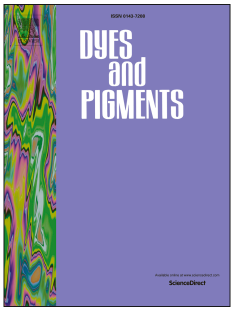

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PII: S0143-7208(15)00212-0

DOI: 10.1016/j.dyepig.2015.05.033

Reference: DYPI 4796

To appear in: *Dyes and Pigments*

Received Date: 14 January 2015

Revised Date: 12 May 2015

Accepted Date: 28 May 2015

Please cite this article as: Chen X, Keyi D, Jun L, Synthesis, identification and application of aldehyde reactive dyes, *Dyes and Pigments* (2015), doi: 10.1016/j.dyepig.2015.05.033.

Synthesis, identification and application of aldehyde reactive dyes

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Abstract: Nine aldehyde reactive dyes, designated $\mathbf{D_1}$- $\mathbf{D_9}$, were synthesized. Among them, $\mathbf{D_1}$ and $\mathbf{D_2}$ were synthesized by “grafting” alizarin red and alizarin yellow GG, respectively, to the α-C of n-butyl-aldehyde; $\mathbf{D_3}$ and $\mathbf{D_4}$ were synthesized by “grafting” alizarin red and alizarin yellow GG, respectively, to the methyl-C of 4-methyl-cinnamaldehyde; $\mathbf{D_5}$- $\mathbf{D_9}$ were synthesized by “grafting” alizarin red, alizarin yellow GG or self-prepared colorants to the α-C of glutaraldehyde. UV-vis, FTIR, ESI-MS, elemental analysis and ^{1}H NMR were applied to identify the target products. Aluminum-tanned wet-white sheep leather was chosen as substrate for the application experiments, and their four dyeing property indexes, i.e., substantivity (S), exhaustion（E）, fixation（F）and reactivity（R）were measured. The results indicated that, without adding of neutral salts and under mild conditions (T = 35-45 °C，pH =4.0-6.5), all these dyes could dye wet-white leather within 1.5 h, and the dyed leather possessed a satisfactory washing-fastness.

Keywords: aldehyde, reactive dyes, synthesis, identification, application

1 Introduction

Reactive dyes are widely used to dye protein fibers (such as wool, silk, fur and leather) and cotton fiber because of their good rub fastness and washing fastness. However, research results [1-3] showed that the problem of the currently available reactive dyes are: (1) the hydrolysis of their reactive groups during the process of storage and application results in the lost as high as 20-50% of reactive dyes; and (2) a large quantity of neutral salts (20-40 g/L) required in the dyeing process may cause environmental pollution.

The idea of reactive aldehyde dyes derived from the research of our laboratory on the color-forming mechanism of natural iridoids (such as genipin, loganin aglycone, oleuropein aglycone and E-6-*O*-methoxycinnamoyl scandoside methyl ester aglycone) with primary amino (–NH_2) containing materials (such as silk, leather and wool) [4-5]. This mechanism indicated that there was an inter-conversion isomer with a glutaraldehyde backbone present in the reaction system, which caused genipin, for example, to crosslink with collagen fiber (Fig. 1). Two effects would produce during this process: collagen fiber was dyed to dark-blue and its hydrothermal stability was increased [4-5].

Glutaraldehyde is a commonly used tanning agent for leather manufacture. During the tanning process a crosslinking reaction could occur between glutaraldehyde and collagen molecules through a Schiff base reaction. This mechanism suggested that a new kind of reactive dye could be made by "grafting" bio-friendly colorants to the backbone of glutaraldehye. Unlike the normally used reactive dyes, this alternative reactive aldehyde dyes do not hydrolysis and neutral salts do not need during their application. Theoretically, a simultaneous tanning — dyeing process could be achieved when this novel kind of reactive dye is applied to leather.

Generally, glutaraldehyde is preserved as a 25% - 50% (w/w) aqueous solution and it is almost impossible to "graft" colorant compounds to its backbone directly. So an "easy to difficult" strategy was adopted, during which colorant compounds were grafted to the α-C of n-butyl-aldehyde and the methyl-C of 3-(4-methyl) phenyl -acrylaldehyde, so that a series of reactive dyes with mono-aldehyde as reactive group was obtained. Their capacity to dye aluminum pre-tanned wet-white leather were investigated; after that, colorant compounds were grafted to the precursor of glutaraldehyde, and target products were obtained by an oxidation reaction or hydrolysis reaction. In this way, nine reactive dyes with aldehyde as the reactive group were synthesized. Their structures were identified and their application properties were investigated.

2 Experimental

2.1 Materials

3,4-Dihydro-2H-pyran-2-methanol(＞97%) was supplied by Huachem Industry Ltd., Japan; sodium 1-amino-4-bromoanthraquinone-2-sulfonate (＞89%) was supplied by Longsheng Dye Chemical Corp., Zhejiang, China；Silica GF254 was supplied by Qingdao Haiyang Chemical Corp., China; n-butyl-aldehyde, N,N-dimethylformamide (DMF), N-chlorosuccinimide (NCS), N-bromosuccinimide (NBS), L-Proline，Alizarin red, Alizarin yellow GG, 4-methylcinnamaldehyde, Benzoyl peroxide (BPO), cyclopentene, dimethyl sulfoxide (DMSO), 1,4-dioxane, sodium 2,4-diamino-benzenesulfonate, m-phenylenediamine, hydroquinone and other commonly used chemicals were supplied by Chengdu Kelong Chemical Corp., China (all analytical grade); aluminum pre-tanned sheep wet white leather was provided by the Leather Department of Sichuan University, China.

2.2 Synthesis of mono-aldehyde reactive dyes

2.2.1 Synthesis of D_1、D_2 based on n-butyl-aldehyde [6]

(1) **Synthesis of α-chlorobutanal**

In a 0 °C ice bath, n-butyl-aldehyde (5 mmol) and L-Proline (1 mmol) were dissolved in CH_2Cl_2 (10 mL), and NCS (6.5 mmol) was added slowly with stirring. After 1 h, the temperature of the solution was raised to 25 °C and the reaction proceeded for another 8 h. After removal of CH_2Cl_2 by rotary evaporation, n-pentane (30 mL) was added to precipitate NCS and other side products. α-chloro butyl-aldehyde was obtained after filtration and removal of n-pentane by evaporation under vacuum (Fig. 2).

（2）Synthesis of D_1

To a 100-mL three-necked flask, alizarin red (1.80 g, 5 mmol), potassium carbonate (2.07 g，15 mmol) and 50 mL of DMF were added，the temperature was raised to 30 °C with stirring. Then α-chloro butyl-aldehyde (1.06 g，0.01 mol）was added and the reaction proceeded for 12 h. After removal of DMF by rotary evaporation, **D_1**, the target product, a red purple powder (1.86 g) was obtained in a yield of 75.4% (Fig. 3).

（3）synthesis of D_2

To a 100-mL three-necked flask, alizarin yellow GG (1.546 g，5 mmol), potassium carbonate (2.07 g，15 mmol) and 50 mL DMF were added，the temperature was raised to 40 °C under stirring, then α-chloro butyl-aldehyde (1.06 g，0.01 mol) was added and the reaction proceeded for 12h. After removal of DMF by evaporation in vacuum, **D_2**, a light yellow powder (1.41 g) was obtained in a yield of 74.6% (Fig.4).

