

A FURTHER INVESTIGATION ON COLLAGEN-Cr(III) INTERACTION AT MOLECULAR LEVEL

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ABSTRACT

As we know, the reaction of chrome tanning primarily occurs at carboxyl groups of collagen, tacitly assumed at aspartic and glutamic side chains. However, the differences of the reactivity and reaction extent at these sites, as well as the effect of environmental conditions on the reaction are still unclear at molecular level. This paper presents a theoretical analysis of the reactivity of collagen carboxyl groups and Cr(III) species based on electrophilicity index (ω), and the driving force for tanning reaction by using density functional theory (DFT) with Lan12dz for chrome atom and 6-31g(d) for non-metal atoms. Glutamic acid (Glu) and aspartic acid (Asp) were used as the models of collagen side chains containing carboxyl group. Based on visual minteq calculation, the main Cr(III) species in chrome tanning liquor were found to be $\text{Cr}(\text{SO}_4)(\text{H}_2\text{O})_4^+$, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, $\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$, and $\text{Cr}_3(\text{OH})_4(\text{H}_2\text{O})_{10}^{5+}$ under the pH range of tanning process, and the content of multi-nuclear Cr(III) species increases with the rise of pH. The reactivity of collagen carboxyl groups is in the sequence of ionized Asp (Asp^-) > ionized Glu (Glu^-) > unionized Glu > unionized Asp, while the reactivity of the main Cr(III) species is sequenced by $\text{Cr}_3(\text{OH})_4(\text{H}_2\text{O})_{10}^{5+}$ > $\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$ > $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ > $\text{Cr}(\text{SO}_4)(\text{H}_2\text{O})_4^+$. The data of thermodynamic driving force for tanning reaction indicate that ionized carboxyl groups have stronger tendency to form more stable carboxyl-Cr(III) complexes compared with unionized carboxyl groups, and the order of the tendency is Glu^- > Asp^- > Asp > Glu. Obviously, for Glu^- and Asp^- or Glu and Asp, the thermodynamic driving force is exactly the opposite with reactivity. Therefore, as for collagen carboxyl groups, the predominant reaction bonding site is determined by both thermodynamic and kinetic conditions. As for Cr(III) species, the order of thermodynamic driving force is $\text{Cr}_3(\text{OH})_4(\text{H}_2\text{O})_{10}^{5+}$ > $\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$ > $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ > $\text{Cr}(\text{SO}_4)(\text{H}_2\text{O})_4^+$ which is consistent with the order of reactivity.

INTRODUCTION

Chrome tanning is the commonest tannage due to the excellent comprehensive performance of chrome tanned leather. Though the use of chrome inevitably leads to chrome discharge that might have potential environmental risks,^{1,2} the complete replacement of chrome is very difficult at this stage, and therefore, it is necessary to explore the real chemistry of the chrome tanning reaction to improve the process. In fact, as early as in 1954, Bows and Kebten had pointed the importance of collagen carboxyl groups in chrome tanning. They proved that the inactivation of collagen carboxyl groups by esterification led to obvious reduction of chrome fixation.³ Afterwards, many modern techniques, such as DSC, UV, XPS, NIR, EXAFS and molecular dynamic (MD) simulation were applied to investigate the basis of tanning, and the key role of collagen carboxyl groups in chrome tanning was confirmed.⁴⁻¹² Experimental work has also cast doubt on the bonding sites, namely aspartic (Asp) and glutamic acid (Glu). The amount of Glu on collagen is about 60 per 1000 residues and about 35 for Asp after liming.¹⁰ It means that Glu is more available during tanning process. However, Asp is favored over Glu because of lower pK_a ($\text{pK}_{a(\text{Glu})}=4.2$, $\text{pK}_{a(\text{Asp})}=3.5$).^{13,14}

In an attempt to obtain direct and quantitative evidence for the chemistry of chrome tanning reaction, quantum chemistry calculation was used to clarify the reactivity of collagen carboxyl groups and Cr(III) species, and the driving force for tanning reaction as well as the stability of the formed complexes was also evaluated in this paper. In order to determine the predominant chemical species of chrome under the pH range of tanning process, visual minteq model was used for predicting of Cr species in $\text{Cr}_2(\text{SO}_4)_3$ solution, which is widely applied in environmental science.¹⁵⁻¹⁷

