Hair Colouring by the Use of Dyestuffs Formed by Oxidation of (+)-Catechin Combined with Photosensitisers Absorbing Visible Light

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Abstract

Hair colouring by using dyestuffs formed by the oxidation of (+)-catechin (Cat.) under light irradiation was studied and the oxidation system was combined with photosensitisers which absorb visible light and generate oxidants. Rose bengal (RB) and Methylene Blue (MB) were used as the visible light photosensitiser. Hair was treated with the solutions containing them and was irradiated with artificial sunbeam in dry condition or in Cat. aqueous solution. It was found that hair is not coloured when it is pretreated with the aqueous solutions containing Cat., RB and MB, and irradiated with the light in the dry condition (dry system). In contrast, hair is coloured most when it is pretreated with the solutions containing RB and MB, and then irradiated with the light in Cat. aqueous solution (wet system). The RB and MB in hair may promote the oxidation of Cat. and production of colourants to give better colouration results, when the treated hair is irradiated with visible light in the solution condition.

Key Words: Hair colouring, (+)-Catechin, Oxidation, Photosensitisier, Visible light

1. Introduction

A milder and safer hair dying technique is desired because the general oxidation hair dye products contain some materials, which cause occasionally sensitization dermatitis and other dermatological symptoms after the dyeing [1 - 4]. The author group has been studying hair colouring by using biobased materials in order to invent a novel milder and safer dyeing technique, which is desired. It was found thereupon that the oxidation products of (+)-catechin (Catechinone), which is contained in tea or several plants, dye white hair yellow, orange and reddish brown [5 - 7]. The dyestuffs are obtained by enzymatic and chemical oxidation processes. The resulting colour of hair can be controlled by the dyeing conditions such as temperature, pH, additives, treatment way, oxidation method, and the colour fastness of the dyed hair to washing and light is high enough. On the other hand, the enzymes used for the dying are still expensive and the careful handling of them is needed. The chemical dying technique requires continuous O₂ gas supply for a long time throughout the dying and this is not practically so useful for low-cost hair dying. Therefore, another colouring technique also should be investigated and be invented to realise safer practical hair dying.

In the study, the oxidation of (+)-catechin (Cat.) under light irradiation was tried to obtain colourants and to colour hair. The oxidation system was combined with photosensitisers which absorb visible light and generate oxidants. Such a technique has advantages. The visible lights such as sunbeam and artificial illumination light from many light sources can be utilised for the technique. People receive visible light on a daily basis and if such light is applied for the hair dyeing, it can contribute to the efficient use of daily light energy. It is expected that a slow hair dyeing by the use of visible light may reduce deleterious effects on human body and could contribute to improve the safety. Rose bengal (RB) [8, 9] and Methylene Blue (MB) [10] were used as the visible light photosensitiser in the study. RB is used as a food dye and MB is used for intravital staining. Hair was treated with the solutions containing with or without Cat. and each of or both of them, and then was irradiated with artificial sunbeam in dry condition (dry system). Hair was also pretreated with the solutions containing each of or both of them, and was irradiated with the light in Cat. aqueous solution (wet system). The relationships between the treatment conditions and the colouration results were investigated in order to find an optimum condition for the effective colouration of hair.
2. Experimental

2.1 Materials

(+) - Catechin hydrate (Cat.; Sigma-Aldrich, \( M_a = 290.27 \) (anhdydrous basis)), rose bengal (RB; Nacalai Tesque (Nacalai), \( M_a = 1017.64 \) (sodium salt)) and Methylene Blue (MB; Nacalai, \( M_a = 373.90 \) (C\(_{16}\)H\(_{18}\)N\(_3\)SCl-3H\(_2\)O)) were used without further purification.

The human hair samples (Beaulax, healthy white hair obtained from Asians) were bundled by a nylon band and washed five times with 600 ml of distilled water at 40 °C for 10 min. The hair samples were air-dried and kept under 18 % of humidity before use.

