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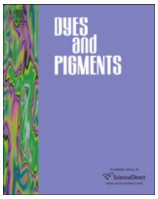

Nonlinear optical properties of selected natural pigments extracted from spinach: Carotenoids

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ABSTRACT

They are report here, for the first time in authors knowledge, results on third order nonlinear optical susceptibilities from a series of natural pigments extracted from spinach. The measurements were performed in-situ at 532 nm wavelength using degenerate four wave mixing technique (DFWM). For comparison third order nonlinear optical susceptibilities of the same pigments were also evaluated using third harmonic generation (THG) set up at 1064 nm. The electronic contribution to the observed properties was also deduced. The measurements were performed on thin films deposited on a thick glass substrate. These pigments were also identified by UV–VIS spectral analysis. All these results were in good agreement with the literature data.

1. Introduction

The design of nonlinear optical (NLO) materials has been the subject of extensive theoretical and experimental investigations in the recent decades because of their potential applications in the development of photonic device such as optical data storage, optical communication, and optical limiting [1–9]. Considerable research efforts have been directed toward understanding the nature of the NLO phenomenon on organic compounds. In particular, the organic charge transfers containing a donor and an acceptor have been widely investigated as a representative of highly efficient NLO materials due to the strong charge transfer (CT) transitions [10–13]. The molecular structures of carotenoids present donor-*p*-acceptor forms, which are very promising candidates for applications in optoelectronics, quantum electronic optical communications, and also in the field of molecular engineering of functional materials [14–17].

Carotenoids are a group of natural pigments occurring in fruits and vegetables flavoring their colours from yellow to red. In human health, their importance is related to their actions as provitamin A, antioxidants, cell differentiation and proliferation regulators, cell–cell communication stimulators, immune function and carcinogen metabolism modulators, as well as blue light filters. There are many studies showing strong correlations between carotenoids intake both with the improvement of the immune system and with the reduction of the risk of some degenerative diseases such as cancer, cardiovascular diseases, cataract and macular degeneration [18–20].

In this paper, a systematic study of third order nonlinear optical properties of carotenoids (β-carotene, xanthophylls and violaxanthin) extracted from spinach is reported. The results on third order nonlinear optical susceptibility ($\chi^{<3>}$) of these chromophores measured by degenerate four wave mixing (DFWM) method at 532 nm wavelength region in solution forms are presented.

The values of carotenoids thin films have been also measured using third harmonic generation (THG) method at a measurement

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wavelength of 1064 nm. These compounds were deposited on glass substrate of 1 mm thickness by the spin-coating method. The film thickness values was measured with a 6M DEKTAK profile-meter, which allows the measurements to be performed in the range of ±5. Third harmonic (TH) signal was analyzed with fused silica as reference material using the Maker fringes technique.

2. Experimental

2.1. Pigment extraction

Torn spinach leaves (500 g) were macerated with EtOH–H_2O (70:30 v/v). After, filtration, the EtOH was evaporated at room temperature and the remaining aqueous solution extracted successively with petroleum ether, $CHCl_3$ and n-BuOH. The n-BuOH extract was chromatographed on silica gel by gradient elution with hexane–EtOAc–MeOH, giving seven fractions. Insulation and purification were performed by TLC on silica gel using CH_2Cl_2–acetone and $CHCl_3$–MeOH with different polarities as eluents and TLC on polyamide DC6 using toluene–MeOH–methylethylketone and water–MeOH–methylethylketone–acetylacetone, leading to seven compounds. These pigments were identified by spectral analysis. All these results were in good agreement with the literature data. The chemical structures of these materials are presented in Fig. 1.

Spin deposition with controlled thickness was used to fabricate thin films of carotenoids on BK7 glass slides. The principle of deposition is based on a homogeneous spreading out of the solution on the rotating substrate with an angular speed of 900–1200 rpm. Immediately after the deposition, thin films were heated in an 80 °C oven for 40 min in order to eliminate any remaining solvent.

2.2. UV spectra

The UV–vis spectra of carotenoids (Fig. 2) in the $CHCl_3$ solutions were performed with a cell having a thickness of about 1 cm containing a very weak concentration $\sim 10^{-5}$ mol/L. These spectra present the typical absorption peak at 400–500 nm which is associated to π–π^* electronic transitions of the carotenoids chromophores from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). These results are in good agreement with the literature (Fig. 2).