2.2.2 Synthesis of D_3、D_4 based on 4-methylcinnamaldehyde[7]

（1）Preparation of 3- (4- (bromomethyl) phenyl) acrylaldehyde

To a 250-mL three-necked flask, 4-methylcinnamaldehyde (4.38 g, 0.03 mol), NBS (6.23 g, 0.035 mol), BPO (10 mg) and 50 mL CCl_4 were added，the temperature was raised to 40 °C with stirring and the reaction proceeded for 4 h. After 2 h at room temperature without stirring, the floating materials were filtered and washed three times (3×10 mL) with CCl_4 and the CCl_4 fractions were combined. Water soluble impurities were removed by washing the CCl_4 solution with 60 mL water in a separatory funnel. The CCl_4 phase was collected and dried by adding $MgSO_4$ (anhyd). $MgSO_4$ was removed by filtration after 12 h, leaving the pure product in CCl_4 solution. CCl_4 was removed by rotary evaporation. The yield of 3- (4-(bromomethyl) phenyl) acrylaldehyde was 4.48 g in a yield of 66.7% (Fig. 5).

(2) Synthesis of D_3

To a 100-mL three-necked flask, alizarin yellow GG (6.18 g，0.02 mol) , potassium carbonate (4.14 g，0.03 mol) , 3- (4- (bromomethyl) phenyl) acrylaldehyde (6.72 g, 0.03 mol) and 100 mL DMF were added，the temperature was raised to 40 °C under stirring and the reaction proceeded for 12 h. After cooling to 25 °C and removal of DMF by evaporation in vacuum, the yellow powder was washed with $CHCl_3$ to remove excess 3- (4- (bromomethyl) phenyl) acrylaldehyde, then filtered and dried. The product, **D_3**, a yellow powder (5.87 g) was obtained in a yield of 64.8% (Fig. 6).

(3) Synthesis of D_4

Alizarin red (7.20 g，0.02 mol), potassium carbonate (4.14 g，0.03 mol), 3- (4-

(bromomethyl) phenyl) acrylaldehyde (6.72 g, 0.03 mol) and 100 mL DMF was combined. The synthesis process was the same as described for the synthesis of $\mathbf{D_3}$. $\mathbf{D_4}$, a dark red powder (7.03 g) was obtained in a yield of 72.4% (Fig. 7).

2.3 Synthesis of reactive dyes with glutaraldehyde backbone

2.3.1 Synthesis of D_5 and D_6 [8]

(1) Preparation of *α*-bromocyclopentene

CCl_4 (50 mL), cyclopentene (6.8 g，0.1 mol), NBS (17 g，0.092 mol) and BPO (30 mg) were combined. The synthesis process was the same as described in section 2.2.2 (1). *α*-bromocyclopentene (9.8 g), a light yellow liquid was obtained in a yield of 71% (Fig. 8).

(2) Synthesis of D_5

To a 250-mL three-necked flask, alizarin red (18 g, 50 mmol), potassium carbonate (20.7 g，150 mmol) and 100 mL DMF were added， the temperature was raised to 50 °C within 0.5 h with stirring, then α-bromocyclopentene (13.8 g) was added dropwise within 0.5 h, and the reaction proceeded for 12 h. After removal of DMF by evaporation in vacuum, the precursor of $\mathbf{D_5}$ (15.8 g) was obtained in a yield of 67%.

The precursor of $\mathbf{D_5}$ (9.84 g) was dissolved in tert-butanol (50mL) in advance. Then, to a 250-mL three-necked flask, H_3WO_3 (0.5 g), B_2O_3 (0.5 g), tert-butanol (100 mL) and H_2O_2 (30% (w/w), 2.4 mL,) were added，the temperature was raised to 35-40 °C within 0.5 h with stirring, then the dissolved precursor of D_5 was added dropwise within 0.5 h and the reaction proceeded for12 h, then $Na_2S_2O_3$ (4.5 g) was added three times (1.5 g ×3) to remove excess H_2O_2. After filtering and removing solvent by evaporation in vacuum, $\mathbf{D_5}$, a red powder (8.72 g) was obtained in a yield of 83% (Fig.9).

(3) Synthesis of D_6

Alizarin yellow GG (28.7 g), potassium carbonate (13.8 g), α-bromocyclopentene (13.8 g), and 100 mL DMF were combined to synthesize the precursor of $\mathbf{D_6}$ (28.5 g) as described in section 2.3.1(2), then the precursor was oxidized by H_2O_2 to give $\mathbf{D_6}$ (26.91 g) in a yield of 87% (Fig. 10).

2.3.2 Synthesis of D_7 and D_8 [9]

(1) Synthesis of 3-Bromo-2, 6-dimethoxytetrahydropyran

To a 100-mL three-necked flask, 3, 4-dihydro-2-methoxy-2H-pyran (15 mL) and 17.5 mL MeOH were combined and put in a –5 °C ice-salt bath, then NBS (17.8 g) was added slowly within 70 min, the temperature was raised to 20-22 °C with stirring and the reaction proceeded for 4 h, then it was filtered and washed two times (2×20 mL) with diethyl ether and the organic fractions were combined. Water soluble impurities were removed by washing the liquid fractions two times (2×20 mL) with saturated $NaHSO_3$(aq.) in a separatory funnel. The organic phase was collected and dried by adding $MgSO_4$ (anhyd). $MgSO_4$ was removed by filtration after 12 h, leaving the pure product in diethyl ether solution, after ether was removed by rotary evaporation, 3-Bromo-2, 6-dimethoxytetrahydropyran was obtained (18.2 g) in a yield of 85% (Fig. 11).

(2) Synthesis of colorant Ⅰ and colorant Ⅱ

Composite catalyst ($n_{(CuSO4•5H2O)}$: $n_{(SnCl2•2H2O)}$ = 1:1 , 20% aq.) was prepared in advance, then sodium 1-amino-4-bromoanthraquinone-2-sulfonate (8.08 g), m-phenylenediamine (2.16 g) and H_2O (50 mL)were added to a 100-mL three-necked flask, the temperature was raised to 65-70 °C with stirring; newly prepared composite catalyst (10 mL) was add dropwise slowly within 10 min, and pH was adjusted to 9-10 with 10% (v/w) Na_2CO_3 aq. The reaction was monitored by thin layer chromatography ($n_{\text{butyl alcohol}}$: $n_{\text{acetic acid}}$: n_{water}= 4:1:5) and the end point was marked as the disappearance of 1-amino-4-bromoanthraquinone-2-sulfonic, usually within 10 h. As soon as the reaction was finished, the solution was filtered and 20 g NaCl was added to the liqiud fractions. After 12 h with stirring, it was put in a separatory funnel, the upper fraction was collected and dried，the product was referred to as **colorant Ⅰ** (Fig. 11).

