Available online at www.sciencedirect.com
ScienceDirect
Phytochemistry 68 (2007) 1740–1745
PHYTOCHEMISTRY
www.elsevier.com/locate/phytochem

# Carotenoids with a 5,6-dihydro-5,6-dihydroxy-β-end group, from yellow sweet potato "Benimasari", *Ipomoea batatas* Lam

Takashi Maoka [a,*], Naoshige Akimoto [b], Koji Ishiguro [c], Masaru Yoshinaga [c], Makoto Yoshimoto [c]

[a] *Research Institute for Production Development, 15 Shimogamo-morimoto-cho, Sakyo-ku, Kyoto 606-0805, Japan*
[b] *Graduate School of Pharmaceutical Sciences, Kyoto University, Yoshida-shimoadachi-cho, Sakyo-ku, Kyoto 606-8501, Japan*
[c] *National Agricultural Research Center for Kyushu Okinawa Region, 6651-2 Yokoichi-cho, Miyakonojo, Miyazaki 885-0091, Japan*

Received 31 October 2006; received in revised form 23 February 2007
Available online 26 April 2007

**Abstract**

A series of carotenoids with a 5,6-dihydro-5,6-dihydroxy-β-end group, named ipomoeaxanthins A (**1**), B (**2**), C1 (**3**) and C2 (**4**) were isolated from the flesh of yellow sweet potato "Benimasari", *Ipomoea batatas* Lam. Their structures were determined to be (5*R*,6*S*,3′*R*)-5,6-dihydro-β,β-carotene-5,6,3′-triol (**1**), (5*R*,6*S*,5′*R*,6′*S*)-5,6,5′,6′-tetrahydro-β,β-carotene-5,6,5′6′-tetrol (**2**), (5*R*,6*S*,5′*R*,8′*R*)-5′,8′-epoxy-5,6,5′,8′-tetrahydro-β,β-carotene-5,6-diol (**3**), and (5*R*,6*S*,5′R,8′*S*)-5′,8′-epoxy-5,6,5′,8′-tetrahydro-β,β-carotene-5,6-diol (**4**) by UV–Vis, NMR, MS and CD data.


*Keywords:* Sweet potato; *Ipomoea batatas*; Convolvulaceae; Carotenoid; Ipomoeaxanthins; Structural determination

## 1. Introduction

There are a variety of flesh colors, such as white, yellow, orange and purple, in sweet potato tubers. β-Carotene (Kimura et al., 2006), luteochrome (β,β-carotene-5,6,5′,8′-diepoxide) (de Almeida et al., 1986; Martin, 1983), and acylated anthocyanins (Yoshinaga et al., 1999) were reported as the principal pigments in orange flesh, white flesh, and purple flesh cultivars, respectively. Obtaining a deeper yellow color is an important characteristic for developing a new sweetpotato varieties, and a sweet potato, "Benimasari" was developed by the National Agricultural Research Center for Kyushu Okinawa Region in 2001 (Ishiguro et al., 2003, 2004). The flesh color of this cultivar deep yellow, and is used for table use and processed foods. However, the components of the yellow pigment remain unknown, despite their yellow flesh cultivars being popular in Japan. In the course of the study on plant carotenoids, recently we isolated a series of new carotenoids with a 5,6-dihydro-5,6-dihydroxy-β-end group, named ipomoeaxanthins (Fig. 1), from the yellow color flesh of sweet potato "Benimasari", *Ipomoea batatas* Lam along with seven known carotenoids. This paper reports the structural elucidation of these new carotenoids and the carotenoid compositions in the flesh of sweet potato "Benimasari".

## 2. Results and discussion

The total carotenoid content in the freeze-dried mature flesh of sweet potato "Benimasari" was found to be 3.1 mg/100 g. The analytical HPLC separations of the carotenoids in the flesh of "Benimasari" are shown in Fig. 2, with the following seven known carotenoids and four new carotenoids identified; β-carotene (10.5% of the total carotenoid), β-carotene-5,8-epoxide (6.5%), β-carotene 5,8;5′,8′-diepoxide (40.5%), β-cryptoxanthin 5′,8′-epoxide (10.5%), β-cryptoxanthin 5,8;5′,8′-diepoxide

* Corresponding author. Tel.: +81 75 781 1107; fax: +81 75 791 7659.
*E-mail address:* maoka@mbox.kyoto-inet.or.Jp (T. Maoka).

