

## LACTOSE TO NATURALIZE TEXTILE DYES

Roberto Bianchini,\*<sup>a</sup> Giorgio Catelani,<sup>b</sup> Elena Frino,<sup>b</sup> Jalal Isaad,<sup>a</sup> and Massimo Rolla<sup>a</sup>

Many natural dyes, for example carminic acid, are soluble in water. We present a simple strategy to naturalize synthetic azadyes through their linkage with lactose to induce their water solubility. The dyeing process of textile fibres then becomes possible in water without additives such as surfactants and mordants, which result in products that are difficult to eliminate. Glyco-azadyes (GADs) we are presenting here are obtained through a diether linker to bond the azadye and the sugar. Tinctorial tests were carried out with fabrics containing wool, polyester, cotton, nylon, and acetate. GADs were found to be multipurpose and capable of dyeing many fabrics efficiently under mild conditions.

*Keywords: Lactose, Conjugation, Dyeing, Azadyes, Ethers*

<sup>a</sup>Dipartimento di Chimica Organica "Ugo Schiff", Università di Firenze, via della Lastruccia 13, 50019 Sesto Fiorentino (FI) (Italy), Fax: +39 0554573531, phone: +39 0554573450

<sup>b</sup>Dipartimento di Chimica Bioorganica e Biofarmacia, Università di Pisa, Via Bonanno, 33 - 56126, Pisa (Italy) \* Corresponding author: roberto.bianchini@unifi.it

## INTRODUCTION

Dyeing chemistry started from an early time, during a period when the majority of dyes were extracted from natural compounds, i.e. from vegetable and animal sources. Currently the global production of textile dyes is estimated to be  $7 \times 10^5$  tons per year (Neamtu et al. 2002), and a significant part of this quantity is eliminated in the effluents of dyeing plants, polluting salt and fresh waters throughout the world.

Dyes are generally applied in an aqueous solution and they require auxiliary chemicals to improve the dyeing process. For instance, surfactants are used to increase solubility, mordants to enhance the fastness of the dye on the fibers, and salts to adjust the pH. Effluent from textile industries therefore can contain a broad spectrum of contaminants, such as highly hydrophobic dyes, suspended solids, chlorinated organic solvents, surfactants in huge concentrations, mordants, metals, etc. (Poon et al. 1999). Reactive dyes are another class of environmentally dangerous textile dyes; as the name suggests, these are very reactive molecules that form covalent bonds with fibers, but they also react with water, leading to inherent losses. Moreover, it's well known that the azo molecules can degrade to aromatic amines, which can further damage the environment if they are released (Neamtu et al. 2000). Selective treatment of effluent is not possible, because the type and extent of contamination varies, depending on the fabric dyed or the class of dye used. Because most pollutants present in the water have different physical and chemical properties, normally the chromophores are attacked using oxidative treatments of the contaminated waters (ozone,  $H_2O_2$ , UV), removing only the visible pollution (Rott and Minke 1999; Bianchini et al. 2002; Selcuk 2005). These treatments are efficient for the depletion of the colour, but the yields of these are variable and the final oxidation products (Mascolo et al. 2002) are often unknown; most importantly, the colorless oxidation products are possibly even more dangerous than the starting dyes (Pierce et al. 2003).

Because of the large variety of species present, a biological approach is also difficult. Therefore, increasing attention has been devoted to natural dyes, with the aim of finding environmentally friendly materials. Natural dyes extracted from plants or animals do not cover all the market requirements, and their isolation from natural sources is difficult.

Furthermore, the impact on the environment is far from negligible when high quantities of dye are required. These factors, together with the cost of these processes, have slowed the development of dyes based on natural products. In order to devise a new strategy to solve these problems, we initiated a naturalization of synthetic dyes, by means of their glycosylation (Bianchini et al. 2004). The aims of this attempt are multiple: a) use of carbohydrates, which are widely and cheaply available, such as lactose, or D-glucose and D-galactose; these compounds often are discarded in huge quantities to the environment, and the environmental impact should not be neglected; b) achievement of hydrophilicity of dyes through their glycoconjugation, so that dyeing processes with dispersed dyes could be carried out without surfactants, which can be very difficult to treat; c) attainment of easier dyeing processes, avoiding high temperatures and high pressures; d) increased affinity towards the textiles, improving efficacy, and reducing waste; e) possibility of efficient and more selective waste treatments using, for instance, live micro-organisms to attack the sugar moiety and consequently the covalently bonded chromophoric part, or the use of enzymes able to destroy dyes; and f) preparation of multipurpose dyes able to dye different fabrics (synthetic, natural, artificial).

