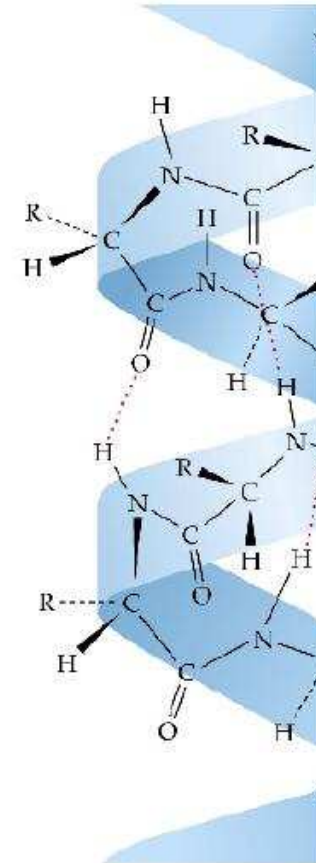
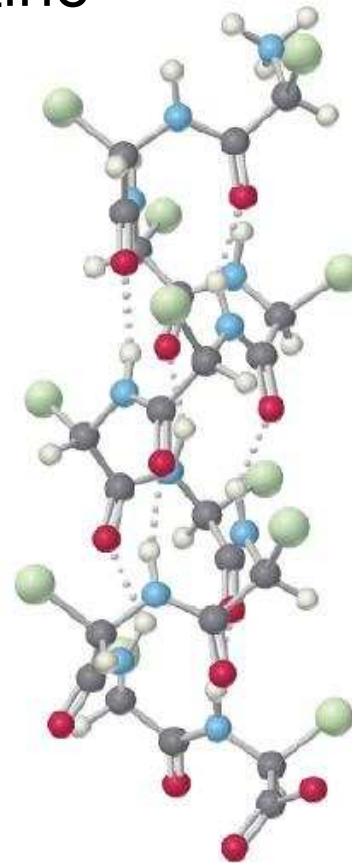
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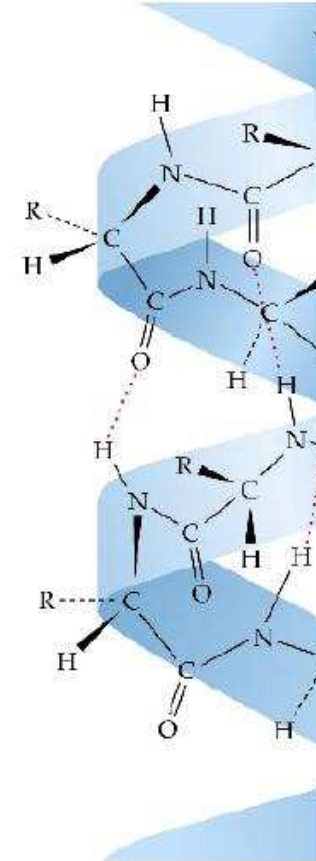
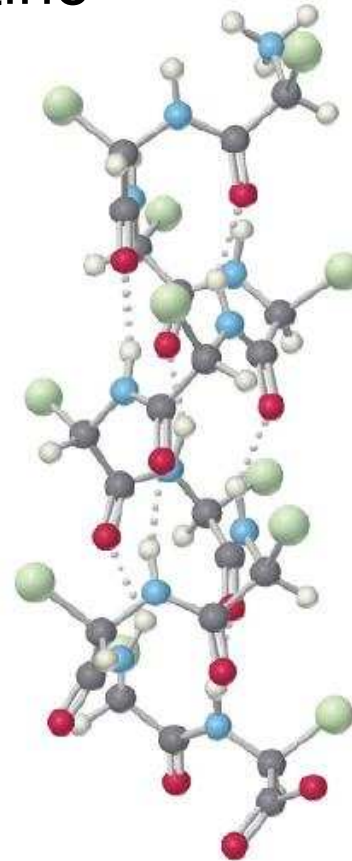
- The dye has to penetrate the fibre to the central α -helices of the protein molecules to be fixed.

