

# Study on Mechanism of Protecting Cr(III) from Oxidation into Cr(VI) in Chrome Leather by Vegetable Extracts\*

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**Abstract:** Vegetable extracts, the Valonia, Tara, and the main components of vegetable extracts, the gallic acid, ellagic acid, as test samples are studied to explore the relationship between reducibility of these materials and ability to prevent chrome (III) from oxidation into chrome(VI).

Abilities of these materials to eliminate free radical were measured by the following tests: Given quantities of materials above on the base of equivalent phenolic value were taken to ascertain reducibility by absorbency method of  $K_3[Fe(CN)_6]$  reduce, eliminating ability against hydroxyl free radical by absorbency method of pyrogallol-red fading, eliminating ability against superoxide anion free radical by the absorbency method of pyrogallol autoxidation. These parameters were considered as the index of ability to prevent Cr(III) from being oxidized into Cr(VI).

Main results: Generally speaking, reducibility of these materials in very large extent accords with their abilities of eliminating various free radicals, with rank based on reducibility from large to small as : ellagic acid, gallic acid, Tara and Valonia. The reducibility of these materials in some extent is different from the ability to prevent Cr(III) from being oxidized into Cr(VI) with result that Valonia although ranks last in the sequence of reducibility, has the highest ability to prevent Cr(III) from being oxidized into Cr(VI). This result could be considered as molecular contracture which is helpful to make Cr(III) form chelate compound so as to lead chemical equilibrium to much Cr(III) other than Cr(VI).

**Key words:** Vegetable extracts; Chromium(VI); Reducibility

## 1 Introduction

Many current researches showed that vegetable tannins mainly composed of phenolic hydroxyl tannin could restrain oxidation of Cr(III) into Cr(VI) in chrome leather, but the report on its preventive mechanism had not been found<sup>[1-4]</sup>. This paper only studied the deoxidization, the antioxidation and the prevention of gallotannin Tara, Valonea extract and their hydrolysis acid gallic acid and ellagic acid and the effects on oxidation of Cr(III) into Cr(VI) to explain the preventive principle. The experiment took advantage of sponge which had large specific surface area, stable property instead of leather, used oleic acid, structural stability, to simulate undersaturation fatliquoring to avoid the disturb from the real leather with agents of fatliquoring, retannin, dyestuff et, let oleic acid, chrome liquid and gallotannin had reaction in sponge and determined the content of the Cr(VI) by interval days. Furthermore this paper also studied the relationship between the structure of gallotannin and its antioxidation, antioxidation and Cr(VI) prevention in chrome leather through measured reducibility to  $Fe^{3+}$ , the antioxidation to hydroxyl radical, lipid peroxy radical and superoxide anion radical.

The gallic acid was used as monocyclic polyhydroxy phenol, ellagic acid was used as gallic acid

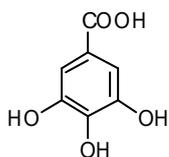
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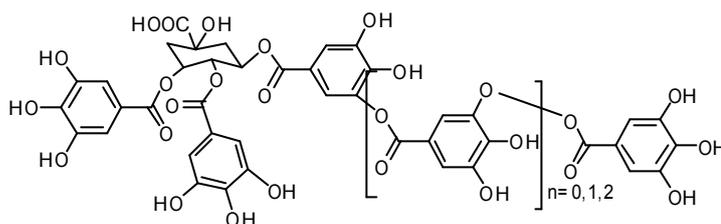
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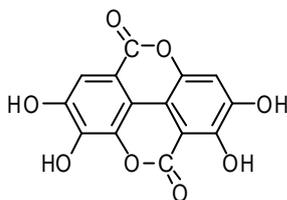
lactone, Tara tannin and Valonia Tannin was used as gallic acid and ellagic acid poly-lactone derivatives in experiment, and their structure were as followed Fig.1, Fig.2, Fig.3 and Fig.4. The experiment used Folin phenol method to measure the total phenols content. And meanwhile reviewed the effect of polyhydroxy phenols' structure on the antioxidation and prevention of Cr(III) into Cr(VI), on the base of same total phenolic value. The  $\text{FeCl}_3/\text{K}_3[\text{Fe}(\text{CN})_6]$  reducibility spectrophotometry was used to represent the reduction of tannin or tannic acid; the pyrogallol-red fading spectrophotometry was used to represent the eliminated rate of hydroxyl radical; the pyrogallol colorimetric spectrophotometry was used to represent the eliminated rate of superoxide anion radical; the peroxide value change of oleic acid was used to represent the antioxidation capacity of the sample to lipid radical.