0031-9422/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.phytochem.2007.03.019

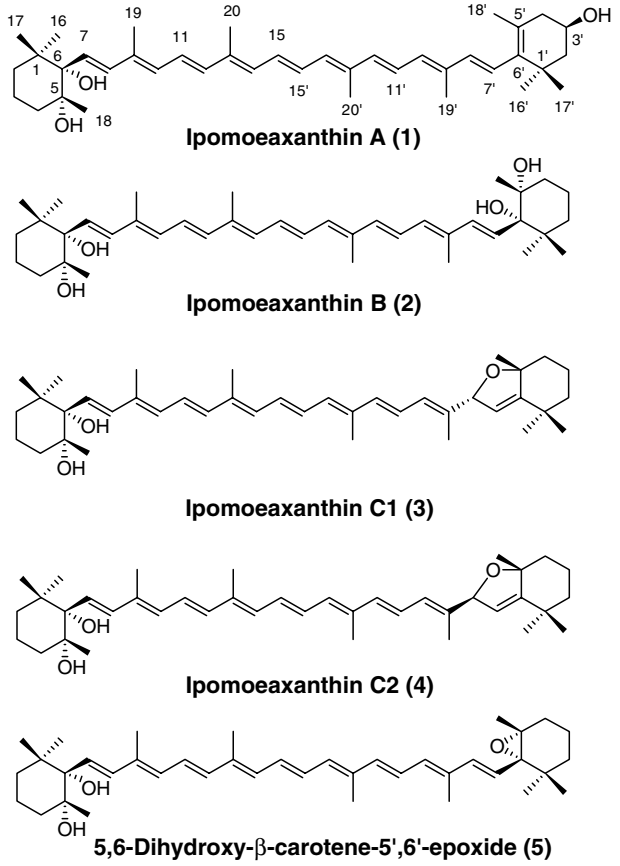


Fig. 1. Structures of new carotenoids.

(5.5%), auroxanthin (2.2%), neochrome (4.5%), ipomoeaxanthin A (**1**) (3.2%), ipomoeaxanthin B (**2**) (0.5%), ipomoeaxanthin C1 (**3**) (2.5%), and ipomoeaxanthin C2 (**4**) (2.5%).

Ipomoeaxanthin A (**1**) showed absorption maxima at 420, 444, and 472 nm. The molecular formula of **1** was determined to be $C_{40}H_{58}O_3$ by high-resolution fast atom bombardment mass spectrometry (HR FABMS). Of the three oxygen atoms, one was ascribed to a secondary hydroxyl group by formation of a mono-acetate by acetylation and an oxy-methine signal at $\delta_H$ 4.00 in the $^1H$ NMR and $\delta_C$ 65.1 in the $^{13}C$ NMR spectra. The remaining two were ascribed to tertiary hydroxy groups by two quaternary carbon signals at $\delta_C$ 75.4 and 79.9. The $^1H$ and $^{13}C$ NMR spectroscopic data for **1**, as assigned by $^1H$–$^1H$ correlated spectroscopy (COSY), $^1H$–$^1H$ nuclear Overhauser enhancement and exchange spectroscopy (NOESY), $^1H$–$^{13}C$ heteronuclear singlet quantum coherence (HSQC), and $^1H$–$^{13}C$ heteronuclear multiple bond coherence (HMBC) experiments, are shown in Table 1. The partial structures of the 3-hydroxy-β-end group and the all *trans* polyene chain were confirmed by the analysis of NMR spectroscopic data by comparison with that of zeaxanthin (Englert, 1995). The structure of the remaining end group (C1–C6 including methyl groups at C16–C18) was elucidated to be 5,6-*cis*-5,6-dihydro-5,6-dihydroxy-β-end group by application of COSY, NOESY, HSQC, and HMBC experiments. The proton and carbon connectivities from C-2 to C-4 were elucidated by COSY and HSQC. The quaternary carbons at C-1, C-5, and C-6 were assigned by analysis of the HMBC spectrum as shown in Table 1. The locations of the tertiary hydroxy groups at C-5 and C-6 were established by HMBC correlations from H-18 to the quaternary carbon at $\delta_C$ 75.4 (C-5) and from H-16, 17, 7 to the quaternary carbon at $\delta_C$ 79.9 (C-6). Therefore, the structure of **1** was determined to be 5,6-dihydro-β,β-carotene-5,6,3′-triol. NOESY correlations between H-17 and H-7 and between H-18 and H-7 established that two tertiary hydroxy groups at C-5 and C-6 were orientated on opposite side of the polyene chain with a *cis* configuration. Therefore, a (5*R*,6*S*) or (5*S*,6*R*) chirality could be considered for **1**. From a biosynthetic consideration as shown in Fig. 3, the (5*R*,6*S*) chirality was proposed for **1**. The NOESY correlations H-19/H-7 and H-11, H-20/H-11 and H-15, H-20′/H-15′ and H-11′, and H-19′/H-11′ and H-7′ confirmed the all-*trans* geometry of the polyene chain. The CD spectrum of **1** showed a similar Cotton effect to that of (3*R*,3′*R*)-zeaxanthin (Bucheker and Noack, 1995), except for the wavelength shift being 10 nm shorter than that of (3*R*,3′*R*)-zeaxanthin, which is attributable to

