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# Provitamin $D_2$ and Provitamin $D_3$ Photo Transformations in Cholesteric Liquid Crystal Mixtures Induced by UV Radiation

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*Shifts of selective reflection peaks under UV irradiation (which can be observed as color changes) are reported for induced cholesteric systems (nematic + optically active dopant) additionally doped with ergosterol (provitamin $D_2$) or 7-dehydrocholesterol (provitamin $D_3$). the effect is based on the photoinduced conversion of ergosterol into vitamin $D_2$, and 7-dehydrocholesterol into vitamin $D_3$, with the vitamins and provitamins having opposite signs of their helical twisting power. The observed shifts of the selective reflection peaks (more than 190 nm after 45 min of UV irradiation) allow both instrumental and visual monitoring of biologically active UV radiation.*

**Keywords:** induced cholesteric; phototransformation; provitamin $D_2$; provitamin $D_3$; UV monitoring



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## INTRODUCTION

The cholesteric mesophase is known as a medium that can be sensitive to the smallest changes in its composition and structure of the constituent molecules [1–6]. Variations of the helical pitch caused by different external factors can be easily recorded using the routinely measured selective reflection/transmission spectra (the maximum selective reflection wavelength $\lambda_{max}$ is equal to $np$, where $p$ is the helical pitch, and $n$ is the average refractivity index). This makes cholesteric liquid crystals a promising base for development of various sensor materials. Extensive studies of changes in helical pitch induced by UV radiation have been carried out for cholesteric systems of different types. UV-induced $\lambda_{max}$ shifts were observed in induced cholesteric LC systems (mixtures of an achiral LC with an optically active mesomorphic or non-mesomorphic dopant) when the cholesteric mixture comprised a conformationally active dye [7] or a photoisomerizable compound as a chiral dopant [8–11], or when a photoisomerizable nematic component was used in induced cholesteric mixtures [12–13].

Recently, it has been proposed to use steroids of the vitamin D group as chiral dopants [14–16], with subsequent monitoring of the UV-induced provitamin D – vitamin D transformation in a liquid crystalline solvent. As the helical twisting power of vitamin D derivatives was too low to produce visible colors in a nematic matrix, the idea acquired practical feasibility when it was proposed that provitamin D should be added to a cholesteric matrix already exhibiting $\lambda_{max}$ in the visible range [17]. In subsequent papers, data on UV-induced $\lambda_{max}$ shifts were reported for systems comprising provitamin $D_2$ in induced cholesteric systems of different composition [18–21].

In this paper, our further studies are reported in detail, involving cholesteric matrices of optimized composition, with both provitamin $D_2$ ($ProD_2$) and $ProD_3$ as photosensitive chiral components.

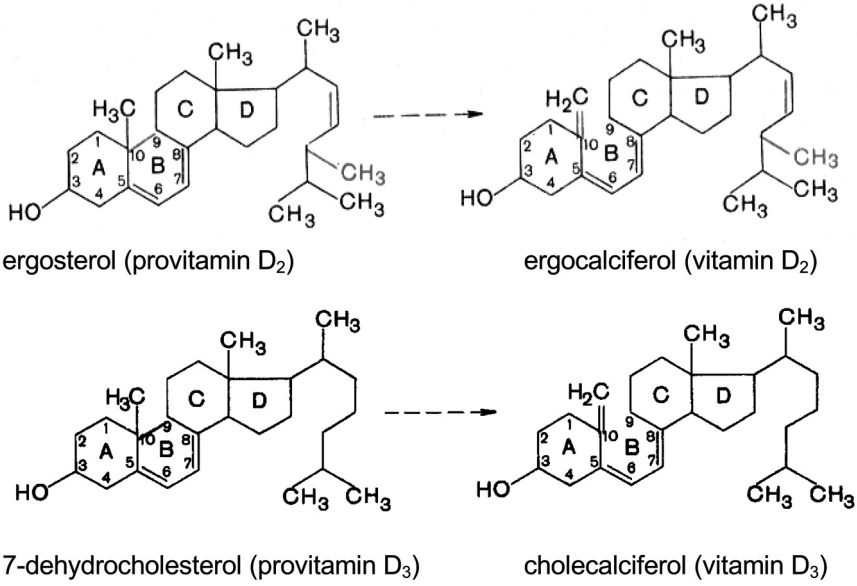
## MATERIALS AND METHODS

The induced cholesteric liquid crystals used in our study should have a broad temperature range of the mesophase. It is important for the UV biosensor that its helical pitch should be temperature independent (or weakly dependent). Moreover, the cholesteric mixture used should be composed of a nematic host and a chiral dopant, both non-photoisomerizable and transparent in the visible and near-UV ranges (down to 250 nm).