On the other hand, also some natural dyes are endowed with saccharidic moieties. For instance, the well known carminic acid is such a dye, but the characteristic is more general, since the hydrosolubility is often a requirement of this class of dyes. Therefore, we devised a completely new approach, consisting on the preparation of glyco azadyes, we will call 'naturalized dyes'. The word naturalize refers to the use of a natural glycide, lactose, that in our process glycoconjugates the dye. As in carminic acid or other similar natural compounds, a chromophore is transformed into a hydrosoluble species through glycoconjugation with a sugar.

## EXPERIMENTAL

### General Methods

The synthetic details of our approach are given in two recent papers (Bartalucci et al. 2007, Bianchini et al. 2007). Red azadye **1a** (Disperse Red 1) is commercially available (Sigma-Aldrich), yellow dye **1b** was prepared according to literature (Podsiadly 2003). Literature methods were used to prepare 6'-O-(1-methoxy-1-methylethyl)-2,3:5,6:3',4'-tri-*O*-isopropylidene lactose dimethyl acetal **2** (Barili et al. 1997).

To measure reflectance a spectrophotometer Varian Cary 4000 was used, endowed with reflectance apparatus. Fastness was measured according to ISO 105 (X-12) C06 standard pattern.

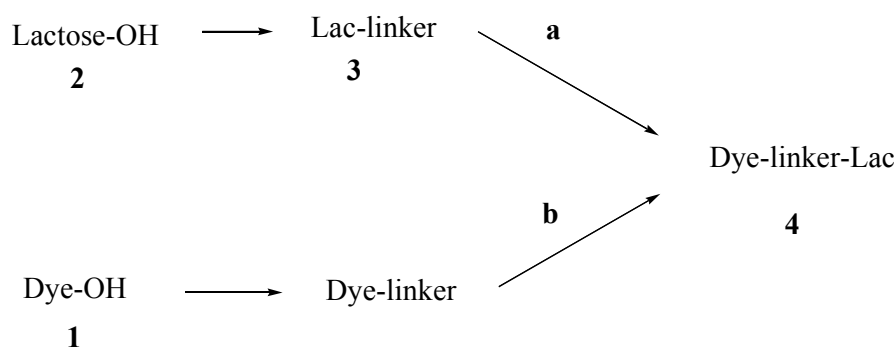
### General Procedure for the Preparation of Protected GADs:

A mixture of the appropriate etherified sugar (1.0 mmol), KOH (4.0 equivalents) and 18-crown-6 ether (0.01 equivalent) in THF (10 ml) was stirred at room temperature for 1 hr, then the dye was added and the mixture left stirring under the same conditions for several hours. The mixture was then neutralized with a saturated aqueous solution of NH<sub>4</sub>Cl and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated, and the resulting residue purified by flash chromatography.

## RESULTS AND DISCUSSION

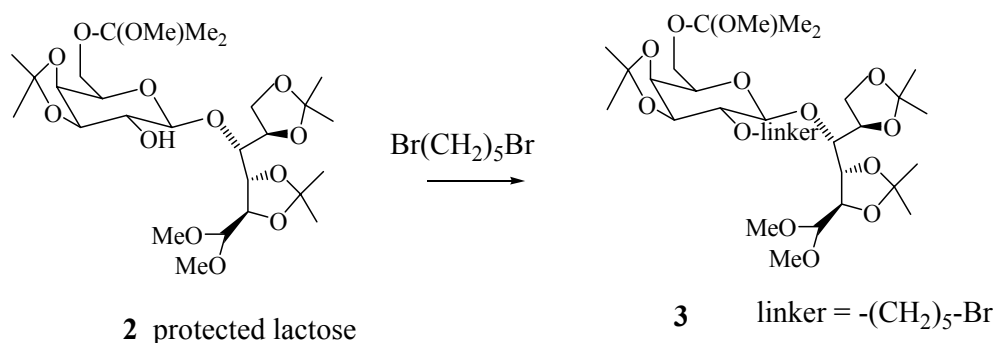
GADs are a new class of naturalized, multipurpose, glycoconjugated dyes, consisting of a synthetic, commercially available dye linked to a saccharide from natural and renewable sources (lactose, D-glucose, D-galactose). The linkage is made using a bifunctional linker.

The modification of the azadyes is carried out on their side chain in order to avoid changes on the chromophoric group and maintain their original colour. The choice of difunctional linkers to be used for the linkage of glycide and dye has been devised on the basis of their ease availability and the simplicity of the practical procedure, with the final aim of an industrial development of the new glycoazadyes. Figure 1 shows two complementary approaches to synthesis these GADs: Path “a” begins by attaching the linker to a protected glycide, while path “b” starts in the reverse order. The resulting structures are diethers, with the formation of two etheric bonds, one between the sugar and the bridge, and a second between the bridge and the hydroxyl group on the side chain of the azadye. Furthermore, the ethers have proven to be stable even under the stressful conditions of dyeing.