**Fig.1 Molecule structure of gallic acid**



**Fig.3 Molecule structure of Tara**



**Fig.2 Molecule structure of ellagic acid**

**Fig.4 Molecule structure of Valonia**

## 2 Experimental

### 2.1 Materials

Oleic acid (analytically pure, Tianjing Sixth Chemical Factory), Chrome B(basicity 33% Lanxess ), Diphenylcarbazide (analytically pure, Shanghai Third Reagent and Chemical Factory), Spectrophotometer (Type: 721, Shanghai Third Analysis and Apparatus Factory), Suoshi Extractor (Type: YG210, Shaanxi Huanyu Equipment Company).

### 2.2 The antioxidation and reducibility experiment of gallotannin

( i )The measuration of total phenolic value: the total phenolic value content of gallic acid, ellagic acid, Tara and Valonia was measured by Folin phenol method. The principle of the measurement was that the phenolic compounds could deoxidize the tungsten and molybdenum acid, and form blue color compounds. This compounds' color had positive correction with the content of phenols and the maximum absorbance wavelength was at 760nm in spectrophotometry. The detail operation was: getting out ellagic acid, Tara, Valonia solution (100mg/L) 5mL, putting into the 50mL capacity bottle, then adding Forint agent 5mL (1:2 dilution), laying for 3min after surging sufficient, adding 10% sodium carbonate solution 5mL, surging enough, and adding water to the scale line of total 50mL capacity bottle, the next reacting in 25 °C constant temperature water for 2h, and doing the control experiment at same time, the last testing

the absorbency at wavelength of 765nm by 722N spectrophotometer, and accounting the total phenolic value with the standard curve of the standard solution of gallic acid<sup>[5]</sup>.

(ii) The measurement of reducibility: the reducibility of samples was measured by  $\text{FeCl}_3/\text{K}_3[\text{Fe}(\text{CN})_6]$  deoxidation spectrophotometry method. The principle of the method was that the phenolic compounds could deoxidize the  $\text{K}_3[\text{Fe}(\text{CN})_6]$  into  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , and the Prussian Blue was of formation by the reaction of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and  $\text{FeCl}_3$  deoxidized. The color of Prussian Blue had the positive correction with its content and the maximum absorbance wavelength was at 700nm in spectrophotometry. According to the basis of total phenolic value in part 1.2(1), the operation of the samples was: taking gallic acid (0.0942g/L), ellagic acid (0.0947g/L), Tara (0.1208g/L), Valonia (0.1239 g/L) solution 0.2mL exactly to the test tube, then adding phosphoric acid buffer solution (pH=6.6) 2mL, adding  $\text{K}_3[\text{Fe}(\text{CN})_6]$  solution (1%) 2mL, laying for 20min at 50 °C after surging, and adding trichloroacetic acid (TCA, 10%) solution 2mL, laying for 10min after surging sufficient, and then taking 2mL and adding water 2mL,  $\text{FeCl}_3$  solution (0.1%) 0.4mL, laying for 10min, measuring the absorbency value at wavelength 700nm when the solution from yellow to blue. In the measurement the sample with the darker color had the better reducibility<sup>[6]</sup>.

(iii) The measurement of hydroxyl radical clearance rate: the hydroxyl radical clearance rate of samples was measured by pyrogallol-red fading spectrophotometry method. The principle of the method was that Fenton system could produce hydroxyl radical. The hydroxyl radical could make the pyrogallol-red fade through oxidation action in alkaline circumstance and also diminish the maximum absorbance value at wavelength 544nm of pyrogallol-red. The phenolic compounds could eliminate hydroxyl radical and indirect cause the speed of pyrogallol-red fading slower. So at the same conditions, the sample which made pyrogallol-red fading slower had the better eliminated ability to hydroxyl radical<sup>[7]</sup>. The detail operation was adding  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  buffer solution (pH=9.2) 2mL, EDTA- $\text{Fe}^{2+}$  solution (0.0038mol/L) 0.7mL, pyrogallol-red (0.0001mol/L) 3.5mL,  $\text{H}_2\text{O}_2$  solution (0.6%, as volumeter) orderly into the 10mL test tube, then adding water at the 10mL scale and putting into the consistence temperature 25°C for 30min, testing the absorbency value at wavelength 544nm. The absorbency value of the system with  $\text{H}_2\text{O}_2$  was  $A_b$ , without  $\text{H}_2\text{O}_2$  was  $A_0$ , then the production of the hydroxyl radical was  $\Delta A = A_0 - A_b$ . The absorbency value of the system separate with gallic acid (0.0942g/L), ellagic acid (0.0947g/L), Tara (0.1208g/L), Valonia (0.1239 g/L) solution before  $\text{H}_2\text{O}_2$  added was  $A_s$ . So the clearance rate of free radical was as followed:

$$S/\% = (A_s - A_b) / (A_0 - A_b) * 100$$

(iv) The measurement of superoxide anion radical clearance rate: the superoxide anion radical clearance rate of samples was measured by pyrogallol colorimetric spectrophotometry method. The principle of the method was that pyrogallol could be autoxidation at alkaline circumstances (pH = 8.2) and produce superoxide anion radical ( $\text{O}_2^- \cdot$ ) and colored substance which had characteristic absorption peak at the wavelength 320nm. The phenolic compounds could deoxidize the singlet oxygen to triplet oxygen for breath. And then the  $\text{O}_2^- \cdot$  formation was restraint, the process of pyrogallol autoxidation was prevented, the absorption value of the system at 322nm was weaken. The detail operation was getting Tris-HCl buffer solution with concentration 50mmol/L, pH8.2, 4.5mL (contained 2mmol/LED $\text{TANa}_2$ ) into the dry colorimetric tube, then separate adding gallic acid (0.0942g/L), ellagic acid (0.0947g/L), Tara (0.1208g/L), Valonia (0.1239 g/L) solution 0.2mL, and putting the tube into the consistence machine with temperature 25°C for 10min, then adding pyrogallol (0.005mol/L) 0.2mL, and measuring the absorbency value at wavelength of 320nm by 30 second instantly. The blank experiment was taking HCl (10mmol/L) instead of pyrogallol solution with the same operation. The comparison experiment was taking deionized

water instead of the samples also with the same operation. Then the regress equation of the curve of the absorbency value along with time changing was founded and its slope was the autoxidation rate of the pyrogallol<sup>[8]</sup>. The clearance rate formula of superoxide anion radical resistance in former 3min was as followed:

$$\text{Clearance rate/\%}=(V_0-V_1)/V_0*100$$

In formula:  $V_0$ —the pyrogallol autoxidation rate without sample system( $\Delta OD/\text{min}$ );  $V_1$ —the pyrogallol autoxidation rate of the sample system ( $\Delta OD/\text{min}$ ).

### **2.3 The gallotannin antioxidant to lipid radical and Cr(III) into Cr(VI)**

#### **2.3.1 Experimental system**

- ( i ) The oleic acid and chromium liquid system, consisting of oleic acid and chrome liquid.
- ( ii ) The gallic acid system, besides component of ( i ), also containing gallic acid (9.42g/L).
- ( iii ) The ellagic acid system, besides component of ( i ), also containing ellagic acid (9.47g/L).
- ( iv ) The Tara system, besides component of ( i ), also containing Tara (12.08g/L).
- ( v ) The Valonia system, besides component of ( i ), also containing Valonia (12.39 g/L).

#### **2.3.2 Experimental process**

25 pieces of sponge were divided into 5 groups, every group containing 5 pieces sponge with every one weighting 2.0g, and named as group ( i )~( v ) respectively and then treated as follow:

Sponges in group ( i ) absorbed oleic acid 4.0g→dried in shade air →absorbed pure water 42.5mL→were irradiated by ultraviolet lamp (220v, 60w) for 2h at 1m upright → absorbed chrome liquid 100mL(20g/L  $\text{Cr}_2\text{O}_3$ ) →were irradiated by ultraviolet lamp (220v, 60w) for 4h at 1m upright distance →proceed to commonly treatment.

Sponges in group ( ii )~( v ) →absorbed oleic acid → dried in shade air →absorbed different samples water solution 42.5mL according to corresponding system → were treated as ( ii ) group after absorbing pure water.

Sponges for commonly treatment → were placed in thermostat/ humidistat at 55 °C and 17% relative humidity for 14 days with interval determination of peroxide value of oleic acid and quantity of chrome (VI) against one piece of sponge in groups by first time after two days and then every three days.