- The α -helix is made of keratine composed of 122 different smaller proteins



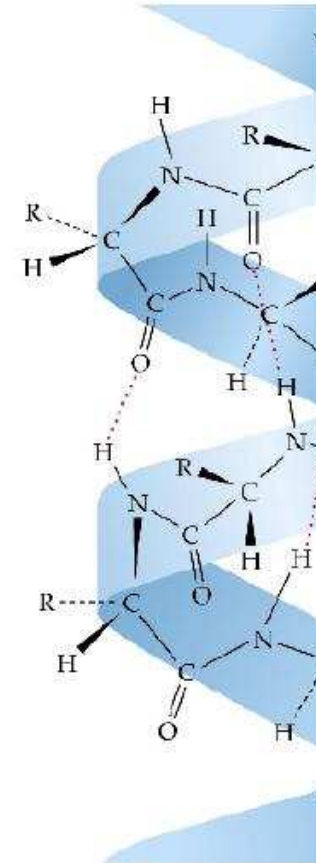
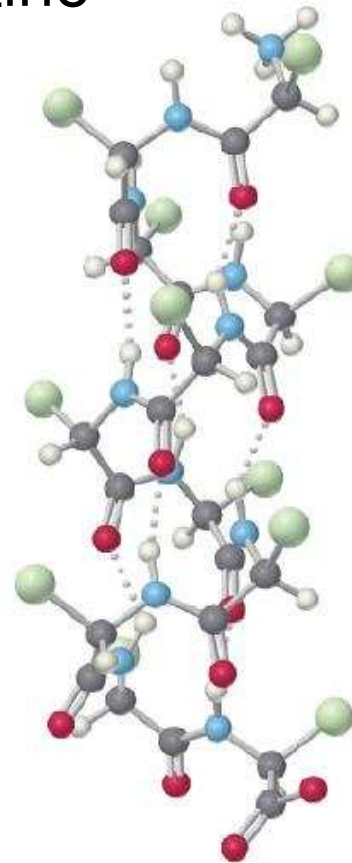
Chemistry of wool

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Chemistry of wool

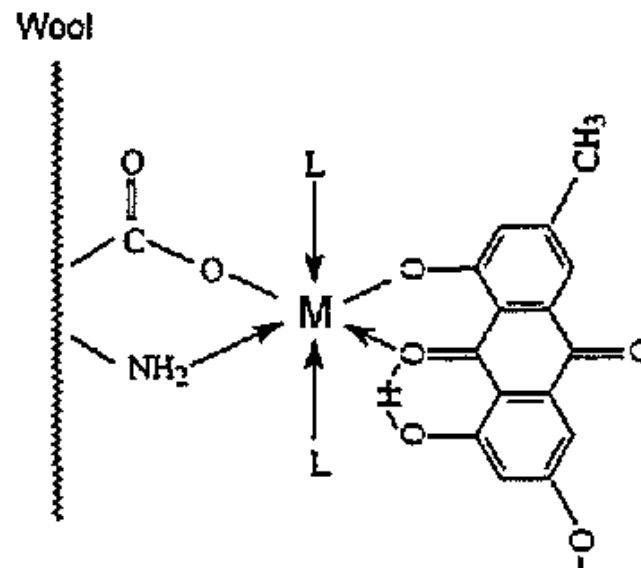
- The α -helix is made of keratine composed of 122 different smaller proteins
- The dyes bind chemically to -NH og -C=O groups. The chemical properties of these groups varies with pH
- The natural pH of pure wool in water is 4.5. The structure of the wool is slowly destroyed when $\text{pH} > 8$





What is the chemistry behind mordanting

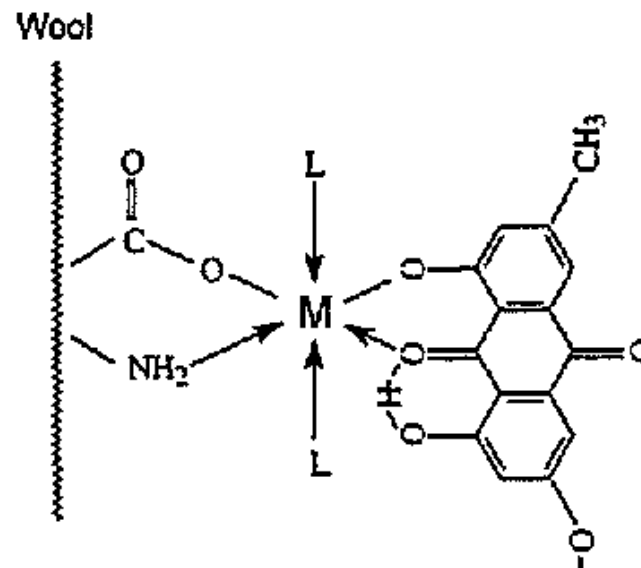
- Binding of emodine to wool by a metal atom





