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International Journal of Pharmaceutics 308 (2006) 155–159
INTERNATIONAL JOURNAL OF PHARMACEUTICS
www.elsevier.com/locate/ijpharm

Incorporation of the sunscreen agent, octyl methoxycinnamate in a cellulosic fabric grafted with β-cyclodextrin

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Received 3 August 2005; received in revised form 25 October 2005; accepted 5 November 2005
Available online 15 December 2005

Abstract

The aim of the study was to investigate the incorporation of the sunscreen agent, octyl methoxycinnamate into cyclodextrin cavities covalently bound to cloth fibres. Tencel, a cellulosic fabric, was grafted with β-cyclodextrin molecules through reaction with monochlorotriazinyl-β-cyclodextrin (β-CDMCT). The finished and untreated textiles were soaked in water-methanol mixtures containing 2% (v/v) of sunscreen agent and subsequently subjected to several washing cycles. The unmodified and modified fabrics were characterized by UV spectrophotometry and thermogravimetric analysis. The level of octyl methoxycinnamate entrapped in the Tencel tissue was determined by high-performance liquid chromatography and was found to be much higher (0.0203%, w/w) for the textile functionalised with β-CDMCT compared to the unmodified fabric (0.0025%, w/w). In addition, spectrophotometric assessment of UV transmission through the fabric samples using the Transpore™ test showed that the in vitro sun protection factor of the textile support was markedly enhanced (3.2-fold increase) by impregnation with octyl methoxycinnamate of the β-CDMCT grafted textile. Hence, even after repeated washings, the β-CD finished fabric exhibits higher sunscreen agent retention and photoprotective properties than the unmodified textile material.

Keywords: Textile; β-Cyclodextrin; Grafting; Sunscreen agent; Octyl-methoxycinnamate; Sun protection factor

1. Introduction

The harmful effects of the solar UV radiation (290–400 nm) on human skin (i.e., erythema, cutaneous photoageing, immune suppression and various forms of skin cancers) have been the object of several studies that led to improved approaches in photoprotection (National Institute of Health, 1989; Gasparro et al., 1998; Green et al., 1999). The strategies advocated by health care authorities to prevent the sunlight-induced damage include reduced sun exposure, topical application of sunscreening preparations and the use of proper clothing (National Institute of Health, 1989; Gasparro et al., 1998; Diffey, 2001; Gambichler et al., 2001; Edlich et al., 2004).

To enhance the sun protection factor of textiles, clothes can be coated with sunscreen agents. This operation has been performed by adding the UV filters directly to the rinsing liquid during the laundry cycles (Edlich et al., 2004). A different approach is described in the present study for the incorporation of sunscreens into fabrics. This innovative procedure is based on cotton tissues grafted with β-cyclodextrin derivatives.

Cyclodextrins are toroidal-shaped cyclic oligosaccharides with a hydrophilic outer surface and an internal hydrophobic hollow interior. Cyclodextrins can entrap a vast number of lipophilic compounds into their hydrophobic cavity, depending on their size and molecular structure. For this reason cyclodextrins behave as hosts and the hydrophobic species are the guests. The driving force for such inclusion process is the enthalpic contribution that arises from non-covalent hydrophobic interactions (Loftsson and Brewster, 1996; Rajewski and Stella, 1996). This complexation phenomenon can modify some physico-chemical and chemical properties of the guest, for example enhancing its stability to oxidant agents and light and increasing its apparent aqueous solubility (Loftsson and Brewster, 1996; Rajewski and Stella, 1996; Uekama et al., 1998).

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doi:10.1016/j.ijpharm.2005.11.007

The remarkable ability of cyclodextrins to include hydrophobic compounds has been exploited in several fields, spanning from pharmaceuticals to cosmetics, from food manufacturing to chromatography and textile finishing (Loftsson and Masson, 2001; Del Valle, 2004; Szente and Szejtli, 2004; Wang and Chen, 2005). The incorporation of cyclodextrins onto fabrics can be carried out by impregnation or spraying of the tissue with a cyclodextrin solution, or through covalent binding (grafting) of the cyclodextrins to the cloth surface (Lo Nostro et al., 2002; Martel et al., 2002). The latter approach has the advantage that it lasts longer than the simple surface adsorption. Grafted specimen retain their complexing properties also after handling and repeated washing cycles (Lo Nostro et al., 2002; Martel et al., 2002).