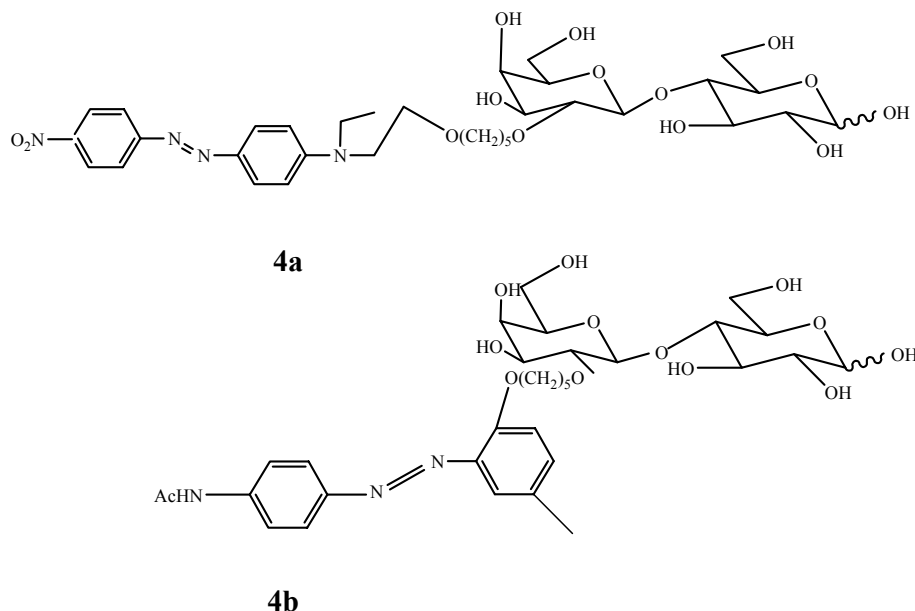
**Figure 1.** Schematic approach to glycoazadyes (GADs)

The study of the influence of GADs glycosidic moiety on the tinctorial properties is the aim of this research. For this purpose, protected lactose (**2**, Fig. 2), together with other protected and linked monosaccharides here not reported for brevity, have been selected in order to prepare a collection of building blocks that can be used to prepare final different GADs.



**Figure 2.** Protected lactose, and linked lactose

These modified glycidides were used to react with a number of azadyes: Here are shown 2 of them, corresponding to the GADs of red disperse 1 (**1a**) and yellow disperse 3 (**1b**, Fig. 3). Of course, products **4a** and **4b** are obtained upon final, single-step, deprotection following the coupling between the linked lactose and the dye, or the linked dye with the protected lactose but bearing a free hydroxyl in position 2'.



**Figure 3.** list of modified dyes

### Tinctorial Tests

Preliminary tinctorial studies were carried out on these GADs, and some of the results are reported in the following tables, thanks to a collaboration with “Italvelluti” SpA Company (Montemurlo, Italy). Later these tests were confirmed and extended by the Lanartex cnc company (Montemurlo, Italy). In Table 1 are shown the conditions of dyeing with this new class of dyes, based on the conjugation with lactose.

**Table 1.** Dyeing with GADs

<i>fabric</i>	<i>polyester</i>	<i>cotton step 1</i>	<i>cotton step 2</i>	<i>acetate</i>	<i>wool</i>	<i>acrylic</i>
Temperature bath (°C)	98	80	98	84	98	98
Time (min)	30	35	15	30	20	30
Bath Ratio <sup>1</sup>	50/1	50/1	50/1	50/1	50/1	50/1
Dye conc. (g/l)	1,0	1,0	1,0	1,0	1,0	1,0
Acetic acid added	1%	--	---	1%	1%	2%
other	---	Na <sub>2</sub> SO <sub>4</sub> (10gr/l)	Na <sub>2</sub> CO <sub>3</sub> (0,5g/l)	--	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	
Fastness <sup>2</sup>	4		4/5	4	3	3/4 <sup>2</sup>

<sup>1</sup>mL of water/fabric(g)