What is the chemistry behind mordanting

- Binding of emodine to wool by a metal atom



- The aluminium atoms from alun bind to combinations of -OH, =O, and -NH₂ groups



Influence of pH on color

- Final colour depends on the nature of the metal ion and on where the metal ion binds to the wool and to the dye molecule.



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Influence of pH on color

- Final colour depends on the nature of the metal ion and on where the metal ion binds to the wool and to the dye molecule.
- The nature of these bindings depends on the pH and on the temperature of the mordanting bath.
- pH can be lowered by adding an acid (e.x. acetic or citric acid)
- pH can be raised by adding a base (e.x. washing soda or ammonia water)

Variations in colors from a single species



Variations in color by dyeing with *C.semisaanguineus* using different pH, different mordants and white/gray wool



Variations in colors from a single species

- A specific fruitbody sometimes contain many dyes with different colors.



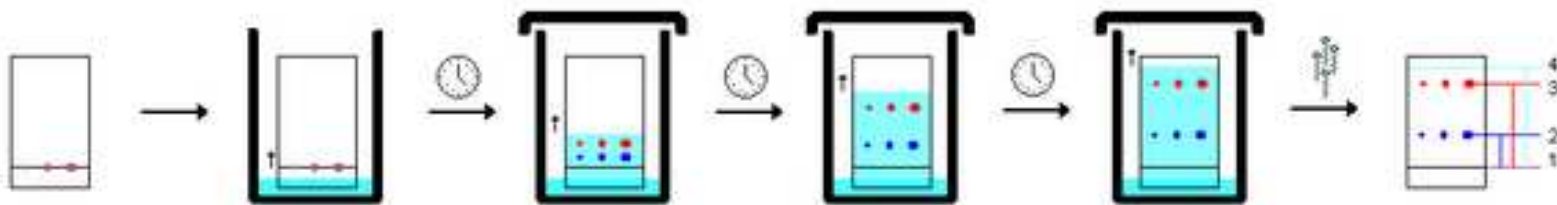
Variations in colors from a single species

- A specific fruitbody sometimes contain many dyes with different colors.
- Extraction of each of the dyes from the fruitbody and binding of the dyes to the wool depends on mordants, temperature and pH.



Variations in colors from a single species

- A specific fruitbody sometimes contain many dyes with different colors.
- Extraction of each of the dyes from the fruitbody and binding of the dyes to the wool depends on mordants, temperature and pH.
- Different dyes can be separated by Thin Layer Chromatography (TLC)