#### **2.3.3 Analysis and determination**

##### ( i ) samples separation

A piece of sponge in experimental group was taken from the thermostat and humidistat and was cut into small chippings. These chippings were placed into a 250ml conical flask, and then added 50mL n-hexane, shaken for 1min, added 100mL  $\text{K}_2\text{HPO}_4/\text{H}_3\text{PO}_4$  buffer solution(0.1mol / L, pH 8.0 ) and then shaken for 3 hours at oscillator, then transferred into separating funnel, hold for 30min. So oleic acid was at upper layer dissolved in n-hexane and the Cr(III), Cr (VI) and polyhydroxy phenol were at under layer dissolved in water solution. The oil phase and the aqueous phase were separated and the oleic acid with the n-hexane in oil phase was separated by rotary evaporator at low temperature. The oleic acid was then put into the drying oven at 50 °C until constant weight was obtained and then taken as sample for determining the peroxide value.

##### ( ii ) Determination of peroxide value

The peroxide value of oleic acid was measured according to National Standard GB/T5338 -1995<sup>[9]</sup>.

##### ( iii ) Determination of chrome (VI)

According to reference <sup>[10-11]</sup>, 10ml sample in 1.3.3 ( i ) was withdrawn by a suction pipette and added to a 50ml measuring flask, then 10ml distilled water and 2ml sulfuric acid was added. The mixed solution was well shaken with then 1ml 1,5-diphenylcarbazide solution added to shake the solution for

2min further and then to stand for 3min. Then 4ml p-methyl benzene sulfonic acid was added accurately and the solution was well shaken up. Then 10ml isoamyl alcohol was added accurately and the solution was shaken again. After that the solution was transferred to a separating funnel, and allowed to separate. 20min later, the water phase was drained and a small piece of absorbent cotton was stuffed into the neck of the funnel. Then the organic phase was filtrated, 3-4 drops per-minute. The control reagent was used as the parallel contrasting sample. Optical density of the organic phase was measured by a spectrophotometer at 540nm in a 2cm cell and the amount of Cr (VI) was calculated by using a calibration curve.

### 3 Results and discussion

#### 3.1 The effect of the reducibility of gallotannin

The measurement of total phenolic value, the concentration of the samples, the reducibility to  $Fe^{3+}$ , the hydroxyl radical ( $OH \cdot$ ) clearance rate of Fenton agent and the superoxide anion radical ( $O_2^- \cdot$ ) clearance rate of pyrogallol autoxidation of gallic acid, ellagic acid, Tara and Valonia were shown in Tab1.

**Tab.1 the reducibility and clearance rate of samples to  $OH \cdot$ ,  $O_2^- \cdot$**

Sample	Total phenolic value	Concentration	Reducibility	The clearance rate to free	
				$OH \cdot$	$O_2^- \cdot$
Gallic acid	100%	0.0942g/L	0.438	63.28%	19.42%
Tara	78%	0.1208g/L	0.433	30.66%	19.38%
Ellagic acid	99.5%	0.0946g/L	1.34	100%	49.81%
Valonia	76%	0.1239g/L	0.386	1.17%	16.89%

According to the method of reducibility measurement in part 1.2, the bigger absorbency value at 700nm wavelength meant the more  $Fe^{2+}$  coordination with the polyhydroxy phenols and the stronger reducibility of the sample. From the Table 1, the result showed that the four polyphenols had different reducibility to the  $Fe^{3+}$  at the same total phenolic value, and the reducibility of the ellagic acid was stronger than others, the gallic acid and Tara followed orderly and the Valonia was weakest. This results meant that the ellagic acid, as the lactone of gallic acid had the strongest reducibility and the gallic acid and its polyester derivatives followed. The reason of the result might be that the ester oxygen atom and ortho-phenolic hydroxyl of ellagic acid formed P track conjugation effect after the esterification of the carboxyl and the hydroxy of the ellagic acid, which made the ortho-phenolic hydroxyl lose hydrogen much easier and formed the more steady semi-quinone structure. Due to the large molecules of Tara and Valonia, the formation of its semi-quinone conformation became difficult with the effect of space obstacle which impaired the ability of hydrogen losing.

