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Efficiency of Photoeffect in BLM with Chlorophyll and Carotene

Wydajność fotoefektu w BLM z chlorofilem i karotenem

Эффективность фотоэффекта для БЛМ с хлорофиллом и каротином

INTRODUCTION

It is well known that β-carotene cooperates with chlorophyll in photosynthesis processes. Its usual functions are: 1° light harvesting and energy transfer to chlorophyll [2,3,7,8], 2° protective function with regard to chlorophyll [1], 3° electron transportation through the membrane [9]. In this work we measured the photoconductivity of artificial lipid membranes (BLM) containing chlorophyll and β-carotene, in order to make more clear some details of the cooperation of them.

MATERIALS AND METHODS

Membranes were formed in a 1.5 mm aperture of a teflon cup. The membrane forming solution consisted of 3 mg/ml lecithin (1:1.5:1.5:2.5 glycerintipalmitat/ L-β, γ dipalmitoyl -α-cephalin/ L-β, γ dimiristoyl α-lecithin/ egg lecithin), 1.74 mg/ml chlorophyll a and 0.2 mg/ml β-carotene in t-butanol and n-decane (2:1). Chlorophyll a and β-carotene, extracted from spinach leaves, were purified by means of thin layer chromatography.

The membrane separated two identical aqueous solutions of KCl 0.1 M, $FeCl_3$ 0.5 mM, $FeCl_2$ 0,5 mM, EDTA 1.7 mM and acetate buffer 0.1 M, pH = 5.5. The short period illumination technique was employed using 150 W halogen lamp and a rotating 2 Hz sector. Optical filters were put between the lamp and the membrane. The characteristics of these filters and the halogen lamp are shown in Fig. 1.

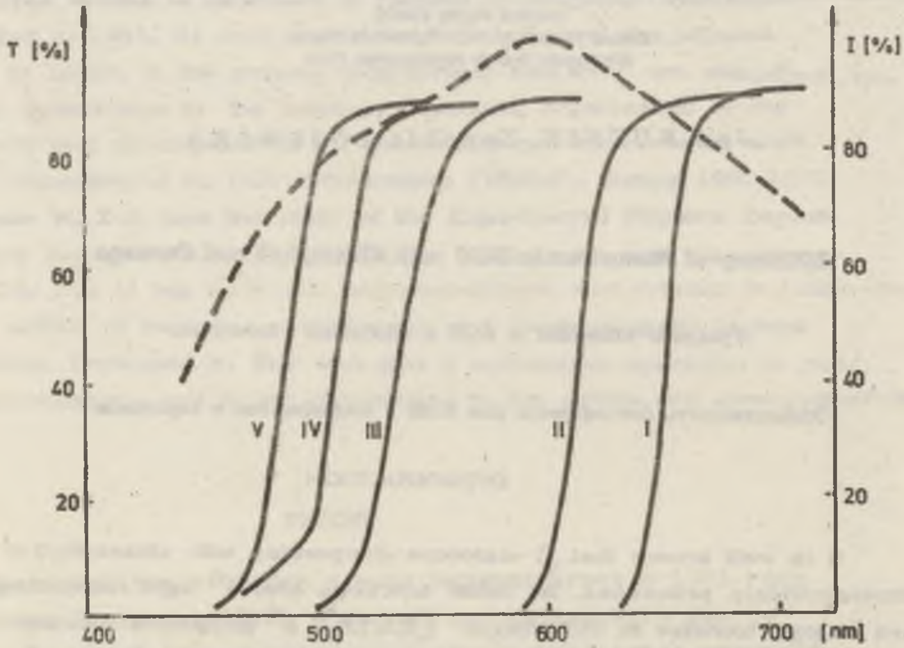

Fig. 1. Transmission of filters - T (continuous line) and the spectral characteristic of the light reaching the membrane after taking into account light absorption in lens and the membrane surrounding solution - I (broken line)

The fast component of photocurrent was measured in a circuit consisting of two calomel electrodes immersed in the compartments of the vessel, a voltage source and a lock-in nanovoltmeter. This experimental arrangement was described in detail in our previously reported article [4].

RESULTS

Values of the fast component of photocurrent were registered after 100s from the beginning of the membrane illumination, because of a fast initial decrease of photocurrent [4]. Different values of photocurrent were obtained using optical filters. The absorption spectrum of the membrane forming solution, measured with a spectrophotometer Specord UV-VIS, Carl Zeiss Jena, is composed in the range 450 nm - 700 nm of five absorption peaks. Four of them belong to chlorophyll a 2 - 541 nm, 3 - 585 nm, 4 - 626 nm, 5 - 672 nm and one 1 to carotene. We presented the chlorophyll peaks as Gaussian components according to W a l z [10] and obtained the β -carotene peak by subtracting the absorption spectrum of pure chlorophyll a from the absorption spectrum of the membrane forming solution (Fig. 2.). Taking into account the spectral characteristic of the light reaching the membrane we calculated absorption peaks of chlorophyll a and β-carotene for each filter (Fig. 3.).