Dyeing of wool with two closely related species

C.sanguineus
from conifer

C.puniceus
from beech

1. dyebath

2. dyebath





TLC of dyeing with two related species

- TLC

C.sanguineus

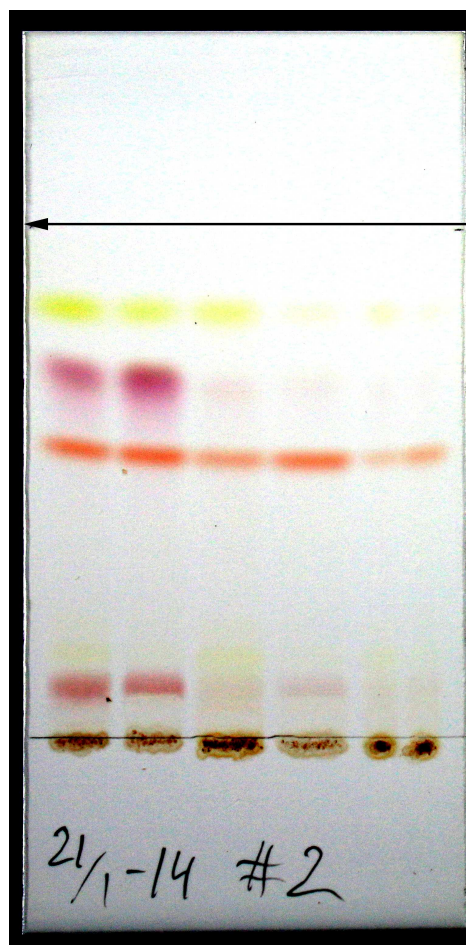
C. puniceus

columns

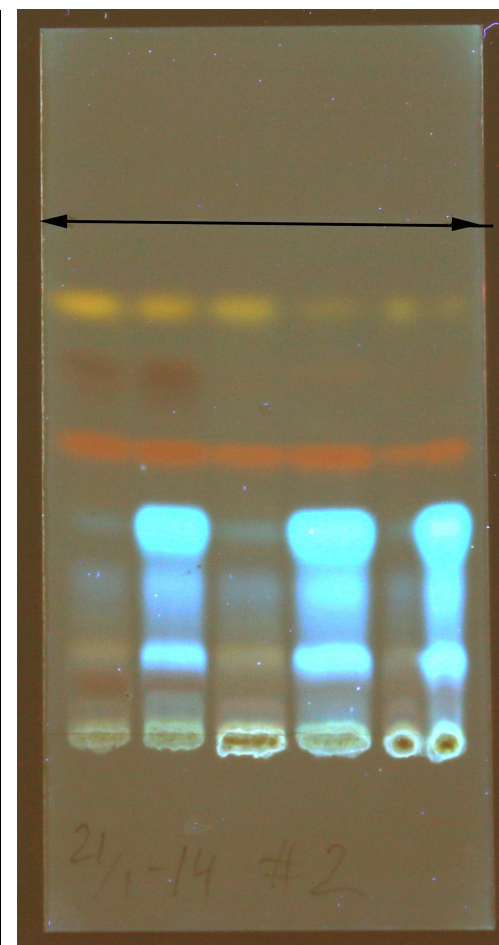
1 3 5

2 4 6

VIS



UV



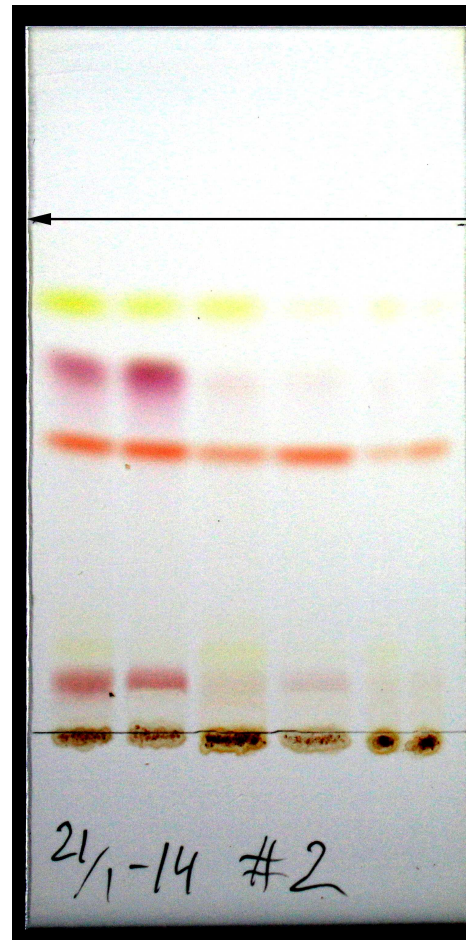


TLC of dyeing with two related species

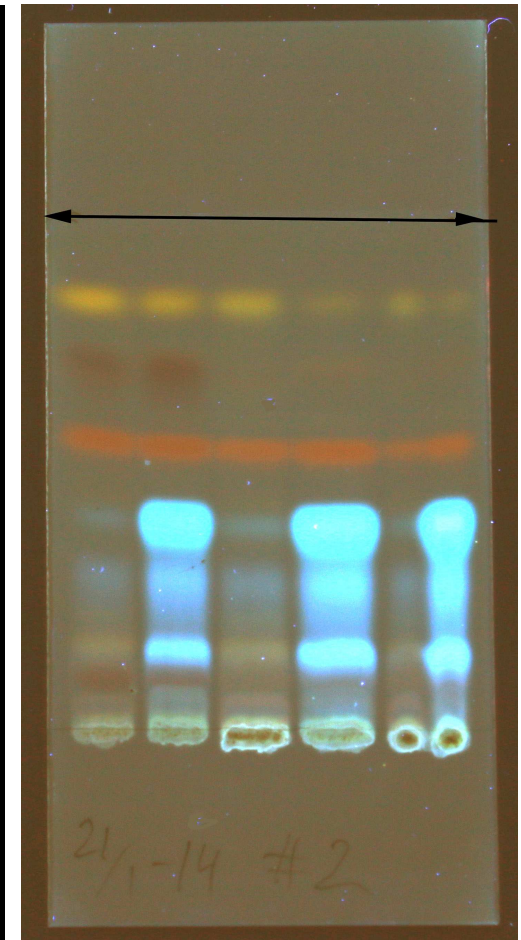
- TLC columns

