Heliyon 5 (2019) e01883

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.heliyon.com

Carotenoid composition of the mushroom Scarlet elf cup *(Sarcoscypha coccinea)*

Péter Molnár [a,*], Erzsébet Ősz [b,†], Erika Turcsi [b], József Deli [a,b]

[a] Department of Pharmacognosy, Faculty of Pharmacy, University of Pécs, Rókus u. 2, H-7624 Pécs, Hungary
[b] Department of Biochemistry and Medical Chemistry, Medical School, University of Pécs, Szigeti út 12, H-7624 Pécs, Hungary

ARTICLE INFO

Keywords:
Food analysis
Organic chemistry
Natural product chemistry
Analytical chemistry
Mushroom
Carotenoids
(Z)-Isomers
Isolation
HPLC analysis
Structure elucidation

ABSTRACT

From the extract of the mushroom Scarlet elf cup (*Sarcoscypha coccinea*) (all-*E*, 2′*R*)- plectaniaxanthin, (all-*E*)-2′-dehydroplectaniaxanthin and a number of sterically unhindered (*Z*)-isomers of these carotenoids were isolated and partially characterized. The carotenoid composition of the Scarlet elf cup extract was determined by HPLC analysis. The structure elucidation of the isolated compounds was carried out by UV/Vis spectroscopy, ^{1}H and ^{13}C-NMR spectroscopy, IR spectroscopy and mass spectrometry. The $NaBH_4$-reduction of (all-*E*)-2′-dehydroplectaniaxanthin resulted in the racemic mixture of (*R*)- and (*S*)-plectaniaxanthin. The isolated (*Z*)-isomers were identified by their UV/Vis spectroscopic properties.

1. Introduction

The mushroom Scarlet elf cup (*Sarcoscypha coccinea*) is an edible fungus, even though it remains rather tough after cooking. It can be collected in Hungary in the Pécs area in the western Mecsek mountains and in the Zselic during February and March. To our knowledge the carotenoid composition of this mushroom has not been investigated and described to date in the literature.

The novelty and the main goal of our work is the determination of the carotenoid composition of the mushroom Scarlet elf cup (*Sarcoscypha coccinea*) by HPLC and CLC, the isolation of its main carotenoids [(all-*E*, 2′*R*)-plectaniaxanthin (**1**) and (all-*E*)-2′-dehydroplectaniaxanthin (**2**); Fig. 1] in highly pure crystalline state, the stucture elucidation of these carotenoids by spectroscopic methods (UV/Vis, ^{1}H- and ^{13}C-NMR, MS, IR), and the isolation of numerous sterically unhindered (*Z*)-isomers of **1** and **2**, and their identification on the basis of their UV/Vis spectroscopic properties. The secondary objective of this study is the confirmation of the (2′*R*) configuration of the naturally occurring (all-*E*)-plectaniaxanthin (**1**).

Plectaniaxanthin [(all-*E*, 2′*R*)-3′,4′-didehydro-1′,2′-dihydro-β,ψ-carotene-1′,2′-diol; **1**] and its mono- and diester have been isolated for the first time from the mushroom *Plectania coccinea* (Arpin and Liaaen-Jensen, 1967a,b) and its occurrence was subsequently demonstrated in several other mushrooms, as well (Bae et al., 1971).

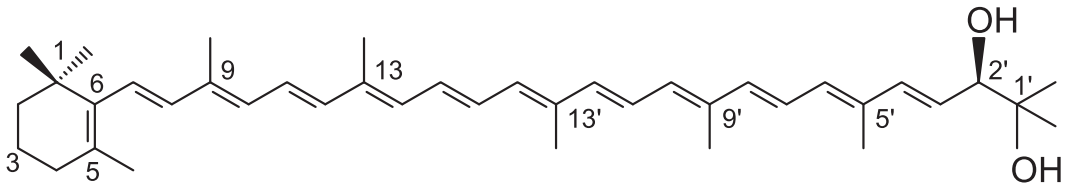
Plectania coccinea and *Sarcoscypha coccinea* are the same species; they are taxonomic synonyms (Korf, 1953; Rønneberg et al., 1982; http://www.mycobank.org/BioloMICS.aspx?TableKey=14682616000000067&Rec=21926&Fields=All).

The constitution of the compound has been determined using spectroscopic methods (UV/Vis, IR, NMR, MS) (Arpin and Liaaen-Jensen, 1967a,b; Hertzberg & Liaaen-Jensen, 1967, 1969; Enzell et al., 1969; Vacheron et al., 1969; Arpin et al., 1970; Bae et al., 1971; Buchecker et al., 1976), however the configuration at C(2') of the isolated compound remained unknown for a long time. On the basis of CD spectroscopic studies carried out in 1982, it was possible to deduce to the (*R*) configuration (Rønneberg et al., 1982).

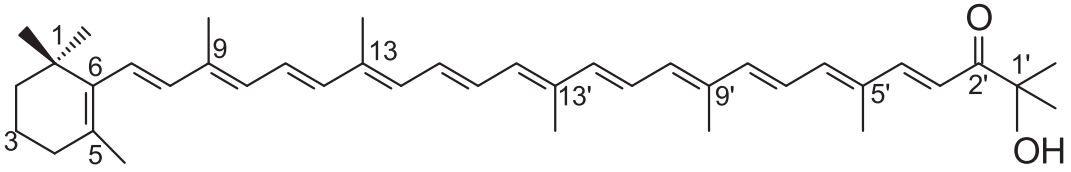
The (2′*R*) configuration has been verified in 1984: The total synthesis of (2′*S*)-plectaniaxanthin was reported, using L-serine as starting material, and based on the comparison of the CD spectra of the natural and the synthetic compound, the (2′*R*)-configuration of the natural compound was established (Dumont and Pfander, 1984). The (2′*R*)-configuration has been confirmed by the result of later investigation (Rønneberg et al., 1985). The natural occurrence of the free (2′*S*)-plectaniaxanthin has not been reported to date, but its glucoside [phleixanthophyll; (2′*S*)-1'-(β-D-glucopyranosyloxy)-3′,4′-didehydro-1′,2′-dihydro-β,