#### 3.2 The scavenging activity of gallotannin to hydroxyl radical

From table 1, the result showed that the four samples had different clearance rate to hydroxyl radical and the clearance rate of samples from large to small was as followed: ellagic acid, gallic acid, Tara and Valonia at the base of same total phenolic value. The clearance rate of Valonia was very low, less than 10% and gallic acid was much bigger than Tara. This result also indicated that the antioxidation of the ellagic acid to hydroxyl radical produced by Fenton reagent was much stronger than monocyclic polyhydroxyl phenol gallic acid, its polyester Tara and its polyester derivative Valonia. In another word the antioxidation

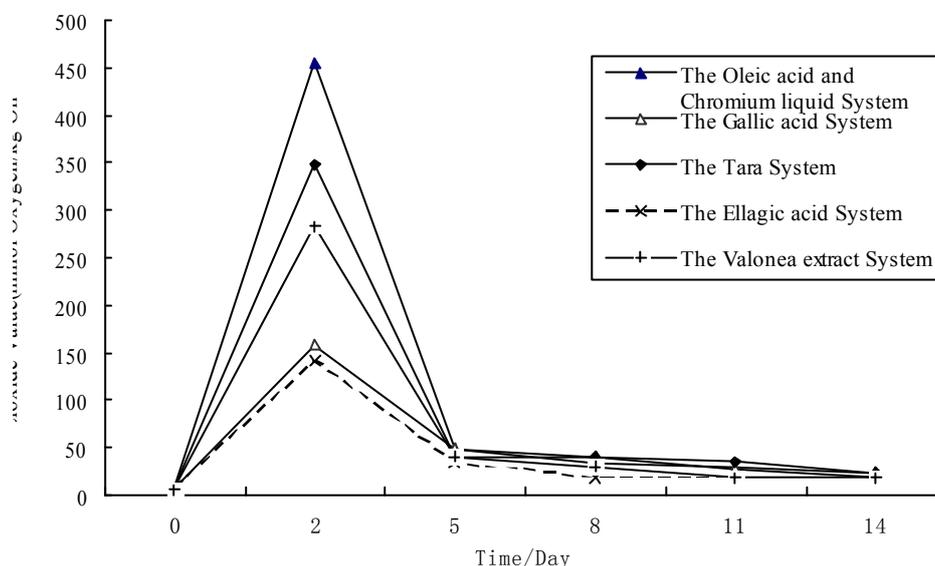
of gallotannin to hydroxyl radical the lactone of gallic acid was strongest. The reason of this result might be that the ellagic acid had not only much easier hydrogen losing with conjugation effect in its structure but also the more coordination ability with  $Fe^{2+}$  which reduced hydroxyl radical formation. This result also indicated that the ellagic acid and polyester derivatives weakened the catalysis of metal ion to free radical reaction through the coordination effect when it scavenged free radical.

### 3.3 The scavenging activity of gallotannin to superoxide anion radical

From the table 1, the result showed that the clearance rate of ellagic acid to superoxide anion radical was almost to 50%, much higher than the clearance rate of others, the gallic acid, Tara and Valonia, which was lower than 20%. The ability to eliminate superoxide anion radical was ranked from large to small as follow: ellagic acid, gallic acid, Tara and Valonia. The order was almost the same with the order of the samples' reducibility to  $Fe^{3+}$  and ability to eliminate hydroxyl radical in Fenton system on the base of the same total phenolic value. The clearance rate of gallotannin to superoxide anion radical comes from hydrogen losing reaction, to form the o-phenolic hydroxyl bond and the o-benzoquinone resonance structure. As regard to the highest clearance rate of ellagic acid, it is because besides the formation of o-phenolic hydroxyl bond and the o-benzoquinone resonance structure, there are two oxygen with P track isolated electron in its molecule inner ester, which made the ortho and para position phenoxyl radical more steady through the resonance effect so as to make phenoxyl produced from ellagic acid more stable and in result of highest clearance rate.

### 3.4 The scavenging activity of gallotannin to lipid radical

The peroxide value in different system was shown along with the time increasing at constant temperature as followed Fig 5.



**Fig.5 The peroxide value of oleic acid in different system and time**

( i ) From the Fig.5 the curves showed that the peroxide value of oleic acid in different system appeared in three phases: peak value phase, low value phase and steady value phase. In another word the peroxide value was all increasing first, reached the tiptop, then declined, reached the lowest value, at last got into steady value phase at the low value. The reason was that when the peroxide value was increasing the oleic acid, as the unsaturated fatty acid, occurred abduction and oxidation reaction and was oxidized

into hydrocarbon peroxide and hydroperoxide; when the peroxide value was reducing the peroxide was decomposed to be aldehyde and ketone or alcohol and carboxyl for more along with the developing of peroxide; when the peroxide value was steady the abduction and oxidation reaction was much slower and the formation rate was the same with the decomposed rate along with the reducing of the oleic acid.