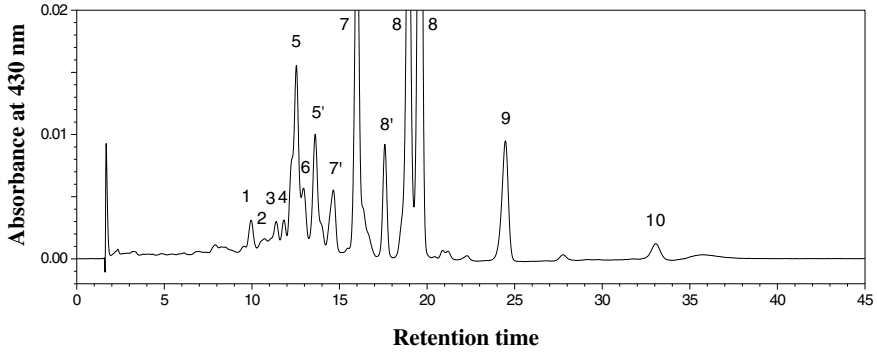


Fig. 2. Analytical scale HPLC of carotenoids from the flesh of yellow sweet potato "Benimasari", *Ipomoea batatas* Lam. HPLC conditions were described in Section 3. Peak identifications 1: neochrome, 2: auroxanthin, 3: ipomoeaxanthin B, 4: ipomoeaxanthin A, 5: β-cryptoxanthin 5,8;5′,8′-diepoxide, 5′: β-cryptoxanthin 5,8;5′,8′-diepoxide (*cis* isomer), 6: ipomoeaxanthin C1 and C2, 7′: β-cryptoxanthin 5′,8′-epoxide (*cis* isomer), 7: β-cryptoxanthin 5′,8′-epoxide, 8′: β-carotene 5,8;5′,8′-diepoxide (*cis* isomer), 8: β-carotene 5,8;5′,8′-diepoxide, 9: β-carotene-5,8-epoxide, 10: β-carotene.

Table 1
$^1$H NMR (500 MHz) and $^{13}$C NMR (125 MHz) spectroscopic assignments of ipomoeaxanthin A (**1**) in $CDCl_3$

