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PAPER

Lignin: a nature-inspired sun blocker for broad-spectrum sunscreens

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We report the evaluation of lignin for development of high-performance broad-spectrum sunscreens. Lignin is added into several commercial sunscreen products. Significant enhancements in ultraviolet (UV) absorbance are observed. The results show that the sunscreen effect of sun protection factor (SPF) 15 could reach to that of SPF 30 with 2wt% lignin addition. Adding 10wt% lignin makes SPF 15 outperform SPF 50. It is also interesting to find that the sunscreen performance improves with UV-radiation time. After two hours of UV radiation, the UV absorbance of the 10wt% lignin SPF 15 lotion increase dramatically. This has been attributed to some synergistic effect between lignin and other sunscreen actives in the lotions, as well as the antioxidant property of lignin. This nature-inspired lignin system may provide a green alternative to replace some synthetic sunscreen actives.

Introduction

Long-time exposure to ultraviolet (UV) radiation is hazardous and causes skin problems. In addition to wearing adequate clothing without impregnation,[1] sunscreen provides protection,[2, 3] commercial sunscreen products are divided into two categories according to their active ingredients, that is, physical and chemical sunscreens. In physical sunscreens, the active ingredients are mainly zinc oxide and titanium dioxide, based on reflection mechanism.[4] Physical sunscreens are healthy, but are not so comfortable, especially for people with dry skins. Compared to physical sunscreens, chemical sunscreens are easier to use, but have their own drawbacks. The active ingredients in chemical sunscreens are often synthetic chemicals. Long-time use of such chemicals may cause unexpected side effects on skins.[5] Natural sunscreens are therefore receiving more and more attention recently. Natural products such as green coffee oil, extracts of carica papaya, rosa kordesii, helichrysum arenarium and so on are proven to have radiation protection functions.[6-9] Usually, many natural sunscreens also have good antioxidant properties. However, most of the natural products are part-spectrum sun blockers and cannot block the full spectrum of UV light. Besides, extraction of the active ingredients from raw materials is costly. The natural sun blockers are often expensive and a large volume commercial production is limited.

Lignin is the only biomass rich in aromatic rings in nature due to its basic phenylpropane unit.[10-14] It also contains UV-absorbing functional groups such as phenolic, ketone and other chromophores.[15-17] Lignin is a natural broad-spectrum sun blocker.[18] In addition to sunscreen property, the free radical scavenging ability of phenolic groups gives lignin an excellent antioxidant property.[19-22] Although 5 to 36×10^8 tons of lignin is produced in nature and over 50 million tons of industrial lignin is produced annually, lignin has never used as sunscreen and antioxidant actives in cosmetics and/or pharmaceuticals due to some safety concerns.[23-25] Except for a small amount of lignosulfonates used as low-end surfactants, such as concrete water reducers, water-coal-slurry dispersants, and dye stuff dispersants, most lignin is burned for energy.[26-28] High-end applications of the industrial lignin at a large scale is still under exploration.

Recently, Ugartondo et al. tested the cell cytotoxicity of four types of industrial lignin and found that the products are safe.[30] Lignin-based products such as microcapsules are not cytotoxic and can be incorporated into cells.[30] These studies resolved doubts about the safety of lignin for potential applications in cosmetics and pharmaceuticals. In this work, alkali lignin recovered from black liquid is investigated for its sunscreen performance. The lignin is added to pure creams and commercial sun protection factor (SPF) 15 sun lotions, as a broad-spectrum sunscreen active. The sunscreen results of SPF 15 sunscreen lotions containing various amounts of lignin are compared to those of SPF 30 and SPF 50 sunscreen products. The irradiation stabilities of the prepared lignin sunscreens are also examined.

Experimental section

Materials

Alkali lignin was obtained from Shuntai technology Corp (Huaihua, Hunan, China). Before use, alkali lignin was purified again by alkali-acid treating for at least three times and continuous washing with DI water. Particle sizes of the dry alkali lignin were ranged from nanometers to micrometers (observed from SEM images in supplementary information). Pure creams were NIVEA refreshingly soft moisturizing cream (75 mL) (Cream-N) and LIFE glycerin hand cream (75 mL) (Cream-L). Sun lotions were LIFE SPF 15, 30, 50 sunscreen lotions (SPF15-L, SPF30-L, and SPF50-L) and BIOTHERM SPF 15, 30, 50 sunscreen lotions (SPF15-B, SPF30-B, and SPF50-B). All these pure creams and sunscreen lotions were bought from SHOPPERS drug market (Hamilton, Ontario, Canada).