(ii) The curve with gallotannin system in Fig.5 compared to the chromium and oleic acid system trended to gentle and its peak value was less obviously. This phenomenon exhibited that gallotannin had inhibitory effect on the oleic acid oxidized, reduced the speed of oleic acid oxidation greatly and also the output of the oleic acid oxidation. The reason was that the oleic acid, as the C-18 unsaturated fatty acid, its hydrogen atom of methylene beside double bond easy became free radical (R·) after the attract of oxygen, and then its autoxidation was beginning. The reaction was as follow <sup>[12]</sup>.

Chain Initiation: (1-1)

Chain Growing: (1-2)

(1-3)

(1-4)

(1-5)

(1-6)

(1-7)

Chain Termination: (1-8)

(1-9)

(1-10)

When the system contained the gallotannin or gallic acid, the polyhydroxy phenol ( InhH ) had reaction with peroxide free radical ( ROO• ) which came from the chain growing period in oleic acid oxidation and created steady polyhydroxy phenol free radical ( Inh• ). This polyhydroxy phenol free radical captured the peroxide free radical and created more steady polyhydroxy phenolic peroxidized hydrocarbon. The reaction was as follow <sup>[11]</sup>:



(1-12)

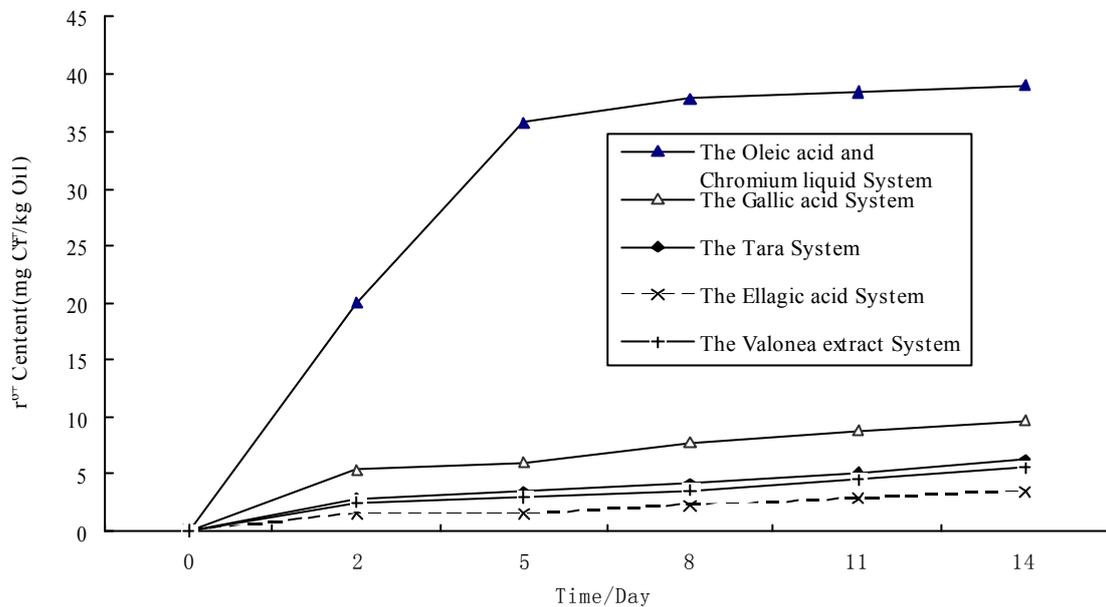
(iii) From the Fig.5 the curves also showed that different sample had different inhibitory effect to peroxide value increasing in the system contained the gallotannin and gallic acid. According the time of the peak value appeared and the highness of the peak, the order of samples in inhibitory ability on the oleic acid oxidized from large to sample was as follow: ellagic acid, gallic acid, Valonia and Tara. It meant that the order of gallotannin to lipid peroxy radical was gallic acid lactone was stronger than the gallic acid and its polyester derivative at the base of same total phenolic value content. That was because when ellagic acid lactone lost hydrogen it formed the more steady benzene oxygen radical and also had better complex ability with Cr(III) which inhibited the catalysis of Cr(III) to lipid radical reaction.