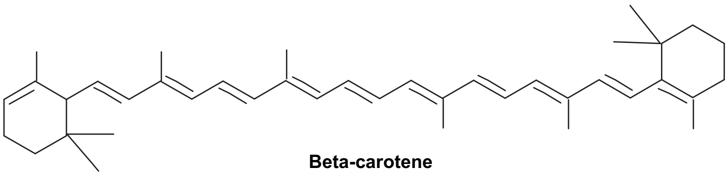
3. Nonlinear optical properties

Various experimental techniques can be used for estimating the third order nonlinear optical susceptibility of the investigated compounds.

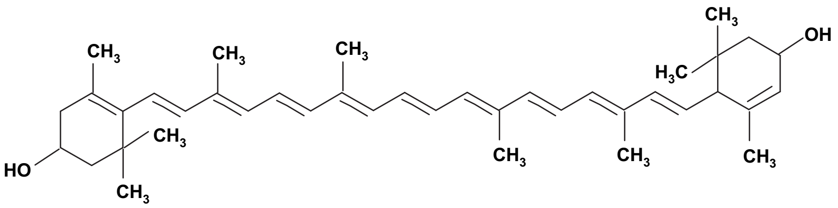
In general, the third order nonlinear optical susceptibilities $\chi^{<3>}(-\omega;\,\omega,\,-\omega,\,\omega)$ and $\chi^{<3>}(-3\omega;\,\omega,\,\omega,\,\omega)$ can be characterized either by degenerate four wave mixing (DFWM) or by third harmonic generation (THG) techniques. THG has the advantage of probing the pure nonresonant electronic nonlinearity while DFWM may include the orientational and dynamic resonant nonlinearity contributions, depending on the experimental conditions. This means that the DFWM technique may be used to measure different contributions, including electronic, orientation and thermal effects.

3.1. DFWM measurements

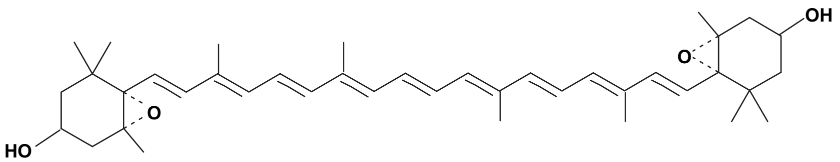
Third order nonlinear optical susceptibilities ($\chi^{<3>}$) of beta-carotene, violaxanthin and xanthophyll solutions were measured by the standard backward degenerate four wave mixing (DFWM) method using Nd:YAG laser working at 532 nm with pulses duration of 30 ps and 1 Hz repetition rate [21,22]. In DFWM geometry, two strong, equal intensity, counter-propagating pump beams and a weak probe beam were temporally and spatially overlapped in the sample. The probe beam makes a small angle ($\theta = 12°$) with respect to the one of the pump beams and its intensity was adjusted to be approximately $I_{\text{probe}} = 6 \times 10^{-2} I_{\text{pump}}$. A phase-conjugated signal generated from these three laser beams of the same frequency (ω) was collected at a reverse direction of the probe beam. This signal



Beta-carotene



Xanthophyll



Violxanthine

Fig. 1. Chemical structures of the investigated pigments.

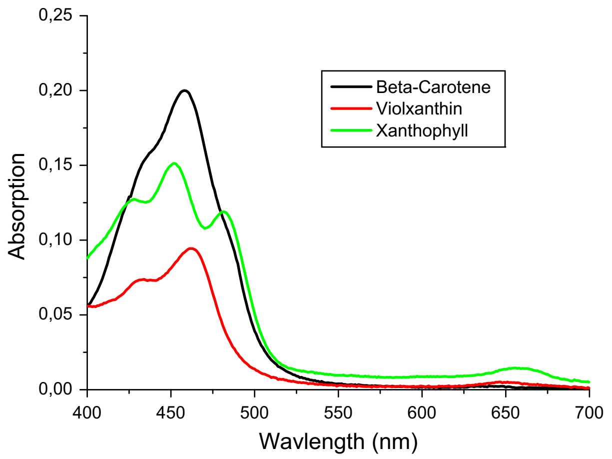


Fig. 2. Absorption spectra of the investigated pigment.

was measured by photomultiplier tube (PMT) and fed to a digital storage oscilloscope (Tektronix TDS 3054). A part of the input laser beam was split off and measured by a sensitive photodiode in order to monitor the input laser energies as well as their related fluctuations.