Sodium 1-amino-4-bromoanthraquinone-2-sulfonic (8.08 g) , hydroquinone (8.8 g) and H_2O (90 mL) were added to a 250-mL three-necked flask, rise temperature to 80-85 °C under stirring, composite catalyst (10 mL) was dripped slowly within 10 min, adjust pH= 9-10 with 10% (v/w) Na_2CO_3 aq. solution. The reaction was monitored by thin layer chromatography ($n_{\text{butyl alcohol}}$: n_{ethanol} : n_{water}= 2：1：1) and making the disappearance of 1-amino-4-bromoanthraquinone-2-sulfonic as the end point, usually the reaction lasted for 18 h. As soon as the reaction was finished, the solution was filtered and 30g NaCl was added to the liqiud fractions. After 12 h with stirring, it was put in a separatory funnel, the upper fraction was collected and dried， the product was referred to as **colorant** Ⅱ(Fig. 11).

(3) Synthesis of the precursor of D_7 and D_8

Water (10 mL) , acetone (10 mL) , 3-bromo-2,6-dimethoxytetrahydropyran (2 mL) and **colorant** Ⅰ (4.1 g) were added to a 50-mL three-necked flask, the reaction was lasted for 3 h under stirring at 0-5 °C, then the temperature was raised to 70 °C and reacted for another 8 h, then it was filtered and the solid product was dissolved in 15mL DMF and filtered for the second time. The liqiud fractions were washed with 100 mL diethyl ether at 5 °C for 1 h and then filtered, the solid product was vaccum dried, it was refered to as precursor of **D_7** (Fig. 11) .

DMF (20 mL) , **colorant** Ⅱ (4.32 g) , NaOH (0.5 g) were added to a 50mL three-necked flask, the reaction was lasted for 2 h under 80-85 °C with stirring, then the temperature was raised to 100 °C, NaI (0.5 g) and 3-Bromo-2,6-dimethoxytetrahydropyran (2 mL) were added and reacted for another 24h; then it was filtered and the solid product was dissolved in 15mL DMF and filtered for the second time. The liqiud fractions were washed with 100 mL diethyl ether at 5 °C for 1 h and then filtered, the solid product was vaccum dried and refered to as precursor of **D_8** (Fig. 11) .

(4) Obtaining the target products D_7, D_8

The precursor **D_7** or **D_8** (2.0 g) and HCl (10 mL, 10% (v/v)) were added to a 50-mL three-necked flask, pH was adjusted to 3-4 with 20% (v/w) $NaHCO_3$ (aq). The reaction was proceed for 3 h at 80-85 °C with stirring, then the solvent was removed by evaporation under vacuum and the product was dried at room temperature. The target products **D_7** and **D_8** were obtained (Fig. 11).

2.3.3 Synthesis of D_9 [10]

(1) Synthesis of colorant Ⅲ

Sodium 1-amino-4-bromoanthraquinone-2-sulfonic (24.30 g), sodium 2,4-diamino-benzene-sulfonic (16.92 g), H_2O (200 mL) and $NaHCO_3$ (18.00 g) were added to a 500-mL three-necked flask, the temperature was raised to 75-85 °C with stirring, newly prepared composite catalyst (30 mL) from section 2.3.2 (2) was added dropwise slowly within 20 min, pH was adjusted to 8.0-8.5 with 10% (v/w) Na_2CO_3 aq. The reaction was monitored by thin layer chromatography ($n_{\text{butyl alcohol}} : n_{\text{2-Propanol}} : n_{\text{ethyl acetate}} : n_{\text{water}} = 2 : 4 : 1 : 3$) and making the disappearance of 1-amino-4-bromoanthraquinone-2-sulfonic as the end point, usually the reaction would last for 12 h. As soon as the reaction was finished, active carbon was added and the solution was filtered, then 80 g NaCl was added to the liqiud fraction. After 12 h with stirring, it was put in a separatory funnel, the upper layer was collected and vaccum dried，24.36 g blue powder, which was referred to **colorant Ⅲ** was obtained with a yield of 85.24% (Fig. 12).

(2) Synthesis of D_9

With DMSO as solvent and KI as catalyst, **colorant Ⅲ** (4.5 g) and 3-Bromo-2, 6-dimethoxytetrahydropyran (2 mL) were reacted as described in section 2.3.2 (3) to obtain the precursor of $\mathbf{D_9}$.

Precursor of $\mathbf{D_9}$ (5 g) and 1,4-dioxane (50 mL, 50% aq. (v/v)) were added to a 100-mL three-necked flask and the pH was adjusted to 2-3 using 1 M HCl aq. and the temperature was raised to 90 °C with stirring. The reaction was monitored hourly by thin layer chromatography ($n_{\text{ethyl acetate}} : n_{\text{pyridine}} : n_{\text{water}} = 6 : 3 : 1$). The reaction was regarded as complete when the size of the spot of D_9 remained unchanged after three consecutive hourly tests. A 1 M solution of HCl (aq.) was added until the product precipitated; then it was filtered and the solid part was dried at room temperature, the target product, $\mathbf{D_9}$, a black powder (3.60 g) in a yield of 82% (Fig. 12) was obtained.

2.4 The isolation and purification of dyes [9]

(1) Isolation

To purify the raw products, 1 g of raw dyestuff was dissolved in 5 mL DMF. Undissolved impurities were removed by filtration and washing with an additional 1 mL DMF. The DMF fractions were combined and DMF was removed by rotary evaporation. The remaining solid material was washed in 50 mL diethyl ether to remove non-polar impurities. Purified product was collected by filtration and the yield was calculated.

(2) Purification

The powdered product from the previous step was mixed with diatomaceous earth and dried in an oven at 80 °C. The dried mixture was added to the top of a column packed with GF254 silica stationary phase. A mixture of n-butyl alcohol and acetic acid (20:1, v/v) was added to the column as mobile phase. Passage of the colored dye through the column was easily monitored, and the main colored band was collected as it was eluted from the column. After removal of solvent by rotary evaporation at 85 °C, the pure sample for UV-vis, FTIR, elemental analysis, ^{1}H NMR and ESI-MS spectrometry analyzing was obtained.

2.5 Identification of dyes

UV-Vis absorption for determination of the λ_{max} of dyes was performed using TU-1901, FTIR (KBr) was performed with FTS3000, elemental analysis were performed on an Carlo-Erba-1106, ^{1}H NMR were recorded on a Bruker Avance DPX – 400 using Methanol-d_4 as solvent and TMS as internal standard, ESI-MS were carried out with Finnigan-LCQ via negative ion mode.

2.6 The measurement of ***S***、***E***、***F***、***R*** (making $\mathbf{D_7}$ as an example) [11]

Aluminum pre-tanned sheep wet-white pelt (5 cm × 5 cm) was weighed and making its weight as reference for other regents: liquor ratio was 300% (w/w), the dosage of $\mathbf{D_7}$ was 2% (w/w), pH of the dye-bath was adjusted to 6.0-6.5 with 10% (w/w) Na_2CO_3 aq., leather pelt was dyed for 30 min under 35-40 °C; then pH was adjusted to 4.0-4.5 with 10% (w/w) HAc aq., and the pelt was dyed for another 60 min under 45 °C. The nine intervals of sample picking for measuring the exhaustion and fixation values were shown as Fig. 13.

(1) Calculation of exhaustion (E_t)

In each interval of ①-⑨, the absorbance (A_t) of the diluted dye solution was measured at the wavelength of maximum absorption (λ_{max}). The exhaustion value of the dye at a certain period (E_t) was calculated as below：

$$E_t\ /\% = (1 - A_t/A_0) \times 100\%$$

Where A_t and A_0 are the absorbance values of the dyeing-bath for a certain period and the original dyeing-bath, respectively.