This study describes the chemical grafting of monochlorotriazinyl-β-cyclodextrin (β-CDMCT) onto Tencel, a cellulosic fabric obtained from wood pulp. β-CDMCT was selected for this investigation since it is commercially available, has no irritating or sensitizing effects (Reuscher and Hinsenkorn, 1996) and represents an efficient tool for surface modification of textiles (Lo Nostro et al., 2003). In addition, the β-cyclodextrin macrocycle has been shown to be the most suitable host for the inclusion of sunscreen agents (Scalia et al., 2002). Tencel was chosen as the clothing material since, while retaining some structural properties that are typical of natural cotton fibres, it exhibits reduced variability in texture, specific weight and specific area (Lo Nostro et al., 2001, 2002, 2003). The present work also reports on the inclusion of octyl methoxycinnamate (OMC), the most widely used sunscreen agent (Scalia et al., 2002), in the β-CD cavities grafted on the textile surface. The influence of the complexed UV filter present on the fabric surface on the sun-protective capacity of the finished textile was then evaluated.

2. Materials and methods

2.1. Materials

Monochlorotriazinyl-β-cyclodextrin (β-CDMCT) was obtained from Wacker-Chemie Italia (Milan, Italy) and used as received. Tencel was kindly provided by Tecnotessile Srl (Prato, Italy). The fabric was carefully rinsed in boiling aqueous Na_2CO_3 for 3 h, and then dried at room temperature before any chemical treatment or test. Octyl methoxycinnamate (OMC; Fig. 1) was supplied by Roche Ltd. (Geneva, Switzerland). Methanol and acetonitrile were high-performance liquid chromatography (HPLC)-grade from Sigma–Aldrich (Steinheim, Germany). All other chemicals were of analytical-reagent grade (Fluka, Milan, Italy).

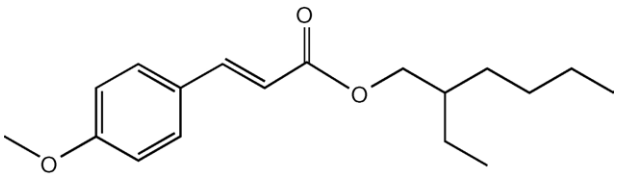

Fig. 1. Chemical structure of octyl methoxycinnamate.

2.2. Grafting of Tencel with β-CDMCT

Permanent grafting of β-CDMCT was carried out according to a previously reported method (Lo Nostro et al., 2003), with minor modifications. The procedure (see Fig. 2) consists in soaking for 5 min the fabric samples (typically 4 cm × 4 cm) at room temperature in an aqueous solution of β-CDMCT (15%, w/v) and Na_2CO_3 (15%, w/v), under magnetic stirring. The samples were then squeezed to remove the excess solution. To minimize the reaction of β-CDMCT with air moisture, the impregnated samples were cured in an oven at 130 °C for 15 min at atmospheric pressure (dry heat), and then carefully rinsed with demineralized water to remove any unreacted β-CDMCT. The tissue was then conditioned in a dry box at constant relative humidity (56%) and room temperature. β-CDMCT was detected on the treated textile surface through UV spectrophotometry. The grafting yield was evaluated by weighing the sample before and after the treatment, with a weight increment of about 5%.

2.3. Impregnation of grafted Tencel with OMC

Modified and unmodified fabric samples were treated with OMC by soaking the textile material for 2 h under stirring in a water-methanol mixture (30:70, v/v) containing 2% (v/v) of the UV filter. The samples were then roll-squeezed, washed several times at room temperature with running tub water, deionized water and 30% (v/v) methanol in water. The latter mixture was found to be more efficient than soapy water for the removal of adsorbed material from the fabric surface.

The OMC uptake of the untreated and grafted Tencel fabrics was evaluated by HPLC, UV and thermal analyses, as described below.

2.4. High-performance liquid chromatography

The HPLC apparatus consisted in a Model LabFlow 3000 pump (LabService Analytica, Bologna, Italy), a Model 7125

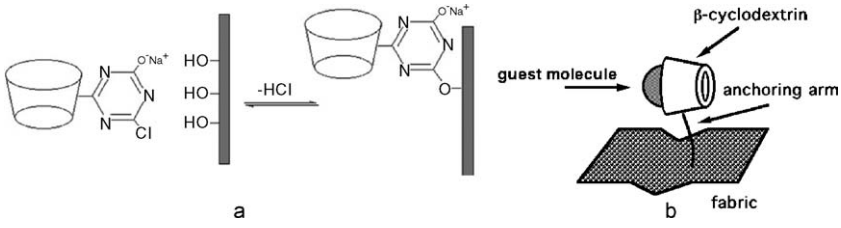

Fig. 2. Chemical grafting of monochlorotriazinyl-β-cyclodextrin onto a cellulosic fibre (a). Scheme of a host-guest inclusion complex grafted on the textile surface (b).