<sup>2</sup>washing and scraping fastness

The first evidence consists in the ‘multipurposity’ that characterizes now the initial aza-dye, that is a disperse dye in origin. But, as a matter of fact, when the naturalization process is carried out, through the glycoconjugation with lactose, the original dye becomes able to dye extremely different fabrics, extending from natural to artificial and synthetic ones. Moreover, the conditions applied for the dyeing processes are extremely mild and easy, especially, for example, upon considering the conditions for polyester. Polyester can be dyed with these GADs in basic conditions, not only using an acidic medium, as usual, and at a temperature near the water boiling point, but far from the 130 °C used for this fabric. Finally, no surface-active agent is added, as reported in the table, which is an evident environmental advantage. Let’s consider the last row. The fastness obtained for each fabric can be considered as the evidence that the dyeing is not a lacquering, but it is in fact a proper dyeing, with good results. Also, here we are reporting on the tristimulus values for each dye and fabrics, so that the colours are well defined in the coordinates of luminosity, chromaticity, and tone, as we can see from Table 2. These tabulated values can be considered as a clear-cut demonstration that dyeing works with naturalized dyes, and that this is now an open research space for textile innovation.

Table 2- Tristimulus values for tissues dyed with GADs

<i>Champion</i>	<i>material</i>	<i>luminosity</i>	<i>Chromaticity</i>	<i>Tune</i>
<b>4a</b>	Wool	53,936	39,920	32,778
<b>4a</b>	Nylon <sup>1</sup>	42,816	61,373	43,612
<b>4a</b>	Acetate <sup>1</sup>	43,921	65,709	41,513
<b>4a</b>	Cotton	66,850	26,393	27,380
<b>4a</b>	Polyester <sup>2</sup>	62,126	46,993	29,776
<b>4a</b>	Polyester <sup>3</sup>	71,917	32,502	32,430
<b>4b</b>	Wool	74,075	47,630	85,632
<b>4b</b>	Nylon <sup>1</sup>	76,454	65,012	85,532
<b>4b</b>	Acetate	73,584	76,054	89,939
<b>4b</b>	Polyester <sup>1</sup>	78,994	60,524	82,505

<sup>1</sup>values read on a multi-fabric witness. <sup>2</sup>Dyed in a basic way (see Table 1)

<sup>3</sup>Dyed in a acid way.

Also we are confident that Table 3 will add important information on the quality of dyeing using these new generations of dyes. And in fact we can see that using ethereal glycoconjugated derivatives of Red (**4a**) or yellow (**4b**) dyes, we gave reflectance values at the two more significant wavelengths, and also K/S values, where K stands for the Kubelka-Munk absorption coefficient and S represents the scattering coefficient at the respective wavelength. Of course where we have high values of reflectance the absorption is low, and scattering is high, and viceversa.

Table 3- Reflectance and K/S Values of Fabrics Dyed with GADs **4a** and **4b**

<b>4a</b>					<b>4b</b>			
febric	R% (500 nm)	R% (700 nm)	K/S (500 nm)	K/S (700 nm)	R% (450nm)	R% (700nm)	K/S (450 nm)	K/S (700 nm)
wool	8	63	7,5	0,2	12	60	2,5	0,1
Nylon	5	65	9,5	0,1	10	63	5,5	0
Acetate	12	75	3,7	0,0	2	55	15	0
Cotton	20	72	1,7	0,1				
Polyester <sup>1</sup>	20	1,6	1,6	0,2	10	72	3,9	0

<sup>1</sup>Dyed in basic conditions (see Table 1)

We think that these data can be considered as a demonstration that environmentally compatible naturalized dyes can work appreciably well in the dyeing processes. The tests showed that these generations of GADs are soluble in water, as expected, and also that these dyes are multipurpose, since they dyed all of the fabrics so far tested. The results of some of these tests are reported in Fig 1. In this case the polyester has been dyed according to the basic procedure reported in Table 1. As far as we know this is the first time that a dye, which is in principle a disperse dye, at the end of story is able to directly dye wool and polyester under mild conditions. These tests, and many others not reported here, since they are covered by a deposited patent, or others on the way, have been carried out under standard conditions and were performed in water without the addition of surfactants, under mild conditions of temperature and pressure. Dispersed dyes, such as the starting azadyes, do not effectively dye wool, and they dye polyester only under drastic conditions (such as high temperature or pressure).



**Figure 1.** Polyester (upper row) and wool (lower row) dyed with **4a** (left) and **4b** (right).

## CONCLUSIONS

A naturalization of industrial commercial dyes has been proposed, in order to maintain their good properties and improve their applications to various textiles. The synthetic modifications applied have brought:

- a higher hydrophilicity of dyes through their glycoconjugation, so that the trial dyeing processes have been carried out without the use of surfactants, or other potential pollutants;
- easier dyeing processes, avoiding high temperatures and high pressures;
- better affinity towards textiles, improving efficacy and reducing waste;
- multipurpose dyes able to dye different fabrics (synthetic, natural, artificial);

- the utilization of carbohydrates largely and cheaply available such as D-glucose, D galactose and lactose; normally discarded in huge quantities in the environment, with not negligible impact;
- new possibilities for efficient and more selective waste treatment by using, for instance, live micro-organisms to attack the sugar moiety and consequently the covalently bonded chromophore, or the use of enzymes able to destroy dyes.