* Corresponding author.
E-mail address: Peter.Molnar@aok.pte.hu (P. Molnár).
† Deceased author.

https://doi.org/10.1016/j.heliyon.2019.e01883
Received 19 November 2018; Received in revised form 7 May 2019; Accepted 30 May 2019



(all-*E*, 2'*R*)-Plectaniaxanthin (**1**)



(all-*E*)-2'-Dehydroplectaniaxanthin (**2**)

Fig. 1. Structure of (all-*E*, 2′*R*)-plectaniaxanthin (**1**) and of (all-*E*)-2′-dehydroplectaniaxanthin (**2**).

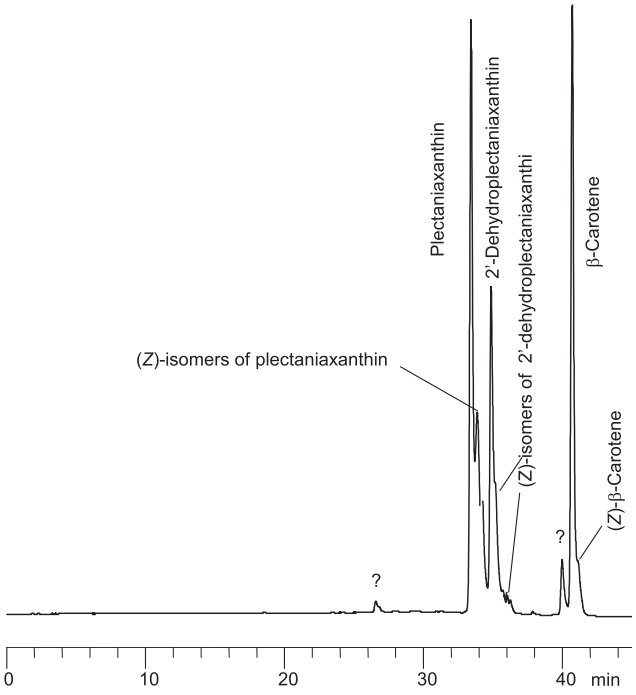


Fig. 2. HPLC analysis of the saponified total extract of mushroom Scarlet elf cup (*Sarcoscypha coccinea*).

ψ-caroten-2′-ol] occurs in nature (Hertzberg and Liaaen-Jensen, 1967; Rønneberg et al., 1985; Britton et al., 2004).

The above mentioned studies reported also the isolation of 2′-dehydroplectaniaxanthin [(all-*E*)-1′-hydroxy-3′,4′-didehydro-1′,2′-dihydro-β,ψ-caroten-2′-one; **2**] and its esters.

2. Materials and methods

2.1. General experimental procedures

All chemicals used in the extraction, in column liquid chromatography (CLC) and during HPLC analysis were analytical grade quality (Sigma-Aldrich Ltd., Budapest, Hungary).

Table 1
Preparative column chromatography of the saponified total extract of mushroom Scarlet elf cup (*Sarcoscypha coccinea*); UV/Vis data of the isolated carotenoids.

Zone	λ_{max} (nm, toluene)	Q*	Carotenoid
111	523, 489, 462, 376	12.3	(all-*E*)-Plectaniaxanthin
132	515, 483, 457, 374	2.3	(13*Z*)- or (13′*Z*)-Plectaniaxanthin
143	515, 482, 457, 373	2.2	(13′*Z*)- or (13*Z*)-Plectaniaxanthin
151	512, 407	5.4	(9*Z*)- or (9′*Z*)-Dehydroplectaniaxanthin
152	505, 400	1.8	(13*Z*)- or (13′*Z*)-Dehydroplectaniaxanthin
222	511, 401	2.0	(13′*Z*)- or (13*Z*)-Dehydroplectaniaxanthin
23	496, 407	2.5	(poly-*Z*)-Dehydroplectaniaxanthin
241	510, 400	1.6	(15*Z*)-Dehydroplectaniaxanthin
243	515, 483, 458, 374	1.6	(15*Z*)-Plectaniaxanthin
31	518, 407	4.9	(all-*E*)-Dehydroplectaniaxanthin
32	503, 408	2.8	(9*Z*,9′*Z*)-Dehydroplectaniaxanthin
4	511, 406	4.9	(9′*Z*)- or (9*Z*)-Dehydroplectaniaxanthin
5	507, 403	2.7	(di-*Z*)-Plectaniaxanthin
6	493, 464	>10	β-Carotene

Carotenoid of zone 31 [(all-*E*)-2′-Dehydroplectaniaxanthin (2)] adsorbed with a blue colour on the $CaCO_3$ column.
* $Q = A_{max}/A_{cis\text{-}peak}$.

The UV/Vis spectra were recorded with a Beckman DU-65 spectrophotometer in toluene.

The NMR experiments were carried out on a Varian Unity Inova 400-WB spectrometer, at 400 MHz (^{1}H) or 100 MHz (^{13}C), in $CDCl_3$ (99.8 atom% D; purchased from VWR International) at a probe temperature of 298K. Chemical shift values (δ) are given in ppm referenced to $(CH_3)_4Si$ (^{1}H) or the residual solvent signals (^{13}C) (Molnár et al., 2006a,b).