### 3.5 The prevention of gallotannin to Cr(VI) in simulated leather system

The Cr(VI) content in different system was shown along with the time increasing at constant temperature and humid as followed in Fig 6.

The curve without gallotannin, was far above the other curves. This result illuminated that in the oleic acid and chromium liquid system the gallotannin and gallic acid had inhibitory effect for Cr(III) oxidized to Cr(VI) indubitability. Connecting with the discussion of Part 3.4, the result came from the inhibition of phenolic hydroxyl to the reaction of free radical oxidation.

In the system with gallotannin or tannic acid, the order of gallotannin to resistance Cr(VI) formation in chrome leather simulated system from large to small was ellagic acid, Valonia, Tara and gallic acid. This order was different to the order gallotannin to Fe<sup>3+</sup> reducibility, hydroxyl radical, superoxide anion radical and lipid radical. It indicated that the gallotannin to Cr(VI) formation was not inevitable with its antioxidation and reducibility.



**Fig.6 The Cr(VI) content in different system and time**

From Fig.6, the curves were also showed that in oleic acid and chromium liquid system, the speed of Cr(VI) increasing before the 5<sup>th</sup> day was much faster than after the 5<sup>th</sup> day, and the fastest stage of Cr(VI) increasing was the time between the 2<sup>nd</sup> and 5<sup>th</sup> days. Combined with the peroxide value changing in Fig.5 it could be found that before the 2<sup>nd</sup> day the reaction of oleic acid in the system was mainly as followed the 1-2 and 1-3, so the peroxide value was increasing quickly; and at the time between 2<sup>nd</sup> and 5<sup>th</sup> day the reaction of oleic acid was mainly as followed 1-4 and 1-5 and the peroxide value was reducing quickly. Therefore, it could be concluded that Cr(VI) formation before the 2<sup>nd</sup> day was mainly effected by the lipid peroxy radical (ROO •) which had low effect on Cr(VI) formation and the speed of Cr(VI) formation was also relatively lower; between the 2<sup>nd</sup> and 5<sup>th</sup> day Cr(VI) formation was mainly effected by the hydroxyl radical (OH •) which had high free energy and the speed of Cr(VI) formation was also relatively higher; after 8<sup>th</sup> day the speed of Cr(VI) formation was very low because of the speed of peroxide formation and decomposition was very low.

From gallic acid system the speed of Cr(VI) formation kept slowly after the 2<sup>nd</sup> day. Combined with

the Tab.1, Fig.5 and reaction process of lipin free radical, the result indicated that the scavenging activity of gallic acid to the three free radical and its reducibility was much stronger than the Valonia and Tara's, but the Cr(VI) formation resistance was much weaker, which meant that the Cr(VI) formation resistance of the gallotannin and the tannic acid was not only depended by its antioxidation and reducibility but also with the coordination effect with the Cr(III). So using the coordination effect of gallotannin to reduce the free ion Cr(III) was also the important method to prevent the Cr(VI). From ellagic acid system the speed of Cr(VI) formation kept lowly and the concentration of Cr(VI) kept lowly. It was because in the earlier phase of oleic acid oxidation it restraint the reaction 1-2 in lipin free radical reaction process by the clearance to superoxide anion radical, in the mid phase it restraint the reaction 1-3 and 1-4 in lipin free radical reaction process by the clearance to lipid radical and in late phase it restraint Cr(VI) formation by the clearance to hydroxyl radical.

#### 4 Conclusions

With regarding to the gallotannin ability to prevent Cr(III) from oxidation into Cr(VI), ellagic acid was best. It had great reducibility, good clearance to lipid peroxy radical, superoxide anion radical and hydroxyl radical. The preventive principle was through hydrogen losing to eliminate superoxide anion radical from earlier free radical reaction, lipid peroxy radical in mid and hydroxyl radical in the end, and meanwhile through reducibility to prevent formation of Cr(VI), and kept the Cr(VI) content at the low concentration.

In chrome leather, oxidation of Cr(III) into Cr(VI) was the result of common action by lipid peroxy radical (ROO •) and hydroxyl radical (OH •). The ability of Valonia and Tara to eliminate the three free radical and its reducibility was much weaker, but the resistance to Cr(VI) formation was much stronger, which meant that the resistance to Cr(VI) formation of the gallotannin and the tannic acid was not only relied on its antioxidation and reducibility but also on the coordination effect with the Cr(III).

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