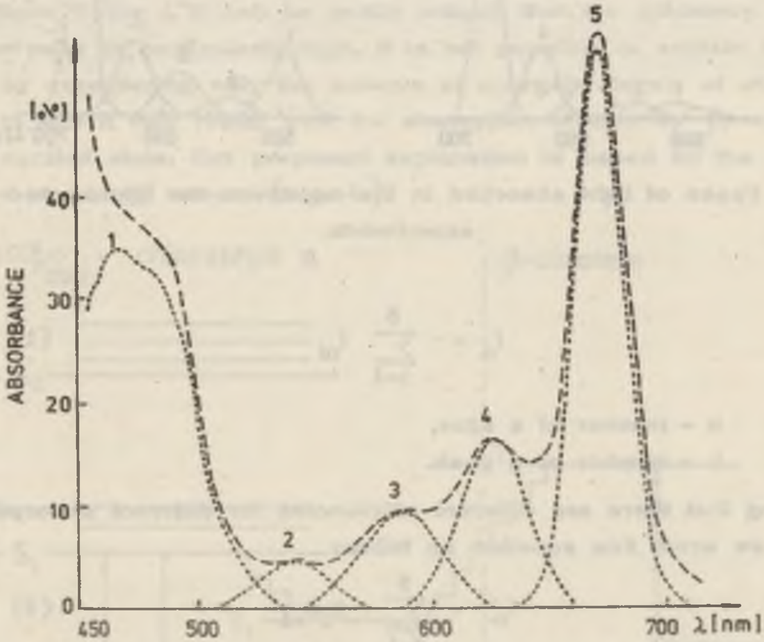

Fig. 2. Components of the membrane forming solution absorption spectrum

The measurements of photocurrent were carried out on the same membrane for each filter separately. The photocurrent for a definite filter can be expressed as a sum of components pertinent to particular peaks:

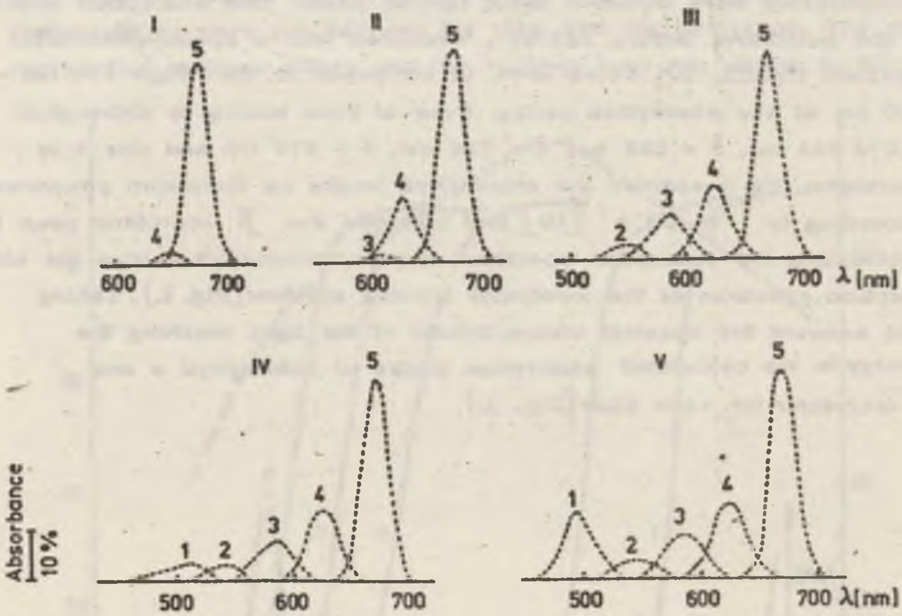

Fig. 3. Peaks of light absorbed in the membrane for filters used in experiments

$$I_n = \sum_{i=1}^{5} I_{ni} \tag{1}$$

where n - number of a filter,

i - number of a peak.

Assuming that there are different efficiencies for different absorption peaks, we wrote this equation as follow:

$$I_n = \sum_{i=1}^{5} k_i A_{ni} \tag{2}$$

where k_i - efficiency pertinent to i-th absorption peak,

A_{ni} - area under i-th peak curve for n-th filter.

Solving the pile of five such equations for a set of five filters we were able to calculate the rates of efficiencies k_i in the range 450 nm - 700 nm. This result is presented in Table 1.

