Isomerization of (all-*E*)-Cucurbitaxanthin A

by **Péter Molnár**[a]), **József Deli**[a]), **Zoltán Matus**[a]), **Gyula Tóth***[a]), **Dorte Renneberg**[b]), and **Hanspeter Pfander***[b])

[a]) Department of Medical Chemistry, Faculty of Medicine, University of Pécs, Szigeti út 12. P.O. Box 99, H-7601 Pécs

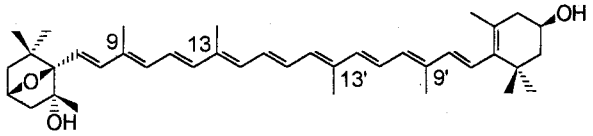
[b]) Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern

Cucurbitaxanthin A (=(all-*E*,3*S*,5*R*,6*R*,3′*R*)-3,6-epoxy-5,6-dihydro-β,β-carotene-5,3′-diol; **1**) was submitted to thermal isomerization and to I_2-catalysed photoisomerization. The structure of the main reaction products (9*Z*)- (**2**), (9′*Z*)- (**3**), (13*Z*)- (**4**), and (13′*Z*)-cucurbitaxanthin A (**5**) was determined by their UV/VIS, CD, ^{1}H-NMR, and mass spectra.

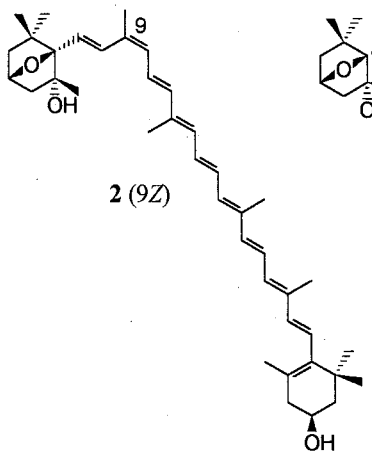
Introduction. – In the course of our investigations of the (*E*/*Z*)-isomerization of carotenoids, the configuration of more than 50 naturally occurring and semisynthetic (mono-*Z*)- and (di-*Z*)-carotenoids have been determined during the last 25 years by our research groups [1–3]. (all-*E*)-Cucurbitaxanthin A ((all-*E*,3*S*,5*R*,6*R*,3′*R*)-3,6-epoxy-5,6-dihydro-β,β-carotene-5,3′-diol; **1**), a naturally occurring carotenoid containing a 7-oxabicyclo[2.2.1]heptyl end group and a 3-hydroxy-β-end group, was isolated from pumpkin and especially from red spice paprika in considerable quantities [4–6]. In continuation of our investigations of the (*E*/*Z*)-isomerization, we report in the present study on the I_2-catalyzed photoisomerization and the thermal isomerization of (all-*E*)-cucurbitaxanthin A (**1**). The structures of the main four products, *i.e.* (9*Z*)- (**2**), (9′*Z*)- (**3**), (13*Z*)- (**4**), and (13′*Z*)-cucurbitaxanthin A (**5**) were established by UV/VIS, CD, ^{1}H-NMR, and mass spectra.

Results. – *Iodine-Catalyzed Photoisomerization.* The I_2-catalyzed photoisomerization of (all-*E*)-cucurbitaxanthin A (**1**) gave the four (mono-*Z*)-isomers (9*Z*)- (**2**), (9′*Z*)- (**3**), (13*Z*)- (**4**), and (13′*Z*)-cucurbitaxanthin A (**5**), which have not been described previously, and a mixture of (di-*Z*)-isomers, which were not further investigated. The qualitative composition of the reaction mixture is in accordance with the pioneering studies of *Zechmeister* [7] and the previous results [1–3][8–12]. The separation of the isomers was carried out by column chromatography (CC) and gave a composition of 49.1% of **1** (all-*E*), 11.7% of **2** (9*Z*), 13.1% of **3** (9′*Z*), 11.1% of **4** (13*Z*), 7.1% of **5** (13′*Z*) and 7.3% of a mixture of (di-*Z*)-isomers.