Preparation of lignin sunscreen samples

All lignin-based sunscreen creams and lotions were prepared by simple magnetic stirring. For example, 5wt% lignin sunscreen

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was prepared by blending 0.10g lignin and 1.90g pure creams at 1000 rpm for 24 hours. The whole blending process was performed under room temperature in a dark room. After blending, these lignin sunscreens were transferred onto transpore tape surface for the measurement of UV transmittance. The dry alkali lignin used in this work was brown. The formulated lignin sunscreen lotions had light brown to brown colors as its content increased.

Sun protection factor (SPF) determination

3M Transpore tape was stickered on clean quartz slides of 2 mm thickness. A tape of 12.5 cm^2 was used to assure measurements on at least five non-overlapping spots. For each sunscreen cream and lotion, a minimum of five samples were prepared for the UV transmittance measurement. At the same time, a reference sample of transpore tape was also prepared. In preparation of the sunscreen samples, 1 mL fine needle syringe was used to transfer the sample. For a 12.5 cm^2 sample size, the slide was placed on an analytical balance and 2 mg/cm^2 of lignin sunscreen sample was distributed on the tape by dotting sunscreen on the slide. The sunscreen was then distributed over entire surface by slowly rubbing the slide surface with a cot coated finger. The sample was then placed in dark room, drying 20 min prior to measurement.

The UV transmittance of lignin sunscreen was measured by Shimadzu UV-3600 with integrating sphere (Shimadzu, Japan). Five spots were scanned for each sample. In each scan, a transmittance (T) measurement per 1 nm was collected in the wavelength range from UVB (290-320nm) to UVA (320-400nm). The SPF value was calculated by the following equation:

$$\mathrm{SPF} = \sum_{290}^{400} E_\lambda S_\lambda \Big/ \sum_{290}^{400} E_\lambda S_\lambda T_\lambda \qquad (1)$$

where E_λ = CIE erythemal spectral effectiveness;[31] S_λ = solar spectral irradiance;[32] T_λ = spectral transmittance of the sample.

Photostability test

The study on photostability of the sunscreen creams with or without lignin was performed on DU 800 UV/visible spectrophotometer (Beckman Coulter, USA). Specifically, the sunscreen samples were prepared according the same procedure as for the SPF measurements and were exposed to UV radiation for two hours. UV source was the deuterium light of the DU 800 UV/visible spectrophotometer. UV absorbance in the UVB and UVA areas (290-400nm) before and after radiation was then determined for the photostability of these sunscreens.

Results and discussion

Lignin added to pure creams

Two kinds of lignin sunscreens were prepared. One was blends of lignin with Cream-N and the other was lignin blended with Cream-L. Because Cream-L was too sticky, 10wt% water was added. The pure Cream-N had no absorbance in the UVA and UVB areas as shown in Figure 1a, while Cream-L with 10wt% water had a little absorbance in 290-310 nm as shown in Figure 1b. It was negligible because its corresponding SPF was only 1.05. The SPF value of the pure Cream-N without UV absorbance was 1. When lignin was added into these pure creams, their UV transmittance decreased and SPF values increased. When the