We have chosen the nematic mixture ZLI-1695 (Merck) as our nematic host, which is a mixture of cyclohexyl cyclohexanes with the

nematic range of 13–72°C. As chiral dopants, we used left-handed ZLI-4571 (S-1011), right-handed ZLI-4572 (R-1011), left-handed MLC-6247 (S-2011) and right-handed MLC 6248 (R-2011).

As it is known, under UV irradiation provitamins $D_2$ and $D_3$ (ergosterol and 7-dehydrocholesterol) are converted into previtamins $D_2$ and $D_3$ by photoinduced ring-opening reactions. These immediate precursors of vitamin D are converted into ergocalciferol (vitamin $D_2$) and cholecalciferol (vitamin $D_3$) by an intramolecular hydrogen shift [22, 23]:




**SCHEME 1**

As it can be seen from the scheme, vitamin $D_2$ and vitamin $D_3$ are formed from ergosterol and from 7-dehydrocholesterol as a result of breaking of the chemical bond between the 9th and 10th carbon atoms in the ring B, which occurs under UV irradiation. Provitamin $D_2$ and provitamin $D_3$ in nematic liquid crystals (LC) induce right-handed helix and vitamin $D_2$ and vitamin $D_3$ induce left-handed helix [24].

In our experiments, we doped right- and left-handed cholesterics with $ProD_2$ and $ProD_3$ and recorded the resulting color changes (i.e., the helical pitch variation) due to photoisomerization of $ProD_2$ and $ProD_3$. To check the general course of the phototransformation reaction, we also doped the cholesteric compositions with vitamin $D_2$ under

the same conditions. All vitamin D group compounds used in our experiments were obtained from Sigma.

The experimental studies were carried out using a standard sandwich-type cell (thickness ~10 μm). The transmission spectra measurements were made at room temperature using a Specord M40 spectrophotometer. A 100 W medium pressure mercury lamp and a filter transparent in the wavelength range 290–400 nm were used in our UV irradiation setup.



## RESULTS AND DISCUSSION

Depending on the handedness of the initial cholesteric structure the pitch after addition of provitamin $D_2$ (provitamin $D_3$) can either increase or decrease. Under UV irradiation, as a result of photo

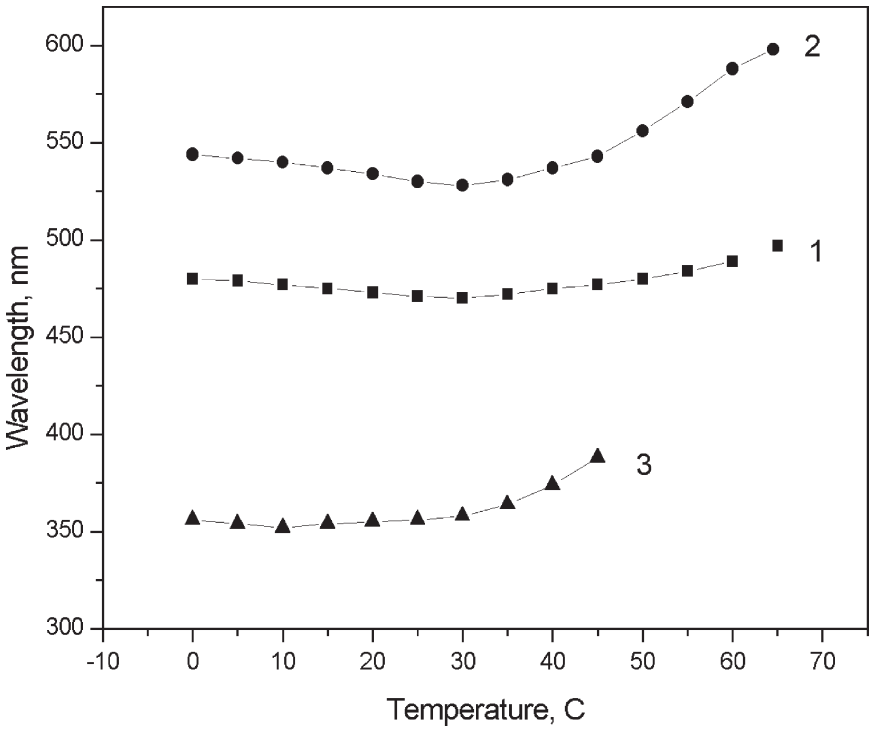



**FIGURE 1** Temperature dependence of the selective reflection peak for mixtures: 1 – 91%ZLI-1695 + 9%1011S; 2 – 90%(91%ZLI-1695 + 9%1011S) + 10% Provitamin$D_2$; 3 – 90%(91%ZLI-1695 + 9%1011S) + 10%Vitamin$D_2$.

