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Relationship between Dyeing Condition and Dyeability in Hair Colouring by Using Catechinone Prepared Enzymatically or Chemically from (+)-Catechin

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Abstract

Hair colouring was carried out by using catechinone prepared from (+)-catechin by enzymatic or chemical oxidation reaction. The difference of dyeability between the catechinone produced by enzymatic reaction (EC) and that produced by chemical reaction (CC) was studied changing the dyeing condition such as dye concentration, dyeing temperature, pH or the sort and concentration of salts. The colour of the hair dyed by EC or CC at 30˚C is yellowish or reddish brown, respectively. The colour of the hair dyed by EC and CC is deeper at a higher dye concentration and at a higher temperature. Hair is dyed deepest by EC or CC at the solution pH = 6.04 or 5.45, respectively. The dyeability is increased by adding NaCl (≤4 M) or $CaCl_2$ (≤1 M), while it is decreased by adding $AlCl_3$. The colour fastness of the dyed hair to washing or ultraviolet light is high enough for practical use. Furthermore, it was found that colourants are obtained from tea extracts which contain catechin derivatives. Hair is dyed reddish brown by the colourants.

Keywords

Catechinone, Hair Dyestuff, Catechin, Dyeability, Tea Extract

1. Introduction

The authors have studied hair dyeing by using biobased materials (obtained from natural materials) to invent novel hair dyeing techniques, which are milder and safer for a human body and eco-friendly, in order to reduce

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the risks accompanying hair dyeing. This is because sensitisation symptoms, dermatitides and systemic symptoms are caused for some people by the use of the oxidation hair dyes [1]-[4]. Then it was found that a dyestuff, catechinone [5], can dye human hair yellow, orange and reddish brown, and the colour of human hair can be controlled by adding biobased materials such as natural pigments and amino acids. Catechinone is obtained from enzymatic oxidation of (+)-catechin which is contained in tea or several plants. The acute skin irritation study according to the OECD Guidelines for the testing of chemicals exhibited that catechinone does not cause skin troubles. The colour fastness to washing or daylight for the hair dyed by catechinone is high enough for practical use. The mechanisms of hair dyeing by catechinone, *i.e.* the dynamics of catechinone in the hair network, catechinone behaviours at fixation and so on, have not been clarified, because the structure of hair is extremely-complex. However, it is envisaged that the interaction between the dyestuffs and hair dye-sites can be van der Waals force, hydrogen bonding and covalent bonding.

The catechinone is also produced by chemical reaction [6] [7]. The chemical preparation of catechinone requires enough O_2 and it should be made in a basic solution for increasing the yield. The enzymatic preparation system is more specific and total reaction rate is higher than that of the chemical preparation [8]. On the other hand, the chemical preparation of catechinone has the advantages that the production condition is not so strict as compared with the enzymatic technique and the technique is economical because of without enzymes.

In the paper, the relationships between dyeing conditions such as the dye concentration of catechinone, dyeing temperature, pH or the sort and concentration of salts added and the dyeability for hair were studied comparing the enzymatically-produced catechinone (EC) with the chemically-produced one (CC). Then, the colour fastness to washing and ultraviolet (UV) light for the hair dyed by catechinone (EC and CC) was investigated. Furthermore, the authors tried to prepare hair dyestuffs from tea extracts, which contain (+)-catechin and catechin derivatives, by the chemical oxidation method, and their dyeability to hair was examined.

2. Experimental

2.1. Materials

(+)-Catechin hydrate (M_w = 290.27, Sigma) and Polyphenon® 70S (Mitsui Norin) were used without further purification. Sunphenon® EGCg, BG-3 and 90S were kindly provided from Taiyo Kagaku and the powders were used as such. The Polyphenon and Sunphenons are the extracts of green tea leaf (*Camellia sinensis*) obtained in India and Kenya and in China, respectively. They contain catechins of high concentration as shown in **Table 1** [9]. Tyrosinase from mushroom (M_w = 1.28×10^5 obtained by sedimentation velocity diffusion, 1.33×10^5 by

Table 1. Composition of catechins in tea extracts [9].

Product name	Polyphenon	Sunphenon		
	70S	EGCg	BG-3	90S
Lot No.	1008271	207051	210041	207311
	Catechins content(a)/wt%			
(+)-Catechin	2.2	0.1	2.7	1.4
(−)-Epicatechin	7.5	0.6	7.9	4.5
(−)-Gallocatechin	6.6	-	4.6	2.3
(−)-Epigallocatechin	18.2	-	16.2	3.8
(−)-Catechin gallate	0.7	-	-	0.8
(−)-Epicatechin gallate	8.9	3.9	7.4	11.9
(−)-Gallocatechin gallate	4.1	0.3	2.7	7.5
(−)-Epigallocatechin gallate	32.0	92.1	51.2	46.8
Total catechin content(a)	80.2	96.8	92.6	78.9
Total polyphenol content(b)	/(c)	≈100	90.8	92.0

(a): Measured by HPLC. The hyphen (-) indicates not detected. (b): Analysed by iron tartrate colourimetric method. (c): Not analysed.

light-scattering measurements and 1.20 × 10^5 by electrophoresis, Sigma) was used as received. Monoethanol amine (MEA, M_w = 61.08, Nacalai tesque), disodium hydrogen phosphate (Na_2HPO_4, F_w = 141.96, Nacalai) and sodium dihydrogen phosphate (NaH_2PO_4, F_w = 119.98, Nacalai) as pH regulators were used without further purification. Water was used after distillation and ethanol (M_w = 46.07, 99.5%, Nacalai) was used without further purification.

