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Applying life sciences as a model for azo and phenoxazinone dyes synthesis

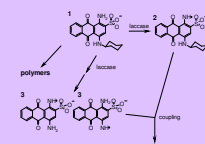
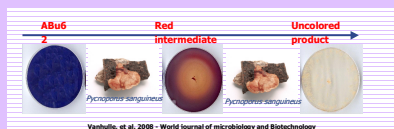


SOPHIED people

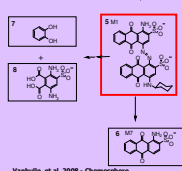


Azoic eco colorants

Azo compounds are not described in nature and their formation by living organisms was only observed in the course of the TNT bioremediation.

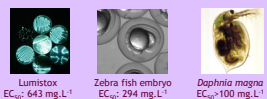


Recently, the finding that an azo-compound was formed during the decolorization of an anthraquinonic dye by white rot fungi (Vanhulle et al. 2008) lead to the analysis of the metabolic pathway, and laccase was found responsible for the formation of an azoic coupling product (Vanhulle et al. 2006). The idea of creating azo dyes through a bioinspired route was born.



Vanhulle, et al. 2008 - *Chemosphere*

Toxicity assessment



	CAS-No	Cto-2 ⁺	Mutagenicity ²	Fish egg ³	Lumistox ⁴
LAR1	2872-52-8	>1	Negative	294	41.2 ⁵
Diopene Red 1	17651-50-4	0.7 ± 0.06	Negative	500-1000	25.9
Diopene Red 28	575-96-0	0.15 ± 0.02	Positive ⁶	<30	3.4
Acid Red 299	57741-47-6	>1	Positive	250-500	50.2

Dyeing properties on polyamide 6 knitted fabric									
Standard depth: 1/1 (2.4 % umf)									
Light fastness: 3									
Washing fastness: ISO 105 B02									
Colour change: 4/5									
Staining: Cellulose acetate 4/5 Cotton 3 Nylon 4/5 Polyester Acrylic 4 Wool 4									
Alkaline perspiration fastness: ISO 105 E04									
Colour change: 3/4									
Staining: Cellulose acetate 2/3 Cotton 2 Nylon 2 Polyester Acrylic 3 Wool 3									

Enaud, et al. 2009 - *submitted in Dyes and Pigments*

A new azo compound SR1 (Sophied Red 1) was proved to be of industrial interest for the dyeing of wool, polyamide and leather. In addition, toxicological assays showed that LAR1 was a non toxic and non mutagenic acid dye. This dye is patented (US 61/078675) and a PCT extension was submitted in July 2009.

Enzyme catalysis is increasingly conjugated to traditional synthetic methods to develop more environmental friendly processes.

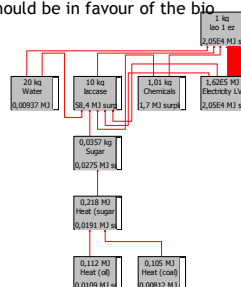
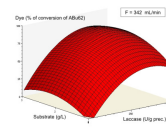
Fungi are known for their ability to synthesise pigments belonging to several chemical classes, such as anthraquinones, terphenylquinones, 2H-Azepine alkaloids, indoles... Observation of natural biosynthetic metabolic pathways can lead to new processes for fine chemical synthesis through original safe biocatalytic ways. In this context, the Sophied project aimed at developing new textile dyes.



Two new processes towards azoanthraquinone and soluble phenoxazinone dyes biosynthesis developed during this project are particularly good examples of bioinspired synthetic routes for new dyes:

Towards eco processes

With the aim of obtaining industrially relevant product, two laccase-catalysed processes were further improved. Continuous processes were preferred to lower the catalyst related costs. The immobilisation of the biocatalyst on cheap carrier and the design of a pilot reactor were undertaken, up to a kg scale of eco colourant synthesis. Experimental design was used to select optimal values for substrate concentration, enzyme amount and flow rate for the production of the dyes. Life cycle assessment of the process at lab scale (1 kg of eco colorant) showed that water and electricity consumption should be in favour of the bio-catalysed process after optimisation and scaling up.



Phenoxazinone eco colorants

Phenoxazinones molecules (cinnabarinic acid, tramesanguin...) confer their bright orange/red colours to *Pycnoporus* species. The cinnabarinic acid is produced by oxidation of 3-hydroxyanthranilic acid.

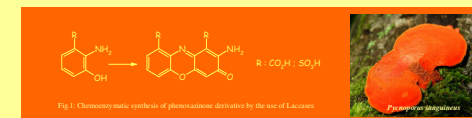
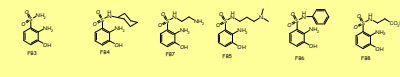


Fig. 1: Chemistry main synthesis of phenoxazinone derivative by the use of Laccase

It is possible to reproduce the reaction *in vitro* using laccase as the oxidation catalyst. However, phenoxazinones are water insoluble when quite some textile applications require water soluble dyes.

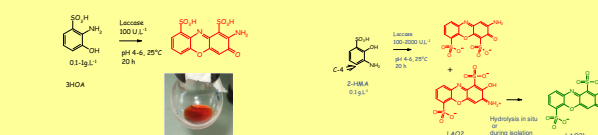
Optimized synthesis of 3-HOA

Sulfonated bioisoster of 3-HAA and related compounds were obtained through directed ortho metalation



Braynard, et al. 2008 - *European Journal of Organic Chemistry*

The biomimetic approach was applied to oxidation of sulfonated bioisoster of 3-hydroxyanthranilic acid catalysed by laccase and proved to be efficient.



The sulfonated coupling product SO2 (Sophied Orange 2) showed excellent colour properties with molecular extinction coefficient close to 14000.M⁻¹.cm⁻¹, and good tinctorial properties as an acid dye with no toxicity/mutagenicity. This type of coupling reaction was further applied to other aminophenolic substrates leading to a family of dyes (SO22, SBr23, SO24, SO25...). These dyes are patented (US 61/078670) and a PCT extension was submitted in July 2009.

Conclusion

Observation of biological pathways led to the development of promising enzyme-catalysed processes for dye synthesis.

Both azoanthraquinone and phenoxazinone eco colorants have interesting properties with regards to textile and cosmetic applications and have been patented by SOPHIED consortium. The two processes were finally evaluated through life cycle assessment demonstrating promising sustainability.