FT-IR spectrum was recorded on an IMPACT 400 spectrometer (Nicolet Analytical Instruments, 5225-1 Verona Road, P.O. Box 4508, Madison, WI 53711-0508, USA; DTGS detector; Δν 400–4000 cm^{-1}; resolution 4 cm^{-1}) in KBr pellets (Lóránd et al., 2002a,b; Molnár et al., 2006a,b).

Mass spectra were recorded using a Varian MA–CH–7A mass spectrometer (Molnár et al., 2006a,b).

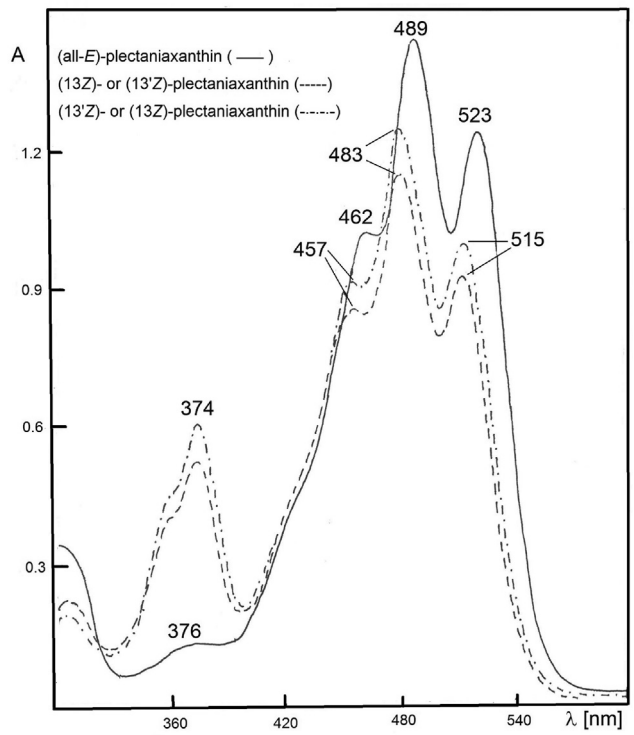


Fig. 3. UV/Vis spectra of (all-*E*)-plectaniaxanthin (**1**) and of its (13*Z*) and (13′*Z*) isomers.

2.2. HPLC measurements

The HPLC separation of the extract of mushroom was performed on a Chromsyl C_{18} (6μm; end-capped) column (250 × 4.6 mm i. d.; 298K), using Dionex 580 pump, HP 1050 detector with ChemStation software; detection wavelength was 450 nm. Gradient elution (in linear steps, and flow rate of 1.25 ml/min) was used with solvents A (H_2O/MeOH 12 : 88), B (MeOH), and C (acetone/MeOH 1 : 1): 0–2 min, 100% A; 2–10 min, to A/B 80 : 20; 10–18 min, to A/B 50 : 50; 18–25 min, to 100% B; 25–27 min, 100% B; 27–34 min, to 100% C, 34–41 min, 100% C (Molnár et al., 2006a,b; Horváth et al., 2010; Agócs et al., 2018). The peak area was used to determine the percentage of individual components in the extract (Pfander and Riesen, 1995).

The chiral HPLC separation of the racemic mixture of plectaniaxanthin enantiomers and a co-chromatography of this mixture with the natural (all-*E*, 2′*R*)-plectaniaxanthin (**1**) was carried out on a Chiralcel OD (3μm) column [Daicel, Chemical Industries Ltd.; 250 × 4.6 mm i. d.; 303K (thermostated)]. The sample was dissolved in MeOH. Isocratic elution (flow rate of 0.7 ml/min) was used with solvents A (*n*-hexane) and B (abs. EtOH): 0–40 min, 5.5% B. The analysis was performed with a Dionex HPLC system (Thermo Fischer Scientific) (Turcsi et al., 2015).

2.3. Extraction

The freshly collected mushroom Scarlet elf cup (2500g) was homogenized with MeOH and extracted three times with MeOH and once with diethyl ether (Et_2O). The three MeOH extracts and the ethereal extract were combined, transferred to a separatory funnel and diluted with Et_2O. The ethereal phase was washed free from MeOH with water and dried over anhydrous Na_2SO_4. This solution was saponified with 30% KOH–MeOH at room temperature overnight (for 18 h). After this process the ethereal solution was washed free from alkali, evaporated to dryness under vacuum and dissolved in benzene. This solution was stored in darkness under nitrogen at –20 °C until further chromatographic separations (Molnár and Szabolcs, 1979; Schiedt and Liaaen-Jensen, 1995; Molnár et al., 2004; Molnár et al., 2005; Molnár et al., 2006a,b; Horváth et al., 2010).

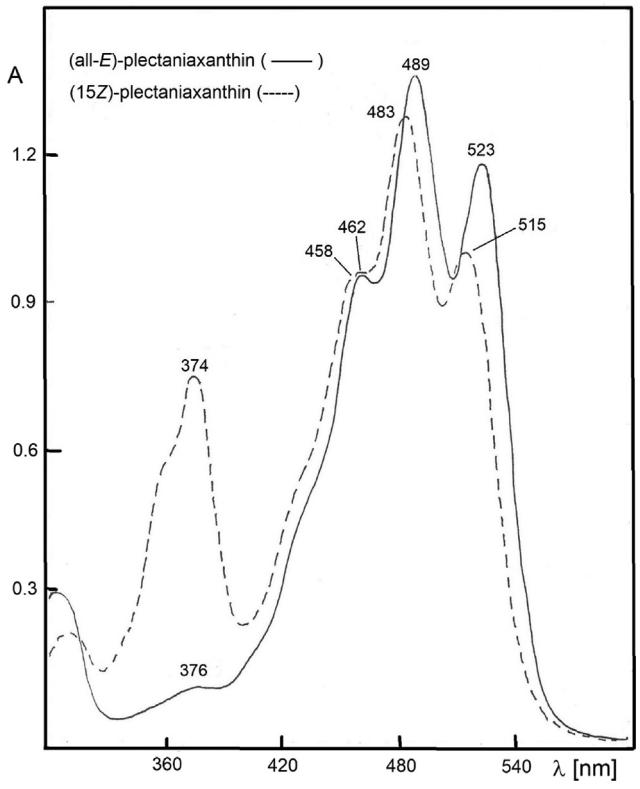


Fig. 4. UV/Vis spectra of (all-*E*)-plectaniaxanthin (**1**) and of its (15*Z*)) isomer.