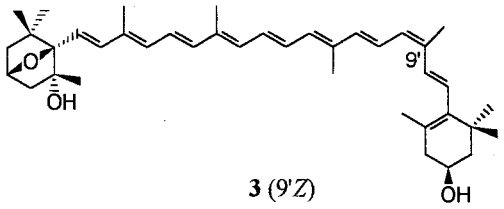
Thermal Isomerization. The thermal isomerization is a well-known and efficient method for the preparation of (13*Z*)- and (13′*Z*)-isomers [2][13]. In accordance with the previous findings, the thermal isomerization of **1** resulted, after CC, in a mixture of 71.1% of **1** (all-*E*), 12.3% of **4** (13*Z*), 14.5% of **5** (13′*Z*), and a mixture of 1.5% of (di-*Z*)-isomers, which were not further investigated. In contrast to the I_2-catalyzed photoisomerization, no significant amounts of the (9*Z*)- and (9′*Z*)-isomers **2** and **3**, respectively, were formed.



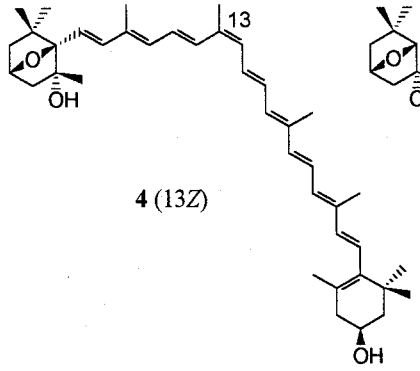
1 (all-*E*)



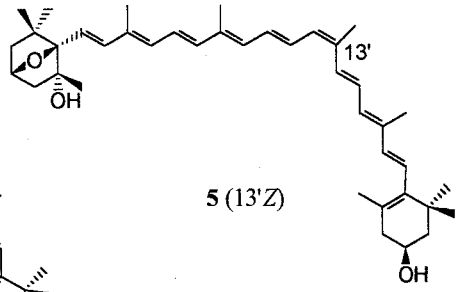
2 (9*Z*)



3 (9'*Z*)



4 (13*Z*)



5 (13'*Z*)

Spectroscopic Characterization. In the UV/VIS spectrum, the isomers **1**–**5** exhibit the main absorption maximum between 450.5 and 458 nm (benzene), corresponding to a decaene chromophore. The isomers **2** and **3** exhibit a hypsochromic shift of the maxima of 5–6 nm, whereas the isomers **4** and **5** show a shift of 7–8 nm. More characteristic is the weak intensity of the *cis*-peak for **2** and **3** (% $A_{cis\text{-peak}}/A_{max} = 8.87$ and 8.78, resp.), which is characteristic for (mono-*Z*)-isomers with a (*Z*)-double bond in a peripheral position (*Fig. 1,a*). In contrast, **4** and **5** exhibit, as expected for polyenes with a (*Z*)-double bond in a more central position of the chain, a strong *cis*-peak at *ca.* 339 nm (% $A_{cis\text{-peak}}/A_{max} = 37.74$ and 43.38; *Fig. 1,b*).