| Position | $^{13}$C mult. | $^1$H mult. (J Hz) | HMBC (H to C) | position | $^{13}$C mult. | $^1$H mult. (J Hz) | HMBC (H to C) |
|---|---|---|---|---|---|---|---|
| 1 | 38.8 *s* | | | 1′ | 37.2 *s* | – | |
| 2 | 37.3 *t* | 1.57 *m* | | 2′ | 48.5 *t* | 1.48 *dd* (12, 12) | C-3′, 4′ |
| | | | | | | 1.77 *ddd* (12, 3, 1.5) | C-3′, 4′ |
| 3 | 18.6 *t* | 1.75 *m* | | 3′ | 65.1 *d* | 4.00 *m* | |
| 4 | 36.5 *t* | 1.77 *m* | | 4′ | 42.6 *t* | 2.04 *dd* (17, 10) | |
| | | | | | | 2.39 *ddd* (17, 5, 1) | |
| 5 | 75.4 *s* | – | | 5′ | 126.3 *s* | – | |
| 6 | 79.9 *s* | – | | 6′ | 137.9 *s* | – | |
| 7 | 129.4 *d* | 5.91 *d* (16) | C-6, C-9 | 7′ | 125.7 *d* | 6.10 *d* (16) | |
| 8 | 134.2 *d* | 6.47 *d* (16) | C-6 | 8′ | 138.5 *d* | 6.15 *d* (16) | |
| 9 | 135.8 *s* | – | | 9′ | 135.8 *s* | – | |
| 10 | 131.8 *d* | 6.23 *d* (11) | | 10′ | 131.4 *d* | 6.16 *d* (11.5) | |
| 11 | 125.9 *d* | 6.62 *dd* (15.5, 11) | | 11′ | 125.6 *d* | 6.65 *dd* (15.5, 11) | |
| 12 | 136.7 *d* | 6.37 *d* (15.5) | | 12′ | 137.9 *d* | 6.36 *d* (15.5) | |
| 13 | 136.3 *s* | – | | 13′ | 136.6 *s* | – | |
| 14 | 132.6 *d* | 6.27 *d* (11) | | 14′ | 132.5 *d* | 6.27 *d* (11) | |
| 15 | 130.2 *d* | 6.65 *m* | | 15′ | 130.1 *d* | 6.65 *m* | |
| 16 | 24.8 *q* | 1.09 *s* | C-1, 2, 6 | 16′ | 28.7 *q* | 1.08 *s* | C-1′, 2′, 6′ |
| 17 | 27.1 *q* | 0.90 *s* | C-1, 2, 6 | 17′ | 30.3 *q* | 1.08 *s* | C-1′, 2′, 6′ |
| 18 | 27.1 *q* | 1.21 *s* | C-4, 5, 6 | 18′ | 21.6 *q* | 1.74 *s* | C-4′, 5′, 6′ |
| 19 | 13.2 *q* | 1.94 *s* | C-8, 10 | 19′ | 12.8 *q* | 1.98 *s* | C-8′,10′ |
| 20 | 12.8 *q* | 1.97 *s* | C-12, 14 | 20′ | 12.8 *q* | 1.99 *s* | C-12′, 14′ |

Chemical shifts were represented as $\delta$ values.

the lack of one double bond at C-5 in **1**. It has been reported that a carotenoid having an 3-hydroxy-β-end group exhibits strong Cotton effects in the CD spectrum, while a carotenoid having a 5,6-dihydro-5,6-dihydroxy-β-end group has a very weak Cotton effect in the CD spectrum (Bucheker and Noack, 1995). Therefore, it was assumed that the CD of **1** reflected the chirality at C-3′. Thus the chirality at C-3′ was determined to be *R*. Therefore, a (5*R*,6*S*,3′*R*) chirality was proposed for **1**.

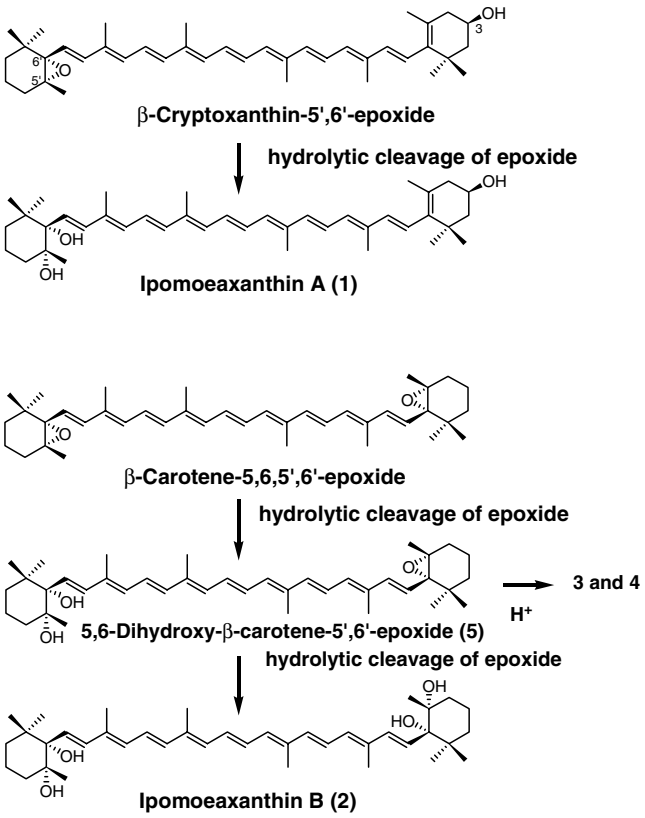


Fig. 3. Proposed biosynthetic pathways of new carotenoids.