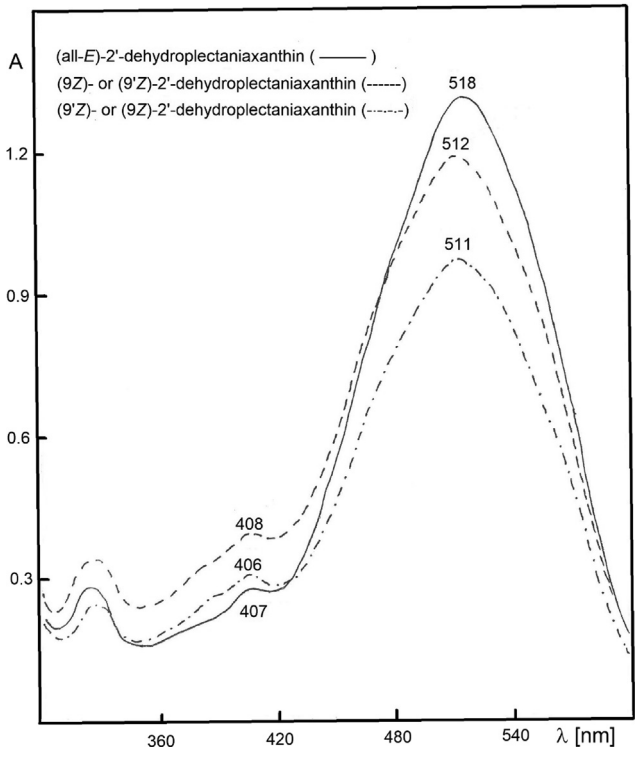


Fig. 5. UV/Vis spectra of (all-*E*)-2′-dehydroplectaniaxanthin (**2**) and of its (9*Z*) and (9′Z) isomers.

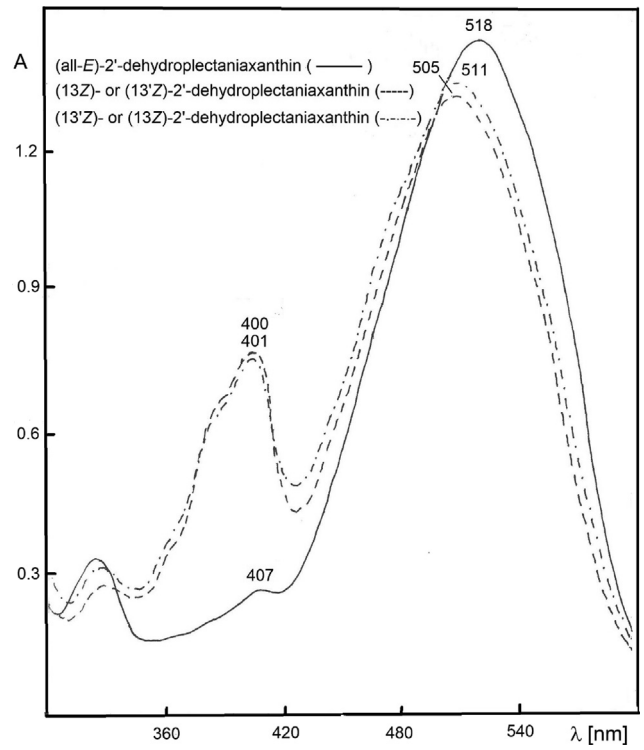


Fig. 6. UV/Vis spectra of (all-*E*)-2′-dehydroplectaniaxanthin (**2**) and of its (13*Z*) and (13′Z) isomers.

2.4. Column liquid chromatography (CLC)

$CaCO_3$ (Ph. Hg. VI., Biogal, Hungary) was used as adsorbent (size of the columns 6 × 30 cm), and the solvents *n*-hexane, 5–10% toluene in *n*-hexane and 0.1–0.5% acetone in *n*-hexane were used as eluents (Molnár and Szabolcs, 1979).

3. Results and discussion

The HPLC analysis of the saponified total extract of the mushroom gave the following carotenoids in order of their decreasing polarity: (all-*E*)-plectaniaxanthin (**1**), (*Z*)-isomers of plectaniaxanthin (all-*E*)-2′-dehydroplectaniaxanthin (**2**), (*Z*)-isomers of 2′-dehydro-plectaniaxanthin, an unidentified carotenoid, β-carotene, and (*Z*)-isomers of β-carotene (Fig. 2).