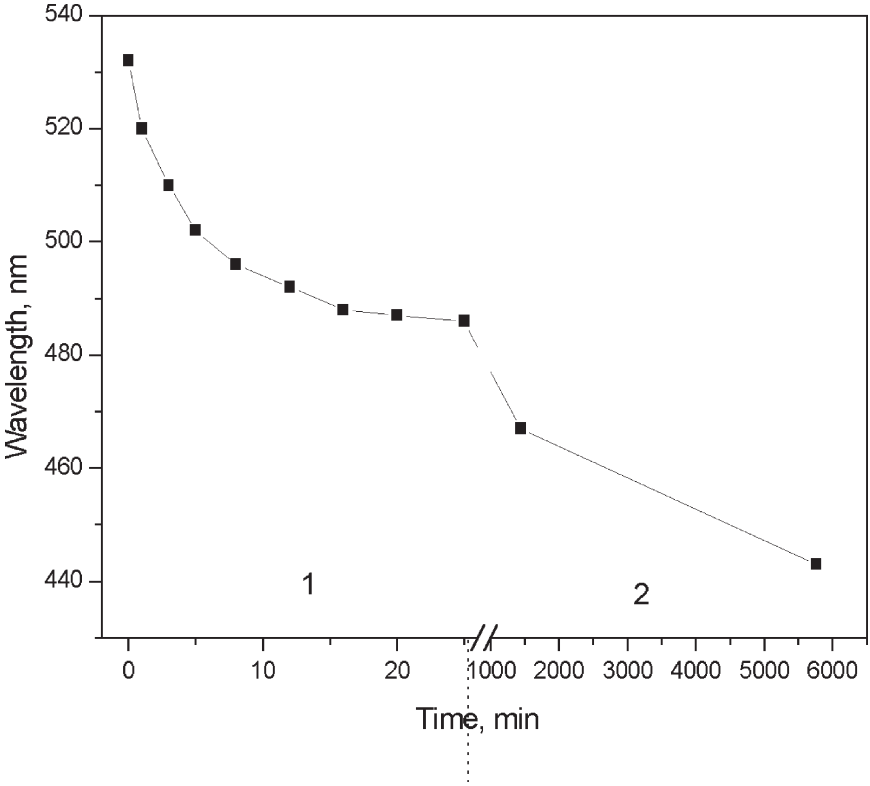



**FIGURE 2** Exposure time dependence of selective reflection peak for the mixture: 90%(91%ZLI-1695 + 9%1011S) + 10%Provitamin$D_2$.

transformation of ergosterol and 7-dehydrocholesterol, the helical pitch changes in the opposite direction, i.e., back to the pitch values for the initial (undoped) cholesteric structure and further on. This is in agreement with the data on the effective helical twisting sense of vitamin $D_2$, known to be opposite to that of ergosterol [24].

In Figures 1 and 3, the selective reflection peak wavelength $\lambda_{max}$ is shown as function of temperature for induced cholesteric systems ZLI-1695 + 1011S (1011R) doped with Pro$D_2$ and $D_2$. In both cases, doping with Pro$D_2$ and $D_2$ shifted $\lambda_{max}$ to opposite directions.

In Figures 2 and 4, changes in $\lambda_{max}$ under UV irradiation (at room temperature) are plotted as functions of exposure time. The plots obtained are essentially similar, accounting for the opposite helix senses induced by the two chiral dopants (1011S and 1011R). Shifts of $\lambda_{max}$ by up to 190 nm could be observed after 45 min of irradiation.