METHODS

The Main Cr(III) Species Under the pH Range of Tanning
MinteqA2 (version 3.1) was used to determine the distribution of main Cr species of 0.05mol/L $\text{Cr}_2(\text{SO}_4)_3$ solution in the pH range of 1 to 7 at 298K.¹⁸

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The Models of Collagen Carboxyl Groups

Glutamic and aspartic acids were chosen as the models of collagen side chains containing carboxyl group. Their N-terminal and C-terminal were closed down with an acetyl group (on the nitrogen atom) and a N-methylamino group (on the carbonyl carbon atom), respectively.¹⁹ With the increase of basicity during the tanning process, more collagen carboxyl groups will dissociate. The ionized Glu and Asp account for only 2.0% and 4.8% at pH=2.5, 16.7% and 34.3% at pH=3.5, and 77.1% and 58.3% at pH=4.5¹⁰, respectively. Then four kinds of states of collagen carboxyl groups were considered, namely unionized Glu, Asp, and ionized Glu⁻, Asp⁻.

The Theoretical Parameters

The equilibrium structures and harmonic vibrational properties of the main Cr(III) species, collagen carboxyl groups, and the complexes formed between them were obtained by density functional theory with B3LYP hybrid functional. Gaussian 09 computational package was used for calculations, and 6-31g(d) basis set was chosen for non-metal atoms, Lan12dz for chrome atom respectively.^{20,21}

For the coordination reactions of tanning, that the partial electron transfers from collagen carboxyl group to Cr(III) contributes to the lowering of the total binding energy. So both the electron accepting capability of Cr(III) and the electron providing ability of collagen carboxyl group would determine the reactivity of tanning. The electrophilicity index (ω) is commonly employed to describe this specific property, which contains two meaningful contributions, the numerator indicating the tendency of the system to acquire an additional amount of electronic charge from the environment, and the denominator representing the resistance to the electronic exchange, as expressed below:²²⁻²⁴

$$\omega = \frac{\mu^2}{2\eta} \quad (1)$$

The electronic chemical potential (μ) and the chemical hardness (η) were obtained from the energies of the highest occupied molecular orbital (ε_H) and lowest unoccupied molecular orbital (ε_L):²⁵⁻²⁷

$$\mu = (\varepsilon_H + \varepsilon_L) / 2 \quad (2)$$

$$\eta = \varepsilon_L - \varepsilon_H \quad (3)$$

For Cr(III) species, the greater ω indicates more reactivity, whereas for collagen carboxyl groups, the lower ω means more reactivity.^{23,24,28}

A viable reaction should have some energetic driving force, which may be a decrease in enthalpy, an increase in entropy, or a combination of the both. The Gibbs energy change ($\Delta_r G$), enthalpy change ($\Delta_r H$), and entropy change ($\Delta_r S$) of reaction were obtained to indicate the driving force for tanning reaction, and the stability of collagen-Cr(III) complex was also evaluated based on following equations.

$$\Delta_r G = \sum G(\text{products}) - \sum G(\text{reactants}) \quad (4)$$

$$\Delta_r H = \sum H(\text{products}) - \sum H(\text{reactants}) \quad (5)$$

$$\Delta_r S = \sum S(\text{products}) - \sum S(\text{reactants}) \quad (6)$$

Where products denote complexes and H₂O, and reactants include collagen carboxyl groups and chrome species. The Gibbs energy change of reaction ($\Delta_r G$) is negative value if the reaction can occurs. The more negative Gibbs energy change of reaction ($\Delta_r G$) indicates higher driving force for tanning reaction and consequently more stable complex.^{29,30}