During the preparative column liquid chromatography (CLC) (Molnár and Szabolcs, 1979) of the saponified total extract the following carotenoids were isolated in order of their decreasing adsorption affinity: (all-*E*)-plectaniaxanthin (**1**), (13*Z*)-plectaniaxanthin [(13*Z*)-**1**], (13′*Z*)-plectaniaxanthin [(13′*Z*)-**1**], (9*Z*)-2′-dehydroplectaniaxanthin [(9*Z*)-**2**], (13*Z*)-2′-dehydroplectaniaxanthin [(13*Z*)-**2**], (13′*Z*)-2′-dehydro plectaniaxanthin [(13′*Z*)-**2**], (15*Z*,5′*Z*(?))-2′-dehydroplectaniaxanthin [(15*Z*,5′*Z*(?))-**2**], (15*Z*)-plectaniaxanthin [(15*Z*)-**1**], (15*Z*)-2′-dehydroplectaniaxanthin [(15*Z*)-**2**], (all-*E*)-2′-dehydroplectaniaxanthin (**2**), (9*Z*,9′*Z*)-2′-dehydroplectaniaxanthin [(9*Z*,9′*Z*)-**2**], (9′*Z*)-2′-dehydroplectaniaxanthin [(9′*Z*)-**2**], (9*Z*,5′*Z*)- or (9′*Z*,5′*Z*)-2-dehydroplectaniaxanthin [(9*Z*,5′*Z*)-**2** or (9′*Z*,5′*Z*)-**2**], β-carotene (Table 1) (all-*E*)-Plectaniaxanthin (**1**; 25 mg) and (all-*E*)-2′-dehydroplectaniaxanthin (**2**, 21 mg) were isolated in a pure crystalline state (m.p. of **1**: 175–176 °C; m. p. of **2**: 146–148 °C) and were identified by UV/Vis spectroscopy, ^{1}H- and ^{13}C-NMR spectroscopy and mass spectrometry. The UV/Vis data are shown in Table 1.

The UV/Vis spectra of (all-*E*)-plectaniaxanthin (1) together with the spectra of its three main (mono-*Z*)-isomers [(13*Z*)-1, (13′*Z*)-1 and (15*Z*)-1], and the UV/Vis spectra of (all-*E*)-2-dehydroplectaniaxanthin (2) together with its four main (mono-*Z*)-isomers [(9*Z*)-2, (9′*Z*)-2 (13*Z*)-2 (13′*Z*)-2] are indicated, as examples on Figs. 3, 4, 5, 6.

Table 2
^{1}H- and ^{13}C-NMR chemical shifts (δ in ppm) of (all-*E*)-plectaniaxanthin (**1**) and of (all-*E*)-2′-dehydroplectaniaxanthin (**2**) in $CDCl_3$.

(all-*E*)-Plectaniaxanthin (1)			(all-*E*)-2′-Dehydroplectaniaxanthin (2)		
C-atom	^{1}H	^{13}C	C-atom	^{1}H	^{13}C
1	-	34.2	1	-	34.3
2	1.46	39.5	2	1.45	39.7
3	1.61	19.1	3	1.60	19.3
4	.012	32.9	4	33.1	
5	-	129.4	5	-	129.4
6	-	137.8	6	-	137.9
7	6.17	126.7	7	6.18	126.9
8	6.12	137.7	8	6.12	137.7
9	-	136.0	9	-	136.1
10	6.14	130.8	10	6.14	130.8
11	6.65	125.1	11	6.66	125.5
12	6.34	137.1	12	6.34	137.1
13	-	?	13	-	-
14	6,23	133.2	14	6.24	135.4
15	6.63130.2	130.2	15	6.66	131.1
16	1.02	28.7	16	1.02	29.0
17	1.02	28.7	17	1.02	29.0
18	1.71	21.5	18	1.71	21.8
19	1.96	12.8	19	1.99	12.8
20	1.96	15.8	20	1.97	12.8
1′	-	73.1	1′	-	75.3
2′	3.99	79.9	2′	-	202.4
3′	5.70	126.2	3′	6.41	116.1
4′	6.37	138.1	4′	7.56	150.0
5′	-	134.0	5′	-	133.0
6′	6.19	132.9	6′	6.60	142.5
7′	6.58	124.2	7′	6.59	123.6
8′	6.38	138.5	8′	6.67	143.3
9′	-	?	9′	-	137.3
10′	6.24	132.4	10′	6.35	136.2
11′	6.61	124.8	11′	6.42	124.6
12′	6.38	138.2	12′	6.45	140.1
13′	-	?	13′	-	136.4
14′	6.27	133.2	14′	6.31	134.4
15′	6.63	130.0	15′	6.63	129.7
16′	1.23	26.3	16′	1.41	26.8
17′	1.17	23.8	17′	1.41	26.8
18′	1.91	12.8	18′	1.97	12.8
19′	1.96	12.6	19′	1.97	12.8
20′	1.96	12.6	20′	1.97	12.8

The UV/Vis spectroscopic properties (λ_{max}-values, fine sructure) of (all-*E*)-**1** and (all-*E*)-**2** were in agreement with the correponding data in the literature (Bae et al., 1971; Røonneberg et al., 1982; Britton, 1995; Britton et al., 2004) confirming the characteristic chromophors (3′, 4′-didehydro-1′,2′-dihydro-β,ψ-carotene, 3′,4′-didehydro-1′, 2′-dihydro-β,ψ-caroten-2′-one respectively) of these carotenoids.

The (*Z*)-isomers of plectaniaxanthin (**1**) and 2′-dehydroplectaniaxanthin (**2**) have not been isolated from natural sources to date. The crystallization of the majority of these isomers was unsuccessful because of their small quantity and special solubility, therefore their structure and geometrical configuration was deduced from their UV/Vis spectroscopic properties (λ_{max}-shifts; Q = $A_{max}/A_{cis\text{-}peak}$; Table 1, Figs. 3, 4, 5, 6) (Zechmeister, 1962; Britton, 1995; Molnár, 2009).