The human hair samples (Mathai Japan, obtained from Asians and decolourised white, length: 11 cm) were bundled by a nylon band and kept under a low humidity. Citric acid (CA, M_w = 192.12, Nacalai), hydrochloric acid (HCl, 35.0 - 37.0 wt%, M_w = 36.46, Nacalai), sodium hydroxide (NaOH, F_w = 40.00, Nacalai), sodium chloride (NaCl, F_w = 58.44, Nacalai), calcium chloride ($CaCl_2$, F_w = 110.98, Nacalai) and aluminium chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, F_w = 241.43, Nacalai) were used without further purification. *p*-Aminophenol (PAP, M_w = 109.13, Katayama Chemical Industries) as an oxidation dye precursor, 5-amino-*o*-cresol (5AOC, M_w = 123.16, Tokyo Chemical Industry) as an oxidation dye coupler and ammonia solution (28 wt%, Nacalai) as a pH regulator were used without further purification. Hydrogen peroxide aqueous solution (H_2O_2, 30 wt%, M_w = 34.01, Santoku Chemical Industries) as an oxidising agent was diluted 5 times with distilled water. Kao Blaune Hair Manicure D13 (colour name: tea brown) was used as a commercially available acid dye, which contains orange II (C.I. 15510, C.I. Acid Orange 7), naphtol blue black (C.I. 20470, C.I. Acid Black 1), acid red (C.I. 45100, C.I. Acid Red 52) and fast acid magenta (C.I. 17200, C.I. Acid Red 33). NLES-227 (Taiko Oil Chemicals) that contains 27 wt% of sodium dodecyloxypolyoxyethylene (*n* = 2) sulphate ($C_{12}H_{25}O\ (CH_2CH_2O)_2\ SO_3Na$) was used as anionic detergent for washing hair.

2.2. Dyestuff Preparation

2.2.1. Enzymatic Oxidation Method

The dyestuff preparation was started by adding 5 ml of tyrosinase (32 kU) phosphate buffer aqueous solution (0.1 M NaH_2PO_4/Na_2HPO_4, pH = 7.0) into 495 ml of (+)-catechin (2.4 mmol) aqueous solution, which was saturated with oxygen by introducing O_2 gas (≥ 99.5 vol%) for over 20 min at 30˚C. The concentration of (+)-catechin in the aqueous reaction solution was 4.8 mM. The reaction was performed under O_2 atmosphere at 30˚C, and 200 ml of ethanol was finally added into the reaction solution to stop the reaction. The reaction solution was filtered and the filtrate was evaporated at 50˚C under below 50 hPa to obtain the powder of catechinone dye. The enzymatically-produced catechinone is abbreviated again here as EC.

2.2.2. Chemical Oxidation Method

The 100 g of (+)-catechin (0.17 $mol \cdot kg^{-1}$) solution was prepared by using MEA (0.10 $mol \cdot kg^{-1}$) water/ethanol mixed solution. The ethanol mass fraction (w_E) and the molar fraction (x_E) in the mixed solution were 0.50 and 0.28, respectively. The reaction was set off by introducing O_2 gas into the (+)-catechin solution at 100 ml min^{-1} of flow rate at 30˚C. The solution was finally concentrated and then the resulting solid was ground to get catechinone dye powder. The chemically-produced catechinone is also abbreviated as CC.

2.2.3. Colourants from Commercial Tea Extracts

The colourant preparation from four kinds of tea extracts was carried out by the chemical oxidation method. Polyphenon 70S, Sunphenon EGCg, BG-3 or 90S was dissolved in MEA (0.50 $mol \cdot kg^{-1}$) water/ethanol solution (w_E = 0.45, x_E = 0.25). O_2 gas was introduced to 100 g of 5.0 wt% tea extract solution at 30˚C, and then the solution was finally evaporated to obtain powder.

2.3. Hair Dyeing

The bleached white hair (0.5 g or 1.0 g) was immersed into the dye solution (50 ml or 100 ml) containing fixed amount of the colourant from (+)-catechin (EC, CC) or tea extract without or with salt (NaCl, $CaCl_2$ or $AlCl_3$), and the solutions were shaken at 100 rpm of shaking speed for 40 min at 30˚C, 40˚C, 50˚C, 60˚C or 70˚C. The pH of the dyeing solution of EC or CC was adjusted by the addition of HCl and NaOH or citric acid, respectively. The dyed hair was washed with 0.27 - 0.81 wt% sodium dodecyloxypolyoxyethylene (*n* = 2) sulphate aqueous solution prepared from NLES-227 and rinsed with distilled water repeatedly at 30˚C or 40˚C. The hair was air-dried at room temperature.

In the oxidation dyeing, PAP (1.4 mmol), 5AOC (1.4 mmol) and ammonia (59 mmol) aqueous solution (50 g) and H_2O_2 (88 mmol) aqueous solution (50 g) were mixed, and then 0.5 g of hair was immersed into the mixed solution and it was shaken at 100 rpm at 30˚C for 40 min. In the dyeing by acid dye, the viscous dye solution was applied to the bundled hair by using a comb and the hair was allowed to stand at room temperature for 20 min. The dyed hairs were washed with 300 ml of distilled water with shaking at 100 rpm and 30˚C for 20 min repeatedly and were air-dried.

2.4. Measurements

The colour of hair was measured by a Konica Minolta CM-2600d spectrocolourimeter and the resulting colour was expressed in $L^*a^*b^*$ standard colourimetric system (CIE 1976). The colour measurements were made employing 10˚-view angle, CIE standard illuminant D_{65} and SCI mode. All the reflection light from the sample including the regular reflection are integrated under the SCI mode. The L^* is the lightness index, and a^* and b^* are the chromaticity coordinates. The positive values of a^* indicate red and the negative values of that indicate green, and the positive values of b^* indicate yellow and the negative values indicate blue. The C^* is the chroma calculated by $C^* = \{(a^*)^2 + (b^*)^2\}^{1/2}$. The measurements of the ultraviolet-visible (UV-Vis) absorption spectra for the dyestuff aqueous solution were made by a Hitachi U-3900H spectrophotometer at 25˚C. The degree of swelling of hair (q) is calculated by $q = m_s/m_d$, where m_s and m_d are the mass of the swollen and dried hair, respectively. The m_s and m_d were measured by a Mettler Toledo HG53 halogen moisture analyser at 120˚C for 15 min.