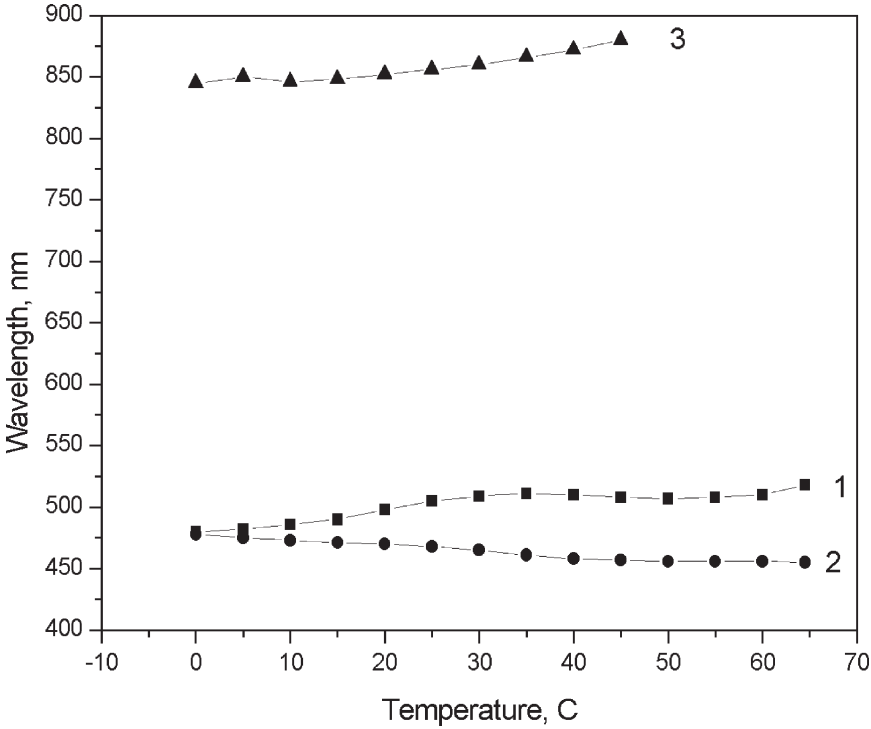



**FIGURE 3** Temperature dependence of selective reflection peak for mixtures: 1 – 91%ZLI-1695 + 9%1011R; 2 – 90%(91%ZLI-1695 + 9%1011R) + 10% Provitamin$D_2$; 3 – 90%(91%ZLI-1695 + 9%1011R) + 10%Vitamin$D_2$.

We also studied changes in $\lambda_{max}$ that occurred after irradiation had been stopped. As shown in Figures 2 and 4, the selective reflection peak is continued to be shifted further on. This fact indicates that not all molecules of provitamin $D_2$ are transformed to vitamin $D_2$ during irradiation. This is also in agreement with the experimental fact that just by means of UV-induced transformation we cannot reach the selective reflection peak values obtained by doping the cholesteric matrix with vitamin $D_2$ (see Figs. 1, 3).

An essentially similar behaviour was observed under the same experimental conditions when we used chiral dopants ZLI-811 [19,21] and ZLI-2011 (R, S) instead of 1011 (R, S), with the only difference that $\lambda_{max}$ changes induced by Pro$D_2$ in the 2011(R)-containing matrix were much smaller as compared with the 1011(R) or 811(R) cases.