The ^{13}C-NMR measurements of the naturally occurring (all-*E*)-plectaniaxanthin (**1**) and (all-*E*)-2′-dehydroplectaniaxanthin (**2**) were carried out for the first time in our laboratory. The ^{1}H- and ^{13}C-NMR chemical shifts are summarized in Table 2. The ^{1}H-NMR chemical shifts of the (all-*E*)-plectaniaxanthin (1), isolated in our laboratory showed a good agreement with that of the natural (2′*R*)- and of the synthetic (2′*S*)-plectaniaxanthin, published earlier (Hertzberg and Liaaen-Jensen, 1969; Bae et al., 1971; Dumont and Pfander, 1984; Madhour et al., 2005); The ^{1}H- and ^{13}C-NMR chemical shifts of naturally occurring (all-*E*)-plectaniaxanthin (1) and of (all-*E*)-2′-dehydroplectaniaxanthin (2) showed also

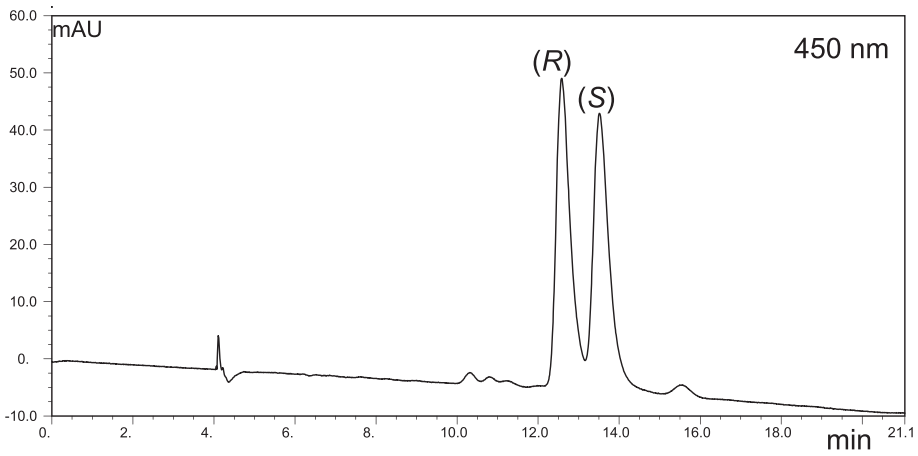


Fig. 7. HPLC separation of the racemic mixture of plectaniaxanthin enantiomers.

a good agrement with the chemical shifts, which were published for the corresponding end groups (Arpin et al., 1970; Englert, 1995).

The MS data of (all-*E*)-plectaniaxanthin (1) were in accordance with literature data (Enzell et al., 1969; Bae et al., 1971; Dumont and Pfander, 1984; Enzell and Back, 1995; Britton et al., 2004). The peak of molecular ion was observed at *m/z* 568 (M^+, $C_{40}H_{56}O_2$), together with fragments at *m/z* 552 ([M-O]$^+$), 550 ([M-H_2O]$^+$), 534 ([M–H_2O–O]$^+$), 532 ([M-2H_2O]$^+$), 510 ([M-CH_3COCH_3]$^+$), 508 ([M-$CH_3CHOHCH_3$]$^+$), 476 ([M-$C_6H_5CH_3$]$^+$), 462 ([M-$C_6H_4(CH_3)_2$]$^+$), 444 ([M–$C_6H_4(CH_3)_2$–H_2O]$^+$), 428 ([M–$C_6H_4(CH_3)_2$–H_2O–O]$^+$), 404 ([M–$C_6H_4(CH_3)_2$–CH_3COCH_3]$^+$), 403 ([M–$C_6H_4(CH_3)_2$–CH_3COCH_3–H]$^+$), 402 ([M–$C_6H_4(CH_3)_2$–$CH_3CHOHCH_3$]$^+$), 209, 197, 171, 157, 145, 119,105, 95, 81, 59, 57, 43.

The MS spectrum of (all-*E*)-2′-dehydroplectaniaxanthin (2) resulted in the following fragment ions, which were in accordance with the data in the literature (Enzell et al., 1969; Vacheron et al., 1969; Arpin et al., 1970; Enzell and Back, 1995; Britton et al., 2004); *m/z*: 566 ([M^+; $C_{40}H_{54}O_2$]), 550 ([M-O]$^+$), 548 ([M-H_2O]$^+$), 507 ([M–CH_3COCH_3–H]$^+$), 474 ([M-$C_6H_5CH_3$]$^+$), 460 ([M-$C_6H_4(CH_3)_2$]$^+$), 368 ([M–$C_6H_4(CH_3)_2$–$C_6H_5CH_3$]$^+$), 209, 197, 183, 145, 119, 105, 95, 81, 69, 59, 43.

In the FT-IR spectrum of (all-*E*)-2′-dehydroplectaniaxanthin (2) the band $\nu = 1668\ cm^{-1}$ (very strong C = O stretching frequency absorption) is characteristic to the 2′-keto group conjugated with the polyene chain (Arpin and Liaaen-Jensen, 1967a,b; Hertzberg and Liaaen-Jensen, 1967; Lóránd et al., 2002a,b; Molnár et al., 2006a,b; Bernhard and Grosjean, 1995).

The $NaBH_4$ reduction of (all-*E*)-2′-dehydroplectaniaxanthin (2) resulted in the formation of the racemic mixture of (*R*)- and (*S*)-plectaniaxanthin verifying the presence of the conjugated 2′-keto group (Arpin and Liaaen-Jensen, 1967a,b; Britton et al., 2004).

The racemic mixture of plectaniaxanthin enantiomers was separated by HPLC using „Chiralcel OD" column (Fig. 7) (Turcsi et al., 2015). The co-chromatography of the racemic mixture with the natural (all-*E*, 2′*R*)-plectaniaxanthin proved the identity of **peak 1** with this carotenoid and of **peak 2** with the corresponding (2′*S*)-enantiomer.

HPLC-ECD measurements were also carried out by stopping the eluent in the HPLC flow cell (Turcsi et al., 2015), but distinct ECD spectra could not be recorded for the separated enantiomers at room temperature, which may be due to the conformational flexibility of plectaniaxanthin.

