Preparation of Four Natural Iridoids and their Tanning/Dyeing Properties to Hide Powder

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Abstract: Four iridoid compounds, genipin(GP), loganin aglucon(LA), oleuropein aglucon(OA) and E-6-*O*-methoxycinnamoyl scandoside methyl este aglucon(EA) were prepared from *Gardenia jasminoides* Ellis, *Lonicera japonica* Thunb, *Olea europare* Linn and *Hedyotis diffusa* (Willd) Roxb respectively, their chemical structures were identified by ESI-MS, ^{1}H NMR and ^{13}C NMR, their tanning and dyeing properties to hide powder were investigated, the relationship between tanning/dyeing properties and the chemical structures were discussed. The results showed that all of the four natural iridoids could react with hide powder under a mild condition (35℃, pH=7.5～8.0), for a short time (about 6 h) and with a low dosage (5% of hide powder, w/w). The hydrothermal stability of hide powder was increased and different colors were induced to hide powder. The experiment also indicated that, the increasing of hydrothermal stability of the tanned hide powder and the color induced to it were closely related to the chemical structure of different iridoids.

Key words: iridoid; tanning agent; natural reactive dye; hide powder

1 Introduction

The previous research work has reported that, a novel iridoid crosslinking-agent, genipin(GP), could increase hide powder's thermal stability and dye it into dark blue by crosslinking reaction. By the combination tanning with aluminum-genipin, the T_p for hide powder by DSC analysis or T_s for bovine leather by classical measurement would be higher than 90 °C[1-3]. These results have suggested the possibility of iridoid compounds as potential tanning agents for leather industry. There are thousands of iridoid compounds in nature and their contents in some plants are fairly abundant. In the present study, four iridoid compounds, genipin (GP), loganin aglucon(LA), oleuropein aglucon(OA) and E-6-*O*-methoxycinnamoyl scandoside methyl este aglucon(EA) were prepared from *Gardenia jasminoides* Ellis, *Lonicera japonica* Thunb, *Olea europare* Linn and *Hedyotis diffusa* (Willd) Roxb respectively, their tanning and dyeing properties to hide powder were investigated, the relationship between tanning/dyeing properties and the chemical structures of the iridoid compounds were discussed.

2 Experimental

2.1 Materials

The four kinds of plants, *Gardenia jasminoides* Ellis, *Lonicera japonica* Thunb, *Olea europare* Linn and *Hedyotis diffusa* (Willd) Roxb were purchased from Wukuaishi Pharmaceutical Plant Market in Chengdu City and identified by Dr. Xiao-ling Wang. Bovine hide powder was provided by the Key Laboratory for Leather Chemistry & Engineering of Education Ministry, Sichuan University. *β*-glucosidase was the product of Sima and provided by Shanghai Bio-chemical Co. Ltd. Other chemicals are analytical class from Chengdu Chemical agents Co. Ltd. All experiments were performed at least twice to evaluate reproducibility.

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2.2 Preparation and identification of iridoid aglycones [5-8]

The four iridoid glycosides were isolated from the four plants respectively, their structures were identified by ESI-MS, ^{1}H NMR and ^{13}C NMR. Then they were hydrolyzed by β- glucosidase and aglycones were obtained.

2.3 Stability of iridoid aglycones

UV-vis were used to verify the stability of the other three iridoid aglycones as that had been done to genipin in the previous work [1]. Each iridoid aglycone was dissolved in PBS (pH ~ 7) to obtain a solution of 0.5 mg/ml and incubated at 35℃. The ultraviolet (UV) spectrum was monitored as a function of time. The absorbance spectrum form 200-400 nm was recorded on a UV-540 (Thermoelectro, USA) at 0.25, 2, 8 and 24 h.

2.4 Tanning

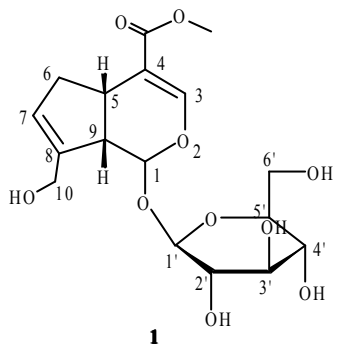
Hide powder was first hydrated with 1500% distilled water in a flask overnight at ambient temperature, filtered and resuspended in phosphate buffered saline (PBS) at pH =7.5-8.0. The tanning processes were evaluated using 0.5 g hide powder in 7.5 ml in a thermostated shaking bath. Tanning parameters were adopted the optimized conditions in the previous work [1]: The dosage for each iridoid was 5% (w/w) (based on the dry weight of hide powder), T=35°C, t = 6h and maintained the pH at 7.5-8.0 during the whole process. At the completion of tanning, the resulting mixture was filtered, the tanned hide powder was washed with distilled water until the effluent was clear. The tanned hide powder was then dried at ambient temperature.

2.5 Determination of thermal stability

Thermal stability of tanned hide powder was determined by differential scanning calorimetry (DSC) on a Differential Scanning Calorimeter model (Perkin-Elmer DSC7). Hide powder samples were prepared for DSC experiments by soaking in distilled water overnight and then blotting on filter paper. Moist, blotted samples (8~10 mg) were weighed into ampoules that were sealed and placed in the calorimeter. The temperature was programmed to record from 30 °C to 90 °C at 5 °C per min.