Ipomoeaxanthin B (**2**) showed absorption maxima at 415, 438, and 468 nm. The molecular formula of **2** was determined to be $C_{40}H_{60}O_4$ by HR FABMS. The $^1$H NMR data (Table 2) indicated that **2** had a symmetrical structure and showed the same chemical shifts and coupling constants as those of H-2 to H-20 of **1**. Therefore, the structure of **2** was determined to be 5,6,5′,6′-tetrahydro-β,β-carotene-5,6,5′6′-tetrol. The $^1$H–$^1$H connectivities of H-2 to H-4 (H-2′ to H-4′), H-7 to H-8 (H-7′ to H-8′), H-10 to H-12 (H-10′ to H-12′), H-14 to H-15 (H-14′ to H-15′), H-19 to H-10 (H-19′ to H-10′) and H-20 to H-14 (H-20′ to H-14′) were also confirmed by a COSY experiment. The (5*R*,6*S*,5′*R*,6′*S*) chirality for **2** was proposed based on biosynthetic considerations as shown in Fig. 3.

Both ipomoeaxanthin C1 (**3**) and C2 (**4**) showed absorption maxima at 398, 420, and 448 nm, and had molecular formulae of $C_{40}H_{58}O_3$. The $^1$H NMR signals of H-2 to H-20 and H-2′ to H-20′ of **3** were identical to those of **2** and (5*R*,8*R*,5′*R*,8′*R*)-aurochrome (5,8,5′,8′-diepoxy-5,8,5′,8′-tetrahydro-β,β-carotene) (Englert, 1995), respectively. Therefore, the structure of **3** was determined to be (5*R*′,8′*R*)-5′,8′-epoxy-5,6,5′,8′-tetrahydro-β,β-carotene-5,6-diol. The $^1$H NMR signals of **4** were almost identical to those of **3** except for the resonances of H-7′, 8′, 16′, 17′, 18′ and 19′. These data suggested that **4** might be a diastereomer of **3**. As well as **3**, the structure of **4** was determined

Table 2
$^1$H NMR (500 MHz) spectroscopic assignments of ipomoeaxanthin B (**2**), C1 (**3**), C2 (**4**) in $CDCl_3$

| Position | Ipomoeaxanthin B (**2**) $^1$H mult. (J Hz) | Ipomoeaxanthin C1 (**3**) $^1$H mult. (J Hz) | Ipomoeaxanthin C2 (**4**) $^1$H mult. (J Hz) |
|---|---|---|---|
| 2 | 1.57 *m* | 1.57 *m* | 1.57 *m* |
| 3 | 1.75 *m* | 1.75 *m* | 1.75 *m* |
| 4 | 1.77 *m* | 1.77 *m* | 1.77 *m* |
| 7 | 5.91 *d* (16) | 5.91 *d* (16) | 5.91 *d* (16) |
| 8 | 6.47 *d* (16) | 6.47 *d* (16) | 6.47 *d* (16) |
| 10 | 6.23 *d* (11) | 6.23 *d* (11) | 6.23 *d* (11) |
| 11 | 6.62 *dd* (15.5, 11) | 6.62 *dd* (15.5, 11) | 6.62 *dd* (15.5, 11) |
| 12 | 6.37 *d* (15.5) | 6.37 *d* (15.5) | 6.37 *d* (15.5) |
| 14 | 6.27 *d* (11) | 6.27 *d* (11) | 6.27 *d* (11) |
| 15 | 6.65 *m* | 6.65 *m* | 6.65 *m* |
| 16 | 1.09 *s* | 1.09 *s* | 1.09 *s* |
| 17 | 0.90 *s* | 0.90 *s* | 0.90 *s* |
| 18 | 1.21 *s* | 1.21 *s* | 1.21 *s* |
| 19 | 1.94 *s* | 1.94 *s* | 1.94 *s* |
| 20 | 1.97 *s* | 1.97 *s* | 1.97 *s* |
| 2′ | 1.57 *m* | n.a. | n.a. |
| 3′ | 1.75 *m* | n.a. | n.a. |
| 4′ | 1.77 *m* | n.a. | n.a. |
| 7′ | 5.91 *d* (16) | 5.17 *s* | 5.23 *d* (1.5) |
| 8′ | 6.47 *d* (16) | 5.16 *s* | 5.07d (1.5) |
| 10′ | 6.23 *d* (11) | 6.19 *d* (11) | 6.20 *d* (11) |
| 11′ | 6.62 *dd* (15.5, 11) | 6.49 *dd* (15.5, 11) | 6.49 *dd* (15.5, 11) |
| 12′ | 6.37 *d* (15.5) | 6.32 *d* (15.5) | 6.32 *d* (15.5) |
| 14′ | 6.27 *d* (11) | 6.22 *d* (11) | 6.22 *d* (11) |
| 15′ | 6.65 *dd* (15, 11) | 6.61 *dd* (15, 11) | 6.61 *dd* (15, 11) |
| 16′ | 1.09 *s* | 1.15 *s* | 1.18 *s* |
| 17′ | 0.90 *s* | 1.10 *s* | 1.11 *s* |
| 18′ | 1.21 *s* | 1.43 *s* | 1.46 *s* |
| 19′ | 1.94 *s* | 1.74 *s* | 1.80 *s* |
| 20′ | 1.97 *s* | 1.94 *s* | 1.94 *s* |

