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BRIEF COMMUNICATIONS

Photochemical Transformations of 7-Dehydrocholesterol

Z. L. Grigoryan, A. I. Martiryan, L. A. Nersesyan, and Sh. A. Markaryan

Yerevan State University, Yerevan, Armenia

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Abstract—Photochemical transformations of 7-dehydrocholesterol were performed with a two-lamp experimental circulation installation equipped with a ferrioxalate actinometer and were monitored by UV spectroscopy and high-performance liquid chromatography. The quantum yields of the overall conversion of 7-dehydrocholesterol at wavelengths of 254, 313, and 365 nm were determined.

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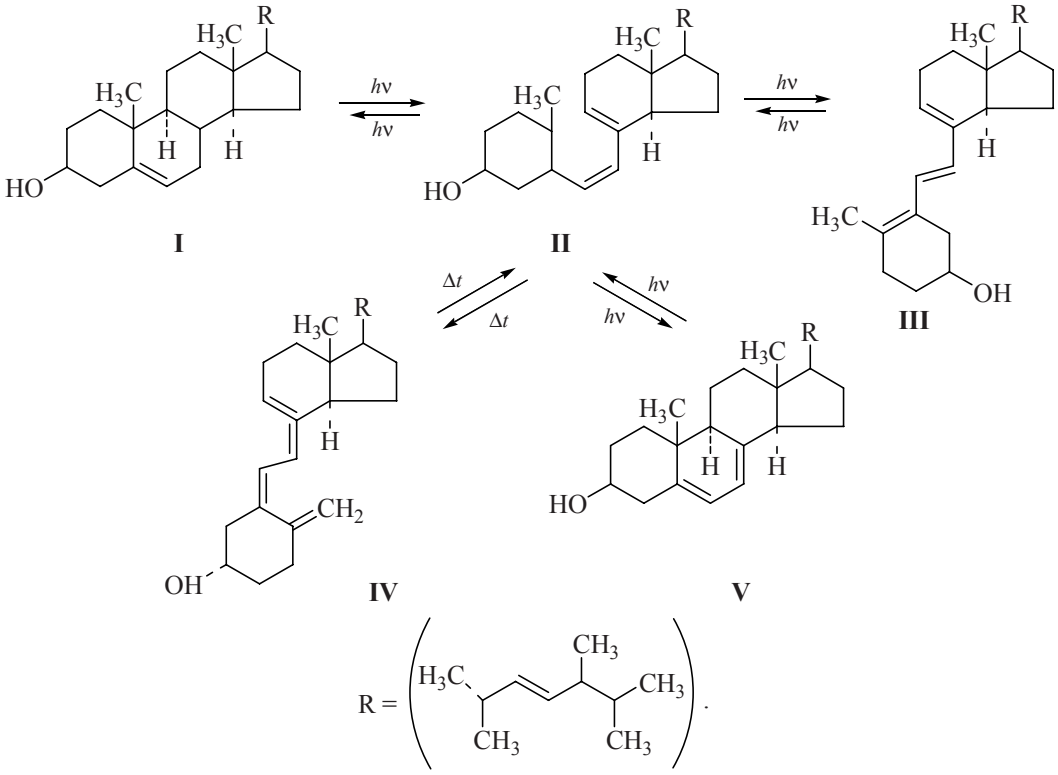
Photochemical transformations of 7-dehydrocholesterol (provitamin D_3, 7-DHC) is the principal precursor for commercial production of cholecalciferol (vitamin D_3) [1–3]. Photolysis of 7-DHC follows Scheme 1.

Photolysis o 7-DHC (**I**) yields a tarry photolyzate consisting mainly of provitamin D_3 (**II**), lumisterol **III**, and also small amounts of tachysterol (**V**) and toxisterols (not shown in the scheme). Vitamin D_3 (**IV**) is produced by the subsequent thermal isomerization of

Scheme 1.