injection valve with a 10 μL sample loop (Rheodyne, Cotati, CA, USA) and a Model 975-UV variable wavelength UV–vis detector (Jasco, Tokyo, Japan) set at 310 nm. Data acquisition and processing were accomplished with a personal computer using Borwin software (JBMS Developpements, Le Fontanil, France). Sample injections were performed with a Model 701 syringe (10 μL; Hamilton, Bonaduz, Switzerland). Separations were performed on a 5-μm Zorbax SB-CN column (150 mm × 3.0 mm i.d.; Agilent Technologies, Waldbronn, Germany) eluted isocratically, at a flow-rate of 0.4 mL/min, with methanol-acetonitrile-water (40:25:35, v/v/v). Chromatography was performed at room temperature. The identity of the OMC peak was assigned by co-chromatography with the authentic standard. Quantification was carried out by integration of the peak areas using the external standardization method.

2.5. Sample preparation

The test samples were obtained by cutting sections (2.5 cm × 2.5 cm) of cloth from the treated and untreated Tencel fabric. The cloth strips were accurately weighed, cut into small pieces and extracted with ethanol (10 mL) under stirring at 70 °C for 10 min. The extraction was repeated with fresh solvent and the combined ethanol fractions were adjusted to volume (20 mL). A portion of the resulting suspension was filtered through 0.45-μm membrane filters (Whatman, Clifton, NJ, USA) and analysed for OMC by HPLC.

2.6. UV spectrophotometry

Absorbance spectra were collected with a Perkin-Elmer Lambda 5 spectrophotometer (Perkin-Elmer, Norwalk, CT, USA) for liquid samples, and with a Perkin-Elmer Lambda 35 instrument, equipped with a 60-mm integrating sphere, for fabrics. In the latter case, each measurement is the average of four scans obtained by rotating the sample by 90°.

2.7. Thermal analysis

Thermogravimetric analysis was performed with an SDT 2960, series Q600 apparatus (TA Instruments, Milan, Italy). The temperature range was 40–300 °C, with a scan rate of 10 °C/min. All runs were performed with a nitrogen flux of 100 mL/min.

2.8. In vitro sun protection factor measurement

The in vitro determination of the sun protection factor (SPF) of the different fabric samples was carried out according to the Diffey and Robson (1989) technique, with minor modifications. The method is based on the measurement of the transmission spectrum of UV radiation (290–400 nm) through Transpore™ tape (a surgical tape fairly transparent to UV and able to simulate the texture of human skin), before and after application of the textile tissue. The samples were cut out from the centre of each fabric specimen and were secured on the tape by gumming the upper and lower edge. The Transpore™ tape was then placed into the spectrophotometer sample compartment over the quartz input optics of the detector. Twelve single measurements were carried out for each sample. The samples were rotated (90 °C) during the test. The spectral data were recorded on a JascoV-530PC UV–vis spectrophotometer, processed with a personal computer and the SPF calculated according to Diffey and Robson (1989).

2.9. Statistical analysis

Statistical analyses were performed by using the unpaired Student's *t*-test (Instat, Graphpad Software, San Diego, CA). *P*-values <0.05 were considered significant.

3. Results and discussion

3.1. Characterization of β-CD modified fabric

Plain Tencel or the fabric functionalised with β-CD (Fig. 2) was charged with OMC, carefully rinsed (see Section 2) and subjected to spectrophotometric analysis (Fig. 3). The UV spectra have been ordered in the vertical direction in order to avoid overlapping of the profiles and improve the clarity of the plot. The methanolic solution (2.0%, v/v) of OMC (open circles) showed the typical peaks at 310, 227 and 211 nm. The untreated Tencel sample (squares) gave almost no absorption between 220 and 360 nm. The fabric material that was simply coated with OMC (diamonds) revealed the presence of OMC through the main peak at 310 nm. After grafting with β-CDMCT, the textile (open downward triangles) exhibited a significant absorption below 280 nm, with a maximum around 230 nm (Fig. 3), due to the triazinyl chromophore (Lo Nostro et al., 2003). The β-CDMCT-grafted sample treated with OMC (bold line, full circles) showed the typical peaks of the β-CDMCT-grafted textile at lower wave-