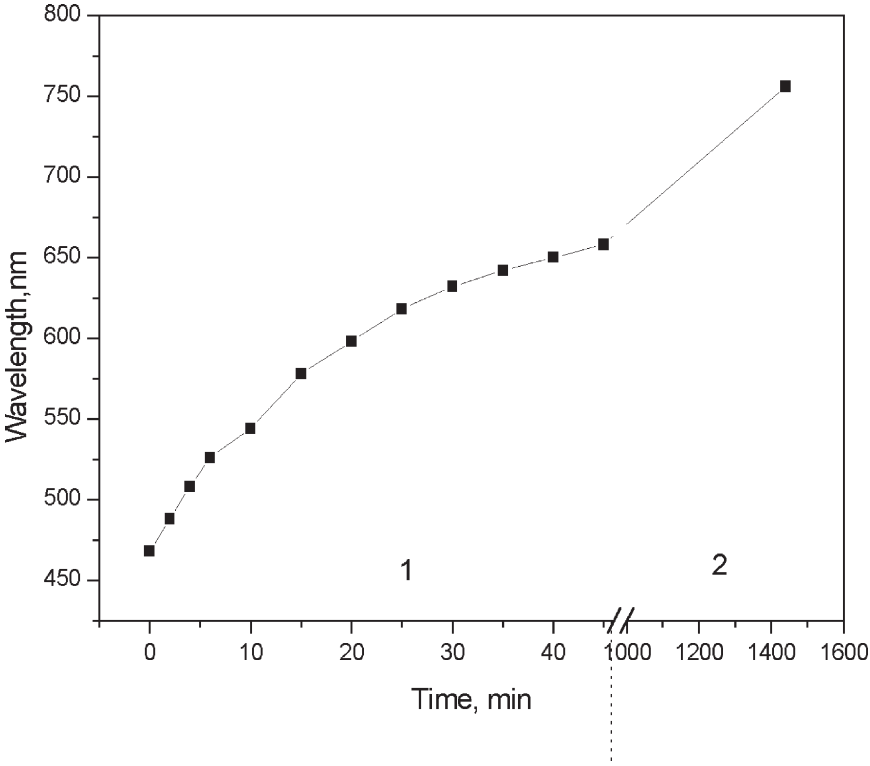



**FIGURE 4** Exposure time dependence of selective reflection peak for the mixture: 90%(91%ZLI-1695 + 9%1011R) + 10%Provitamin$D_2$.

Comparing the results obtained with similar cholesteric matrices that differ only in the handedness of the chiral dopant (e.g., 1011 S in Figs. 1, 2 and 1011 R in Figs. 3, 4), an interesting observation can be made. It appears that when $\lambda_{max}$ shifts to longer wavelengths (upon addition of Pro$D_2$, or upon UV-irradiation), the absolute values of these shifts are comparatively larger than in the case when $\lambda_{max}$ shifts to shorter wavelengths. This may reflect an anticipated fact that the process of helical twisting involves larger relative changes in thermodynamic free energy of the system than the inverse process of "untwisting".

In another set of experiments, cholesteric matrices of a different type have been used. Namely, they contained a nematic mixture of 4-butyl- and 4-hexylcyclohexanecarboxylic acids (4CHCA + 6CHCA, 1:1) and a mixture of several cholesterol 3β-derivatives (e.g.,

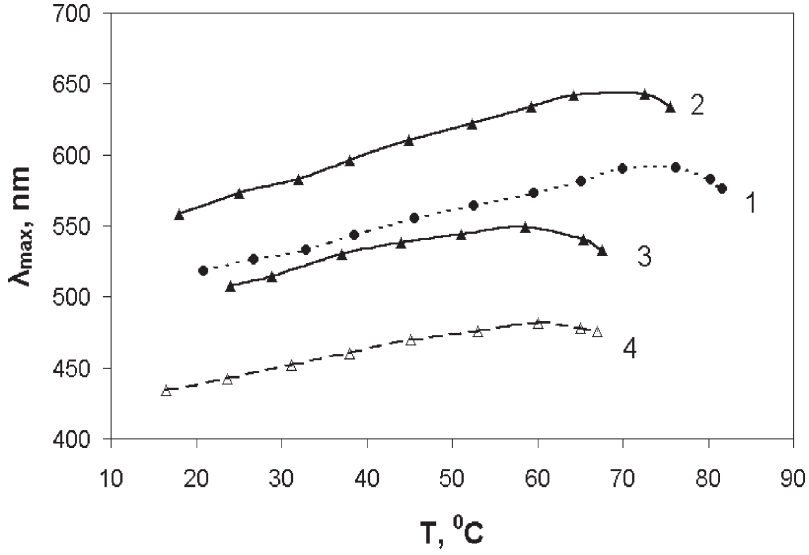



**FIGURE 5** Maximum reflection wavelength vs. temperature for different mixtures: 1 – Matrix 8; 2 – 95% Matrix 8 + 5% $ProD_2$; 3 – 95% Matrix 8 + 5% $ProD_2$ after 60 min irradiation; 4 – 95% Matrix 8 + 5% $D_2$.