The studied compounds were dissolved in dichloroethane and contained in a 1 mm thick cuvette. The solvent produced signal under the experimental conditions. Third order nonlinear optical susceptibility of dichloroethane was estimated to be $\chi^{<3>} = 0.13 \cdot 10^{-20}$ [m^2/V^2]. We used carbon disulfide (CS_2) as reference material to calibrate DFWM measurements. Third order nonlinear optical susceptibility of CS_2 was estimated to be $\chi^{<3>} = 1.94 \cdot 10^{-20}$ [m^2/V^2].

The DFWM reflectivity (R) was calculated from the propagation equations of the interacted beams, which were deduced from the Maxwell equations using the approximation of slow amplitude variation taking into account the linear and nonlinear absorption (eq. (1a)) or only the linear absorption coefficients (eq. (1b)). The DFWM reflectivity (R), defined as the total DFWM signal intensity divided by the incident probe–pulse intensity, is plotted as a function of the pump–pulse intensity. The DFWM reflectivity (R) can be expressed as follows [21–25]:

$$R = \frac{I_4(0)}{I_3(0)} = \left(\frac{48\pi^3}{n^2 c\lambda}\right)^2 \frac{\left(\left(\chi_R^{<3>}\right)^2 + \left(\chi_I^{<3>}\right)^2\right) I_1(0) I_2(0)}{\left[q\coth(qL) - \frac{\phi}{2}\right]^2} \tag{1a}$$

$$R = \frac{I_4(0)}{I_3(0)} = \left(\frac{48\pi^3}{n^2 c\lambda}\right)^2 \frac{\left(\chi^{<3>}\right)^2 I_1(0) I_2(0) \exp(-\alpha L)}{\left[p\coth(pL) + \frac{\alpha}{2}\right]^2} \tag{1b}$$

where

$$\begin{aligned} q^2 &= \left(\frac{\phi}{2}\right)^2 - \left(\frac{48\pi^3}{n^2 c\lambda}\right)^2 \left(\left(\chi_R^{<3>}\right)^2 \right. \\ &\quad \left. + \left(\chi_I^{<3>}\right)^2\right) I_1(0) I_2(0), \\ \phi &= -\alpha - 2\beta(I_1 + I_2), \text{ and} \\ p^2 &= \frac{\alpha^2}{4} - \left(\frac{48\pi^3}{n^2 c\lambda}\chi^{<3>}\right)^2 I_1(0) I_2(0). \end{aligned}$$

The parameters α, β, L, λ, n, c, $\chi_R^{<3>}$ and $\chi_I^{<3>}$ are respectively the linear absorption coefficient, the two-photon absorption coefficient, the sample thickness, the used laser wavelength, the linear refractive index of the considered material, the light velocity in vacuum, the real and imaginary parts of the third order nonlinear optical susceptibility ($\chi^{<3>}$).

The nonlinear transmission was calculated using the following expression [21,22]:

$$T = \frac{I_T(L)}{I_1(0)} = \frac{\alpha \exp(-\alpha L)}{\alpha + \beta I_1 (1 - \exp(-\alpha L))} \tag{2}$$

where α is the linear absorption coefficient; $\beta = 24(\omega\pi^2/n^2c^2)\chi_I^{<3>}$, the two-photon absorption (TPA) coefficient; L, the thickness of the sample; I_1 and I_T, respectively the incident and transmitted intensities.