(2) Calculation of fixaion (F_t)

In each interval of ⑤-⑨, the dyed leather sample was picked up and soaped-off using a weakly anionic detergent (2 g/L) at 40 °C for 10 min. The soap-bath was diluted to a certain volume and its absorbance value (A_t) was measured at the wavelength of maximum absorption (λ_{max}). The fixation value of the dye at a certain interval (F_t) was calculated as below：

$$F_t /\% = (1–A_t/A_0) \times 100\%$$

Where A_t and A_0 are the absorbance values of the soap-bath for a certain period and the original dye-bath (2 g/L detergent was added also), respectively.

Making dyeing time as *X*-axe, E_t and $\mathrm{F_t}$ as *Y*-axe, the exhaustion and fixation curve of $\mathbf{D_7}$ was achieved (Fig. 14). According to Fig. 14, *S* (substantivity), *E* (exhaustion), *F* (fixation) and *R* (reactivity) of D_7 could be obtained, where the value of *S* refers to the exhaustion value when t = 30 min; *R* refers to the value of fixation when t = 35 min, i.e., after 5 min of the adding of HAc; *E* and *F* refer to the final value of exhaustion and fixation, respectively.

The values of *S*, *E*, *F* and *R* of the other eight dyes could be obtained in the same way as above. These values are very useful in dyeing practice, especially for the choice of color-matching dyeing process when two or more than two dyes are needed to be combined [11].

2.7 The washing fastness testing

The washing color fastness of the dyed leather was tested according to Chinese standard methods GB/TC3921-97.

3 Results and discussion

3.1 Identification of dyes

$\mathbf{D_1}$: $C_{18}H_{13}O_8SNa$, purple-red powder, λ_{max} = 525 nm. IR (KBr): 2852 cm^{-1}, 2742 cm^{-1} (double $\upsilon_{C\text{-}H}$ of the aldehyde), 2744cm^{-1} (quinone $\upsilon_{C=O}$), 1345 cm^{-1} ($-SO_3$), 1256 cm^{-1} (Ar-OH), 1047 cm^{-1} (Ar-O-CH). ESI-MS, *m/z*: 389.13 $[M-Na]^-$. ^{1}H NMR: δ_H: 9.23 (d, 8.7 Hz, 1H), 8.01 (dd, 6.4, 4.5 Hz, 1H), 7.73 (s, 1H), 6.84 (m, 1H), 6.82 (m, 1H), 6.79 (m, 1H), 4.25 (dd, 6.7, 4.3 Hz, 1H), 2.13 (m, 1H), 1.87 (m, 1H), 0.96 (t, 7.4 Hz, 3H). Elemental Anal. Calcd：C，52.47; H, 3.16; O, 31.76; S, 7.78; Na, 5.58. Found：C，52.43; H, 3.18; O, 31.72; S, 7.75; Na, 5.56%.

$\mathbf{D_2}$: $C_{17}H_{14}O_6N_3Na$, yellow powder, λ_{max} = 353 nm. IR (KBr): 2850 cm^{-1}, 2742 cm^{-1} (double $\upsilon_{C\text{-}H}$ of the aldehyde), 1447 cm^{-1} ($\upsilon_{-N=N-}$), 1390 cm^{-1} (υ_{-NO2}), 1067 cm^{-1} (Ar-O-CH). ESI-MS, *m/z*: 356.12 $[M-Na]^-$. ^{1}H NMR: δ_H: 9.28 (d, 8.1 Hz, 1H), 8.47 (t, 1.7 Hz, 1H), 8.41 (d, 6.5 Hz, 1H), 8.21 (m, 1H), 8.18 (m, 1H), 8.17 (m, 1H), 7.43 (t, 6.7 Hz, 1H), 7.36 (d, 8.1 Hz, 1H), 4.23 (m, 1H), 2.05 (m, 1H), 1.87 (m, 1H), 1.06 (t, 7.3 Hz, 3H). Elemental Anal. Calcd：C，53.87; H, 3.69; O, 25.33; N, 11.08; Na, 6.06. Found：C，53.79; H, 3.66; O, 25.37; N, 11.10; Na, 6.02%.

D$_3$: $C_{23}H_{16}O_6N_3Na$, yellow powder, λ_{max} = 381 nm. IR (KBr): 2852 cm^{-1}, 2745 cm^{-1} (double $\upsilon_{C\text{-}H}$ of the aldehyde), 1451 cm^{-1} ($\upsilon_{\text{-}N=N\text{-}}$), 1390 cm^{-1} ($\upsilon_{\text{-}NO2}$), 1069cm^{-1} (Ar-O-CH). ESI-MS, *m/z*: 430.21 $[M\text{-}Na]^-$. ^1H NMR: δ_H: 9.18 (dd, 8.1, 2.3 Hz, 1H), 8.70 (s, 1H), 8.12 (t, 1.7 Hz, 1H), 7.92 (m, 1H), 7.88 (m, 1H), 7.79 (m, 1H), 7.67 (dd, 14.3, 2.3 Hz, 1H), 7.63 (m, 3H), 7.25 (m, 3H), 6.84 (dd, 14.3, 8.1 Hz, 1H), 5.44 (s, 2H). Elemental Anal. Calcd：C，60.98; H, 3.53; O, 21.19; N, 9.27; Na, 5.07. Found：C, 60.10; H, 3.55; O, 21.16; N, 9.25; Na, 5.05%.

D$_4$: $C_{24}H_{15}O_8SNa$, red powder, λ_{max} = 535 nm. IR (KBr): 2851 cm^{-1}, 2740 cm^{-1} (double $\upsilon_{C\text{-}H}$ of the aldehyde), 2746cm^{-1} (quinone $\upsilon_{C=O}$), 1358cm^{-1} ($\text{-}SO_3$), 1254cm^{-1} (Ar-OH), 1047cm^{-1} (Ar-O-CH_2). ESI-MS, *m/z*: 463.08 $[M\text{-}Na]^-$.^1H NMR: δ_H: 9.29 (d, 4.8 Hz, 1H), 8.56 (s, 7.4 Hz, 1H), 8.40 (d, 4.8 Hz, 1H), 8.10 (m, 1H), 8.08 (m, 1H), 8.07 (m, 1H), 7.85 (d, 12.3 Hz, 1H), 7.79 (d, 6.7 Hz, 2H), 7.36 (d, 6.7 Hz, 2H), 6.64 (dd, 12.3, 4.8 Hz, 1H), 4.58 (s, 2H). Elemental Anal. Calcd：C，59.31; H, 3.09; O, 26.34; S, 6.65; Na, 4.73. Found：C, 59.22; H, 3.12; O, 26.37; S, 6.49; Na, 4.69%.