n.a. not assigned.

to be (5′*R*,8′*S*)-5′,8′-epoxy-5,6,5′,8′-tetrahydro-β,β-carotene-5,6-diol by comparison with the $^1$H NMR spectroscopic data of **2** and (5*R*,8*S*,5′*R*,8′*S*)-aurochrome (Englert, 1995). The $^1$H–$^1$H connectivities and relative stereochemistry of both compounds were also confirmed by COSY and NOESY data (see Section 3). The CD of **3** and **4** gave almost mirror image spectra of each others and were reflected in their (8′*R*) and (8′*S*) chiralities, respectively. The (5*R*,6*S*) chirality of both compounds was proposed based on biosynthetic considerations as shown in Fig. 3 and the results of NOESY data. It is well known that 5,8-epoxides are derived from the corresponding 5,6-epoxide by acid catalysis (Schiedt and Liaaen-Jensen, 1995). Therefore, it was assumed that the precussor/nature form of both compounds was (5*R*,6*S*,5′*R*,6′*S*)-5′,6′-epoxy-5,6,5′,6′-tetrahydro-β,β-carotene-5,6-diol (**5**) , which was named as 5,6-dihydroxy-β-carotene-5′,6′-epoxide.

### 2.1. Concluding remarks

Concerning the naturally occurring carotenoids having a 5,6-dihydro-5,6-dihydroxy-β-end group (Britton et al., 2004), only azafrin and its derivatives have a 5,6-*trans* configuration (Eschenmoser et al., 1982). On the other hand, the ipomoeaxanthins have 5,6-*cis* configuration, although carotenoids with a 5,6-*cis*-5,6-dihydro-5,6-dihydroxy-β-end group have not been reported yet in nature.

Carotenoids with a 5,6-*cis*-5,6-dihydro-5,6-dihydroxy-β-end group might be derived from the corresponding 5,6-epoxy carotenoid by hydrolytic cleavage of an epoxide. Therefore, β-cryptoxanthin 5′,6′-epoxide was assumed to be a precursor of ipomoeaxanthin A. Similarly, β-carotene 5,6,5′,6′-diepoxide might be a precursor of ipomoeaxanthins B, C1 and C2 as shown in Fig. 3.

## 3. Experimental

### 3.1. Plant material

A sweet potato, "Benimasari" was cultivated at the National Agricultural Research Center for Kyushu Okinawa Region in 2005. The planting density was 0.75 m × 0.30 m. Compost was applied at 10 t/ha and chemical fertilizer ($N:P_2O_5:K_2O = 8:12:20$) at 600 kg/ha. The cultivar was transplanted in May and harvested in October. The harvested tubers were freeze-dried and kept at −30 °C until use.

### 3.2. General experimental procedures

The UV–Vis spectra were recorded with a Shimadzu-UV-240 spectrophotometer in $Et_2O$ at a concentration of about 5 μg/ml. Spectral fine structure were indicated as value of %III/II (Britton, 1995). The positive ion FABMS spectra were recorded using a JEOL JMS-HS 110A mass spectrometer, with *m*-nitrobenzyl alcohol as a matrix. The $^1H$ NMR (500 MHz $CDCl_3$) and $^{13}C$ NMR (125 MHz $CDCl_3$) spectra were recorded with a Varian UNITY *INOVA* 500 spectrometer in $CDCl_3$ with TMS as an internal standard. The CD spectra were recorded in $Et_2O$ at room temperature with a Jasco J-720 WI spectropolarimeter. HPLC was performed on a Shimadzu LC-6AD with a Shimadzu SPD-6AV spectrometer set at 450 nm.