3.2. THG measurements

Third order nonlinear optical susceptibility of the investigated compound was also evaluated by THG measurements. In that case, the measurements were performed on thin films using a Q-switched Nd:YAG laser working at 1064 nm with a pulse duration of 16 ps, 10 Hz frequency and a pulse power of 1.6 mJ. A half wave plate has been seated between two polarizers that controlled the polarization and the power of the fundamental beam. The intensity at the input face of the sample is taken for being a Gaussian distribution in space and time. The beam diameter was 0.65 mm at the film of 120 nm thickness and the applied power density was 2 GW/cm^2. The beam was focused on the sample passing through lens having a focal distance of 25 cm. The films were mounted on a rotation stage. A transmitting filter (at 355 nm) was used to absorb the pump beam before crossing the photodetector. Also the density filters were used in order to reduce the intensity involved from the nonlinear medium. Third harmonic signal was detected by photomultiplier tube (Model: Hamamatsu), which was integrated with a boxcar and processed by a computer. A portion of the input beam was selected and measured by fast photodiode to monitor the input energy. Finally, so-called Maker fringes [26] were obtained, which were generated by rotating the sample through the range ±50° to the normal. The SiO_2 was used as a reference material to calibrate THG measurements. Third order nonlinear optical susceptibility of SiO_2 was estimated to be $\chi^{<3>} = 2.00 \cdot 10^{-22}$ [m^2/V^2] [27].

The intensity of the generated TH is given by the following formula [28,29]:

$$\chi^{(3)} = Cte \cdot \frac{A_3 I_{3\omega}}{A_1 \left\{\exp\left[i3\omega l \left(N_\omega^{(2)} - N_{3\omega}^{(2)}\right)/c\right] - 1\right\}} \tag{3}$$

$$A_1 = \frac{N_{3\omega}^{(2)} + N_\omega^{(2)}}{N_{3\omega}^{(3)} + N_{3\omega}^{(2)}},$$

$$A_3 = 1 - \left(\frac{N_{3\omega}^{(1)} - N_{3\omega}^{(2)}}{N_{3\omega}^{(1)} + N_{3\omega}^{(2)}}\right) \left(\frac{N_{3\omega}^{(3)} - N_{3\omega}^{(2)}}{N_{3\omega}^{(3)} + N_{3\omega}^{(2)}}\right) e^{i6\omega N_{3\omega}^{(2)} l/c}$$

$$N_{\omega,3\omega}^j = n_{\omega,3\omega}^j \cos\theta_{\omega,3\omega}^j$$

where $n_{\omega;3\omega}^{(j)}$ is the refractive index of the jth medium corresponding to the fundamental frequency ω; 3ω, the frequency of the third harmonic signal and l, the film thickness. The $\chi^{<3>}$ is the third order nonlinear optical susceptibility of the film; $I_{3\omega}$, the power of the generated third harmonic signal and θ, the rotation angle.

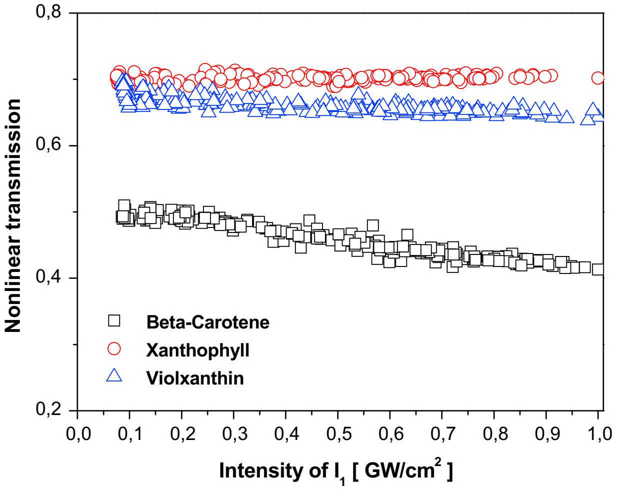


Fig. 3. Nonlinear transmission of beta-carotene, violaxanthin and xanthophyll as a function of input pump intensity.