D$_5$: $C_{19}H_{13}O_9SNa$, red powder, λ_{max} = 522 nm. IR (KBr): 2849 cm^{-1}, 2738 cm^{-1} (double $\upsilon_{C\text{-}H}$ of the aldehyde), 2744 cm^{-1} (quinone $\upsilon_{C=O}$), 1356 cm^{-1} ($\text{-}SO_3$), 1266cm^{-1} (Ar-OH), 1049 cm^{-1} (Ar-O-CH_2). ESI-MS, *m/z*: 417.15 $[M\text{-}Na]^-$.^1H NMR: δ_H: 9.27 (d, 4.8 Hz, 1H), 9.08 (t, 7.4 Hz, 1H), 8.68 (s, 1H), 8.13 (t, 1.8 Hz, 1H), 7.91 (m, 1H), 7.89 (m, 1H), 7.76 (m, 1H), 4.20 (m, 1H), 2.75 (m, 2H), 2.26 (m, 1H), 2.10 (m, 1H). Elemental Anal. Calcd：C，51.86; H, 2.96; O, 32.73; S, 7.29; Na, 5.22. Found：C, 51.62; H, 3.01; O, 32.75; S, 7.26; Na, 5.18%.

D$_6$: $C_{18}H_{14}O_7N_3Na$, yellow powder, λ_{max} = 361 nm. IR (KBr): 2852 cm^{-1}, 2745 cm^{-1} (double $\upsilon_{C\text{-}H}$ of the aldehyde), 1443 cm^{-1} ($\upsilon_{\text{-}N=N\text{-}}$), 1529 cm^{-1} ($\upsilon_{\text{-}NO2}$), 1249 cm^{-1} (Ar-O-CH). ESI-MS, *m/z*: 385.12 $[M\text{-}Na]^-$.^1H NMR: δ_H: 9.38 (d, 4.5 Hz, 1H), 9.29 (t, 7.3 Hz, 1H), 8.74 (brs, 1H), 8.62 (d, 1.8 Hz, 1H), 8.25 (m, 1H), 8.24 (m, 1H), 8.20 (dd, 8.4, 1.8 Hz, 1H), 7.65 (t, 8.0 Hz, 1H), 7.42 (d, 8.4 Hz, 1H), 4.20 (m, H), 2.43 (m, 2H), 2.31 (m, 1H), 2.15 (m, 1H). Elemental Anal. Calcd：C，52.99; H, 3.43; O, 27.45; N, 10.29; Na, 5.63. Found：C，52.94; H, 3.46; O, 27.48; N, 10.23; Na, 5.69%.

D$_7$: $C_{25}H_{21}O_7N_3S$, dark-blue powder, λ_{max} = 634 nm. IR (KBr): 2847 cm^{-1}, 2741 cm^{-1} (double $\upsilon_{C\text{-}H}$ of the aldehyde), 2743 cm^{-1} (quinone $\upsilon_{C=O}$), 1624cm^{-1} ($\upsilon_{\text{-}NH\text{-}}$), 1577cm^{-1} ($\upsilon_{\text{-}NH2}$). ESI-MS, *m/z*: 506.11 $[M\text{-}H]^-$.^1H NMR: δ_H: 9.31 (d, 4.6 Hz, 1H), 9.25 (t, 7.1 Hz, 1H), 9.16 (brs, 1H), 8.15 (m, 1H), 8.13 (m, 1H), 8.09 (m, 1H), 8.08 (m, 1H), 7.75 (brs, 1H), 7.59 (s, 1H), 7.21 (m, 1H), 6.89 (m, 1H), 6.43 (m, 1H), 6.30 (m, 1H), 3.65 (m, 1H), 2.64 (m, 2H), 1.97 (m, 2H). Elemental Anal. Calcd：C，59.22; H, 4.14; O, 22.09;N, 8.28; S, 6.32. Found：C，59.17; H, 4.11; O, 22.07; N, 8.26; S, 6.29%.

D$_8$: $C_{25}H_{19}O_9NS$, purple-red powder, λ_{max} = 498 nm. IR (KBr): 2851 cm^{-1}, 2745

cm^{-1} (double $\upsilon_{C\text{-}H}$ of the aldehyde), 2741cm^{-1} (quinone $\upsilon_{C=O}$), 1620cm^{-1} ($-SO_3$), 1465cm^{-1} ($\upsilon_{Ar\text{-}NH2}$). ESI-MS, *m/z*: 508.25 $[M\text{-}H]^-$. ^{1}H NMR: δ_H: 9.41 (d, 4.6 Hz, 1H), 9.27 (t, 7.3 Hz, 1H), 8.10 (m, 1H), 8.07 (m, 1H), 8.04 (m, 1H), 8.00 (m, 1H), 7.50 (s, 1H), 7.20 (d, 8.2 Hz, 2H), 6.87 (d, 8.2 Hz, 2H), 4.27 (m, 1H), 2.64 (m, 2H), 2.35 (m, 1H), 2.14 (m, 1H). Elemental Anal. Calcd：C，58.99; H, 3.73; O, 28.29;N, 2.75; S, 6.29. Found：C, 58.93; H, 3.76; O, 28.25; N, 2.79; S, 6.25%.

D$_9$: $C_{25}H_{21}O_{10}N_3S_2$, black powder, UV-Vis analysis indicated it had an mean absorption within 400-600nm. IR (KBr): 2858 cm^{-1}, 2795 cm^{-1} (double $\upsilon_{C\text{-}H}$ of the aldehyde), 2733cm^{-1} (quinone $\upsilon_{C=O}$), 1489cm^{-1} ($-SO_3$), 1498cm^{-1} ($\upsilon_{Ar\text{-}NH\text{-}Ar}$). ESI-MS, *m/z*: 586.32 $[M\text{-}H]^-$. ^{1}H NMR: δ_H: 9.07 (d, 4.8 Hz, 1H), 9.05 (t, 4.9 Hz, 1H), 8.10 (brs, 1H), 8.06 (m, 1H), 8.04 (m, 1H), 7.83 (m, 1H), 7.67 (d, 6.4 Hz, 1H), 7.65 (brs, 1H), 7.52 (d, 6.5 Hz, 1H), 6.45 (dd, 6.5, 1.8 Hz, 1H), 6.41 (d, 1.8 Hz, 1H), 5.91 (brs, 1H), 5.40 (brs, 1H), 4.01 (m, 1H), 2.35 (m, 2H), 2.14 (m, 2H). Elemental Anal. Calcd：C，51.15; H, 3.58; O, 27.26;N, 7.16; S, 10.63. Found：C，51.12; H, 3.61; O, 27.24; N, 7.19; S, 10.61%.

The above analysis data not only identified the target products, but confirmed the feasibilities of the synthesis routes also.

3.2 The application properties of dyes

3.2.1 The advantage for the dyeing process of the dyes

Unlike the normally used reactive dyes, aldehyde reactive dyes don’t hydrolysis during storage and application process. The dyeing practice of the nine aldehyde reactive dyes showed that, they could dye wet-white leather at a condtion of 35-45 °C, pH=4.0-6.5 within 1.5 h, this condition is relatively mild comparing with the commonly used reactive dyes at present; and what was more, no neutral salts were needed during the dyeing process. So, enegy would be saved and the environmental pollution from waste water could be reduced.

3.2.2 The *S*、*E*、*F*、*R* values and Washing fastness

From Table 1, we could notice that, *S*、*E*、*F*、*R* values of the five reactive dyes with glutaraldehyde back-bone were superior than that of mono-aldehyde reactive dyes. Nevertheless, washing fastness values for all of the nine reactive dyes reached 4 grade and possessed the fundamental property of reactive dyes; the washing fastness values of the five reactive dyes with glutaraldehyde back-bone reached 5 grade, i.e., the highest grade.