RESULT AND DISCUSSION

The States of Cr₂(SO₄)₃ and Collagen Carboxyl Groups Under Tanning Condition

Figure 1 shows that the distribution of Cr(III) species in aqueous solution varies obviously with pH in the range of tanning. At the initial stage of tanning (pH 2.5), Cr(III) monomers Cr(SO₄)(H₂O)₄⁺ and Cr(H₂O)₆³⁺ account for 98%, and the other ions are nearly negligible. When the solution is basified to pH 3.5, Cr(SO₄)(H₂O)₄⁺ and Cr(H₂O)₆³⁺ decrease to 45% and 15%, respectively, whereas Cr₂(OH)₂(H₂O)₈⁴⁺ and Cr₃(OH)₄(H₂O)₁₀⁵⁺ increase to 25% and 10%, respectively. At the final stage of tanning (pH 4.5), the percentages of Cr(SO₄)(H₂O)₄⁺, Cr(H₂O)₆³⁺, Cr₂(OH)₂(H₂O)₈⁴⁺ and Cr₃(OH)₄(H₂O)₁₀⁵⁺ are 1.31%, 7%, 19% and 66%, respectively. Then Cr(SO₄)(H₂O)₄⁺, Cr(H₂O)₆³⁺, Cr₂(OH)₂(H₂O)₈⁴⁺ and Cr₃(OH)₄(H₂O)₁₀⁵⁺ were defined as the models of main Cr(III) species in tanning liquor.

The Reactivity of the Reactants

The structures of optimized Cr(III) species, ionized and unionized collagen carboxyl groups are shown in Figure 2, and their electrophilicity indexes (ω) were calculated to indicate their reactivity (Table I).

As electron donor, a lower electrophilicity index (ω) of collagen carboxyl group indicates that it has higher reactivity to coordinate with Cr(III). As shown in Table I, the ω value of ionized Glu⁻ and Asp⁻ is 0.51eV and 0.83eV lower than that of Glu and Asp, respectively, and the ω value of ionized Asp⁻ is 0.11eV lower than Glu. These imply that ionized collagen carboxyl group is more reactive to coordinate with Cr(III) compared with the corresponding unionized one, which is consistent with the experimental results.³ Furthermore, ionized Asp⁻ possesses slightly higher reactive than Glu⁻ on the basis of electrophilicity index.

On the other hand, as electron acceptor, a bigger electrophilicity index (ω) of Cr(III) species indicates that it has higher reactivity to coordinate with carboxyl group. Table I shows that the reactivity of the main Cr(III) species is in the sequence of Cr₃(OH)₄(H₂O)₁₀⁵⁺ > Cr₂(OH)₂(H₂O)₈⁴⁺ >

$\text{Cr}(\text{H}_2\text{O})_6^{3+} > \text{Cr}(\text{SO}_4)(\text{H}_2\text{O})_4^+$. With the increase of basicity, collagen carboxyl groups are ionized while Cr(III) ions are “polymerized”. Thus, basification results in higher reactivity for both carboxyl group and Cr(III).^{10,31-33} An interesting thing is that the ω value of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is much higher than that of $\text{Cr}(\text{SO}_4)(\text{H}_2\text{O})_4^+$, which suggests SO_4^{2-} considerably lower the coordination reaction. This observation confirms that SO_4^{2-} can act as masking agent in chrome tanning.

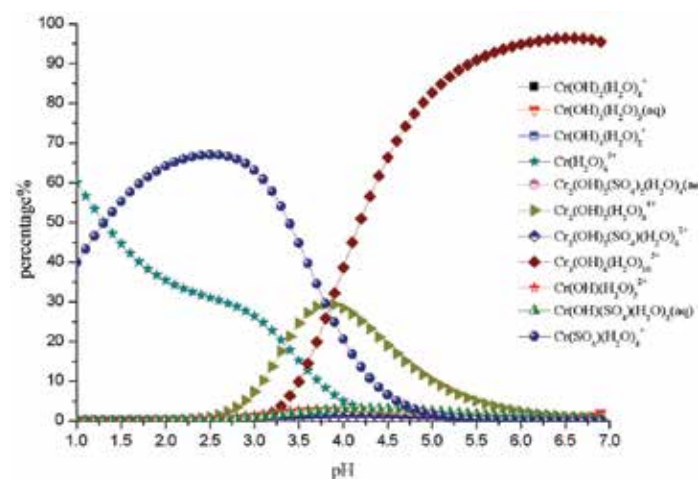


Figure 1. The distribution of chrome species in tanning liquor.