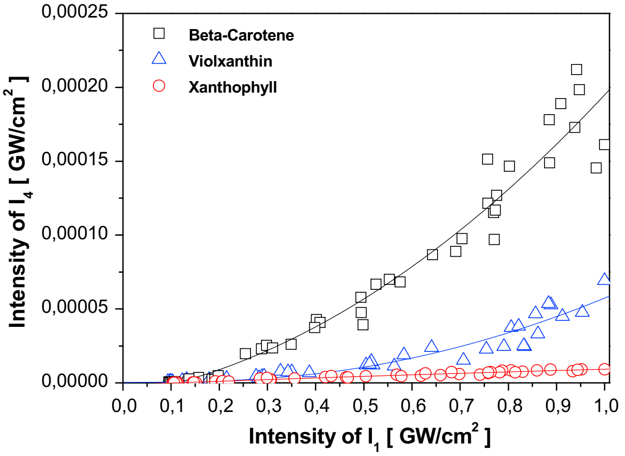


Fig. 4. The DFWM reflectivity (R) of beta-carotene, violaxanthin and xanthophyll as a function of input pump intensity.

4. Results and discussion

In general, the third order nonlinear optical susceptibility ($\chi^{<3>}$) is considered to be a complex quantity $\chi^{<3>} = \chi_R^{<3>} + i\chi_I^{<3>}$ where the real part, ($\chi_R^{<3>}$), is related to the nonlinear refractive index changes, which can be extracted from DFWM measurements. The imaginary part, ($\chi_I^{<3>}$), is related to the two-photon absorption coefficient (β) calculated from nonlinear transmission (NLT) measurement.

Fig. 3 displays the nonlinear transmission behaviour of beta-carotene and violaxanthin. It means that the nonlinear transmission decrease with an increase of the incident intensity. Therefore, these samples reveal the nonlinear absorption. The values of TPA coefficient (β), which can be related directly to the imaginary parts of third order nonlinear optical susceptibility ($\chi_I^{<3>}$), were extracted from dependencies of experimental data and eq. (2). The obtained values of TPA coefficients (β) for beta-carotene and violaxanthin dissolved in dichloroethane are presented in Table 1.

In the case of xanthophyll a nonlinear transmission curve constant with the incident intensity was obtained and the transmission value was lower than unity (see Fig. 3). This allowed to consider only a one-photon contribution to the absorption and to conclude that the third order nonlinear optical susceptibility is a real parameter at the excitation wavelength of 532 nm, ($\chi_I^{<3>} = 0$). All values of the linear absorption coefficient (α) of the investigated compounds, which were deduced from $T = \exp(-\alpha L)$, are reported in Table 1.

The typical plots of the DFWM reflectivity (R) versus input intensity are shown in Fig. 4. During the DFWM experiments, the quadratic dependence of the phase conjugate signal to the input intensity has been verified for all the samples. Fig. 4 presents also the theoretical fitting results of DFWM reflectivity (R) data recorded for beta-carotene and violaxanthin (eq. (1a)) and xanthophyll (eq. (1b)) compounds at a measurement wavelength of 532 nm. All obtained values of the third order nonlinear optical susceptibility ($\chi^{<3>}$) are presented in Table 1.

Table 1
The values of linear absorption coefficient (α), two-photon absorption coefficient (β), the imaginary part of third order nonlinear optical susceptibility ($\chi^{<3>}$) and the absolute value of third order nonlinear optical susceptibility ($\chi^{<3>}$) of beta-carotene, violaxanthin and xanthophylls dissolved in dichloroethane at a measurement wavelength of 532 nm, respectively.

Pigments	α [cm^{-1}]	β [cm/GW]	Im $\chi^{<3>} \cdot 10^{20}$ [m^2/V^2]	$\lvert\chi^{<3>}\rvert \cdot 10^{20}$ [m^2/V^2]
Beta-Carotene	6.63	8.68	2.65	2.87
Violaxanthin	3.94	1.87	0.57	0.63
Xanthophyll	3.59	≈0	–	0.35

From Fig. 3 and Table 1 it is seen that the values of linear absorption (α) and two-photon absorption (β) coefficients as well as imaginary part of third order nonlinear optical susceptibility ($\chi^{<3>}$) of beta-carotene are about two and four times bigger than violaxanthin, respectively. From Fig. 4 and Table 1 it can be noticed that the absolute value of third order nonlinear optical susceptibility ($\chi^{<3>}$) of beta-carotene is about four times bigger than violaxanthin and about eight times than xanthophyll. Such behaviour is not surprising because beta-carotene is a highly conjugated compounds and possesses hydrocarbon lacking functional groups. The molecular structure of beta-carotene does not consist of oxygen atoms. In comparison with beta-carotene, xanthophyll is oxidized derivatives of carotenes and it contains hydroxyl groups. Contrary to the carotenes, hydroxyl groups substitute some hydrogen atoms and/or oxygen atoms substitute some pairs of hydrogen atoms. Xanthophyll is also more polar than carotenes.