The colour fastness was estimated by the colour difference, ΔE^*, for the dyed hair between before and after repeatedly washed, or the colour difference for the hair between before and after under UV irradiation. The ΔE^* is calculated by $\Delta E^* = \{(L^*_t - L^*_i)^2 + (a^*_t - a^*_i)^2 + (b^*_t - b^*_i)^2\}^{1/2}$ where L^*_t, a^*_t, b^*_t, L^*_i, a^*_i, b^*_i are L^*, a^*, b^* of treated (washed or UV irradiated) and freshly-dyed hair, respectively. In the experiments for colour fastness to washing, the dyed hair was washed with 0.27 wt% sodium dodecyloxypolyoxyethylene ($n = 2$) sulphate aqueous solution at 30˚C for 20 min, rinsed twice with distilled water at 30˚C for 20 min and dried by a Yamato Scientific DN400 constant temperature oven at 45˚C for 1 h. The colour was measured by the spectrocolourimeter after every washing. The experiments for colour fastness to UV light for the dyed hair was made by using a Sen Lights HL100G high-pressure mercury lamp. The intensity of the light was 20.0 mW·cm^{-2} at 254 nm, 11.0 mW·cm^{-2} at 310 nm and 9.8 mW·cm^{-2} at 365 nm. The irradiation was performed for 10 h under ambient humidity. The colour was measured in the same way at each irradiation time.

3. Results and Discussion

3.1. Dyeability of EC and CC

Catechinone is prepared by both of the enzymatic oxidation in aqueous solution and the chemical oxidation in water/ethanol solution. The amount of the formed dye by the chemical method is over 20 times higher than that by enzymatic method, for the higher concentration of (+)-catechin in the water/ethanol reaction solution. However, the yield of catechinone by enzymatic preparation is 1.4 times higher than that by chemical preparation. The UV-Vis absorption spectra of EC and CC aqueous solution are approximately same but parts of the spectrum, especially at short wavelength (UV region), are little different. Both of the dyestuffs consist of catechinone (4-(3,4-dihydro-3*α*,5,7-trihydroxy-2*H*-1-benzopy-ran-2*α*-yl) 1,2-benzoquinone) chiefly and contain by-products [5]. The by-products are dimers, trimers and multimers, of which oxidised parts and their degrees are various. The results indicate that the EC and CC consist chiefly of catechinone and they may be different in the species and composition of the small amounts of by-products. The enzymatic oxidation reaction is specific and its rate is higher. Meanwhile, the chemical one proceeds longer under basic condition although the rate is lower than that of the enzymatic one [6] [8].

Figure 1 shows the photographs of undyed and dyed hair with EC or CC solution. The hair is coloured by both the catechinones, and the colour of EC-dyed-hair is more yellowish and vivid, while that of CC-dyed-hair is reddish brown and deeper.

The hair samples differ a little in the dyeability depending on the production lot, because the samples are human hair and, strictly speaking, no two are ever the same. Two kinds of hair differing in the lot, of which dyeability was slightly different, were used for the experiments. One was hair sample used for EC and another was for CC. Therefore, attention was focused on the tendency of the change in values of colour depending upon dyeing condition for each sample dyed by EC or CC rather than the absolute values.

(a) (b) (c)

Figure 1. Photographs of the part of undyed hair (a), and hair dyed with catechinone produced by enzymatic method (EC; (b)) and chemical method (CC, (c)). The dye concentration was 1.0 wt%.

The measured colour data expressed in chromaticity coordinates and in chroma-lightness index as a function of the dye concentration (c_D) are shown in **Figure 2**. The colour of the hair dyed by EC becomes more yellowish and reddish, and the a^* and b^* increase with c_D. On the other hand, the colour obtained by CC becomes more dull, and the a^* and b^* decrease gradually with c_D. The colour of the hair dyed by both catechinones is deeper at higher c_D and the L^* decreases with c_D. The change in the colour with c_D becomes gradual for 0.60 wt% and over of EC or 1.0 wt% and over of CC. The results show that the dyeability and the tendency of the variation in the colour with the dye concentration for CC are different from those for EC. The catechinone obtained by enzymatic method consists of mainly 4-(3,4-dihydro-3*α*,5,7-trihydroxy-2*H*-1-benzopyran-2*α*-yl) and by-products [5]. Then the results indicate the difference in the dyestuff composition for EC and CC. In fact, the enzymatic oxidation reaction is specific, whereas the chemical one is not so specific and the preparation time is longer [6].

3.2. Effect of Dyeing Temperature

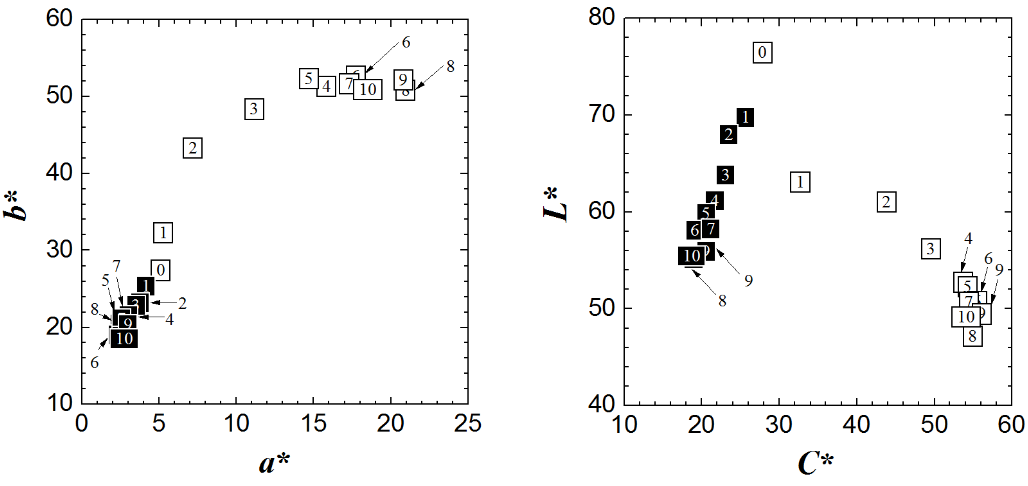
The heating effect on the dyeability of hair by catechinone was investigated in order to shorten the dyeing time. The colour of hair dyed by EC and CC at 30˚C - 70˚C for 40 min was measured.

The colour of hair dyed by 0.60 wt% and over of EC is about the same, and the same for 1.0 wt% and over of CC. Therefore, 0.6 wt% of EC and 1.0 wt% of CC were adopted in the temperature effect experiments taking into account also the little different dyeability of each hair sample as described above.