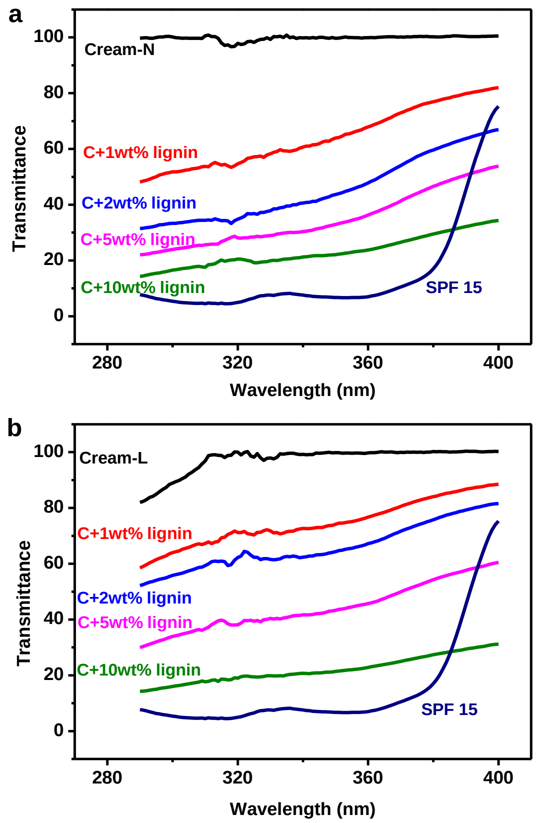

Fig. 1 UV transmittance of the pure creams blended with different amounts of lignin in UVB and UVA areas. The purchased SPF 15 sunscreen provides a reference. (a) Cream-N + lignin; (b) Cream-L + lignin.

Table 1. SPF values of the pure creams blended with different amounts of lignin.

Lignin (wt%)	0	1	2	5	10
Cream-N	0.99±0.01	1.82±0.13	2.74±0.30	3.68±0.30	5.72±0.26
Cream-L	1.06±0.01	1.48±0.01	1.69±0.03	2.68±0.17	5.33±0.47

amount of lignin increased to 10wt%, SPF of the lignin + Cream-N increased to 5.72, while SPF of the lignin + Cream-L increased to 5.33. Table 1 summarizes SPF values of the pure creams blended with different amounts of lignin.

As expected, UV transmittance of the pure cream+10wt% lignin was higher than that of LIFE SPF 15 sunscreen lotion. The latter contained two kinds of active ingredients with the total weight percent over 10wt% (refer to Table S1 in the supplementary information). However, the transmittance of the lignin sunscreens in UVA area, especially between 385~400nm was lower than that of SPF 15. It suggested that lignin is a very good natural candidate for broad spectrum sunscreens.

Lignin added to sunscreen lotions

It is known that sunscreen effect of the green coffee oil itself is not obvious, but the oil can help to improve performance of the synthetic sunscreen active.[6] This sunscreen enhancement has been attributed to antioxidants in the green coffee oil. Similarly, lignin is not only a natural sun blocker, it is also well known for antioxidant activities due to its phenolic hydroxyl groups.

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Therefore, sunscreen enhancement of the commercial SPF 15 sunscreen lotions with added lignin was investigated and compared with the sunscreen performance of SPF 30 and 50 sunscreen products.

It can be seen in Figure 2a that the UV transmittance of SPF 15-B + 2wt% lignin was close to that of SPF 30, but it was lower than that of SPF 50 in the UVA area, especially in the range of 380~400 nm. The SPF values of SPF 15-B blended with different lignin amounts, as well as SPF 30-B and SPF 50-B, were measured and summarized in Table 2. Unfortunately, further increase in the lignin amount did not improve the sunscreen effect. When lignin was increased to 10wt%, the sunscreen effect disappeared and the SPF level retuned to the original SPF 15 lotion. This was mainly caused by poor dispersion of lignin in SPF 15-B at such a high loading. SPF 15-B with 10wt% lignin dried quickly when it was distributed on the transpore tape.