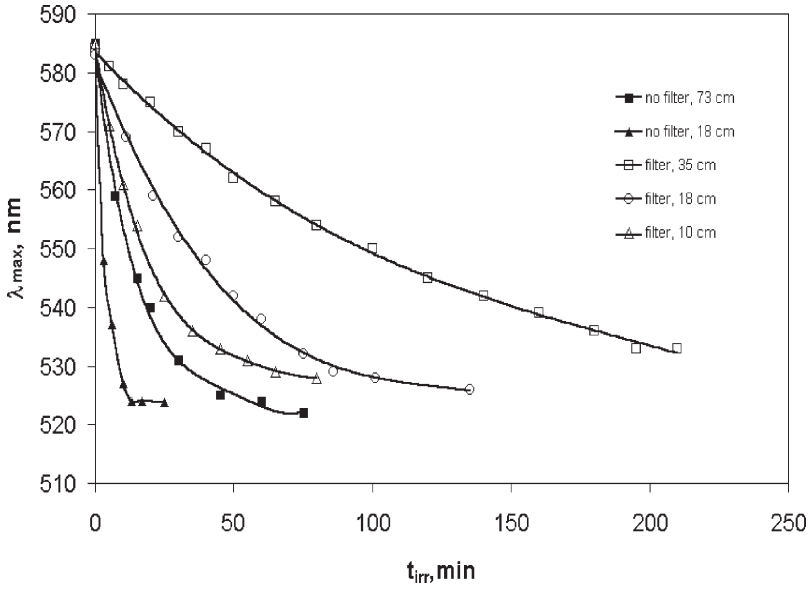



**FIGURE 6** Maximum reflection wavelength vs. irradiation time at different distances from the UV source (95% Matrix 8 + 5% $ProD_2$, with and without filter).

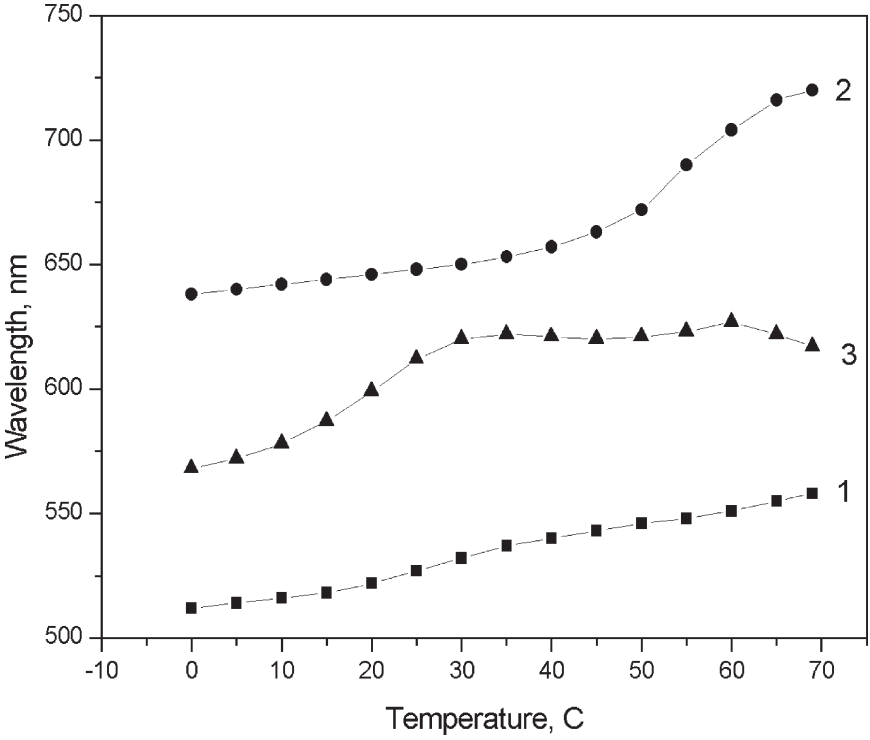



**FIGURE 7** Temperature dependence of the selective reflection peak for mixtures: 1 – 74%ZLI-1695+26% 2011 S; 2 – 90%(74%ZLI-1695+26% 2011 S) + 10% ProvitaminD$_2$; 3 – 90%(74%ZLI-1695 + 26% 2011 S) + 10% Provitamin D$_3$.

cholesteryl nonanoate, butyrate, and chloride) [20]. The mass fraction of the nematic constituent was 60% (Matrix 8). The obtained temperature dependences of $\lambda_{max}$ (Fig. 5) are qualitatively similar to those shown in Figure 1 (one should note that Matrix 8 is "left-handed").

Changes in $\lambda_{max}$ under UV irradiation are shown in Figure 6. In this set of experiments, a PRK-4 UV lamp was used, both with and without a K8 filter effectively cutting out the region below 290 nm.

Thus, in several variants of cholesteric matrices doped with ergosterol, it was clearly and unambiguously shown that monitoring the helical pitch changes caused by the photo induced transformation of ProD$_2$ to vitamin D$_2$ can really be a feasible way for detection (and possibly dosimetry) of biologically active UV radiation.