## ACKNOWLEDGMENTS

We thank Italvelluti SpA and Lanartex CNC companies, Montemurlo (Prato), and Cassa di Risparmio di Firenze for financial support.

This contribution was an original presentation at the *ITALIC 4 Science & Technology of Biomass: Advances and Challenges* Conference that was held in Rome, Italy (May 8-10, 2007) and sponsored by Tor Vergata University. The authors gratefully acknowledge the efforts of the Conference Organizers, Prof. Claudia Crestini (Tor Vergata University, Rome, Italy), Chair, and Prof. Marco Orlandi (Biococca University, Milan, Italy), Co-Chair. Prof. Crestini also is Editor for the conference collection issue to be published in *BioResources*.

## REFERENCES CITED

- Barili, P. L., Catelani, G., D'Andrea, F., De Rensis, F., and Falcini, P. (1997). "Improved preparation of 2,3:5,6:3',4'-tri-O-isopropylidenelactose dimethyl acetal and its 6'-O-(1-methoxy-1-methylethyl) derivative," *Carbohydr. Res.* 298, 75-84.
- Bartalucci, G., Bianchini, R., Catelani, G., D'Andrea, F., and Guazzelli, L. (2007). "Naturalized dyes: a simple straightforward synthetic route to a new class of dyes – glycoazadyes (GADs)" *Eur. J. Org. Chem.* 588-595.
- Bianchini, R., Bartalucci, G., Catelani, G., and Seu, G. (2004). "Coloring agent containing a mono- or disaccharide" *European Pat. Appl.* no. 04005253.4, deposit 03/05/2004.
- Bianchini, R., Calucci, L., Lubello, L., and Pinzino, C. (2002). "Intermediate free radicals in the oxidation of wastewaters" *Res. Chem. Intermed.* 28, 247-256.
- Bianchini, R., Catelani, G., Cecconi, R., D'Andrea, F., Guazzelli, L., Isaad, J., and Massimo Rolla, M. (2007). "Ethereal glycoconjugated azodyes (GADs), a new group of water soluble, naturalized dyes," accepted for publication on *European Journal of Organic Chemistry*.
- Bock, K., and Pedersen, C. (1983). "Carbon-13 nuclear magnetic resonance spectroscopy of monosaccharides" *Adv. Carbohydr. Chem. Biochem.* 41, 27-66.
- Mascolo, G., Lopez, A., Bozzi, A., and Tiravanti, G. (2002). "By-products formation during the ozonation of the reactive dye Uniblu-A [Uniblue A]" *Ozone-Science & Engineering* 24(6), 439-466.
- Neamtu, M., Siminiceanu, I., Yediler, A., and Kettrup, A. (2002). "Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/H<sub>2</sub>O<sub>2</sub> oxidation," *Dyes and Pigments* 53, 93-99.
- Perrin, D. D., Armarengo, W. L. F., and Perrin, D. R. (1980). *Purification of Laboratory Chemicals*, 2nd Ed., Pergamon Press, Oxford.
- Pierce, C. I., Lloyd, J. R., and Guthrie, J. T. (2003). "The removal of colour from textile wastewater using whole bacterial cells" *Dyes and Pigments* 58, 179-196.

- Podsiadły, R., Sokołowska, J., Marcinek, A., Zielonka, J., Chrześcijańska, E., and Socha, A. (2003) "Electrochemical and photochemical reduction of a series of azobenzene dyes in protic and aprotic solvents" *Coloration Technology* 119, 269-274.
- Poon, C. S., Huang, Q., and Fung, P. C. (1999). "Degradation kinetics of cuprophenyl yellow RL by UV/H<sub>2</sub>O<sub>2</sub>/ultrasonication (US) process in aqueous solution" *Chemosphere* 38, 1005-1014.
- Rott, U., and Minke, R. (1999)." Overview of wastewater treatment and recycling in the textile processing industry" *Water Sci. Technol.* 40, 137-144.
- Selcuk, H. (2005). "Decolorization and detoxification of textile wastewater by ozonation and coagulation processes" *Dyes and Pigments* 64, 217-22.

Article received by journal: July 27, 2007; First round of peer-review completed: Sept. 16, 2007; Revised version received and accepted: Oct. 15, 2007; Article published Oct. 17, 2007.