2.2 Hair dyeing

2.2.1 Light irradiation treatment in dry system

Each of the (1) Cat. (4.0 mM), (2) RB (0.20 mM), (3) Cat. (4.0 mM) / RB (0.20 mM), (4) MB (0.010 mM), (5) Cat. (4.0 mM) / MB (0.010 mM), (6) RB (0.10 mM) / MB (0.010 mM) and (7) Cat. (4.0 mM) / RB (0.10 mM) / MB (0.010 mM) aqueous solutions was prepared with distilled water as treatment solutions. A bundled hair (0.10 mM) / MB (0.010 mM) aqueous solutions were prepared with distilled water as treatment solutions. The coloration species in order to compare the colouring results. The colours of hair samples treated with the solutions which contain RB and/ or MB turn pink, blue or reddish purple, because RB and MB are

2.2.2 Light irradiation treatment in wet system

The (9) RB (0.10 mM), (10) MB (0.010 mM) and (11) RB (0.10 mM) / MB (0.010 mM) aqueous solutions were prepared with distilled water as treatment solutions. A bundled hair (0.8 g) was immersed into each of the treatment solutions (100 g) and the treatment bottles were shaken in the dark 40 °C for 40 min. The liquor ratio was 125 : 1. The treated hair was dried by inserting between two sheets of filter paper and was immersed into 500 ml of 4.0 mM Cat. aqueous solution in a polystyrene cell culture flask. The flask was irradiated with the artificial sunbeam by the SUNTEST XLS+ (light total intensity: 765 W m\(^{-2}\)). The flask transmits light with the wavelength being longer than 300 nm. The temperature of the Cat. solution was 25 °C before the irradiation and 50 °C at 4 h of the irradiation time. The hair was air-dried after a fixed time of irradiation.

2.3 Measurements

The colour and spectrophotometric of treated hair samples were measured by a Konica Minolta CM-2600D spectrophotometer employing 10°-view angle, CIE standard illuminant D65, and specular component included (SCI) mode. All reflected lights from a sample including the regular reflection are integrated and received under the SCI mode of the equipment. The measurements at the areas of a hair sample were made three times and arithmetic mean values were calculated. The obtained colour values were expressed in \( L^*a^*b^* \) standard colourimetric system (CIE 1976). The \( L^* \) is the lightness index, and \( a^* \) and \( b^* \) are the chromaticity coordinates. The positive values of \( a^* \) indicate red colours and its negative values indicate green ones, and the positive values of \( b^* \) indicate yellow ones and its negative values indicate blue ones. The \( K/S \) value is defined from Kubelka-Munk theory \([11, 12]\) and calculated as \( K/S = (1 - R_s)^2 / 2R_s \), where \( K \) is the absorption coefficient, \( S \) the scattering coefficient and \( R_s \) the reflectance of the light at a wavelength \( \lambda \). Higher \( K/S \) value indicates higher intensity of a colour, i.e., deeper colour or higher optical density of colour. The measurements of hair colour were conducted at five points of each sample (measured area: 3 mm\(^2\)). The arithmetic mean was calculated from the obtained values excluding outliers.