Since chemical structure of ProD$_2$ and ProD$_3$, as well as photochemistry of ProD$_2$-D$_2$ and ProD$_3$–D$_3$ transformations, are believed to be

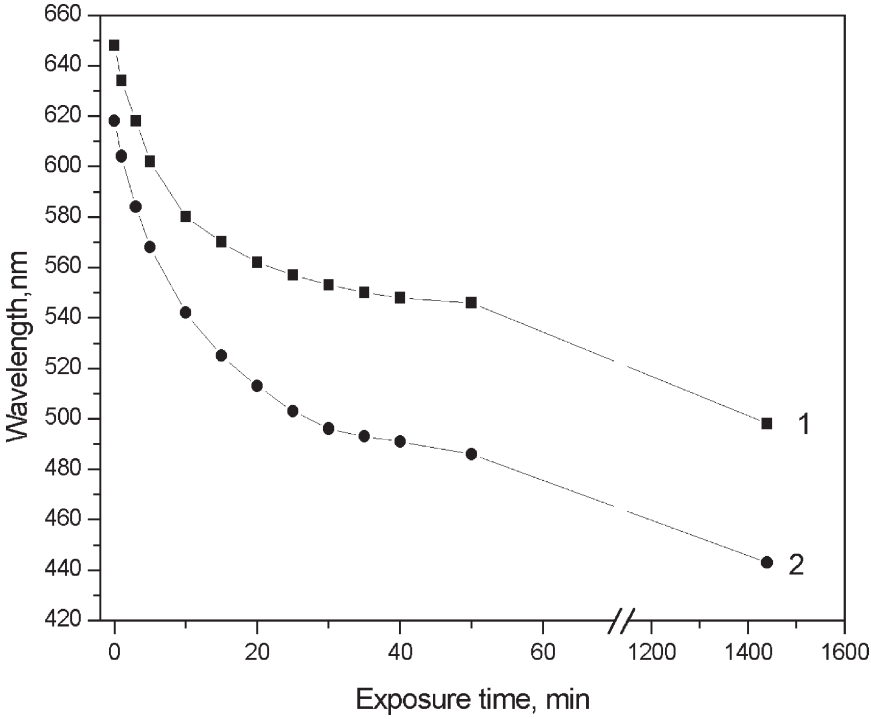



**FIGURE 8** Exposure time dependence for mixtures: 1 – 90% (74%ZLI-1695 + 26% 2011 S) + 10% Provitamin$D_2$; 2 – 90% (74%ZLI-1695 + 26% 2011 S) + 10% Provitamin$D_3$.

essentially similar, we have also checked up the behaviour of Pro$D_3$ under similar conditions, expecting similar effects of UV-irradiation. Examples of the results obtained are shown in Figures 7, 8. It could be noted that $\lambda_{max}$ shifts caused by introduction of Pro$D_3$ into a cholesteric matrix were smaller as compared with Pro$D_2$; from the other side, Pro$D_3$ appeared to show better solubility, which could ensure higher sensitivity to UV radiation in appropriately composed sensor mixtures with higher Pro$D_3$ content.

Some of the results obtained with higher Pro$D_3$ concentrations are shown in Figures 9, 10. It was noted that temperature dependences of $\lambda_{max}$ at 15% Pro$D_3$ showed an anomalous behaviour as compared with lower concentrations. This could be tentatively ascribed to formation of certain supramolecular structures affecting the short-range order of the "quasi-supersaturated" solutions. These features require further detailed investigations.