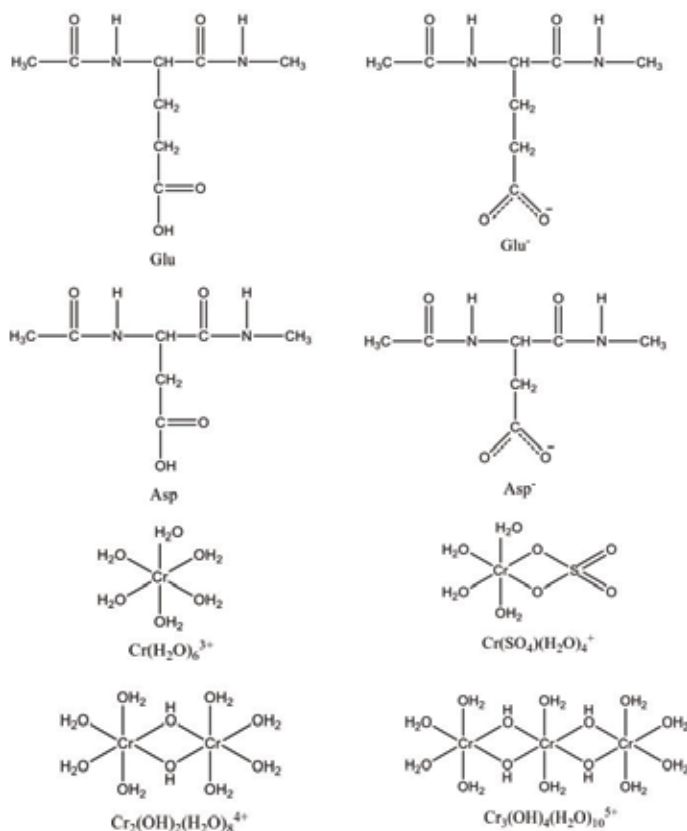


Figure 2. The structures of the reactants.

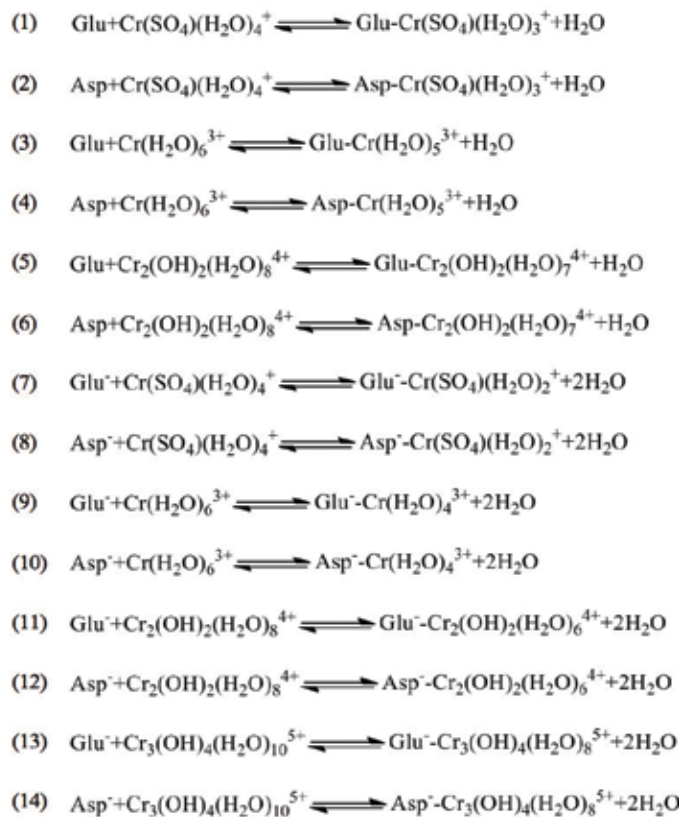
TABLE I
The electrophilicity indexes (ω) of collagen carboxyl groups and Cr species.