The results obtained by observation with the naked eye show that the colour of hair dyed by both of the EC and CC becomes deeper with an increase in the dyeing temperature. It was found that the dyeability for hair by using both of the EC and CC solution increases with increasing temperature, and the dyeing time required decreases. **Figure 3** shows the L^*, a^* and b^* for the hair dyed by EC or CC for 40 min as a function of the dyeing temperature (T). The data values obtained at 30˚C differ a little from the values shown in **Figure 2**. This was caused by the variation of the dyeability of hair samples.

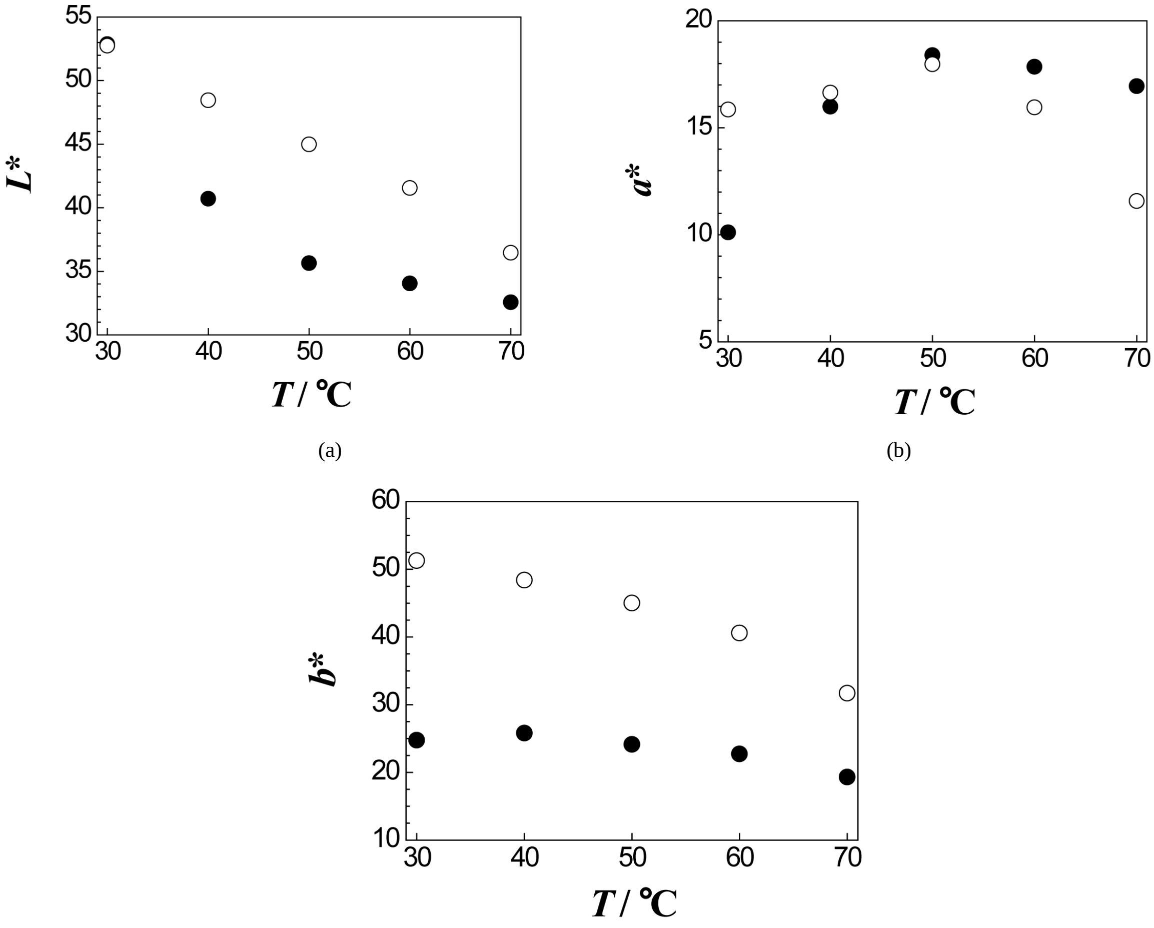
The L^* for the EC- and CC-dyed hair decreases with T. The a^* slightly increases with T up to 50˚C and it decreases over 50˚C for EC-dyed hair. The changing behaviour of a^* for CC-dyed hair is similar to that forEC-dyed one though the magnitude of the change at lower temperatures is larger than that at higher temperature. The b^* for EC- and CC-dyed hair decreases monotonously with T. It can be said that dyeability for hair by both of the EC and CC solution increases with increasing temperature up to 70˚C.

The higher temperature is favourable for accelerating the dyestuff molecules diffusion in a diffusion medium (here this is hair) and depresses dye adsorption onto dye-sites and the fixation in general. However, the amount of catechinone dye molecules fixed on hair has not determined and dyeing process has not clarified. It can be said at least that the dyestuff molecules diffusion dominates the dyeability for the catechinone hair dyeing sys-



(a) (b)

Figure 2. Chromaticity coordinates (a) and chroma-lightness index (b) relationships for hair dyed by EC at 30˚C for 40 min (□) and that dyed by CC (■), and undyed one (0). The dye concentration (c_D) is 0.10 (1), 0.15 (2), 0.30 (3), 0.60 (4), 0.80 (5), 1.0 (6), 1.2 (7), 1.5 (8), 1.8 (9) or 2.0 (10) wt%. The numbers in the round brackets correspond with those in the figures.



(a) (b)

(c)

Figure 3. Dyeing temperature (T) dependence of the L^*(a), a^*(b) and b^*(c) for hair dyed by 0.60 wt% EC solution (○) or 1.0 wt% CC solution (●) for 40 min.

tem under the conditions. The obtained results, however, show the higher temperature is favourable for obtaining higher dyeability in a shorter time and for rapid dyeing from the practical point of view. A local heating technique, for example, may be required to realise the practical dyeing.

On the other hand, the variation of a^* for the EC and CC system is not monotonously. The colour change of dye solution during dyeing hair at higher temperature was observed. This indicates an alteration of dye molecules caused by heating. Then it was examined whether the dyestuff is altered by heating.