### 3.3. Extraction and isolation of carotenoids

The $Me_2CO$ (3 l for 24 hrs) extract of the freeze dried flesh of sweet potato (1500 g) was evaporated and saponified with 5% KOH/MeOH at room temperature for 3 h. Unsaponifiable materials were extracted with $Et_2O$ and washed with water and concentrated. The residue so obtained was then subjected to silica gel CC using an increasing percentage of $Et_2O$ in *n*-hexane and $Me_2CO$. The fraction eluted with *n*-hexane:$Et_2O$ (1:1) was subjected to preparative HPLC on ODS, LiChrospher RP-18 (e) (250 × 10 mm i.d., 10 μm, Cica-Merck, Darmstadt, Germany), with $CHCl_3$–MeCN (1:9), at a flow rate of 2.0 ml/min, to yield ipomoeaxanthin C1 (**3**) (1.5 mg, Retention time (Rt.) 42.3 min) and C2 (**4**) (1,5 mg, Rt. 40.0 min). The fraction eluted with $Et_2O$ (1:1) was subjected to preparative HPLC on ODS, with $CHCl_3$–MeCN (1:9) to yield ipomoeaxanthin B (**2**) (0.2 mg, Rt. 26.8 min) and ipomoeaxanthin A (**1**) (3 mg, Rt. 30.0 min). Analytical scale HPLC was performed on a Wakopack Navi C30-5 (250 × 30 mm i.d., 5 μm, Wako Chemicals Co. Ltd., Osaka, Japan) column with MeCN (solvent A) and MeCN/MeOH/$CHCl_3$ (75:10:15) (solvent B) as eluents at a flow rate of 0.85 ml/min at 35 °C. The elution profiles were as follows: solvent B conc. 0–100% linear gradient (0–15 min), 100% (15–30 min), 100–0% linear gradient (30–31 min), 0% (31–45 min) with detection at 430 nm.

### 3.4. Carotenoid content and compositions

The total carotenoid content was calculated using the extinction coefficient of $E = 2500$ at $\lambda$ max (Schiedt and Liaaen-Jensen, 1995). The percentage compositions of individual carotenoids were calculated from the peak area of analytical HPLC. The identification of seven known carotenoids, β-carotene, β-carotene-5,8-epoxide, β-carotene 5,8;5′,8′-diepoxide, β-cryptoxanthin 5′,8′-epoxide, β-cryptoxanthin 5,8;5′,8′-diepoxide, auroxanthin, and neochrome, was based on UV–Vis, FABMS and $^1H$ NMR spectroscopic data.

### 3.5. Ipomoeaxanthin A (*1*)

Yellow solid; for $^1H$ NMR (500 MHz $CDCl_3$) and $^{13}C$ NMR (125 MHz $CDCl_3$) spectroscopic assignments, see (Table 1); HR FABMS: Calc. for $C_{40}H_{58}O_3(M^+)$: 586.4386; Found 586.4388; CD (20 μg/ml in $Et_2O$) $\lambda$ ($\Delta\varepsilon$): 210 (−7.7), 226 (0), 248 (+6.2), 256 (0), 275 (−12.0), 310 (0), 333 (−3.6). Key NOESY correlations; H-17/H-7, H-18/H-7, H-19/H-7, H-19/H-11, H-20/H-11, H-20/H-15, H-20′/H-15′, H-20′/H-11′, H-19′/H-11′, H-19′/H-7′, H-16′/H-3′. Acetylation of **1** with acetic anhydride in pyridine at room temperature for 5 h gave a mono-acetate, which had a molecular ion at *m*/*z* 628 in FABMS.

### 3.6. Ipomoeaxanthin B (*2*)

Yellow solid; for $^1H$ NMR (500 MHz $CDCl_3$) spectroscopic assignments, see (Table 2); HRFABMS: Calc. for $C_{40}H_{60}O_4$ ($M^+$): 604.4486; Found 604.4486.