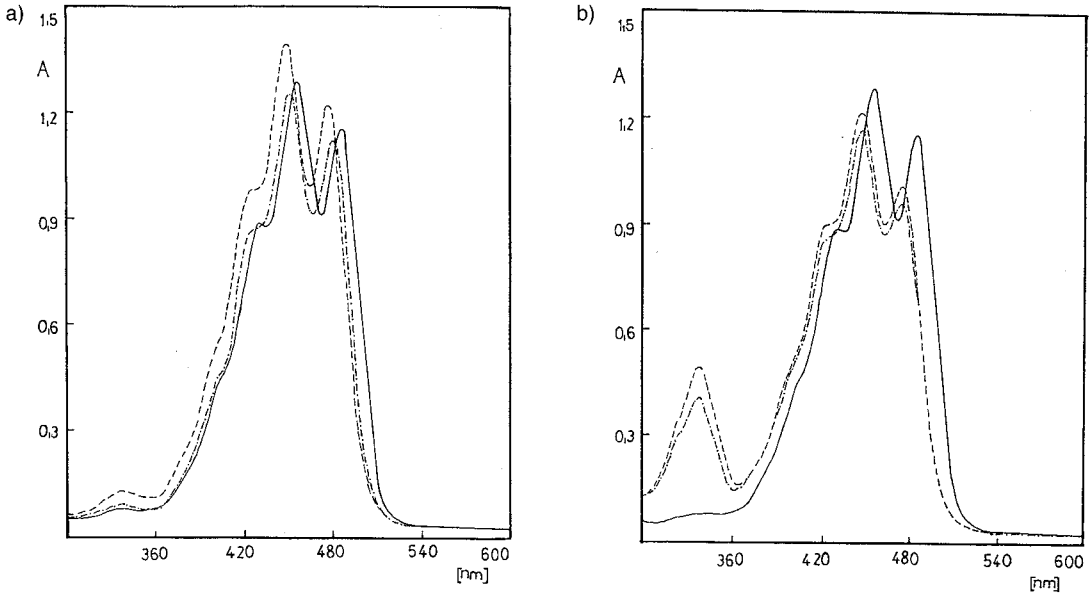


Fig. 1. *UV/VIS Spectra* a) *of (9*Z*)-cucurbitaxanthin A* (**2**; - - - -), *(9′*Z*)-cucurbitaxanthin A* (**3**; ·-·-·-·-·-·), *and (all-*E*)-cucurbitaxanthin A* (**1**; ––-) *in benzene and* b) *of (13*Z*)-cucurbitaxantin A* (**4**; - - - -), *(13′*Z*)-cucurbitaxanthin A* (**5**; ·-·-·-·-·-·), *and (all-*E*)-cucurbitaxanthin A* (**1**; ––-) *in benzene*

^{1}H-NMR, ^{1}H,^{1}H-COSY, and ^{1}H,^{1}H-T-ROESY Experiments allowed complete ^{1}H-signal assignments for the isomers **2**–**5**, and the δ(H) and J(H,H) values (see *Exper. Part*), as well as the isomerization shift data ($\Delta\delta = \delta_Z - \delta_{\text{all-}E}$) were identical with the corresponding data from the literature [1–3][14][15]. Based on these results, the configuration at the C=C bonds was established as (9*Z*) for **2**, (9′*Z*) for **3**, (13*Z*) for **4**, and (13′*Z*) for **5**.

In the CD spectra of the (*Z*)-isomers **2**–**5**, all signs are reversed, compared to the (all-*E*)-isomer **1**, which is characteristic for (mono-*Z*)-isomers of carotenoids with a conservative CD spectrum [16]. In addition, the spectra of **2**–**5** exhibit a characteristic fine structure between 400–500 nm (*Fig. 2*).

In the mass spectrum, all isomers **1**–**5** exhibited the same pattern with the molecular-ion peak at *m*/*z* 584 (= $C_{40}H_{56}O_3$) and fragments at 566 ($[M-18]^+$), 504 ($[M-80]^+$), 492 ($[M-92]^+$), 221, 197, 155 and 43. In addition, strong peaks were observed at *m*/*z* 286 and 160, which are characteristic for carotenoids with the 3,6-epoxy-end group [3][17].

Discussion. – The (*Z*)-isomers **2**–**5** represent new semi-synthetic (*Z*)-carotenoids, which have not yet been found in Nature. The isolated compounds may serve as reference compounds for further investigations of the carotenoid composition of red spice paprika and other natural sources, containing cucurbitaxanthin A. As expected, the photoisomerization and the thermal isomerization of the (all-*E*)-isomer **1** resulted in a different composition of the reaction products. Whereas in the I_2-catalyzed photoisomerization, the (*Z*)-isomers were formed in amounts of the same magnitude,