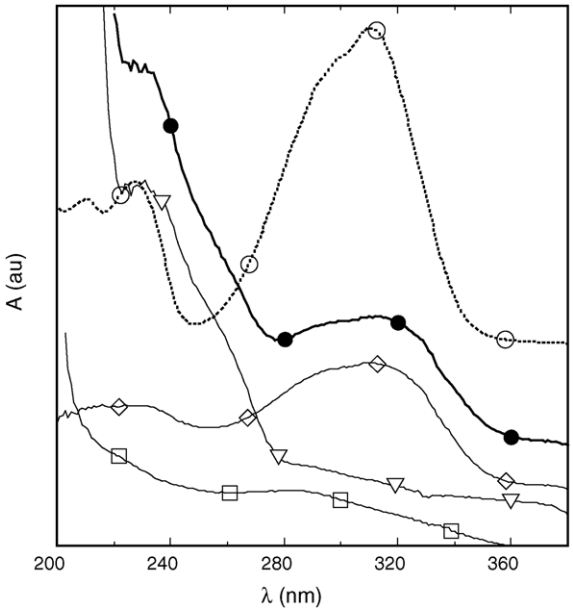

Fig. 3. UV spectra of: (◯) OMC (2.0%, v/v) in methanol; (□) untreated Tencel; (◊) Tencel loaded with OMC; (▽) Tencel grafted with β-CDMCT; and (●) Tencel grafted with β-CDMCT and loaded with OMC.

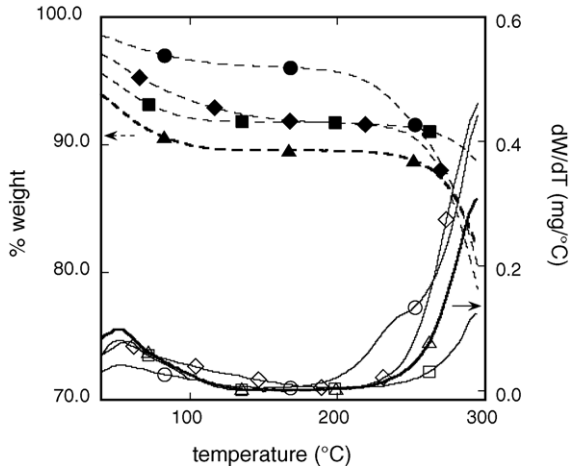

Fig. 4. Thermal analysis profiles between 40 and 300 °C. Variation in sample weight (left *y*-axis, full symbols) and d*W*/d*T* (right *y*-axis, open symbols) for: untreated fabric (circles), fabric grafted with β-CDMCT (diamonds), untreated fabric loaded with OMC (squares), and β-CDMCT-grafted fabric loaded with OMC (triangles).

lengths and a small bathochromic shift to 314 nm for the main peak of OMC (Fig. 3). This red shift can be ascribed to the more hydrophobic environment experienced by OMC (Sabaté and Estelrich, 2003; De Garcia Venturini et al., 2005) and suggests the formation of the host-guest inclusion complex between OMC and β-CD at the fabric's surface.

The thermogravimetric study of the Tencel fabrics indicated that, as expected, the untreated sample is sensitive to the temperature gradient, with a consistent loss of mass above 200 °C (Fig. 4). All the modified textiles appeared to be more stable, with a significant mass decrement only above 250 °C (Fig. 4). The analysis of the derivative (right *y*-axis) showed higher d*W*/d*T* (d*W* is the change in sample weight with a change in temperature, d*T*) levels for the untreated sample and for the β-CDMCT-grafted Tencel specimen. The clothes treated with OMC (included into the cyclodextrin cavities or simply adsorbed on the fabric fibres) were more stable, presumably because of the higher hydrophobicity of the textile surface.

In order to quantify the actual amount of OMC entrapped in the different Tencel supports, the UV filter was extracted from the fabric specimen and assayed by HPLC. Several parameters affecting the release of the sunscreen agent from the textile material were examined, including different liquid solvents (i.e., methanol, ethanol, acetonitrile), the use of mixing or ultrasonication, the extraction temperature and time. The highest sunscreen levels were produced by two sequential 10 min extractions of the tissue in ethanol at 70 °C, under magnetic stirring. The recovery of OMC from the fabric was evaluated by subjecting the samples, processed according to the method outlined above, to Soxhlet extraction with ethanol for 6 h. Less than 13.6% of the total UV filter content remained in the textile material (as determined by Soxhlet extraction and HPLC analysis), thus indicating a satisfactory extraction efficiency. In the unmodified Tencel tissue impregnated with OMC, the UV filter concentration was 0.0025% ± 0.0013 (w/w), while the sunscreen concentration measured in the β-CD grafted textile sample was