The results obtained from CC are presented here and **Figure 4** shows the absorption spectra of its aqueous solution. The signal intensity of the absorption spectrum increases with the rise in temperature. New signals donot appear during the development of the spectrum with temperature and the shape undergoes very little change in appearance. The temperature change in the spectra of EC is similar to that of CC. The results meanthat the colourant in aqueous solution is increased by heating. The prepared catechinone dyestuff contains colourless materials such as unreacted (+)-catechin. Removing them from the dye powder and purification are difficult because the solubility and molecular weight of (+)-catechin are very close to those of catechinone. The unreacted (+)-catechin is oxidised further at higher temperature to give catechinone because of the dye solution was exposed to air during the measurement procedure and the dyeing process. The formation of coloured dimers or other coloured multimers in the solution at higher temperature may also be assumed. The formation can affect the dyeing results.

3.3. Effect of Dyeing pH

The dye solution pH is thought to be important factor for hair dyeing. Because the degree of swelling of hair and electric charge of the hair protein vary according to the pH and this may affect the dyestuff penetration into/diffusion in hair and dyestuff fixation. Moreover, the aggregation state of dye molecules in solution may also depend upon the pH. Then the effect of the pH of dyeing solution on the dyeability of hair dyed by catechinone was investigated. The solubility of CC in each the dyeing solution of which pH is different is lower than that of EC. Then the pH-effect experiments for CC were made at higher temperature (50˚C) than those for EC (30˚C). The results obtained by visual observation show the colour of the hair dyed by EC is yellowish and this is almost same at pH = 1.83 - 6.04. The colour of hair dyed at pH = 6.04 by EC is deepest, and the hair is poorly dyed at pH = 8.38. Meanwhile, CC dyes hair reddish brown at pH = 4.09 - 7.48, and the colour is deepest at pH = 5.45.

Figure 5 shows the relationships between the pH and the resulting colour of hair dyed by EC or CC. The dye concentration of EC or CC was set to 0.6 or 1.0 wt% for the same reason described above. The dyeability of EC cannot be compared with that of CC in absolute terms. Here, only the tendency of each change with pH should be focused.

The L^* may take minimum and the a^* reach maximum between pH = 3 and pH = 6 for hair dyed by EC. Its b^* decreases with an increase in pH. On the other hand, the results for CC system show that L^* of the dyed hair

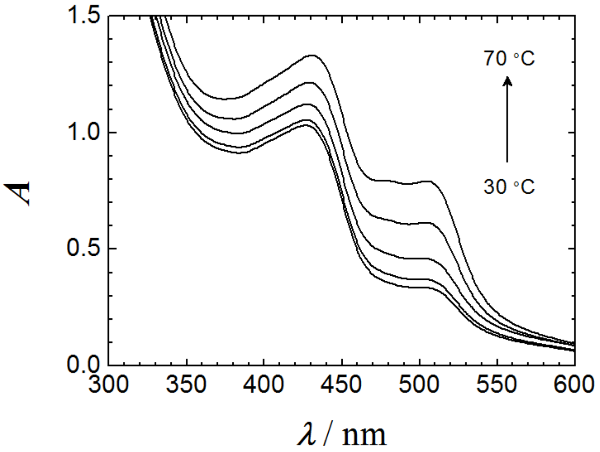
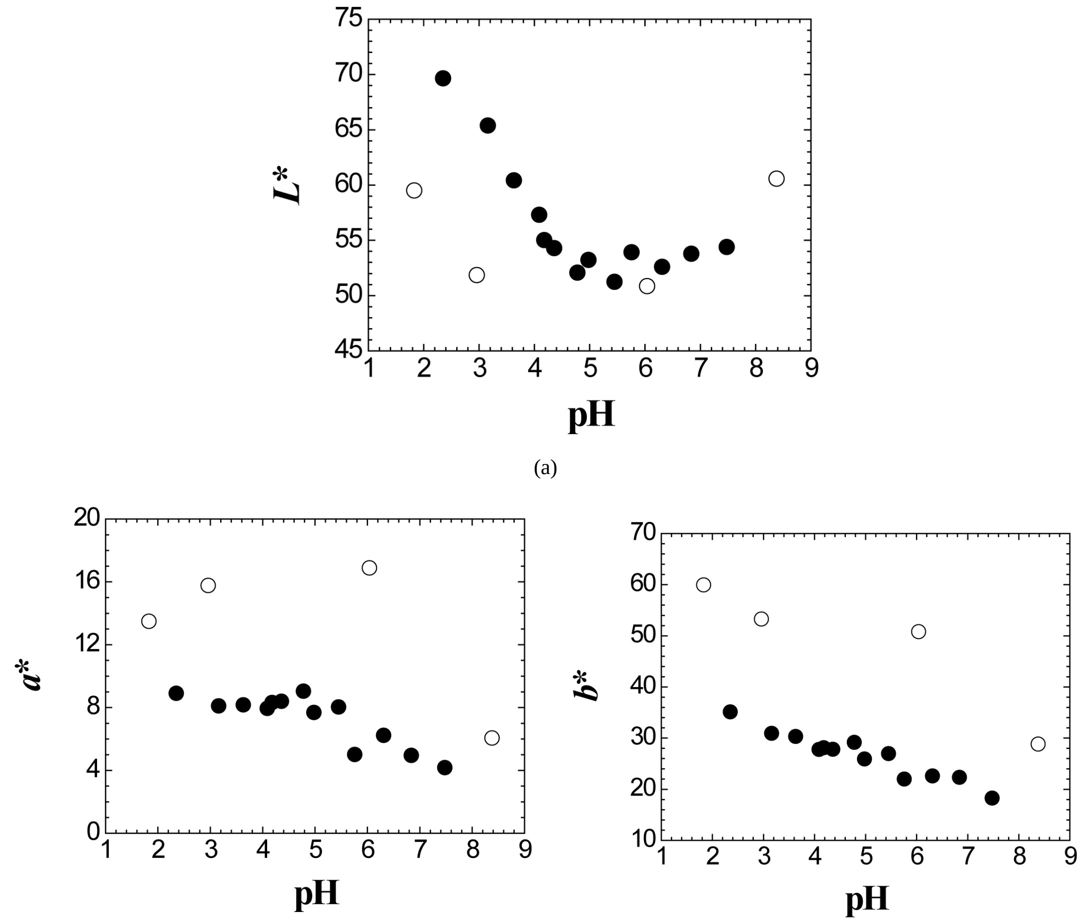


Figure 4. Absorption spectra of 0.025 wt% CC aqueous solution. The temperature of the solution was raised from 30˚C to 40˚C, 50˚C, 60˚C and 70˚C with being stirred.