### 3.7. Ipomoeaxanthin C1 (*3*)

Yellow solid; for $^1H$ NMR (500 MHz $CDCl_3$) spectroscopic assignments, see (Table 2); HRFABMS: Calc. for $C_{40}H_{58}O_3(M^+)$: 586.4386; Found 586.4388; CD (20 μg/ml in $Et_2O$) $\lambda$ ($\Delta\varepsilon$): 210 (+5.6), 230 (−1.5), 248 (+4.6), 270 (0), 308 (−0.8), 380 (0). Key NOESY correlations; H-17/H-7, H-18/H-7, H-19/H-7, H-19/H-11, H-20/H-11, H-20/H-15, H-20′/H-15′, H-20′/H-11′, H-19′/H-11′, H-19′/H-7′, H-18′/H-8′.

### 3.8. Ipomoeaxanthin C2 (*4*)

Yellow solid; for $^1H$ NMR (500 MHz $CDCl_3$) spectroscopic assignments, see (Table 2); HRFABMS: Calc. for $C_{40}H_{58}O_3(M^+)$: 586.4386; Found 586.4386; CD (20 μg/ml in $Et_2O$) $\lambda$ ($\Delta\varepsilon$): 210 (−5.0), 230 (−1.0), 248 (+4.0), 270 (0), 308 (+0.2), 380 (0). Key NOESY correlations; H-17/H-7, H-18/H-7, H-19/H-7, H-19/H-11, H-20/H-11, H-20/H-15, H-20′/H-15′, H-20′/H-11′, H-19′/H-11′, H-19′/H-7′.

## Acknowledgements

We thank Dr. H. Yasui, Kyoto Pharmaceutical University for measurement of CD spectra.

## References

Britton, G., 1995. UV/visble spectrometry. In: Britton, G., Liaaen-Jensen, S., Pfander, H. (Eds.), Carotenoids, vol. 1B. Birkhäuser Verlag, Basel, pp. 13–62.

Britton, G., Liaaen-Jensen, S., Pfander, H., 2004. Carotenoids Handbook. Birkhäuser Verlag, Basel.

Bucheker, R., Noack, H., 1995. Circular dichroism. In: Britton, G., Liaaen-Jensen, S., Pfander, H. (Eds.), Carotenoids, vol. 1B. Birkhäuser Verlag, Basel, pp. 63–116.

de Almeida, L.B., Penteado, M.deV.C., Simpson, K.L., Britton, G., Acemoglu, M., Eugster, C.H., 1986. Isolation and characterization of (5*R*,6*S*,5′*R*,8′*R*)- and (5*R*,6*S*,5′*R*,8′*S*)-luteochrome from Brazilian sweet potatoes (*Ipomoea batatas* Lam.). Helv. Chim. Acta 69, 1554–1558.

Englert, G., 1995. NMR spectroscopy. In: Britton, G., Liaaen-Jensen, S., Pfander, H. (Eds.), Carotenoids, vol. 1B. Birkhäuser Verlag, Basel, pp. 147–160.

Eschenmoser, W., Uebelhart, P., Eugster, C.H., 1982. Synthesis of (+)-(5*S*,6*S*)-azafrin methyl ester. Absolute configuration of aeginetic acid or further vicinal apocarotene-diol. Helv. Chim. Acta 35, 353–364.

Ishiguro, K., Yamakawa, O., Kumagai, T., Kai, Y., Nakazawa, Y., 2003. Benimasari: new sweet potato cultivar for table use. Sweetpotato Res. Front 15, 3.

Ishiguro, K., Yamakawa, O., Kumagai, T., Yoshinga, M., Kai, Y., Hidaka, M., 2004. Benimasari: new sweet potato cultivar for table use. Bull. Natl. Agric. Res. Center Kyushu Okinawa Reg. 43, 59–85.

Kimura, M., Kobori, C.H., Rodriguez-Amaya, D.B., Nestel, P., 2006. Screening and HPLC methods for carotenoids in sweetpotato, cassava and maize for plant breeding trials. Food Chem. 100, 1734–1746.

Martin, F.W., 1983. The carotenoid pigments of white-fleshed sweet potatoes. J. Agric. Univ. Puerto Rico 67, 494–500.

Schiedt, K., Liaaen-Jensen, S., 1995. Isolation and analysis. In: Britton, G., Liaaen-Jensen, S., Pfander, H. (Eds.), Carotenoids, vol. 1B. Birkhäuser Verlag, Basel, pp. 81–108.

Yoshinaga, M., Yamakawa, O., Yoshimoto, M., 1999. Genotypic diversity of antocyanin content and composition in purple-fleshed sweet potato (*Ipomoea batatas* (L.) Lam.). Breed. Sci. 49, 43–47.