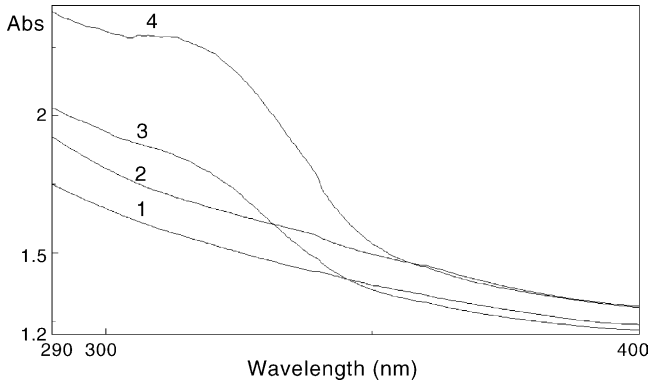

Fig. 5. Wavelength scans obtained by the Transpore™ assay. Curves: 1, unmodified Tencel; 2, β-CDMCT-grafted Tencel; 3, unmodified Tencel loaded with OMC; 4, β-CDMCT-grafted Tencel loaded with OMC.

0.0203% ± 0.0086 (w/w). The high dispersion of the OMC assay results can be probably traced to the non-homogeneous structure of the fabric surface. In addition, according to the producer's specification, one or more (two to three) triazinyl groups can be bound to a single cyclodextrin macrocycle (Fig. 2). Since it is the triazinyl chlorine atom, which reacts with the nucleophilic residues (e.g., hydroxyls, amines) present in the textile fibres (Fig. 2), also the number of anchoring arms between the hosting species and the fabric can be variable. However, the β-CD finishing of Tencel fabric markedly enhances its sunscreen agent retention capacity (8.1-fold increase), even after several washing cycles of the textile material in water and water-methanol.

3.2. Sun protective properties

The sunlight-protective properties afforded by clothing fabrics have been assessed by their UV protection factor (UPF), which is analogous to the more frequently used "sun protection factor" (SPF) associated to sunscreens (Diffey, 2001). The UPF is determined in vitro by measuring spectrophotometrically the UV transmission across the fabric sample (Gambichler et al., 2001). Since, in this study, the textile material is coated with a UV filter, the well-known Transpore™ test for the in vitro evaluation of the SPF (Diffey and Robson, 1989) was selected. This procedure represents a valuable tool to analyze the transmittance of opaque samples such as semisolid preparations (creams, gels, pastes), nano- and micro-particles containing sunscreen agents (Wissing and Müller, 2002; Scalia et al., 2004). Fig. 5 shows the results of the Transpore™ assay on the unmodified and β-CDMCT-grafted textile materials. The untreated fabric showed high absorption values (SPF, 41.4 ± 3.9) since, as expected, the textile yarns are opaque to the UV radiation, the only possible way for the radiation to pass across the fabric is across the spaces between the yarns (Gambichler et al., 2001). The fabric grafted with β-CDMCT (with no sunscreen agent) gave results close to those of the control (Fig. 5) with an SPF of 47.4 ± 8.6 ($P > 0.05$ compared to plain Tencel). The curve of the fabric material obtained by simple surface adsorption of the UV filter, exhibited the characteristic absorption pattern of OMC and an increase of the SPF value to 60.3 ± 2.8. A remarkable decrease of the spec-

tral UV transmission (Fig. 5) was attained by the β-CDMCT finished Tencel tissue loaded with OMC, which produced a 3.2-fold increase of the SPF (SPF, 133.1 ± 8.5) as compared to the control sample. The obtained absorption curves (Fig. 5) indicate that the fabric functionalised with β-CD exhibits higher photo-protective capacity than unmodified Tencel, even after repeated washing cycles of the cloth material.

4. Conclusions

The results reported in this study demonstrated that textile finishing with β-CDMCT increases the uptake of OMC by the tissue material thereby enhancing the UV screening properties of the clothing fabrics. In addition, the covalent binding of β-CD to the textile fibres improves the resistance of the entrapped sunscreen agent to washing cycles, prolonging the UV protective effect afforded by the fabric. The chemical grafting of cyclodextrins onto cotton fibres represents a useful strategy for the production of sun-protective clothing.

Acknowledgments

The authors are grateful to MIUR (Ministero per l'Istruzione, l'Università e la Ricerca) and CSGI (Consorzio per lo Sviluppo dei Sistemi a Grande Interfase) for financial support.

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