Table 1. Relative efficiencies of photoeffect for different wavelengths

Peak No.	Wavelength nm	k
1	480	0.27 ± 0.25
2	541	2.94 ± 1.00
3	585	0.64 ± 0.15
4	626	0.63 ± 0.15
5	672	1.00 ± 0.07

DISCUSSION

From Table 1 it can be easily noticed that the efficiency for the 541 nm peak is particularly high. It is not possible to explain this effect by considering only the scheme of energetic levels of chlorophyll a but in fact it may result from the absorption of light by β -carotene in an excited state. Our proposed explanation is based on the following scheme of energy transfer (Fig. 4.).

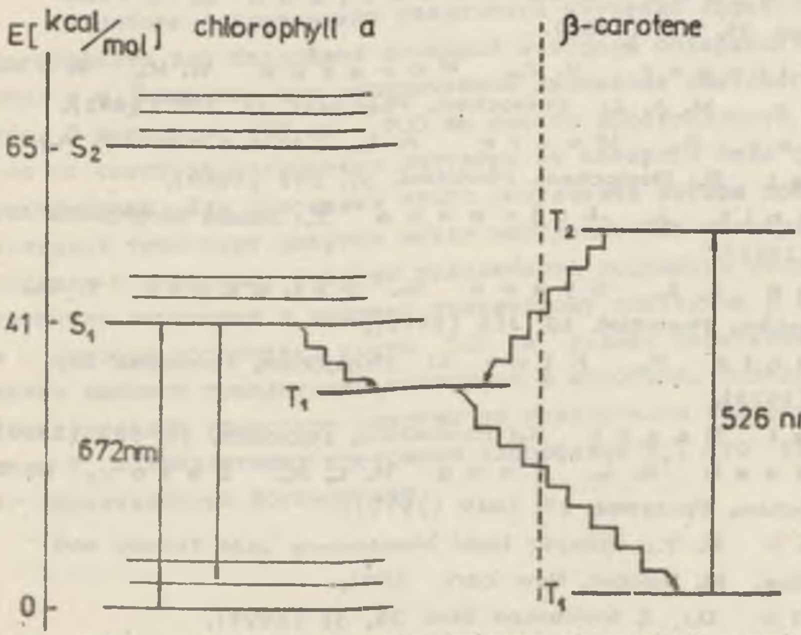

Fig. 4. Scheme of energy transfer between chlorophyll a and β -carotene. /\/\/- nonradiative transitions

672 nm light excites the singlet chlorophyll state S_1, and subsequently the chlorophyll triplet state T_1 becomes excited. The life time of this state 10^{-3}s is long enough for the photochemical reaction to elicit electron release. According to the result of M a t h i s and K l e o [6] there is an energy transfer from the triplet state of chlorophyll to the forbidden lowlying triplet state of β-carotene, which is 29 kcal/mol below the chlorophyll triplet state, as reported by L a n d, S y k e s and T r u s c o t t [5]. As a result of this energy transfer, the 526 nm absorption peak of β -carotene then appears for the chlorophyll- carotene mixture. Therefore if the light spectral range is 510 - 700 nm the excitation of the higher triplet state of carotene T_n is reached. Assuming the possibility of energy transfer from this T_n triplet state of β -carotene to the triplet state of chlorophyll a, which is relatively lower, the increase effect of the photoconductivity could be understandable.

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STRESZCZENIE

W pracy badana była, przy ograniczonym zakresie spektralnym światła, wydajność fotoefektu w dwuwarstwowych membranach lipidowych (BLM) zawierających chlorofil a i β-karoten. Obserwowano rozbieżność pomiędzy wydajnością fotoefektu a widmem absorpcyjnym roztworu do formowania membran. Dla wyjaśnienia tego efektu autorzy założyli wzajemne przekazywanie energii pomiędzy cząsteczkami chlorofilu a i β-karotenu w stanie wzbudzonym. Energia trypletowego stanu chlorofilu a jest częściowo przekazywana do niżej leżącego trypletowego stanu β-karotenu i w konsekwencji tego może być wzbudzany wyższy stan trypletowy T_n poprzez absorpcję światła (526 nm). Ostatecznie następuje przekazanie energii z trypletowego stanu T_n β-karotenu do trypletowego stanu T_1 chlorofilu a, co powoduje zwiększenie wydajności fotoefektu.

РЕЗЮМЕ

В работе представлены результаты изучения эффективности фотоэффекта для бислойной липидной мембраны содержащей хлорофилл а и β каротин при ограниченном диапазоне светового спектра. В диапазоне 450 нм - 700 нм спектр эффективности не согласен со спектром поглощения раствора из которого были формированы мембраны. Для обяснения этого результата авторы предлагают взаимный транспорт энергии между возбуждёнными молекулами хлорофилла и каротина. Энергия триплетного состояния хлорофилла частично переходит к низшему триплетному состоянию β каротина и с помощью поглощения света 526 нм делает возможным возбуждение высшего триплетного состояния β каротина. Вследствие того происходит транспорт энергии от триплетного состояния каротина $T_н$ к триплетному состоянию хлорофилла T_1, что увеличивает эффективность фотоэффекта.

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