(a)

(b) (c)

Figure 5. Relationships between pH of the dye solution and L^* (a), a^* (b) or b^* (c) for the hair dyed by 0.60 wt% EC solution at 30˚C for 40 min (○) or 1.0 wt% CC solution at 50˚C for 30 min (●).

decreases with increasing pH from 2.32, takes minimum at pH = 5.45 and increases slightly from pH = 5.45 and over. Its a^* decreases with increasing pH from 5.45 and b^* decreases monotonously with an increase in pH.

Subsequently, the relationship between the solution pH and the degree of swelling of hair was studied in order to clarify the mechanism of the pH effect on the dyeing. **Figure 6** shows the degree of swelling of hair (q) in CC solution against the solution pH. The q is high at pH = 3.00 - 3.20 and 6.50 - 7.10. The isoionic and isoelectric points of human hair were evaluated as 5.6 - 6.2 [10] and 3.67 [11], respectively. Therefore, the q of hair can be low approximately between pH = 3.7 and 6.2 because of the low electric interaction among hair proteins. The q takes minimum at pH $\approx$ 4 in fact as shown in **Figure 6**. The q decreases at very low and high pH and takes low values. The pH of the dyeing solution was controlled by using HCl and NaOH or citric acid, and the ionic strength for each of the solution was not adjusted. It can be thought that the decrease in the degree of swelling of hair at the very low and high pH is caused by the high ionic strength in the solution. The high ionic strength shields the electric charge repulsion among the hair protein and the hair network shrinks. The experimental results of pH-q relationship do not show clear correlation with the relationship between pH and the dyeability as seen in the Figures, although the L^* minimum appears near at the isoionic point of hair. Therefore, the pH dependence of the dyeability is not explained by the variation of q. Further investigation should be made to clarify the pH effect on the catechinone dyeability.

3.4. Effect of Added Salts

It is well known that salts play important role in dyeing of charged fibres such as wool [12]. Here, the effect of

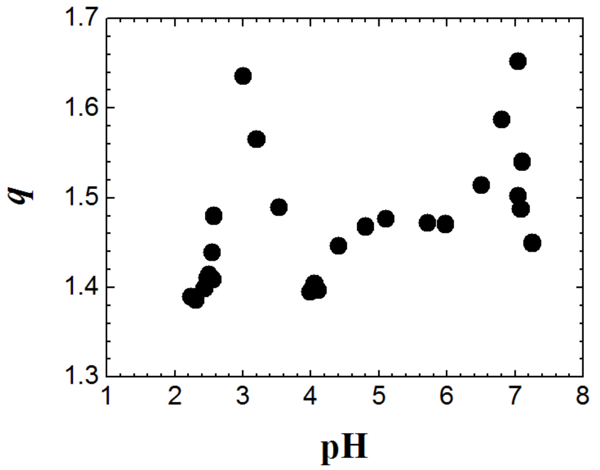


Figure 6. Relationship between solution pH and the swelling ratio of hair (q) in 1.0 wt% CC aqueous solution.

the addition of sodium chloride, calcium chloride or aluminium chloride on the dyeing by CC at 70˚C and at pH = 6.7 - 7.5 was studied. The colour of the hair dyed with NaCl is deepest at c_S = 1.0 M, and it is deepest for $CaCl_2$ at c_S = 0.050 M, while it becomes paler with an increase in c_S for $AlCl_3$ in naked-eye observation. **Figure 7** shows the colour values of hair dyed with each the salt as a function of the salt concentration (c_S). The L^* of dyed hair decreases on addition of a small amount of NaCl ($c_S \leq 1.0$ M) or $CaCl_2$ ($c_S \leq 0.050$ M), and it increases on addition of $AlCl_3$. The a^* increases on addition of NaCl or $CaCl_2$ ($c_S \leq 0.5$ M). The hair has negative charge as a whole in the CC solution of pH = 6.7 - 7.5 and the hydroxylphenyl groups of catechinone dissociate a little to give negative charge. The results that the addition of smaller amount of NaCl and $CaCl_2$ increases the dyeability and the addition of larger amount of salts reduces the dyeability are consistent with the negative charge state of hair and catechinone dyestuff and the shielding effect of salts. Furthermore, catechinone becomes insoluble in the solution with NaCl of $c_S \geq 2.0$ M or with $CaCl_2$ of $c_S \geq 1.0$ M. The shielding effect of Ca^{2+} is higher than that of Na^+ for the larger positive charge. The charge of Al^{3+} may be too large to promote the dyeability.

It is concluded that the addition of a small amount of NaCl or $CaCl_2$ are most effective and practical to improve the dyeability in the dyeing conditions (temperature, pH and salt addition) by comparing **Figure 3**, **Figure 5** and **Figure 7**.