Table 1 Values of *S*、*E*、*R*、*F* and washing fastness of nine reactive dyes (mean of values from three experiment times)

Dye number	*S*/%	*E*/%	*R*/%	*F*/%	Washing fastness (grade)
D_1	52.54	57.87	48.35	52.17	4
D_2	55.73	61.07	50.94	56.21	4
D_3	60.35	65.27	53.74	59.86	4
D_4	58.43	63.21	51.25	57.33	4
D_5	84.22	91.37	82.05	83.27	5
D_6	85.47	88.33	82.85	84.12	5
D_7	83.26	90.65	81.93	86.14	5
D_8	82.54	89.77	81.47	85.92	5
D_9	85.25	92.13	82.76	84.32	5

4 Conclusions

(1) The analysis results from FTIR、UV-Vis、ESI-MS indicated that, some colorant compounds such as alizarin red and alizarin yellow GG could be “graft” to the back-bone of glutaraldehyde or some mono-aldehyde, so that a novel series of aldehyde reactive dyes could be developed.

(2) The dyeing practice to wet-white leather indicated that, without the adding of neutral salts, the dyeing process could be undertaken at a relatively mild condition of 35-45 °C, pH=4.0-6.5 within 1.5 h; all of the washing fastness values of the nine reactive dyes reached 4 grade and possessed the fundamental property of reactive dyes.

(3) *S* (substantivity), *R* (reactivity)，*E* (exhaustion) and *F* (fixation) values of the five reactive dyes with glutaraldehyde back-bone were superior than that of mono-aldehyde reactive dyes, and their washing fastness values reached the highest grade, i.e., 5 grade.

The authors wish to thank National Natural Science Foundation (“The color-forming mechanism and structural — property relationship for natural iridoids and their structural-like synthesis products”, Project No. 21176202) for financial support.

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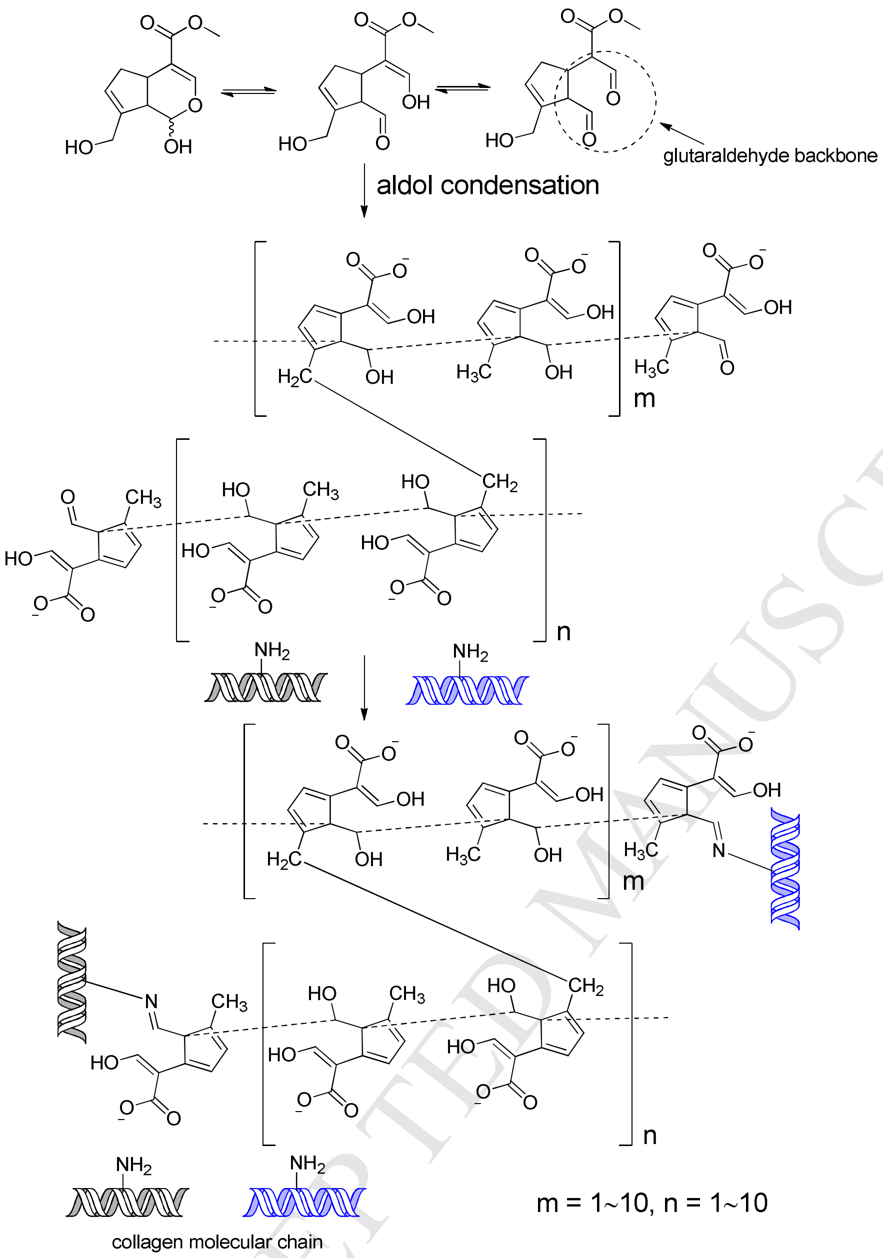
thesis of Southwest University for nationalities, Chengdu, China (2014)