4. Conclusion

In this study, we described the determination of the carotenoid composition of the mushroom Scarlet elf cup (*Sarcoscypha coccinea*) by HPLC and CLC, the determination of the ^{13}C-NMR chemical shifts of the naturally occurring (all-*E*)-plectaniaxanthin (**1**) and (all-*E*)-2′-dehydroplectaniaxanthin (**2**), and the isolation and partial characterization of three sterically unhindered mono-*cis* isomers of plectaniaxanthin (**1**) [(13*Z*)-**1**, (13′*Z*)-**1** and (15*Z*)-**1**], five mono-*cis* isomers of 2′-dehydroplectaniaxanthin (**2**) [(9*Z*)-**2**, (9′*Z*)-**2** (13*Z*)-**2**, (13′*Z*)-**2** and (15*Z*)-**2**], three di-*cis* isomers of 2′-dehydroplectaniaxanthin (**2**) [(9*Z*,5′*Z*)-**2** or (9′*Z*,5′*Z*)-**2**, and probably (15*Z*,5′*Z*)-**2**], and one poly-*cis* (tri-*cis*) isomer of 2′-dehydroplectaniaxanthin (**2**) [probably (9*Z*,9′*Z*,5′*Z*)-**2**], for the first time. The main carotenoids [(all-*E*)-plectaniaxanthin (**1**) and (all-*E*)-2′-dehydroplectaniaxanthin (**2**)] were isolated in highly pure crystalline state. The structure elucidation of these carotenoids was carried out by spectroscopic methods (UV/Vis, ^{1}H- and ^{13}C-NMR, MS, IR). The majority of the isolated (*Z*) isomers were identified and characterized only on the basis of their UV/Vis spectroscopic properties [λ_{max}-shifts; Q-values ($Q = A_{max}/A_{cis\text{-}peak}$)] (Zechmeister, 1962; Britton, 1995; Molnár, 2009; Molnár at al., 2017).

Besides of the main achivements of our work mentioned above, the (2′*R*)-configuration of the naturally occurring (all-*E*)-plectaniaxanthin (**1**) was also confirmed.

Declarations

Author contribution statement

Péter Molnár: Conceived and designed the experiments; Performed the experiments; Wrote the paper.

Erzsébet Ősz, Erika Turcsi: Performed the experiments; Analyzed and interpreted the data.

József Deli: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Funding statement

This work was supported by a grant from OTKA 115931 (Hungarian Scientific Research Fund), and from COST Action (European network to advance carotenoid research and applications in agro-food and health, EUROCAROTEN, CA15136).

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Acknowledgements

We are grateful to Ms. Zs. Götz, Mr. N. Götz and Mr. R. Lukács for their skillful assistance. We thank Prof. Dr. L. Barthó (University of Pécs, Medical School, Department of Pharmacology and Pharmacotherapy) for collecting and professional identification of the mushroom, Dr. T. Lóránd (University of Pécs, Medical School, Department of Biochemistry and Medical Chemistry) for recording the FT-IR spectrum, Dr. A. Giger and Dr. S. Werner (DSM Nutritional Products, Basel) for recording the mass spectra, Prof. Dr. T. Kurtán (University of Debrecen, Department of Organic Chemistry) for performing the HPLC-ECD measurements and Prof. Dr. H. Pfander (University of Berne, Department of Chemistry and Biochemistry) for his useful comments.

The present scientific contribution is dedicated to the 650th anniversary of the foundation of the University of Pécs, Hungary.

References

Agócs, A., Murillo, E., Turcsi, E., Béni, Sz., Darcsi, A., Szappanos, Á., Kurtán, T., Deli, J., 2018. Isolation of allene carotenoids from mamey. J. Food Compos. Anal. 65 (1), 1–5.

Arpin, N., Fiasson, J.L., Lebreton, P., 1970. Modern methods of structural analysis of carotenoids. 2. Les Carotenoides des champignons. Prod. et Probl. Pharmaceutiques 25 (1), 21–34.

Arpin, N., Liaaen-Jensen, S., 1967a. Chemotaxonomic research on fungi. Fungal carotenoids IV. Isolation and identification of a new natural xanthophyll. Recherces chimiotaxinomiques sur les champignons. Fungal carotenoids. 4. Les carotenoides de *Phillipsia carminea* (PAT) le gal. – isolement et identification dune xanthopylle naturelle nouvelle. Bull. Soc. Chim. Biol. 49 (5), 527–536.

Arpin, N., Liaaen-Jensen, S., 1967b. Recherches chimiotaxinomiques sur les champignons. Fungal carotenoids. 3. – nouveaux carotenoides notamment sous forme d'esters tertiaires, isoles de *Plectania coccinea* (Scop. ex Fr.) fuck. Phytochemistry 6 (7), 995–1005.

Bae, M., Lee, T.H., Yokoyama, H., Böttger, H.G., Chichester, C.O., 1971. The occurrence of plectaniaxanthin in *Cryptococcus laurentii*. Phytochemistry 10 (3), 625–629.

Bernhard, K., Grosjean, M., 1995. Infrared spectroscopy. In: Britton, G., Liaaen-Jensen, S., Pfander, H. (Eds.), Carotenoids: Spectroscopy, 1B. Birkhäuser, Basel-Boston-Berlin, pp. 117–134.

Britton, G., 1995. UV/Visible spectroscopy. In: Britton, G., Liaaen-Jensen, S., Pfander, H. (Eds.), Carotenoids: Spectroscopy, 1B. Birkhäuser, Basel-Boston-Berlin, pp. 13–62.

Britton, G., Liaaen-Jensen, S., Pfander, H. (Eds.), 2004. Carotenois Handbook. Birkhäuser, Basel-Boston-Berlin.

Buchecker, R., Arpin, N., Liaaen-Jensen, S., 1976. Absolute configuration of aleuriaxanthin. Phytochemistry 15 (6), 1013–1014.