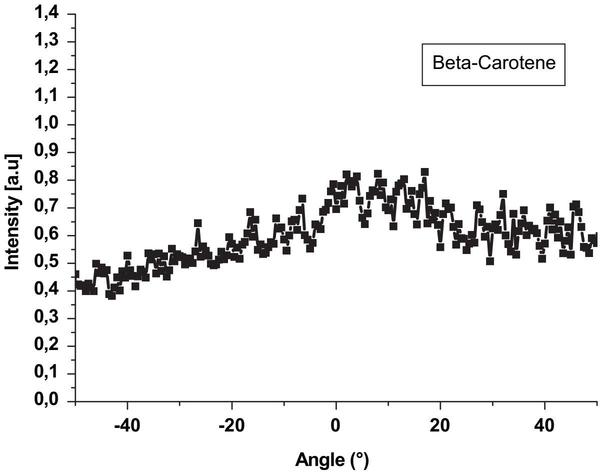


Fig. 5. Third harmonic intensity as a function of the incident angle.

Table 2
The values of thickness of thin films (l) and third order nonlinear optical susceptibility ($\chi^{<3>}_{THG}$) of pigments thin films obtained from THG experiment.

Pigments	l [nm]	$\chi^{<3>}_{THG} \cdot 10^{20}[m^2/V^2]$
Beta-carotene	200	0.87
Violaxanthin	200	0.27
Xanthophyll	200	0.19

Moreover, xanthophyll is the pigment from the carotenoid group, which the molecular structure is based on carotenes. In the case of violaxanthin, it is a natural xanthophyll pigment. Therefore, beta-carotene is a pure carbohydrate compounds. In contrary to beta-carotene, xanthophyll and violaxanthin contain oxygen groups.

Nonlinear optical characterisation has been also performed by third harmonic generation (THG) measurements. To extract the third order nonlinear optical susceptibility of the sample, the analysis of experimental results was carried out on the basis of the Maker fringes technique [30]. It can be assumed that third harmonic signal (TH) is generated in a very thin film; and the medium is being without losses and dispersion.

Fig. 5 illustrates the experimental result of TH intensity as a function of incident angle. The $\chi^{<3>}_{THG}$ values of carotenoids thin films were evaluated by comparing the TH signal with that from reference material. In our calculations using eq. (3), the refractive index of carotenoids thin films was assumed to be the same as that of the fused silica glass substrate. The data were corrected for air contributions. The values derived from THG measurements of the investigated materials are listed in Table 2.

The values of third order nonlinear optical susceptibility of pigments thin films at a measurement wavelength of 1064 nm have been estimated between $0.19 \cdot 10^{-20}$ and $0.87 \cdot 10^{-20}$ $[m^2/V^2]$ (Table 2). These values are one order of magnitude larger than $\chi^{<3>}_{THG}$ value of silica, which is the reference material for THG method. Also, it can be noticed the good agreement between the results obtained using THG and DFWM techniques (see Tables 1 and 2). Therefore, we can conclude that the nonlinear optical properties of the studied pigments decrease in the order of Beta-carotene > Violaxanthin > Xanthophyll.

5. Conclusion

Third order nonlinear optical properties of beta-carotene, xanthophylls and violaxanthin dissolved in dichloroethane, which are the natural pigments extracted from spinach, were investigated using DFWM method at 532 nm. Electronic contribution of third order nonlinear optical susceptibility ($\chi^{<3>}_{THG}$) of our pigments was evaluated on thin film form using THG technique at 1064 nm. It can be noticed that the highest value of third order nonlinear optical susceptibility ($\chi^{<3>}$) was obtained for beta-carotene in the both cases of DFWM and THG measurements. Such behaviour is not surprising because beta-carotene is highly conjugated compounds and possesses hydrocarbon lacking functional groups. Also, it can be seen that the $\chi^{<3>}$ value of violaxanthin is higher than xanthophyll. Finally the carotenoids are considered as promising compounds for photonic applications.

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