List of Figures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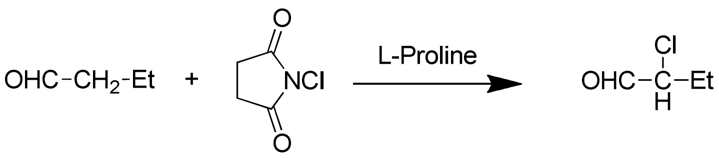
aldol condensation
m
n
m
n
collagen molecular chain
m = 1~10, n = 1~10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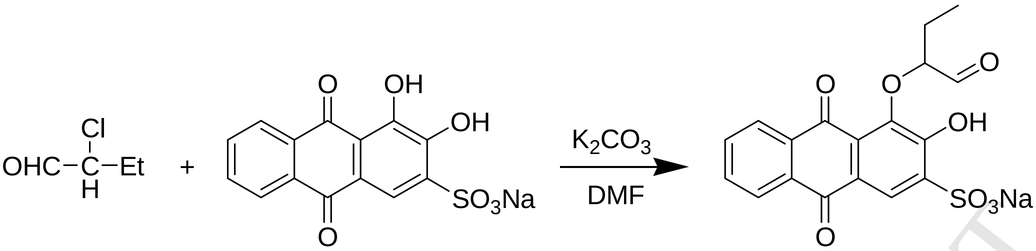
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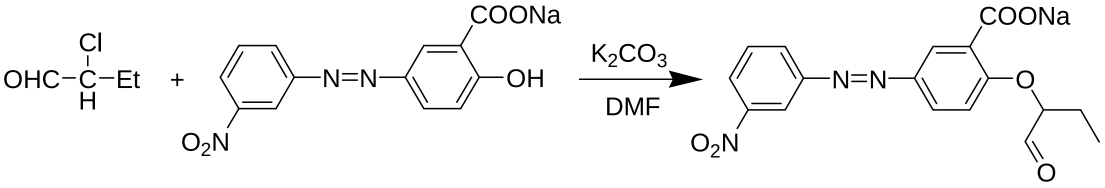
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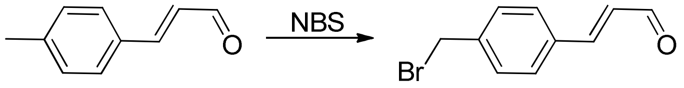
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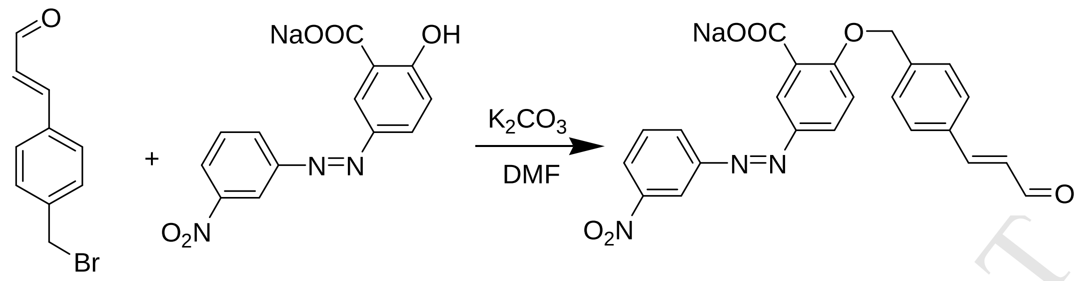
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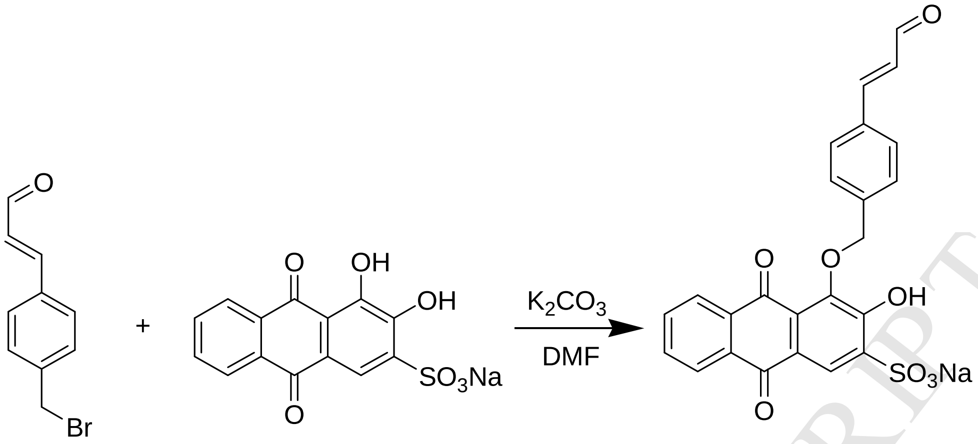
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O
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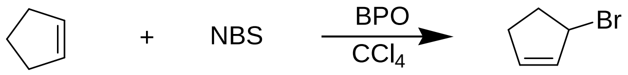
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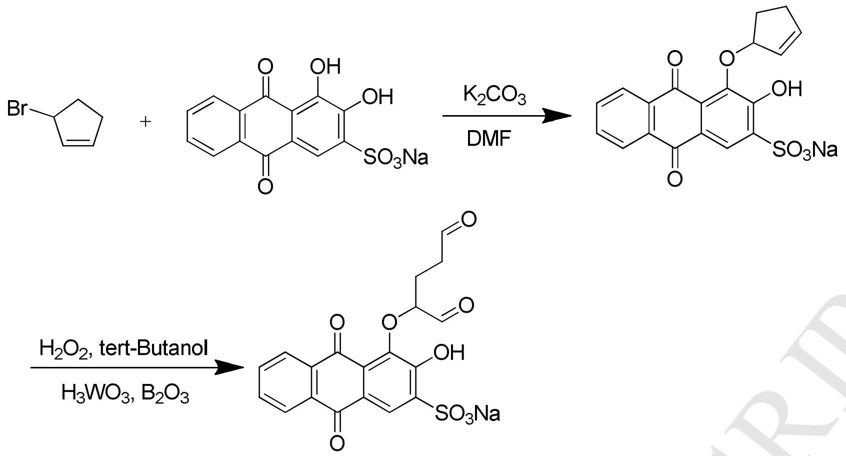
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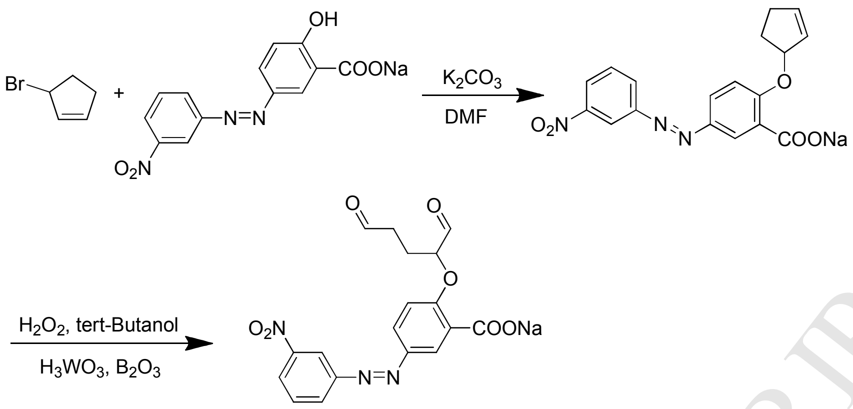
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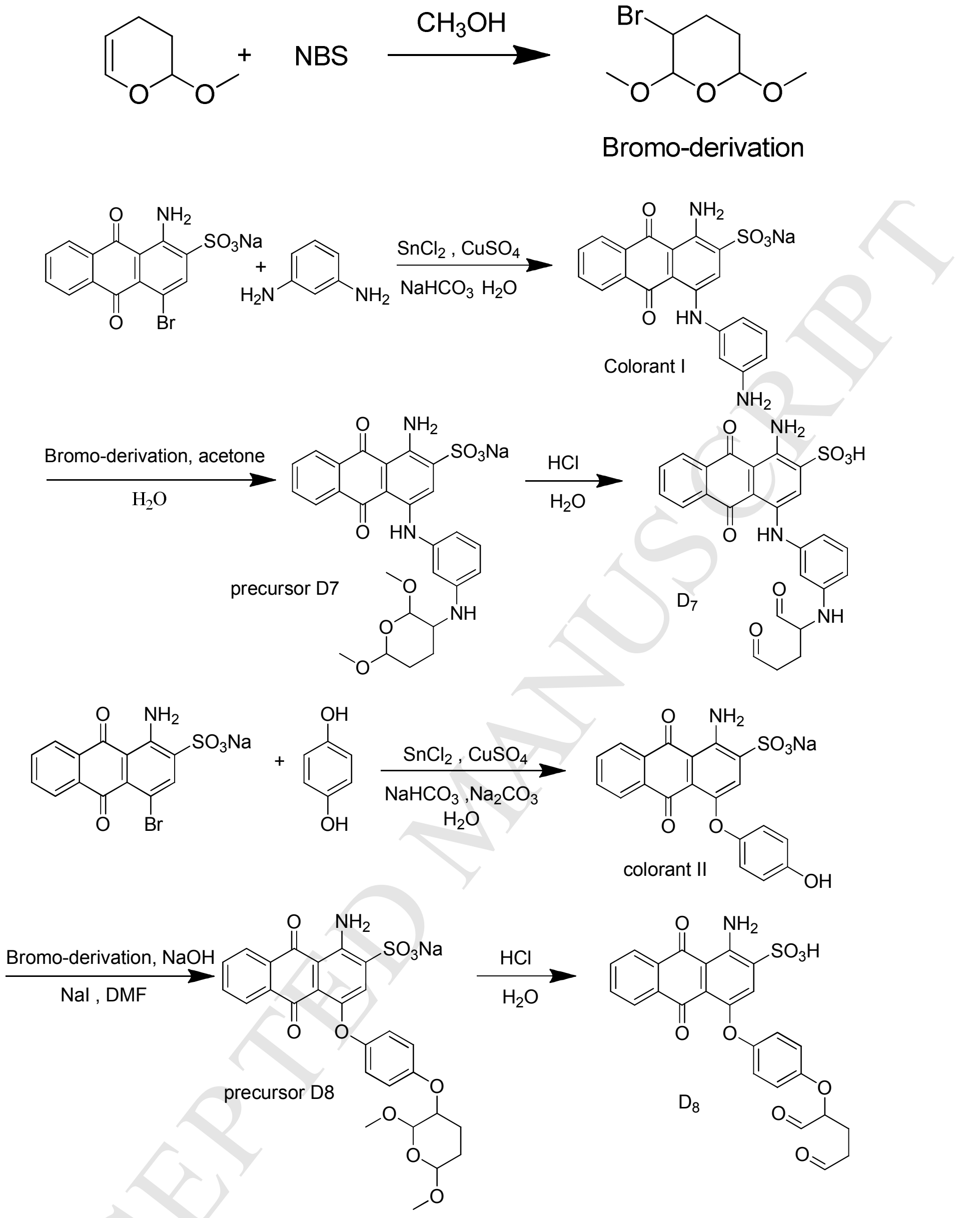
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Bromo-derivation
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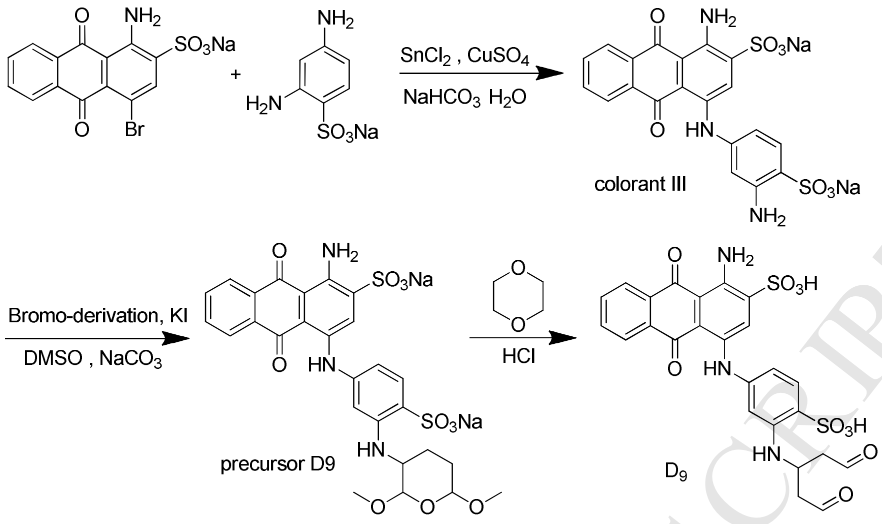
NaHCO3 H2O
HN
Colorant I