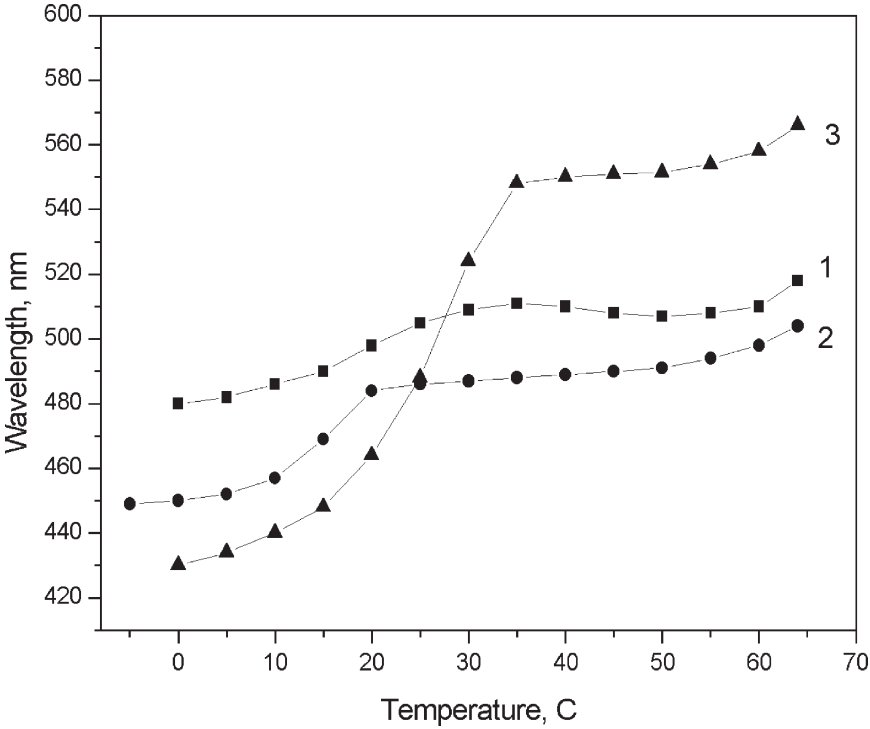



**FIGURE 9** Temperature dependence of selective reflection peak for mixtures: 1 – 91%ZLI-1695 + 9%1011R; 2 – 90%(91%ZLI-1695 + 9%1011R) + 10% Provitamin$D_3$; 3 – 85%(91%ZLI-1695 + 9%1011R) + 15%Provitamin$D_3$.

## CONCLUSIONS

Peculiar features of the helical pitch variation due to UV-induced provitamin D transformations have been studied for a number of different cholesteric matrices. The apparent response (provitamin D photoisomerization) relevant for monitoring of the biologically active UV radiation, as well as physico-chemical mechanisms of the processes involved, were shown to be essentially similar in cholesteric matrices of different types, e.g., comprising chiral components of steroid nature (mixtures of cholesterol derivatives) or non-steroid optically active dopants of "chiral nematic" type (accounting for the handedness of the induced helix).

The recorded sensitivity to UV radiation shows that cholesteric liquid crystal mixtures can be considered as a promising sensor material for bioequivalent detectors of UV radiation (with either

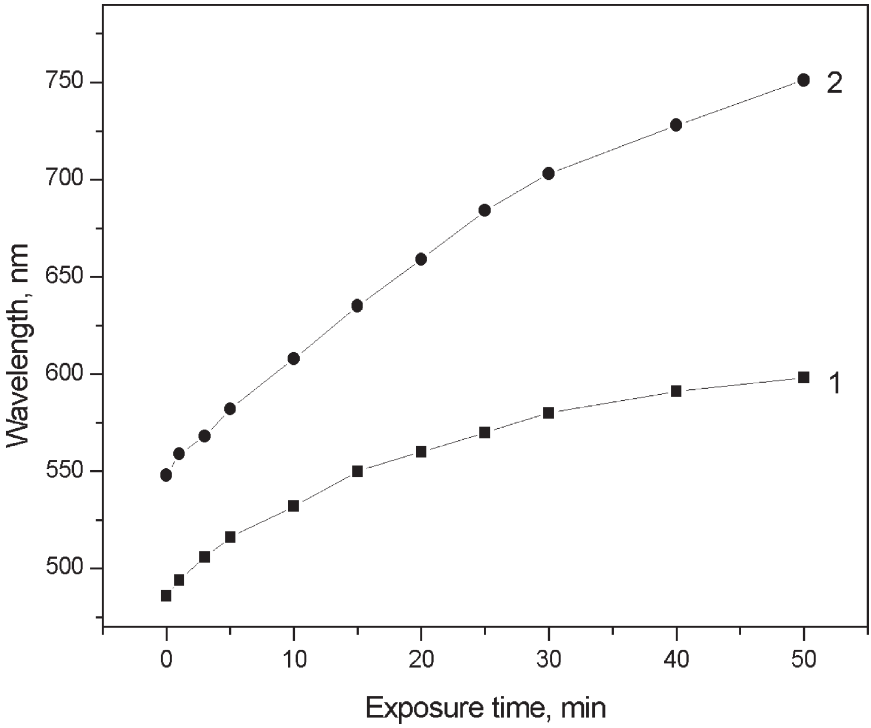



**FIGURE 10** Exposure time dependence for mixtures: 1 – 90%(91%ZLI-1695 + 9%1011R) + 10%ProvitaminD$_3$; 2 – 85%(91%ZLI-1695 + 9%1011R) + 15%ProvitaminD$_3$.

provitamin D$_2$ or provitamin D$_3$ used as a photosensitive component). Differences related to higher provitamin D$_3$ solubility, different helical twisting power and possible peculiarities in interaction features are, however, to be considered.

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