C.sanguineus	1 3 5
C. puniceus	2 4 6
- bath before dyeing 1 2
- after first dyeing 3 4
- after second dyeing 5 6

VIS



UV



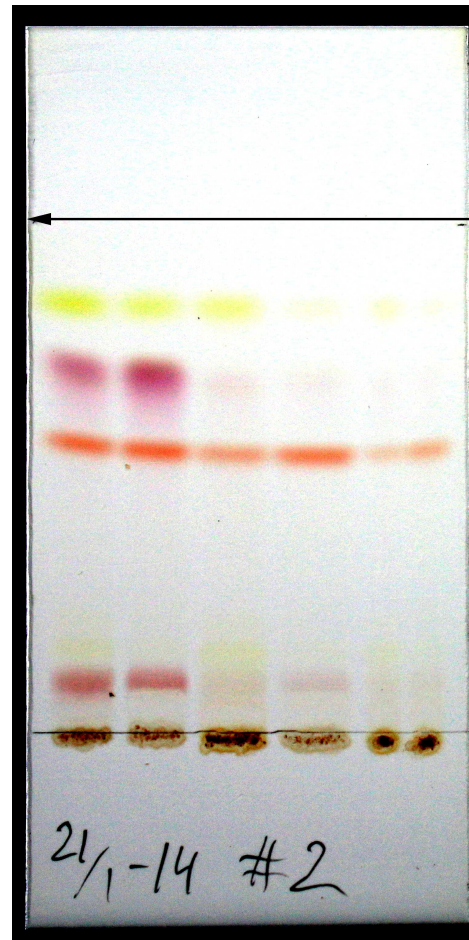


TLC of dyeing with two related species

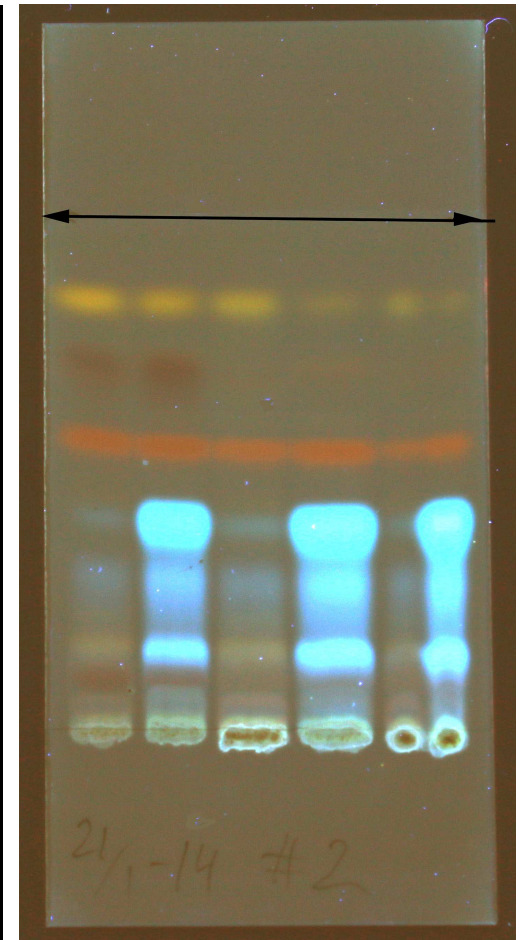
- TLC columns

C.sanguineus	1 3 5
C. puniceus	2 4 6
- bath before dyeing 1 2
 after first dyeing 3 4
 after second dyeing 5 6
- TLC using Toluene
 Ethylacetate
 Ethanol, and Formic acid
 volume ratios 10:8:1:2