Dumont, R., Pfander, H., 1984. Synthese von (*S*)-Plectaniaxanthin. Helv. Chim. Acta 67 (4-6), 1283–1290.

Englert, G., 1995. NMR spectroscopy. In: Britton, G., Liaaen-Jensen, S., Pfander, H. (Eds.), Carotenoids: Spectroscopy, 1B. Birkhäuser, Basel-Boston-Berlin, pp. 147–260.

Enzell, C.R., Back, S., 1995. Mass spectrometry. In: Britton, G., Liaaen-Jensen, S., Pfander, H. (Eds.), Carotenoids: Spectroscopy, 1B. Birkhäuser, Basel-Boston-Berlin, pp. 261–320.

Enzell, C.R., Francis, G.W., Liaaen-Jensen, S., 1969. Mass spectrometric studies of carotenoids. 2. A Survey of fragmentation reactions. Acta Chem. Scand. 23 (3), 727–750.

Hertzberg, S., Liaaen-Jensen, S., 1967. Bacterial carotenoids XX.* the carotenoids of *Mycobacterium phlei* strain Vera. 2. The structure of the Phleixanthophylls – two novel tertiary glucosides. Acta Chem. Scand. 21 (1), 15–41.

Hertzberg, S., Liaaen-Jensen, S., 1969. The structure of myxoxanthophyll. Phytochemistry 8 (7), 1259–1280.

Horváth, G., Molnár, P., Farkas, Á., Szabó, L.G., Turcsi, E., Deli, J., 2010. Separation and identification of carotenoids in flowers of *Chelidonium majus* L. And inflorescences of *Solidago canadensis* L. Chromatographia 71 (S1), 103–108.

Korf, R.P., 1953. The new rules of typification as they affect *Sarcoscypha* and *Velutaria*. J. Mycol. 45 (2), 296–301.

Lóránd, T., Deli, J., Molnár, P., Tóth, G., 2002a. FT-IR study of some carotenoids. Helv. Chim. Acta 85 (6), 1691–1697.

Lóránd, T., Molnár, P., Deli, J., Tóth, G., 2002b. FT-IR study of some seco- and apocarotenoids. J. Biochem. Biophys. Methods 53 (1-3), 251–258.

Madhour, H., Anke, H., Mucci, A., Davoli, P., Weber, R.W.S., 2005. Biosynthesis of the xanthophyll plectaniaxanthin as a stress response in the red yeast *Dioszegia* (tremellales, Heterobasidiomycetes, Fungi). Phytochemistry 66, 2617–2626.

Molnár, P., 2009. Research of the (*E/Z*)-isomerization of carotenoids in Pécs since the 1970s. Arch. Biochem. Biophys. 483 (2), 156–164.

Molnár, P., Deli, J., Ősz, E., Tóth, G., Zsila, F., Herrero, C., Landrum, J.T., 2006a. Preparation and spectroscopic characterization of 3'-oxolutein (ketolutein). Lett. Org. Chem. 3 (10), 723–734.

Molnár, P., Kawase, M., Motohashi, N., 2005. Isolation, crystallization and handling of carotenoids and (*E/Z*)-isomerization of carotenoids. In: Motohashi, N. (Ed.), Functional Polyphenols and Carotenes with Antioxidative Action. Research Signpost, Trivandrum, Kerala, India, pp. 111–131.

Molnár, P., Ősz, E., Turcsi, E., Kurtán, T., Deli, J., 2017. 18th International Symposium on Carotenoids, 9–14. July, Lucerne (Switzerland), p. 106. Abstracts.

Molnár, P., Szabolcs, J., 1979. Alkaline permanganate oxidation of carotenoid epoxides and furanoids. Acta Chim. Acad. Sci. Hung. 99 (2), 155–173.

Molnár, P., Szabó, Z., Ősz, E., Oláh, P., Tóth, G., Deli, J., 2004. Separation and identification of lutein derivatives in processed foods. Chromatographia 60 (S), 101–105.

Molnár, P., Ősz, E., Tóth, G., Zsila, F., Deli, J., 2006b. Preparation and spectroscopic characterization of (9Z,9'Z)-lutein (neolutein C). Helv. Chim. Acta 89 (4), 667–674.

Pfander, H., Riesen, R., 1995. Chromatography: Part IV, high-performance liquid chromatography. In: Britton, G., Liaaen-Jensen, S., Pfander, H. (Eds.), Carotenoids: Isolation and Analysis, 1A. Birkhäuser, Basel-Boston-Berlin, pp. 145–190.

Røonneberg, H., Andrews, A.G., Borch, G., Berger, R., Liaaen-Jensen, S., 1985. CD correlation of C-2' substituted monocyclic carotenoids. Phytochemistry 24 (8), 309–319.

Røonneberg, H., Borch, G., Buchecker, R., Arpin, N., Liaaen-Jensen, S., 1982. Chirality of plectaniaxanthin. Phytochemistry 21 (8), 2087–2090.

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

Turcsi, E., Murillo, E., Kurtán, T., Szappanos, Á., Illyés, T.Z., Gulyás-Fekete, G., Agócs, A., Avar, P., Deli, J., 2015. Isolation of β-cryptoxanthin-epoxides, precursors of cryptocapsin and 3'-deoxycapsanthin, from red mamey (*Pouteria sapota*). J. Agric. Food Chem. 63 (26), 6059–6065.

Vacheron, M.J., Michel, G., Guillary, R., Arpin, N., 1969. Etude par spectrometrie de masse d'un carotenoide isole d'un discomicete, *Plectania coccinea*. Phytochemistry 8 (5), 897–903.

Zechmeister, L., 1962. *Cis – Trans*' Isomeric Carotenoids, Vitamins A and Arylpolyenes. Springer, Wien.