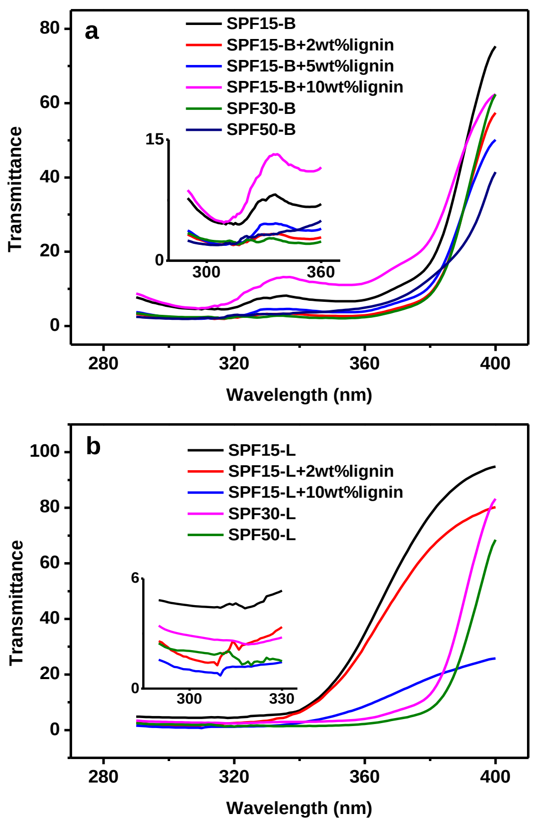

Fig. 2 UV transmittance of the commercial SPF 15 sunscreen lotions containing different lignin amounts in the UVB and UVA areas. The corresponding SPF 30 and 50 sunscreen lotions are included as reference. (a) BIOTHERM brand sunscreen lotions; (b) LIFE brand sunscreen lotions.

Table 2. Measured SPF values of the commercial sunscreen lotions and the sunscreen lotions with different amounts of added lignin.

Lignin (wt%)	0(15*)	2	5	10	0(30*)	0(50*)
BIOTHERM	20.25 ±0.82	44.36 ±6.22	39.41 ±6.68	16.63 ±0.35	41.25 ±1.54	58.30 ±4.03
LIFE	18.22 ±0.92	35.32 ±1.85	------	89.58 ±12.15	36.67 ±1.36	58.95 ±5.09

*Commercial sunscreen lotions with SPF of 15, 30 and 50, without lignin addition.

The sunscreen effect enhancement in SPF 15-L was not so obvious with 2wt% lignin addition. However, when the lignin amount was increased to 10wt%, the sunscreen effect was enhanced dramatically. The blended lotion not only became much better than SPF 15-L, but also significantly outperformed SPF 50-L, especially in the UVA area, as shown in Figure 2b. The SPF value of SPF 15-L+10wt% lignin reached 89.58 (in Table 2). SPF 15-L and SPF 15-B contained different active ingredients. It was also easier to disperse lignin in SPF 15-L than in SPF 15-B.

Radiation-enhanced sunscreen effect

We then evaluated photostability of the lignin-modified sunscreen lotions. There could be a concern about the service lifetime of lignin as UV blocker in the lotions. To our surprise, when the lignin-modified sunscreens were exposed to UV radiation for two hours, the UV absorbance in the UVA and UVB areas increased several times, as shown in Figure 3a. In comparison, there was little change in the UV absorbance with the commercial sunscreen lotions without lignin, as shown in Figure 3b and 3c. This result was unexpected and promising. How could the sunscreen performance of the lignin lotions get better with UV radiation? We made effort to elucidate the underlying mechanisms. The first suspect was the effect of radiation on lignin. The UV-radiated lignin somehow became a better UV blocker. To validate this assumption, the photostability of a pure cream was used as a reference. Different from the lotions, the cream contained no active sunscreen ingredients. Figure 3d shows the radiation effect on Cream + 10wt% lignin sample. Although there was a little increase in the UVB area after two hours of UV radiation, the absorbance in the UVA area was not obvious at all. Therefore, the radiation effect on lignin alone could not explain the observed results with the lignin lotions. Another possibility might be some synergistic effect of lignin and synthetic sunscreen actives in the lotions, such as homolete, avobenzone and so on. During the two hours of UV radiation, lignin might interact and/or react with some active ingredients, forming higher performance UV blockers. We hope this work provoke further studies on the actual molecular processes involved in these interactions and/or reactions. It should also be pointed out that lignin is an excellent antioxidant. Sunscreen actives such as avobenzone and octinoxate do not have good photostability and can easily form free radicals by photolysis.[33] Lignin is an effective radical scavenger and stops further formation of free radicals.