Reactants	ϵ_{H} (eV)	ϵ_{L} (eV)	μ (eV)	η (eV)	ω (eV)
Glu	-6.54	0.21	-3.16	6.75	0.74
Glu ⁻	-0.42	2.91	1.25	3.33	0.23
Asp	-6.88	-0.45	-3.67	6.43	1.05
Asp ⁻	-1.67	4.02	1.17	5.69	0.12
$\text{Cr}(\text{SO}_4)(\text{H}_2\text{O})_4^+$	-11.53	-7.03	-9.28	4.50	9.57
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	-22.80	-17.23	-20.02	5.57	35.96
$\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$	-23.13	-18.16	-20.65	4.97	42.91
$\text{Cr}_3(\text{OH})_4(\text{H}_2\text{O})_{10}^{5+}$	-24.13	-19.41	-21.77	4.72	50.23

(ϵ_{H} , ϵ_{L} , μ , η represent energy of highest occupied molecular orbital and lowest unoccupied molecular orbital, electronic chemical potential, and chemical hardness, respectively. With these parameters, ω was calculated according to equation 1.)

The Driving Force of Typical Reaction of Chrome Tanning

The states of both collagen carboxyl groups and chrome species vary with pH of solution, and the possible tanning reaction during basifying process are shown as the follows.



The extents of the tanning reactions above are determined by the thermodynamics of reactants and products. All these reactions have a feature of $\Delta_r G < 0$, as shown in Table II, which means they are viable reactions. The more negative the $\Delta_r G$, the more stable the complex.

Collagen carboxyl groups exist in two kinds of states, namely unionized and ionized states during tanning process. The unionized Glu and Asp react with Cr(III) primarily at the initial stage of tanning, such as reactions (1) to (6). In general, the $\Delta_r G$ of tanning reaction involving Asp is more negative than that involving Glu except reaction (6), especially for the coordination reaction with $\text{Cr}(\text{SO}_4)(\text{H}_2\text{O})_4^+$. For example, the $\Delta_r G$ of reaction (2) is about 96 kJ/mol more negative than that of reaction (1). This means the thermodynamic driving force of the coordination reaction between unionized Asp and Cr(III) is greater than that between unionized Glu and Cr(III) for the same chrome species. With the increase of basicity, ionized carboxyl groups present much more negative Gibbs energy change of reactions compared with the unionized carboxyl. For example, the $\Delta_r G$ of reaction (9) is about 1086 kJ/mol more negative than that of reaction (3), where Glu⁻ and Glu coordinate with the same Cr(III) species of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, respectively. Moreover, for the same Cr species, the $\Delta_r G$ of the

coordination reaction between Glu⁻ and Cr is 52-144 kJ/mol more negative than that between Asp⁻ and Cr. These results indicate that thermodynamic driving force of reaction involving ionized Glu⁻ is greater than that of Asp⁻, which is exactly the opposite with the case of unionized carboxyl group. The thermodynamics data of tanning reaction showed that, with the increase of basicity, the reaction potential of ionized carboxyl with Cr(III) is much greater than that of the unionized, and Glu⁻ plays a more important role than Asp⁻ in tanning reactions. At the same time, $\Delta_r G$ values of tanning reactions also imply that ionized carboxyl can form more stable complexes with Cr(III) compared with the unionized. The complex formed by Glu⁻ is more stable than by Asp⁻.

