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RESONANCE RAMAN SPECTRA OF EXCITED TRIPLET-STATES OF β-CAROTENE ISOMERS

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The resonance Raman spectra of the electronically excited triplet-state of β-carotene, which was produced from the all-*trans*, 9-*cis*, 13-*cis*, and 15-*cis* isomers by means of flash-photolysis using a sensitizer, were recorded. They were very similar to one another. Isomerization of each isomer under the condition of Raman measurements was followed by HPLC. Isomerization from the *cis* isomers to the all-*trans* isomer was predominant. The results suggested that the isomers should have a common configuration in the lowest triplet-state.

Resonance Raman (RR) spectroscopy is a powerful tool to study the molecular structure not only in the ground-state but also in an electronically excited-state. It has been used to reveal the configurations of conjugated polyenes such as carotenoid or retinal in the lowest triplet-state.1-5) However, there remain a few open questions and one of them is whether the electronically excited triplet-state depends on the kind of starting isomers or not. Recently, the RR spectra of the lowest triplet-state of all-*trans* and 15-*cis*-β-carotene which was produced using pulse radiolysis and optical excitation were presented.1-4) Wilbrandt and Jensen suggested that the triplet configuration which is twisted around the 15-15' C=C double-bond should be predominant, since the triplet Raman spectrum which was obtained from all-*trans*-β-carotene was identical to that from 15-*cis*.4) We extended the RR study to the other β-carotene isomers, namely 9-*cis* and 13-*cis* in order to investigate the structure of the excited triplet-state.

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The 9-cis and 13-cis isomers of β-carotene were isolated from a mixture of isomers (which was obtained by thermal isomerization of the all-trans isomer) by means of high performance liquid chromatography (HPLC) using $Ca(OH)_2$ and acetone/hexane.$^{6)}$ The all-trans isomer was purified by recrystallization and the 15-cis isomer was a gift from Prof. C. H. Eugster of Zürich-Irchel University.

The excited triplet-state was produced by triplet energy transfer from a photosensitizer (anthracene), which was excited by the use of the 337 nm beam of a N_2 laser (NDC JL-1000L, 1MW). The RR scattering was probed at 532 nm by the use of the second harmonic of a Q-switched Nd:YAG laser (Quantel YG480, 6-7 mj/pulse), which was electrically delayed by approximately 1 μs in reference to the above pumping beam. The spectrum was recorded on a spectrometer (JASCO TRS-200) which was equipped with a SIT detector and an OMA-2 data processor (EG & G PAR 1254,1215 and 1216). The sample solution were spouted from a nozzle as a flat jet-stream at the rate of ≈1 m/s and circulated. They were kept under a nitrogen atmosphere by the use of a quartz jacket. The pump-beam, probe-beam and the optical axis of the spectrometer were set at the right angle to each other.

Figure 1 shows the Raman spectra of the triplet-state of β-carotene which was produced from the all-trans, 9-cis, 13-cis, and 15-cis isomer. The Raman lines in the region of 900-1300 cm^{-1}, which are ascribable to the coupled vibrations of C-H in-plane bendings and C-C stretching, are expected to be the most sensitive to the configuration. Actually, the ground-state RR spectra of the isomers were quite different from one another reflecting their configurations.$^{7-9)}$ On the other hand, the triplet RR spectra of the isomers were similar to one another, although the relative intensities were slightly different as shown in Fig. 1 and the Raman frequencies of C=C stretching were also identical (not shown), indicating the presense of a common triplet configuration.

Figure 2 illustrates the isomerization of each isomer under the same conditions of Raman measurements except for longer exposure. Hard lines show the elution profiles by the HPLC analyses of the sample solutions after the exposure of 6000 pulses of both pump and probe beams. Broken lines show elution profiles before exposure. The main peak in each profile is nomalized. In the case of the all-trans isomer (Fig. **2a**), both lines coincided, showing that no isomerization took place under the present conditions. The 15-cis isomer (**2d**) isomerized only into the all-trans isomer. As for the 9-cis and the 13-cis isomers (**2b** and **2c**), the major product of isomerization was the all-trans isomer. However, as a minor-