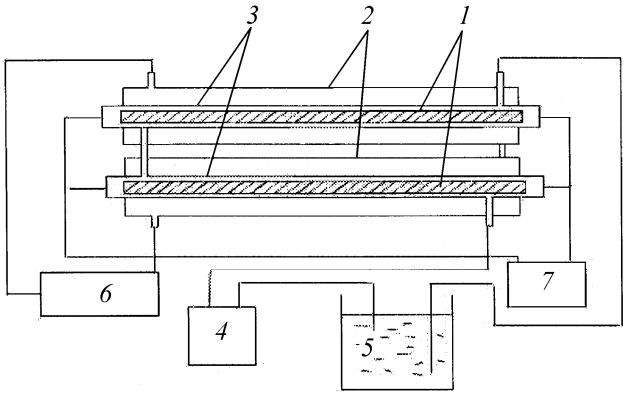


Fig. 1. Two-lamp experimental circulation installation: (*1*) ultraviolet irradiation lamps, (*2*) temperature-control system, (*3*) reaction zone, (*4*) circulation pump, (*5*) vessel with the reaction mixture, (*6*) power supply to lamps, and (*7*) thermostat.

provitamin D_3. Photolysis is usually performed with 20–30-W low-pressure mercury lamps. It was found [2] that, to ensure high selectivity with respect to provitamin D_3, it is appropriate to use luminophores with which the major fraction of the emission power of the mercury lamp would correspond to a wavelength λ = 300–310 nm.

In some studies, with the aim to increase the yield of provitamin D_3, the photochemical process is performed in two steps: solutions of 7-DCH in various solvents (ethanol, diethyl ether, etc.) are irradiated with a laser first at λ = 248–254 and then at λ = 350–400 nm [4–7]. In the first step, the product of the photochemical reaction is tachysterol, and in the second step, tachysterol transforms into provitamin D_3 [6, 7]. To accelerate the transformation of tachysterol into provitamin D_3 [5], such sensitizers are used in the second step as anthaquinone, benzpyrene, or anthracene. The mechanism of photolysis of 7-DHC upon laser irradiation was examined in [7–9].

Despite numerous studies on photochemical transformations of 7-DHC, available data on the kinetic relationships of the 7-DHC photolysis and quantum yield of the process are scarce.

The goal of this study was determination of the quantum yields of the process at various wavelengths and elucidation of kinetic relationships of the photochemical transformations of 7-DHC.

EXPERIMENTAL

The quantum yields of photochemical transformations of 7-DCH at various wavelengths were determined with a ferrioxalate actinometer [3]. The UV spectra were recorded with a Specord 50 PC spectrometer.

Kinetic experiments were performed with a two-lamp experimental circulation installation schematically shown in Fig. 1.

Irradiation was performed with 30-W low-pressure mercury lamps made of Uviol glass. Walls of one of the lamps were coated with a luminophore having the emission maximum at 310–313 nm, and the second lamp had no luminophore coating, and its emission maximum was at 254 nm. The circulation rate of 7-

(a) (b)