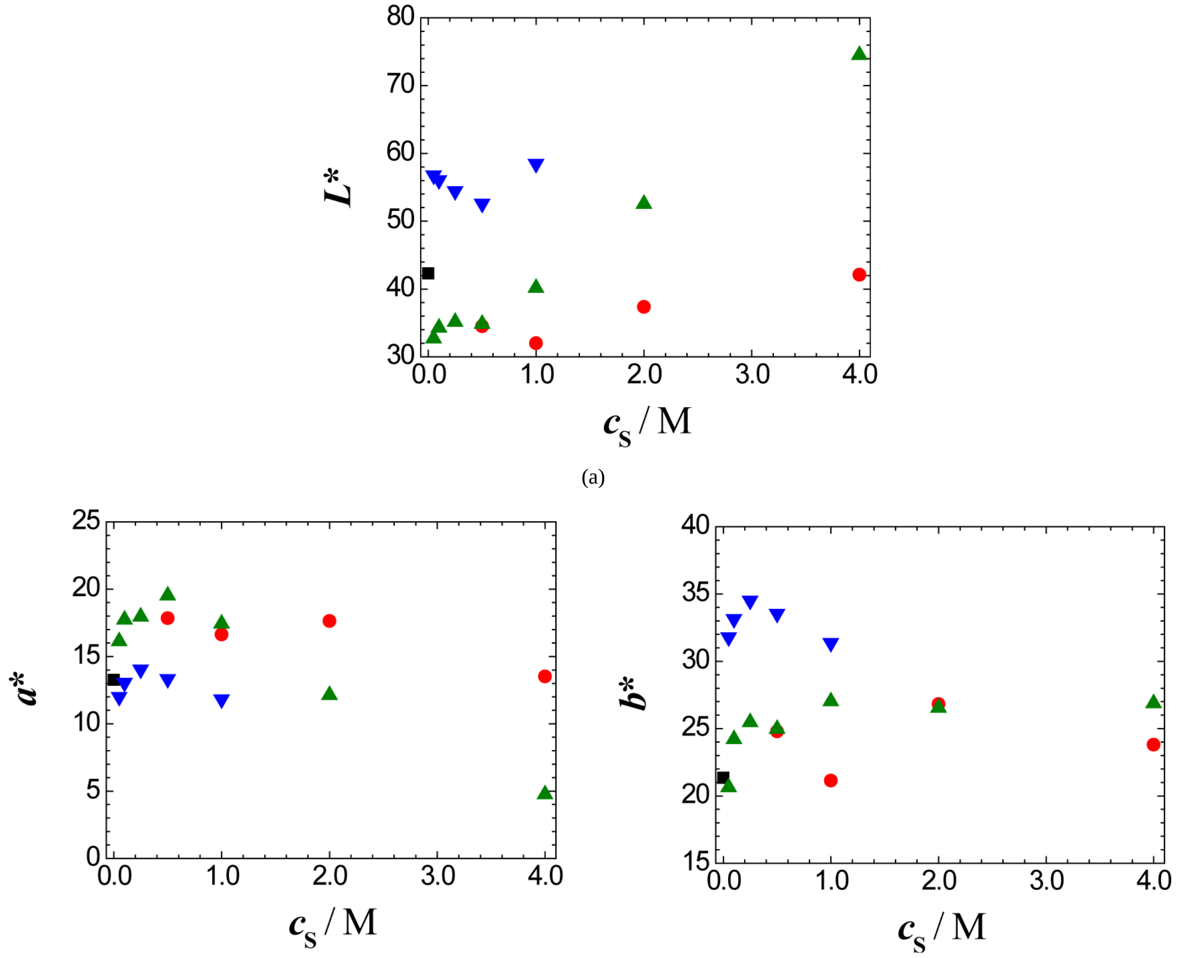
3.5. Colour Fastness to Washing and UV Light

Colour fastness of hair dyed by catechinone to washing and UV light is important property for practical hair dyeing. The colour fastness of hair dyed by catechinone to washing was first examined comparing with that of hair dyed by other colourants. The colours of the hair dyed by EC, CC, an oxidation dye (PAP + 5AOC) or an acid dye are dark brownish orange, dark yellowish orange, dark reddish brown or dark reddish brown, respectively. The colour of hair dyed by each the method was not same because adjusting the colour of hair samples is not easy the important point is the comparison of the difference in the colour change.

Figure 8 shows the change in the colour difference (ΔE^*) between unwashed and washed hair dyed by each the method, as a function of number of washing (n). The ΔE^* of the hair dyed by the oxidation dye increases finally by approximately 6 with n and ΔE^* for the acid dye increases to a great extent. In contrast, the ΔE^* of the hair dyed by EC or CC at both temperatures increases by 12 - 15. However, the ΔE^* for EC and CC systems changes very slightly for $n > 6$. The change in colour is very small for visual observation. The results demonstrate that the hair dyed by EC or CC has sufficient colour fastness to washing for practical purposes.

Figure 9 shows the change in the ΔE^* between unirradiated and UV-irradiated hair dyed by each the method, as a function of UV irradiation time (t). The ΔE^* of the hair dyed by the oxidation dye or the acid dye increases with t, and it is about 6 or 9 at t = 10 h, respectively. The change in the ΔE^* of the hair dyed by EC or CC are almost as same as that of the hair dyed by the oxidation dye or the acid dye.

However, the changing behaviours of ΔE^* for [the EC and CC system] and [the oxidation and acid dyes sys-



(a)

(b)

(c)

Figure 7. Change in L^* (a), a^* (b) and b^* (c) for the hair dyed by 1.0 wt% CC solution at 70˚C with NaCl (●), $CaCl_2$ (▲) or $AlCl_3$ (▼) as a function of the salt concentration (c_S). The black-closed square (■) indicates the colour values for hair dyed without salt.

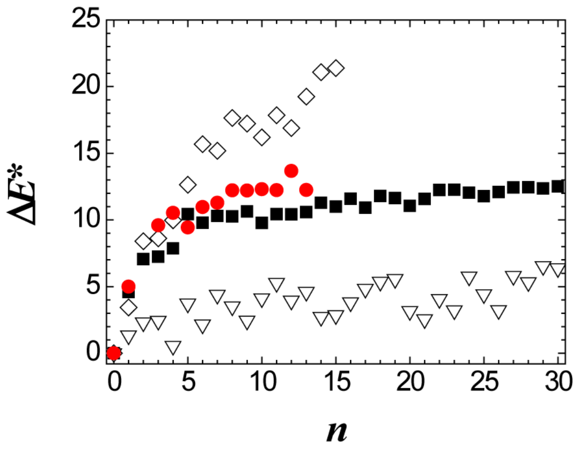


Figure 8. Change in colour difference (ΔE^*) of hair dyed by EC (■; T = 30˚C), CC (●; T = 30˚C), oxidation dye (▽; T = 30˚C) or acid dye (◇; room temp.) as a function of number of washing (n). The initial value at n = 0 means the value of the hair washed once after dyeing.