3. Results and Discussions

3.1 Light irradiation treatment in dry system

The white hair dyed with catechinone shows orange or reddish orange yellow, orange and reddish brown as described above \([5, 6]\). The targeted colours of the resulting hair samples treated with light irradiation are colours like those obtained in the previous studies. The colour values of the targeted ones are as follows: \( L^* \): 40 - 50, \( a^* \): 10 - 17 and \( b^* \): 25 - 52 \([6]\). While the colour of the hair sample treated only with the Cat. solution scarcely changes, those of the hair samples treated with the solutions which contain RB and/ or MB turn pink, blue or reddish purple, because RB and MB are colourants. The hair samples were treated with aqueous solutions, which contained the systematically different combinations of the species in order to compare the colouring results. The colours of hair samples due to RB and MB fade away with the light irradiation. It was not observed that the colour of the hair samples treated in the dry system turns to the targeted ones with the light irradiation for 18 h. The obtained average colour values for the hair samples before the pretreatment with each of the solutions are as...
follows: $L^*$: 70, $a^*$: 3.5, $b^*$: 23. The obtained colour values for the hair samples before light irradiation (after the pretreatment), at 3 h of light irradiation and at 18 h of light irradiation are summarised in Table 1. The results show that $L^*$ value for hair decreases a little after the treatment with Cat. solution, it is distributed from 43.3 to 51.8 after the treatment with the solutions containing RB and/or MB. The $a^*$ value increases from ca. 3 - 4 after the treatment with the solutions containing RB, especially highly with RB only or Cat./RB, and $a^*$ value shows negative ones after the treatment with the solutions containing MB only or Cat./MB. The $b^*$ value decreases from 21 - 24 to negative values after the treatment with the solutions containing RB and/or MB and decreases to a great extent after the pretreatment with the solutions containing RB / MB. The $L^*$ for the hair treated only with the Cat. solution (1) decreases a little with light irradiation time $t$ (64.0 at 18 h). The $L^*$ for the hair treated with the solutions containing the photosensitisers (2 - 7) increases with $t$ and the values even at $t =$ 18 are larger than those of the targeted one. The $a^*$ and $b^*$ for the hair treated only with the Cat. solution change very little with $t$. The $a^*$ for the hair treated with the solutions containing RB decreases (2, 3, 6, 7) and it for MB only or Cat./MB solution (4, 5) increases slightly with $t$. All of the $a^*$ values at $t =$ 18 are smaller than the targeted ones. The $b^*$ for the solutions containing the photosensitisers increases with $t$ and the values at $t =$ 18 are also smaller than the targeted ones.

The spectrophotometric of the samples was measured and their $dK/dS$ spectra were obtained. The $K/S$ spectra of hair samples dyed with catechins show higher values below 500 nm [7]. The $K/S$ spectra of the hair samples treated with the solution containing RB and/or MB show signal peaks at 560 nm (RB) and 670 nm (MB), which are not the index of the hair dyeability. Both of the signals decrease with the light irradiation. The $K/S$ value at 430 nm ($K/S_{430}$) is chosen to evaluate the dyeability of hair in the study. This is because there are reasons. The highest signal in the visible region of the $K/S$ spectrum for the hair treated with RB or MB covers chiefly the wavelength from 460 to 740 nm and the signal decreases with the light irradiation due to the decay of RB and MB. Therefore, a $K/S$ value at from 380 to 450 nm in the visible region should be used for monitoring the colouration of the hair samples. The large change in the $K/S$ value is favourable to monitoring the colouring process. However, the $K/S$ value change is larger at shorter wavelength for hair treated with Cat.+RB+MB and irradiated in the dry system, whereas it is larger at longer wavelength for hair treated with Cat. only and irradiated in the dry system, hair without treatment and irradiated in the wet system to be described, and hair treated with RB+MB and irradiated in the wet system. Moreover, it was found that the $K/S$ values at 440 and 450 nm are influenced by the decay of RB and MB in some sample systems. It was finally concluded by taking into account the results that $K/S_{430}$ is adopted and used in the figures of the report. The light irradiation time ($t$) course of $K/S_{430}$ for the hair samples treated in the dry system is shown in Fig. 1. All of the $K/S_{430}$ values for the samples scarcely change with $t$ as shown in the figure.

It is concluded that hair is not coloured by the light irradiation treatment in dry system. The adsorption of Cat. onto hair in the pretreatment process and/or the production of colourants in the dried hair under the light may not proceed effectively in the system. The distribution and the positional relationships of Cat., RB and MB in hair should be appropriate for the effective colouration in dry condition, because they cannot move to react under such condition.

### 3.2 Light irradiation treatment in wet system

The light irradiation in wet condition was then tried to colour hair according to the results obtained by the light irradiation treatment in the dry system. As described above, RB and MB work as colourants. If the light irradiation to hair pretreated with Cat. solution is made in the RB and/or MB solution, they might be adsorbed onto hair too much during the irradiation process, and they might absorb light chiefly in the vicinity of the solution surface and the effective oxidation and production of colourants from Cat. at hair could not proceed. The colouration of hair with RB and/or MB is not the purpose of the study, and the colour due to RB and MB fade away easily under light. Therefore, the light irradiation to hair pretreated with the RB and/or MB solutions was performed in Cat. aqueous solution first of all in the study.