Bromo-derivation, acetone
H2O
precursor D7
NH
HCl
H2O
SO3H
D7
OH
SnCl2 , CuSO4
NaHCO3 ,Na2CO3
H2O
colorant II
Bromo-derivation, NaOH
NaI , DMF
precursor D8
HCl
H2O
D8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precursor D9
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D9
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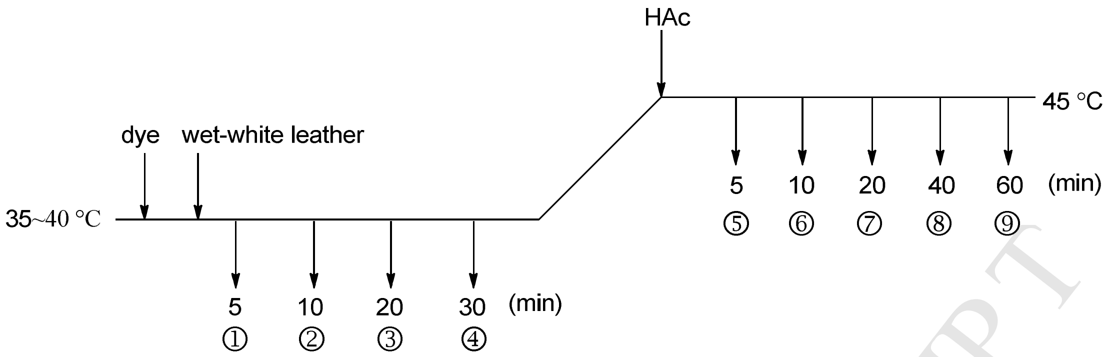
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dye
wet-white leather
35~40 °C
5
10
20
30
(min)
①
②
③
④
5
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20
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60
(min)
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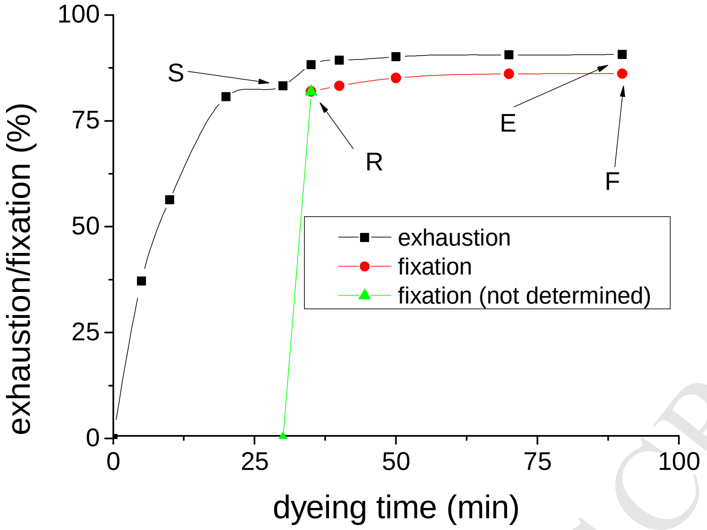
⑥
⑦
⑧
⑨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25
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exhaustion/fixation (%)
dyeing time (min)
S
R
E
F
exhaustion
fixation
fixation (not determined)

- -CHO was introduced into reactive dyes as reactive group for the first time.
- Nine aldehyde reactive dyes were synthesized and identified.
- These dyes could dye leather at mild conditions without adding of neutral salts.
- The dyed leather possessed a satisfactory washing-fastness.
- These dyes do not hydrolysis during the process of storage and application.