As we described above, there are four kinds of main Cr(III) species in chrome liquor, $\text{Cr}(\text{SO}_4)(\text{H}_2\text{O})_4^+$, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, $\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$, and $\text{Cr}_3(\text{OH})_4(\text{H}_2\text{O})_{10}^{5+}$. With the increase of basicity, the Cr(III) ions are "polymerized". From Table II, it can be found that the polymerization improves driving force of tanning reaction no matter collagen carboxyl group is ionized or not, and higher polymerization leads to more negative $\Delta_r G$ in reacting with same carboxyl. For example, the reactions (7), (9), (11), and (13) involve the same ionized Glu⁻, and the contribution of Cr(III) species to thermodynamic driving force is in the sequence of $\text{Cr}_3(\text{OH})_4(\text{H}_2\text{O})_{10}^{5+} > \text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+} > \text{Cr}(\text{H}_2\text{O})_6^{3+} > \text{Cr}(\text{SO}_4)(\text{H}_2\text{O})_4^+$. Furthermore, the data of $\Delta_r G$ also indicate the stability of carboxyl-Cr(III) complexes is in the sequence of trinuclear Cr(III) species > binuclear Cr(III) species > mononuclear Cr(III) species.

For the mononuclear Cr(III) species, carboxyl- $\text{Cr}(\text{SO}_4)(\text{H}_2\text{O})_4^+$ is less stable than carboxyl- $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. It should be noticed that $\Delta_r G$ of coordination reaction between carboxyl and $\text{Cr}(\text{SO}_4)(\text{H}_2\text{O})_4^+$ is much less negative than that between carboxyl and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. For example, $\Delta_r G$ of reaction (7) is about 927 kJ/mol less negative than that of reaction (9). These results indicate that the SO_4^{2-} existing in Cr(III) species cannot accelerate tanning reaction nor stabilize carboxyl-Cr(III) complexes. So SO_4^{2-} seems unfavorable to tanning reaction, which is somewhat inconsistent with previous results³⁴. But, as we speculated before, the SO_4^{2-} may act as masking agent in chrome tanning since it reduces the reactivity of Cr(III) species. On the other hand, SO_4^{2-} may work as acceptor of hydrogen bond instead of participating the coordinative reactions.³⁵ However, the role of SO_4^{2-} should be further investigated.

CONCLUSION

Two quantitative kinetic and thermodynamic evidences for understanding mechanism of chrome tanning reaction were obtained in this paper, which clearly reflect the reactivity of collagen carboxyl groups and main Cr(III) species, and the driving force for the reactions, respectively.

TABLE II
The thermodynamics data of the possible tanning reactions (298K).

Reaction	$\Delta_r H$ (kJ/mol)	$\Delta_r S$ (J·mol ⁻¹ ·K ⁻¹)	$\Delta_r G$ (kJ/mol)
(1)	-21.82	-54.98	-5.44
(2)	-125.55	-80.26	-101.64
(3)	-344.29	52.72	-360.00
(4)	-392.87	19.61	-398.72
(5)	-420.55	24.78	-427.93
(6)	-406.75	-19.59	-400.92
(7)	-483.29	63.16	-519.31
(8)	-422.05	111.48	-455.27
(9)	-1419.97	88.22	-1446.26
(10)	-1294.09	113.40	-1327.88
(11)	-1566.17	160.46	-1613.98
(12)	-1515.85	154.07	-1561.75
(13)	-1838.74	164.45	-1887.73
(14)	-1704.22	133.36	-1743.96

($\Delta_r H$, $\Delta_r S$, $\Delta_r G$ represent enthalpy, entropy and Gibbs energy change of reaction, respectively.)

On the basis of kinetic data, aspartic acid has faster reaction rate with Cr(III) species, whereas the thermodynamic data indicate that glutamic acid possesses stronger tendency to form more stable complexes with of Cr(III) species. Therefore, the favorable bonding site for Cr(III) species is inconsistent from the points of thermodynamics and kinetics, and consequently, the predominant reaction sites are influenced by reaction conditions.

As for main Cr(III) species, the case is relatively simple. The increase of basicity leads to formation of larger Cr(III) species, which simultaneously present higher reactivity and stronger tendency to form more stable complexes with collagen carboxyl. However, the role of SO_4^{2-} in tanning process needs further investigation.

This research may shows that calculational chemistry is an effective tool in revealing the mechanisms implied in leather processing. The particular scientific principles and the processes to obtain the thermodynamic and kinetic data by using calculational chemistry may be a little bit sophisticated. But, as it might be seen in this paper, the easily understandable

conclusions can be clearly presented through reasonably selecting and analyzing the key parameters obtained.

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