The hair samples, which were untreated, treated with RB solution, treated with MB solution and treated with RB / MB solution were immersed into Cat. aqueous solution and irradiated with light in wet system. The hair samples treated with the solutions which contain RB and/or MB turn pink, blue or reddish purple as mentioned above. The colours of hair due to RB and MB fade away with the light irradiation in a similar manner as the dry system. The colour of the untreated hair turns light brown (8), that of the hair treated with RB turns from pink to reddish brown (9), that with MB turns from blue to pale gray (10), that with RB / MB turns from
reddish purple to deep reddish brown (11) with the light irradiation for 4 h. It was observed that the obtained colours of the hair samples pretreated with the solution containing RB are close to those of the targeted one. The colour obtained in the system containing MB only is not well favourable one, whereas the colours obtained by the RB system are favourable ones. The obtained colour values for hair samples before light irradiation (after the pretreatment), at 3 h of light irradiation and at 4 h of light irradiation are summarised in Table 1. The results show that $L^*$ value for the untreated hair decreases from 69.6 to 56.8 at $t = 4$ h. On the other hand, the $L^*$ for the hair treated with the photosensitiser solutions decreases more with $t$ under the light and the value for the hair pretreated with RB / MB is 46.6 at $t = 4$. This value is slightly larger than that of the targeted one. However, it is sufficiently low for practical uses. The change in $a^*$ and $b^*$ with $t$ for the hair treated with RB / MB is large in contrast to that for the untreated hair, where it is very small. The $a^*$ values of the hair samples pretreated with the solution containing RB at $t = 4$ h are close to those of the targeted one, while the $b^*$ values of the hair samples pretreated with the solutions containing RB at $t = 4$ h are smaller than those of the targeted one, it was found that the values increase with time and approach the targeted one under light after the hair dried.

The light irradiation time course of $K/S_{430}$ for the hair samples treated in the wet system is shown in Fig. 2. All of the $K/S_{430}$ values for the samples increase with $t$ as shown in the figure. The $K/S_{430}$ for the hair samples pretreated with the solution containing RB / MB increases most steeply and the values are highest at $t = 3$ and 4 h. The $K/S_{430}$ values of the hair samples pretreated with the photosensitiser solutions are higher at $t = 4$ h than that of the untreated one. These results show that the treatment of hair with RB and/or MB solution promotes the colouration of the hair under light irradiation in wet system. This indicates that such photosensitisers contribute to the effective oxidation of Cat. to give colourants. The highest colouration is obtained by the solution containing both of the RB and MB. This indicates that light with broader wavelength could be utilised to oxidise Cat. and it contributes to produce higher amount of colourants, when RB is combined with MB. In

![Fig. 2 Time course of $K/S_{430}$ for hair samples irradiated with artificial sunbeam in wet condition.](image)

Table 1 $L^*$, $a^*$ and $b^*$ values of hair samples treated in dry system and wet system before light irradiation, at 3 h irradiation, at 18 h irradiation (dry system) and at 4h irradiation (wet system).