Conclusions

Lignin is evaluated as a nature-inspired broad-spectrum sun blocker in sunscreen lotions. As expected, lignin enhanced the sunscreen performance when it was added to commercial sunscreen lotions. However, the enhancement level was unexpectedly high. The UV absorbance of lignin-containing sunscreen lotions increased several times. It was particularly interesting to find that the performance improved with the UV radiation time. Although the underlying mechanism remained to be elucidated, it was attributed a synergistic effect between lignin and other sunscreen actives, as well as antioxidant property of lignin. This work demonstrated potential of lignin in such value-added applications as cosmetics.

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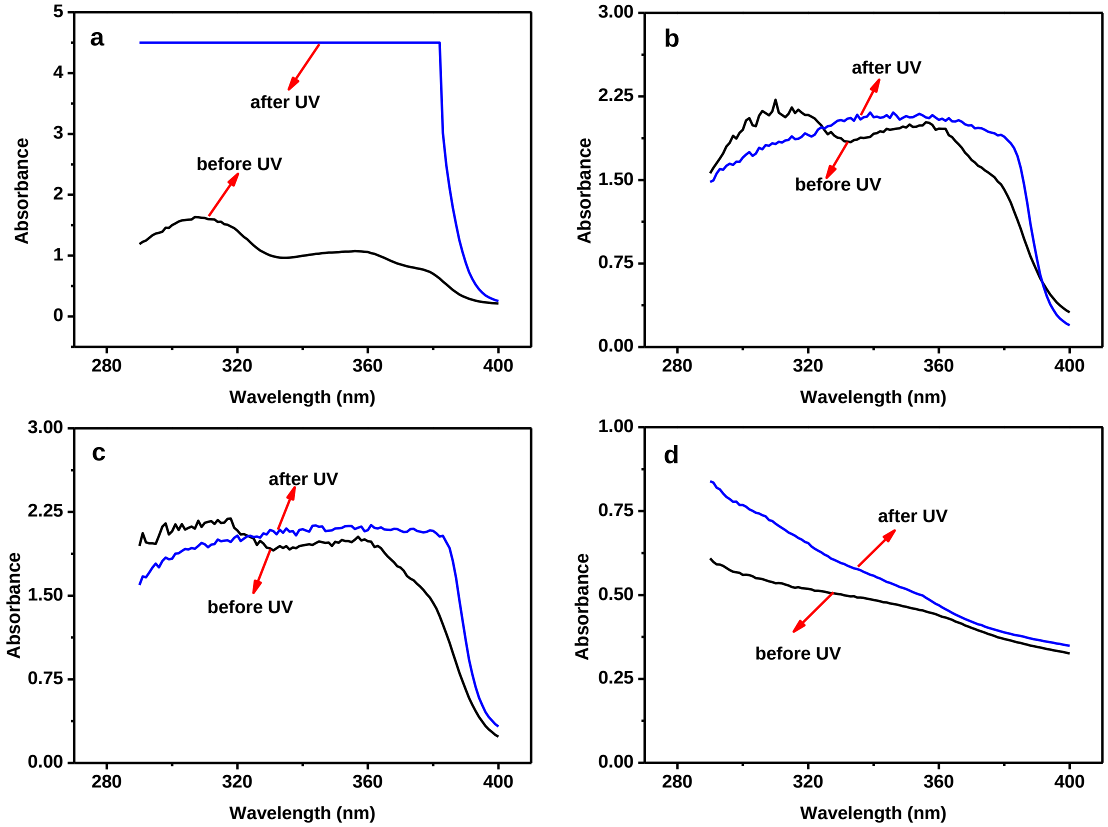

Fig. 3 UV absorbance of the sunscreens before and after two-hour UV radiation: (a) SPF 15-L+10wt% lignin; (b) SPF 15-L; (c) SPF 30-L; (d) Cream-L+10wt% lignin.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Active and inactive ingredients of purchased sunscreen lotions and pure creams. See DOI: 10.1039/b000000x/

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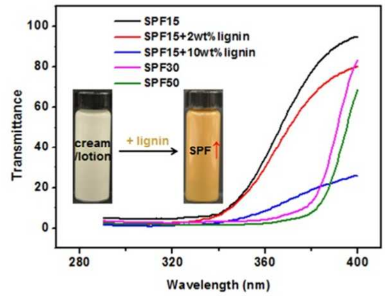

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