3 Results and discussion

3.1 The chemical structure of four iridoid glycosides



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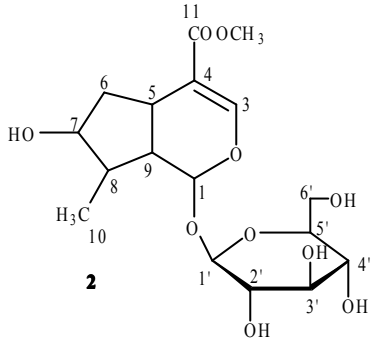

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Fig.1 Chemical structures of four iridoid glucosides (1: genipin; 2: loganin; 3: oleuropein; 4: E-6-O-methoxycinnamoyl scandoside methyl este)

3.2 Iridiods stability

The UV spectra of the four iridoids solutions that were incubated in PBS (pH ~ 7) at 35 °C after 0.25, 2, 8 and 24 h were illustrated in Figure 4. The characteristic peak for GP(a) and EA（d） remained at 242 nm and 239 nm respectively during the whole incubated period. The two characteristic peaks of OA(c) were remained at 232 nm and 280 during the whole incubated period; the two characteristic peaks of LA (b) were remained at 229 nm and 307nm during the whole incubated period (Figure 4).

These results were consistent with the result reported in the previous work [1], which indicated that, iridoid aglycones would not polymerized in PBS, or only limited polymerization occurred.

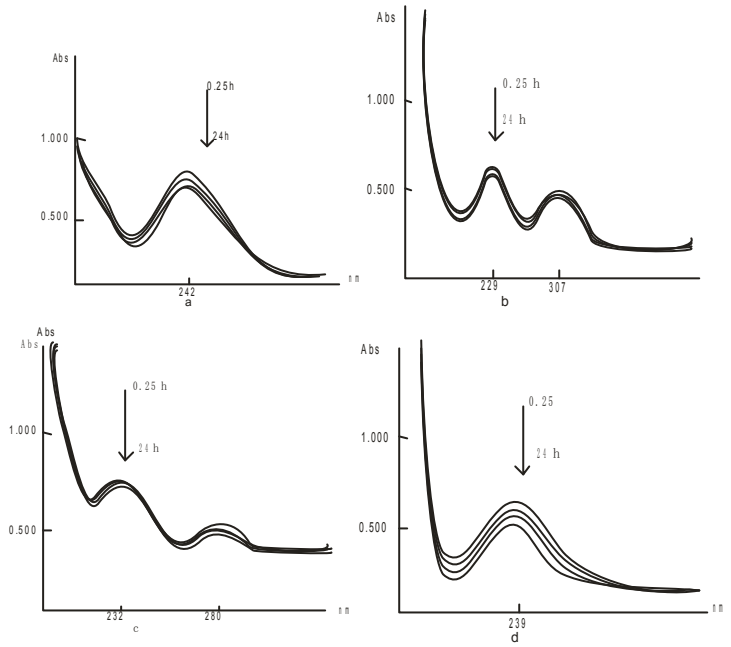

Fig. 2 UV-vis spectra for GP (a), LA (b), OA (c) and EA (d) in PBS solution at different storage time

3.3 Tanning and dyeing properties to hide powder

The tanning and dyeing results of four iridiods to hide powder were showed in Table 2.

Table 2 Tanning and dyeing results of 4 iridiods to hide powder

	Control	GA	LA	OA	EA
T_p(°C)	60	80	82	85	83
Color	white	dark blue	yellow	light yellow	mauve

Increases in thermal stability (shrinkage temperature) of a hide, hide powder, or even collagen are often cited as evidence of the tanning potential of the process responsible for the increase. The results of this study show that, the four iridoids could be effective at increasing the thermal stability of hide powder. Under conditions where hide powder suspended in PBS (pH=7.5-8.0) and were treated with each iridoid (5% w/w basis on dry weight of hide powder) for 6h at 35 ℃, T_p of all of the tanned hide powder were≥ 80 °C. These results further confirmed that, the special structure of the hexa-ring with an alkene-ether

from iridoids (including secoiridoids) is the key factor for the crosslinking reaction. Side groups have some effect on the increases in thermal stability. Oleuropein aglucon (OA) and E-6-*O*-methoxycinnamoyl scandoside methyl este aglycone (EA), which have phenol-hydroxyl groups in the molecular structures, would be advantage for increasing the thermal stability of tanned hide powder.

During the previous work [1], we have known that genipin could dye hide powder to dark blue; and this color is produced during the crosslinking reaction, not from genipin itself. This kind of dyeing mechanism is basically different with the dyeing process by natural dyes, acid dyes, reactive dyes, or any other dyes currently applied in the industry. Since then, we were wondering whether we could find some other iridoids which could dye protein to other colors (red, yellow, ect). If so, we might find a kind of "natural reactive dyes" special for protein fibers and give some guidance for their total synthesis. Needless to say, these kinds of natural reactive dyes would be environmental friendly and have good fastness property.

From the results showed in Table 2, we could see that yellow and mauve could be induced to hide powder by OA, LA and EA. The reason might be that, chromophares with complicated molecular structure were formed during the crosslinking reaction of iridoids with hide powder; and the side groups combined with the hexa-ring backbones of different iridoids were acted as auxochrome. Different auxochromes would produce different colors. Of course, the exact mechanism for this process need further research yet.

4 Conclusions

(1) The stability experiment results indicated that, polymerization did not occur or only limited polymerization occurred in iridoid-PBS solutions, i.e., most iridoid aglycones crosslinked with hide powder via monomer.

(2) Beside genipin, the other three iridoids also show considerable promise as potential tanning agent also. This means that, the special structure of the hexa-ring with an alkene-ether from iridoids (including secoiridoids) is the key factor for the crosslinking reaction. Side groups have some effect on the increases in thermal stability.

(3) Different color could be induced to hide powder by different *iridoids*. The reason might be that, chromophares with complicated molecular structures were formed during the crosslinking reaction; and the side groups combined with the hexa-ring backbones of different iridoids were acted as auxochrome. This result suggested the potential for iridoids to perform as a bio-friendly "natural reactive dye" for protein materials, such as leather, silk, wool, or even for human hair.

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