VIS



UV





Dynamics of dyeing with *C.semisanguineus*

- Final result from a danish workshop for the first and second dyebath using *C. semisanguineus*



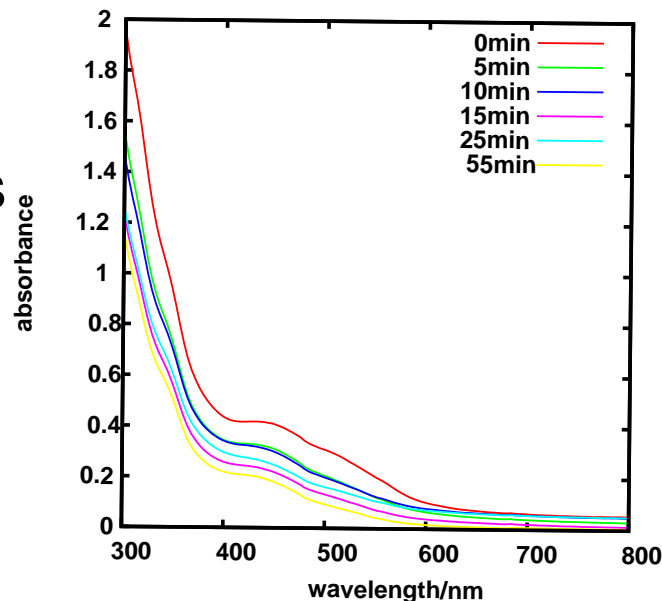


Dynamics of dyeing with C.semisanguineus

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- Spectrum for samples from first dyebath taken at different times after start of dyeing



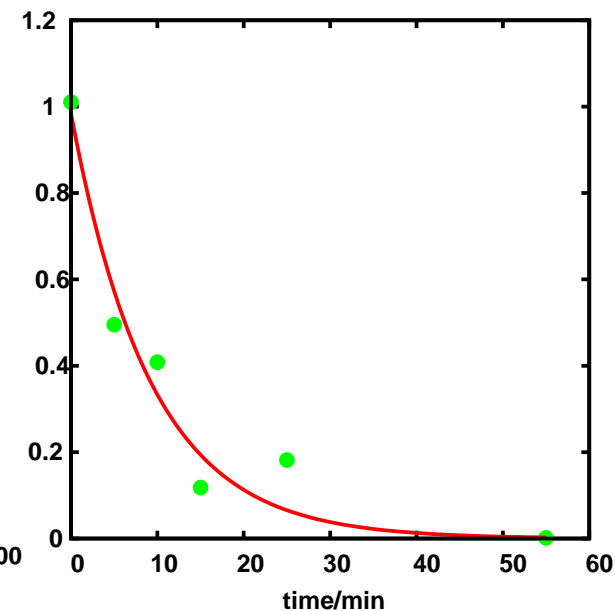
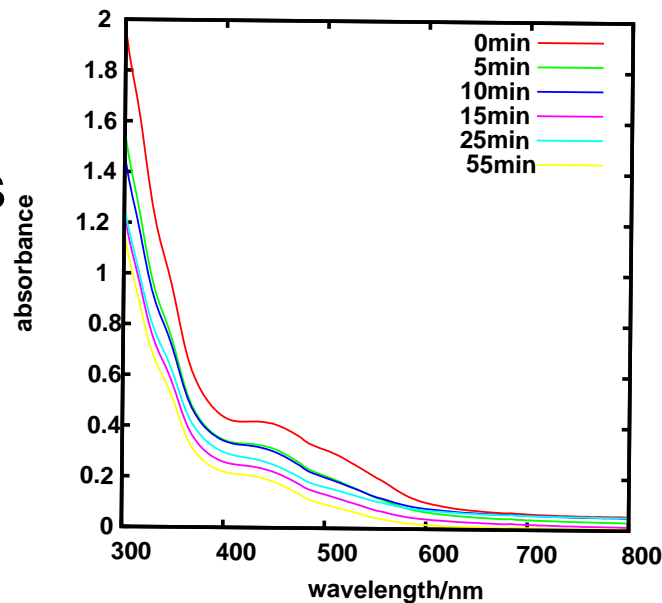