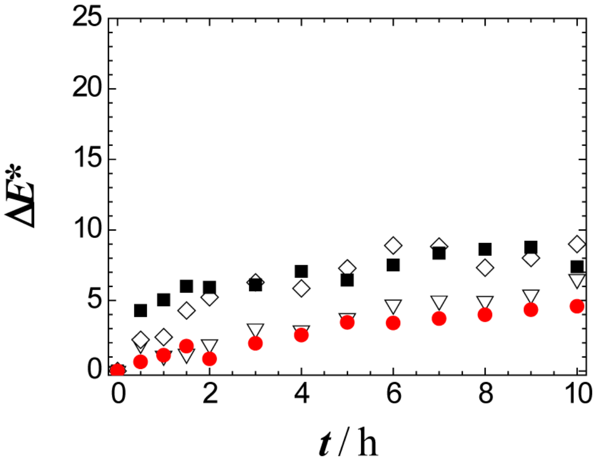


Figure 9. Change in ΔE^* of hair dyed by EC (■; T = 30˚C), CC (●; T = 30˚C), oxidation dye (▽; T = 30˚C) or acid dye (◇; room temp.) as a function of UV irradiation time (t).

tem] are different. The time change in L^* of hair dyed by each the method under UV irradiation is shown in **Figure 10**. While L^* for the oxidation and acid dyes system increases monotonously with t, L^* for the EC and CC system decreases until t = 8 h. The results demonstrate that the hair dyed by the oxidation or acid dye only discolours by UV irradiation, whereas it dyed by EC or CC is coloured further and turns darker by the UV.

The results indicate that the hair dyed by EC or CC has enough high colour fastness to UV light. In addition, the colour fastness to visible light for the hair dyed by catechinone is also enough high [5]. Therefore, it can be said that catechinone has practical colour fastness to daily light including sunshine. Furthermore, the colour-changing into deeper for the hair dyed by EC or CC under UV irradiation is a special property of catechin. This is thought to be caused by the further progress of oxidation of (+)-catechin attaching hair with UV light.

3.6. Dyestuff Formation from Tea Extracts and Its Dyeability

It is important for the practical production of hair dyestuffs to prepare them from a massive amount of low materials. It was found that colourants are also prepared by the chemical oxidation method from four commercial tea extracts, which contain (+)-catechin and other catechin derivatives. Then, hair dyeing by using the colourants obtained from tea extracts was next examined and the high dyeing temperature (70˚C) was adopted at first. The resulting colour of hair samples expressed in $L^*a^*b^*$ colourimetry, which are dyed by the obtained colourants from the tea extracts is summarised in **Table 2**. The results show that hair can be dyed by the dyestuffs obtained from tea extracts. The dyeability of them is somewhat lower than that of CC. The dyeability of the colourants prepared from Polyphenon 70S and Sunphenon BG-3 is relatively higher among them and the results imply that the dyeability depends on the composition of catechins in the tea extracts. The Polyphenon 70S and Sunphenon BG-3, which contain non-gallate catechins at a higher rate, give dyestuffs showing higher dyeability as shown in **Table 1** and **Table 2**. The non-gallate catechins such as (+)-catechin, (−)-epicatechin, (−)-gallocatechin and (−)-epigallocatechin may be profitable to obtain efficient dyestuffs. In addition, hair dyestuffs are obtained also by enzymatic oxidation of the tea extracts.

The hair dyeing by using organic compounds such as mulberry fruits, alizarin, curcumin and juglone was also tried [13]. The dyeability of the compounds is not enough high and then benzyl alcohol and 2-propernol were added to promote the dyeability. Longer dyeing time is required for mulberry fruits as 12 h at 25˚C and the dyeing time is 30 min for other organic compounds. The colour fastness to washing or light for the dyed hair samples was not reported. On the other hand, guaiacol, acetosyringone, vanillic acid, syringic acid, gallic acid, homovanillyl alcohol, *p*-coumaric acid, vanillin, syringaldehyde, acetovanillone, ferulic acid, catechinand etc. were treated by laccase and used to dye hair [14]. Hair is dyed various colour by mixing a couple of the phenolic compounds. It takes 22 h to dye hair at 28˚C. The change in colour of hair samples dyed by gallic acid + syringic acid, ferulic acid + syringic acid orcatechin + catechol was reported to be negligible up to three times of washing.

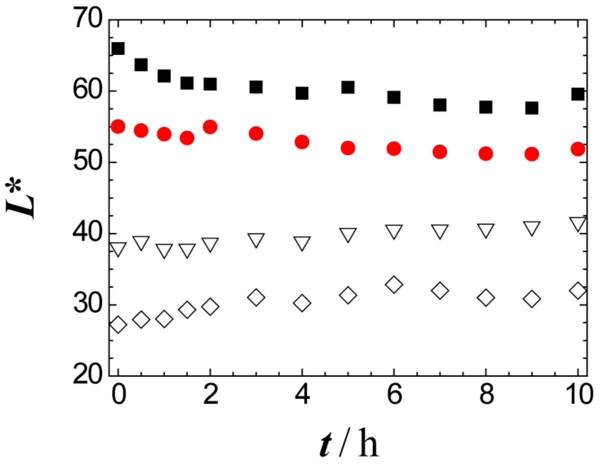


Figure 10. Change in L^* of hair dyed by EC (■; T = 30˚C), CC (●; T = 30˚C), oxidation dye (▽; T = 30˚C) or acid dye (◇; room temp.) as a function of *t*.

Table 2. The colourimetric values for undyed and dyed hairs.

Sample hair dyed with	undyed	CC	dyestuffs from Polyphenon 70S	dyestuffs from Sunphenon EGCg	dyestuffs from Sunphenon BG-3	dyestuffs from Sunphenon 90S
L^*	70.8	33.3	49.2	53.4	42.7	55.7
a^*	4.47	14.5	10.7	4.54	8.77	4.01
b^*	25.8	19.3	22.7	18.8	20.0	19.3
C^*	26.2	24.1	25.1	19.3	21.9	19.7

Dyeing conditions: c_D = 1.0 wt%, T = 70˚C and t = 40 min.

4. Conclusion

Catechinone is obtained from (+)-catechin by both the enzymatic and chemical oxidation method. Hair is dyed deeper red brown of the higher dye concentration, for longer dyeing time and at higher dyeing temperature. Hair is dyed darkest by EC at pH = 6.04 and by CC at pH = 5.45. A small amount of NaCl and $CaCl_2$ addition into the dye solution increases the dyeability. The colour fastness to washing and UV light for the hair dyed by catechinone is high enough for practical use. Hair dyestuff is obtained from commercially available tea extracts.

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