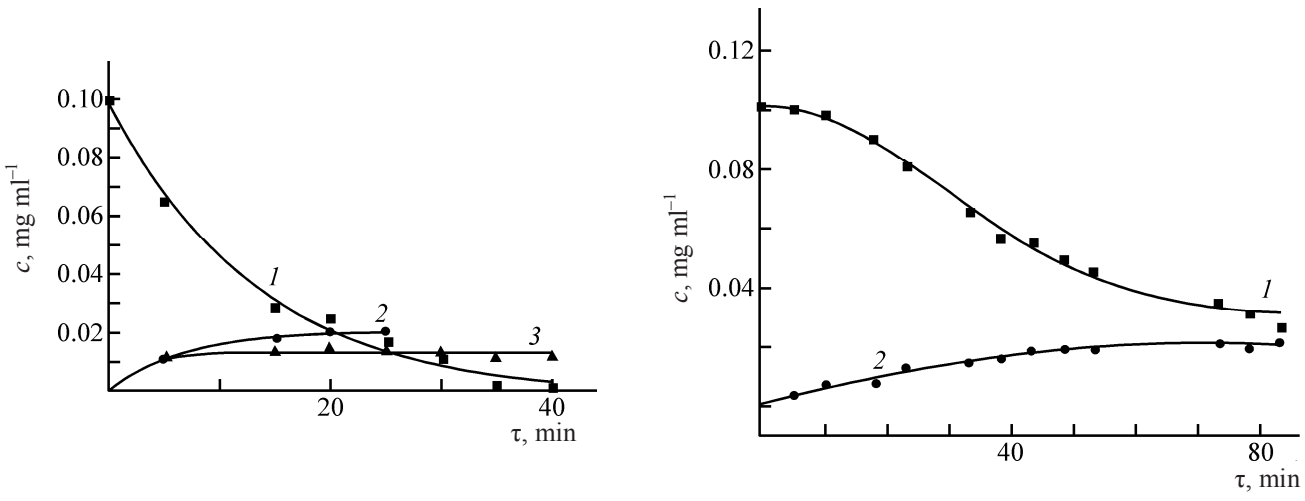


Fig. 2. Irradiation of 7-dehydrocholesterol with a lamp having the emission maximum at (a) 254 and (b) 313 nm. (*c*) Concentration and (τ) irradiation time; the same for Fig. 3. (*1*) Unchanged 7-DHC, (*2*) provitamin D_3, and (*3*) vitamin D_3; the same for Fig. 3.

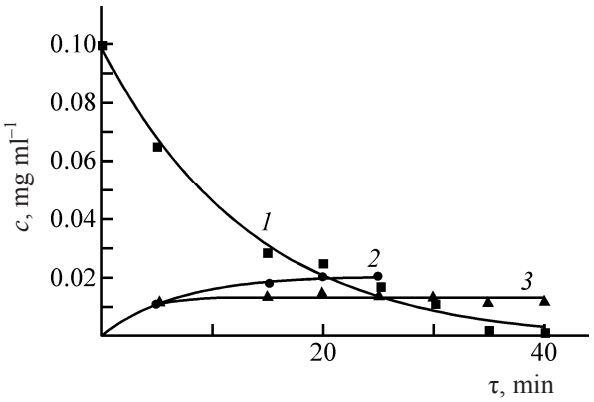


Fig. 3. Successive irradiation of 7-dehydrocholesterol at λ = 254 and 313 nm.

DHC solutions was 14–15 ml s^{-1}. Analysis of the initial substances and reaction products was performed on a Waters 486 high-performance liquid chromatograph equipped with a tunable absorbance detector, a Waters 6005 controller, and a Waters 626 pump. The UV detector operated at λ = 265 nm. The column (150 × 4.6 mm) was packed with C_{18} adsorbent. The eluent was acetonitrile–methanol (75 : 25), elution rate 1 ml min^{-1}.

7-DHC (main substance content 98%) was purchased from Aldrich–Sigma. Ethanol, methanol, and acetonitrile were purified by published procedures [10].

The quantum yields of the overall conversion of 7-DHC were determined at λ = 254, 313, and 365 nm. From the results obtained (φ_{254} = 0.35, φ_{313} = 0.42, and φ_{365} = 0.05, respectively), it follows that the wavelength of 313 nm is optimal.

The kinetics of photochemical transformations of 7-DHC were studied by taking samples from the flask at 5-min intervals for chromatographic analysis to determine the content of the unchanged 7-DHC and reaction products, provitamin and vitamin D_3. Figures 2 and 3 show the kinetic curves of variation of the 7-DHC and reaction product concentrations in the course of irradiation at λ = 254 and 313 nm and successive irradiation first at λ = 254 and then at λ = 313 nm.

The results obtained show that, upon irradiation of a 7-DHC solution with a lamp having an emission maximum at 254 nm, the reaction products contain vitamin D_3 along with provitamin D_3, and 7-DHC is completely consumed in 60 min. A similar pattern is observed when 7-DHC is irradiated at λ = 254 and 313 nm successively. In this case, 7-DHC is completely converted in 40 min. Upon 7-DHC irradiation at λ = 313 nm, only provitamin D_3 was found in the reaction products, with no vitamin D_3 detected, and the 7-DHC conversion after irradiation for 80 min was 75%. It should be noted that vitamin D_3 was detected in 7-DHC irradiation products for the first time. It was believed previously that the products of 7-DHC irradiation are provitamin D_3, lumisterol, tachysterol, and toxisterols. Detection of vitamin D_3 indicates that the generally accepted mechanism of 7-DHC photolysis should be revised.

CONCLUSIONS

(1) The optimal quantum yield of the overall conversion of 7-dehydrocholesterol is observed at the irradiation wavelength of 313 nm.

(2) Along with provitamin D_3, the products of photochemical transformations of 7-dehydrocholesterol contain vitamin D_3.

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