Dynamics of dyeing with C.semisanguineus

- Final result from a danish workshop for the first and second dyebath using *C. semisanguineus*



- Spectrum for samples from first dyebath taken at different times after start of dyeing
- Time variation in amount of remaining dye in dyebath



Variations in duration of mordanting



Dyeing with *Cortinarius semisanguineus* at 90°C

Left group: Time in mordant bath 10, 20, 30, 40, 50, 60 min
Time in dyeing bath 60 min.

Right group: Time in mordant bath 60 min
Time in dyeing bath 15, 30, 45, 60 min.



Samples of wool mordanted and
dyed at different pH and
temperatures



Overview of presented samples

- Ringlabels **Semi-3 Semi-7 Semi-9** are 10g wool samples dyed with *Cortinarius semisanguineus* at pH=3 pH=7 and pH=9



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- Ringlabels **Sch-3 Sch-7 Sch-9** are 10g wool samples dyed with *Phaeolus schweinitzii* at pH=3 pH=7 and pH=9



Details of explanation sheet Semi-7

Semi-7

Samples of 10g wool mordanted at 90°C and dyed with *Cortinarius semisanguineus* caps at pH 7.
weight of caps/weight of wool = 0.8. % = % o.w.f. Tin is stannous chloride.

Sample id:	Mordanting 90°C-100°C				Dyeing 90°C-100°C	Colour
Al+Ci	Alum	10%	Citric acid	10%	pH=7	dark bright red
Al+Vin	Alum	10%	Cream of tartar	10%	pH=7	darker bright red
Al	Alum	10%			pH=7	dark bright red
Tn+Ci	Tin	2%	Citric acid	10%	pH=7	bright red
Tn+Vin	Tin	2%	Cream of tartar	10%	pH=7	bright red
Tn	Tin	2%			pH=7	weak red

Conclusion: Mordanting using citric acid or cream of tartar give similar results for Al and Tin, but the colours using Tin gives a less dark red. Mordanting with Tin without lowering pH by adding citric acid or cream of tartar gives a much weaker red. Note that using alum and cream of tartar gives a slightly darker colour than using alum and citric acid.

Compare colours with **Semi-3** and **Semi-9**.



Overview of presented samples

- Ringlabel **Semi-a** are 10g wool samples mordanted at room temperature and dyed with *Cortinarius semisanguineus* at 90°C



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- Ringlabel **Pax-b** are 10g wool samples mordanted at room temperature and dyed with *Paxillus atrotomentosus* at 90°C
- Ringlabels **Semi-t** are 10g wool samples mordanted at 90°C and dyed with *Cortinarius semisanguineus* using different timespans.



Overview of presented samples

- Ringlabel **Semi-1-cold** are 10g wool samples mordanted for 24 hours at room temperature and dyed with *Cortinarius semisanguineus* at 90°C



Overview of presented samples

- Ringlabel **Semi-1-cold** are 10g wool samples mordanted for 24 hours at room temperature and dyed with *Cortinarius semisanguineus* at 90°C
- Ringlabel **Semi-2-cold** are 10g wool samples mordanted for 24 hours at room temperature and dyed with *Cortinarius semisanguineus* at 90°C and at room temperature.



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- Time for dyeing at 90°C may be reduced to 30 min.



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- The concentrations of metal salt in the mordant bath can be significantly reduced, without compromising the result.
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- Dyeing is possible at room temperature by increasing the dyeing time to 24 hours, but final colours may change.



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- Mordanting at room temperature is possible by increasing the time for mordanting to 24 hours, but the final sample colours may change.
- The concentrations of metal salt in the mordant bath can be significantly reduced, without compromising the result.
- Time for dyeing at 90°C may be reduced to 30 min.
- Dyeing is possible at room temperature by increasing the dyeing time to 24 hours, but final colours may change.
- Avoid washing final product in alkaline soap, use detergents based on SDS.