<table>
<thead>
<tr>
<th>Sample before light irradiation treated with</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>before light irradiation</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) 4.0 mM Cat.</td>
<td>67.9</td>
<td>3.58</td>
<td>20.9</td>
<td>63.8</td>
<td>3.07</td>
<td>18.2</td>
<td>64.0</td>
<td>3.41</td>
<td>17.8</td>
</tr>
<tr>
<td>(2) 0.20 mM RB</td>
<td>50.4</td>
<td>34.4</td>
<td>-5.10</td>
<td>59.5</td>
<td>14.6</td>
<td>9.50</td>
<td>67.9</td>
<td>3.74</td>
<td>17.8</td>
</tr>
<tr>
<td>(3) 4.0 mM Cat. / 0.20 mM RB</td>
<td>47.8</td>
<td>32.3</td>
<td>-5.18</td>
<td>55.0</td>
<td>16.4</td>
<td>6.03</td>
<td>62.2</td>
<td>5.47</td>
<td>14.8</td>
</tr>
<tr>
<td>(4) 0.010 mM MB</td>
<td>51.8</td>
<td>-15.4</td>
<td>-5.74</td>
<td>51.0</td>
<td>-12.1</td>
<td>-2.46</td>
<td>53.9</td>
<td>-8.06</td>
<td>1.86</td>
</tr>
<tr>
<td>(5) 4.0 mM Cat. / 0.010 mM MB</td>
<td>48.2</td>
<td>-14.4</td>
<td>-4.05</td>
<td>49.3</td>
<td>-12.4</td>
<td>-1.68</td>
<td>52.8</td>
<td>-8.95</td>
<td>1.85</td>
</tr>
<tr>
<td>(6) 0.10 mM RB / 0.010 mM MB</td>
<td>43.3</td>
<td>15.6</td>
<td>-14.7</td>
<td>44.2</td>
<td>9.57</td>
<td>-6.62</td>
<td>53.6</td>
<td>4.46</td>
<td>3.37</td>
</tr>
<tr>
<td>(7) 4.0 mM Cat. / 0.10 mM RB / 0.010 MB MB</td>
<td>45.0</td>
<td>13.5</td>
<td>-11.0</td>
<td>48.8</td>
<td>8.20</td>
<td>-2.00</td>
<td>58.8</td>
<td>2.96</td>
<td>9.87</td>
</tr>
<tr>
<td>Dry system</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8) Nothing (Untreated)</td>
<td>69.6</td>
<td>3.07</td>
<td>21.9</td>
<td>58.4</td>
<td>6.64</td>
<td>17.2</td>
<td>56.8</td>
<td>6.52</td>
<td>17.3</td>
</tr>
<tr>
<td>(9) 0.10 mM RB</td>
<td>53.1</td>
<td>28.1</td>
<td>-1.81</td>
<td>55.0</td>
<td>10.5</td>
<td>13.8</td>
<td>51.5</td>
<td>10.9</td>
<td>13.9</td>
</tr>
<tr>
<td>(10) 0.010 mM MB</td>
<td>51.7</td>
<td>-15.4</td>
<td>-5.74</td>
<td>48.9</td>
<td>-0.73</td>
<td>8.50</td>
<td>49.3</td>
<td>0.245</td>
<td>11.9</td>
</tr>
<tr>
<td>(11) 0.10 mM RB / 0.010 mM MB and light-irradiated in Cat. aqueous solution</td>
<td>43.3</td>
<td>15.6</td>
<td>-14.7</td>
<td>45.2</td>
<td>11.6</td>
<td>6.50</td>
<td>46.6</td>
<td>9.10</td>
<td>8.94</td>
</tr>
<tr>
<td>Wet system</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(12) 0.10 mM RB / 0.010 mM MB and light-irradiated in water (without Cat.)</td>
<td>43.3</td>
<td>15.6</td>
<td>-14.7</td>
<td>65.0</td>
<td>1.12</td>
<td>13.2</td>
<td>66.8</td>
<td>1.51</td>
<td>16.0</td>
</tr>
</tbody>
</table>
fact, RB and MB absorb visible light between 460 and 580 nm and between 480 and 700 nm in aqueous solution, respectively. The wet condition throughout the light irradiation also works favourably for the colouration of hair. Hair is coloured in the process that the active oxidants generated from RB and MB by the light irradiation react with Cat. to give colourants and they penetrate into hair matrixes and are adsorbed onto hair. It is thought that the Cat. solution gives favourable condition for the process and the colouration proceeds effectively. It could be said that the continuous supply of Cat. from the solution to the process throughout the light irradiation treatment might also increase the hair colouration. Higher efficiency of the colouration and more effective hair dyeing will be pursued as a future study by the authors.

4. Conclusions

Hair is not coloured, when it is treated with the aqueous solutions containing (+)-catechin, rose bengal and Methylene Blue, and then irradiated with artificial sunbeam in the dry condition. In contrast, hair is coloured, when it is pretreated with the aqueous solutions containing rose bengal and then irradiated with the light in (+)-catechin aqueous solution. The highest colouration is obtained for the hair pretreated with the aqueous solution containing both of rose bengal and Methylene Blue. It is concluded that the photosensitisers promote the colouration of hair, when hair pretreated with them is irradiated with visible light in the wet condition.

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References