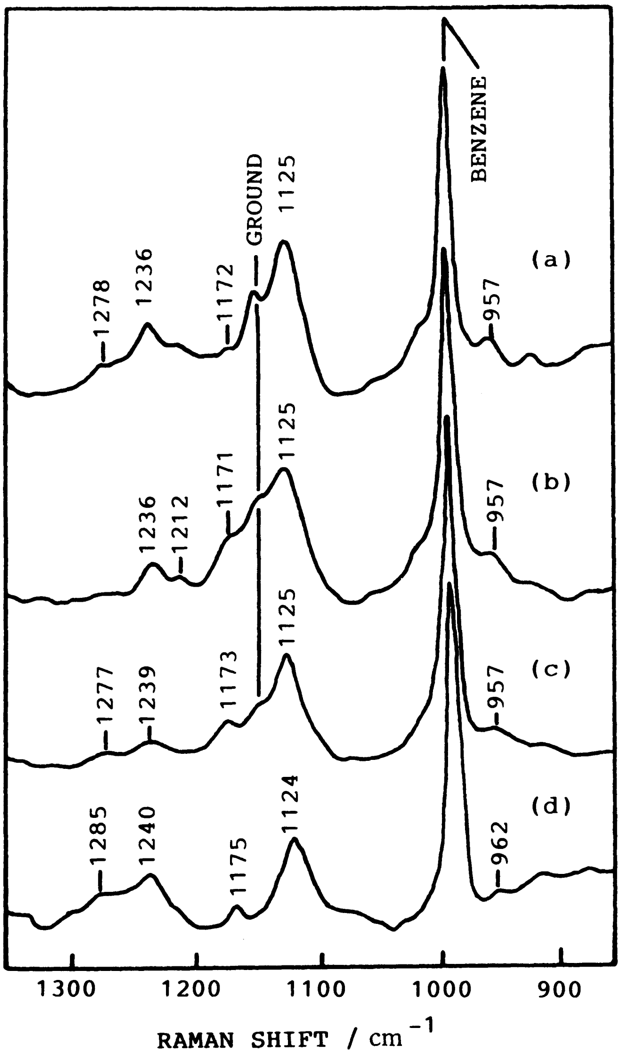

Fig. 1. RR spectra of electronically excited triplet-state of β-carotene isomers, (a) all-*trans*, (b) 9-*cis*, (c) 13-*cis*, and (d) 15-*cis*. The Raman lines marked by GROUND and BENZENE are due to the sample in the ground state and solvent. 1.0 x 10^{-4} M of each isomer and 1.0 x 10^{-2} M anthracene were dissolved in benzene. 500 Runs (10 Hz) of the Raman spectral data were accumulated and the dark back-ground of the SIT detector was subtracted.

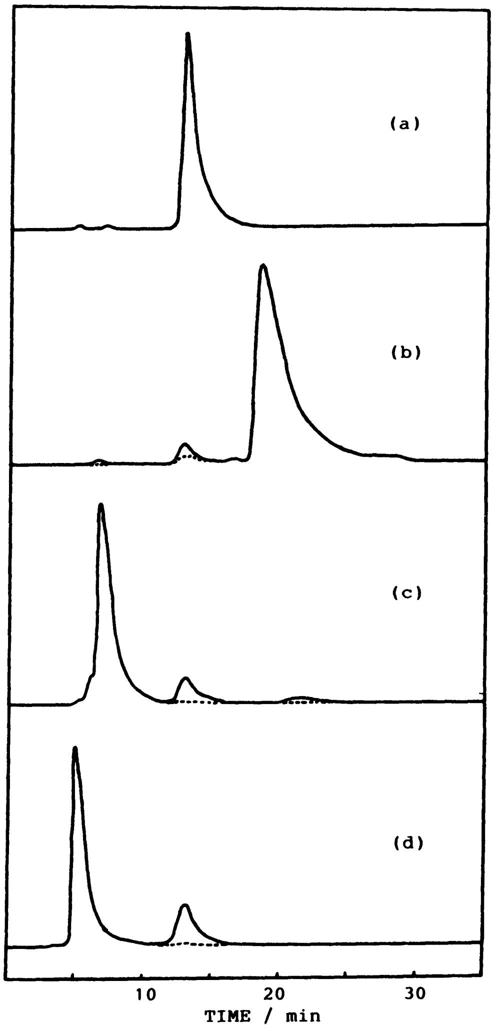

Fig. 2. Isomerization of the (a) all-*trans*, (b) 9-*cis*, (c) 13-*cis* and (d) 15-*cis* isomers of β-carotene under the conditions of Raman measurements. Hard lines show the HPLC elution profile (detection at 450 nm) of each sample solution after the exposure of 6000 pulses of both the pump and the probe beams. Broken lines show elution profiles before exposure.

product, the 9-*cis* isomer produced the 13-*cis* isomer, and the 13-*cis* isomer produced the 9-*cis* isomer. The results indicate that each *cis* configuration transforms mainly into the all-*trans* configuration after forming a relaxed triplet configuration ; most probably, the RR spectra reflect this triplet configuration. Then, what is the common triplet configuration like ? Sugimoto et al. reported that the 15-cis isomer was considered to take a central-twisted configuration based on its electronic absorption[10)] and theoretical calculations also predicted it to be the most stable.[11,12)] Wilbrandt and Jensen assumed that the triplet configuration which was obtained from the all-trans and 15-cis isomers should be 15-perpendicular.[4)] Accordingly, the common triplet configuration which was obtained from the 9-cis and 13-cis isomers also may be 15-perpendicular. If this is the case, 9-cis and 13-cis isomers must isomerize through the discrete two steps of rearrangement. One more reasonable candidate we can speculate as the common triplet configuration is a configuration which is twisted around the 9-, 13-, and 15-C=C double-bonds simultaneously with the rotation angles less than 90°. The speculation is an extension of the idea of dynamical double torsion.[13)]

The present investigation revealed a common triplet configuration for β-carotene isomers. However, detailed discussion should be postponed until the following set of data will become available. (1) T_n-T_1 absorption for each isomer. (2) The dependence of the triplet Raman profile and of the isomerization products for each isomer on the kind of sensitizers. (3) The time-resolved RR spectrum for each isomer.

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