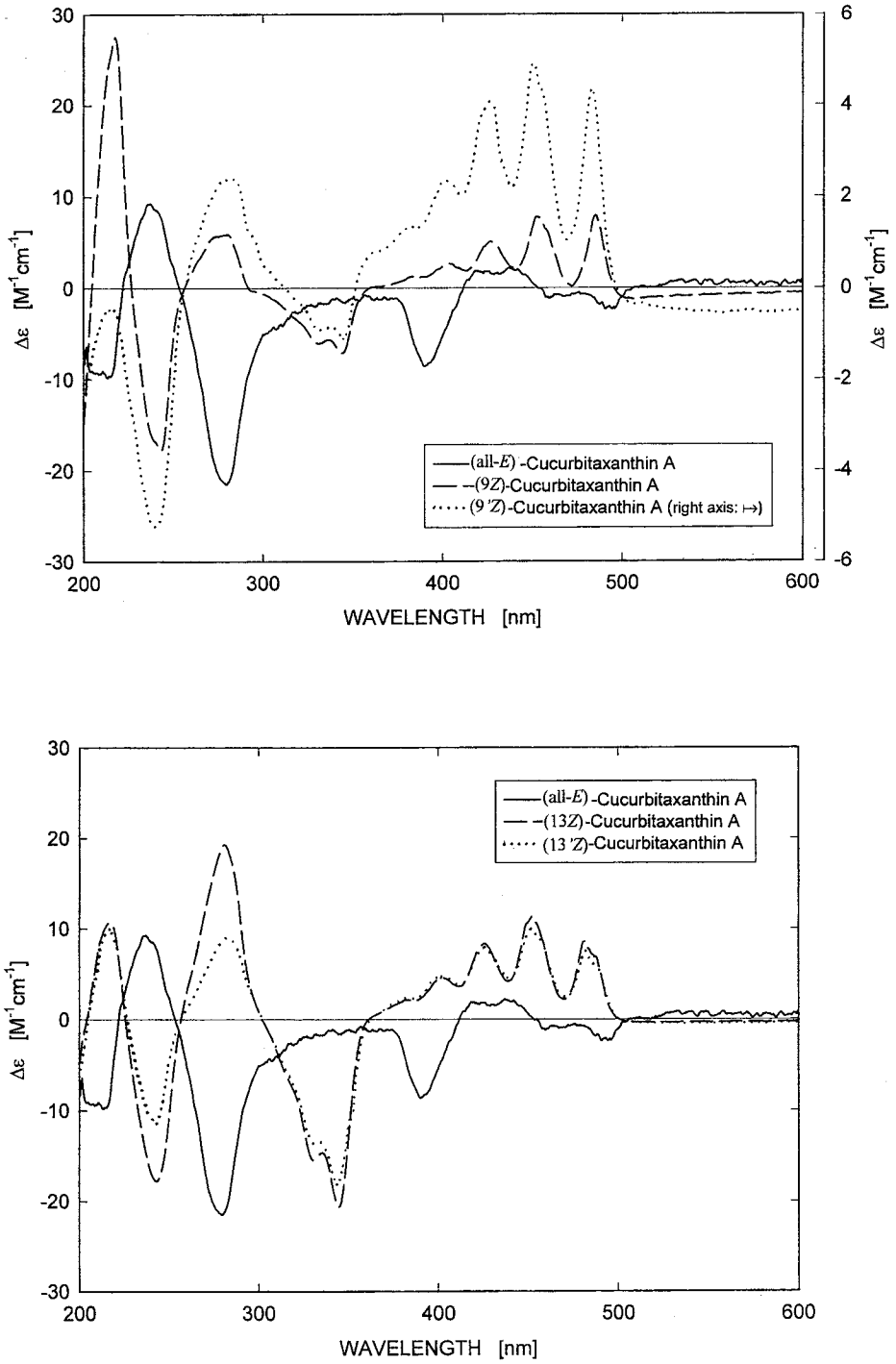


Fig. 2. *CD Spectra of cucurbitaxanthin A isomers* **1**–**5** *in* Et_2O*/isopentane/EtOH 5 : 5 : 2* (EPA) *at* $-180°$

the thermal isomerization gave exclusively the (13*Z*)- and the (13′*Z*)-isomers **4** and **5**, respectively, in significant amounts. Therefore, the thermal isomerization of **1** is a suitable method for the preparation of **4** and **5**.

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Experimental Part

1. *General*. See [6].

2. *Iodine-Catalyzed Photoisomerization*. A soln. of 80 mg of (all-*E*)-cucurbitaxanthin A (**1**; m.p. 160–162°; purity (HPLC) >95%) in 800 ml of benzene was isomerized under N_2 in filtered daylight in the presence of 1.6 mg of I_2 (2% to the carotenoid) [2][7][12]. The isomerization was monitored by UV/VIS, and when the quasi-equilibrium was reached (*ca*. 40 min), the soln. was washed free of I_2 with 5% $Na_2S_2O_3$ soln. After the usual workup [18], the mixture was submitted to CC.

3. *Thermal Isomerization*. A soln. of 40 mg of (all-*E*)-cucurbitaxanthin A (**1**) in 400 ml of benzene was refluxed for 2 h under N_2 in the dark [2][7][13], and after usual workup, the mixture was submitted to CC.

4. *Isolation*. The reaction mixtures were separated by CC (6 × 30 cm columns, 16 columns for photoisomerization, 6 columns for thermal isomerization) with $CaCO_3$ and benzene/hexane 3:7. Typical picture after development (for photoisomerization): 10 mm pale yellow (*Zone 1*; mixture of (di-*Z*)-isomers of **1**); 5 mm of intermediate zone; 25 mm ochre (*Zone 2*; **1**); 8 mm of intermediate zone; 10 mm yellow (*Zone 3*; **3**); 2 mm of intermediate zone; 15 mm pale yellow (*Zone 4*; **5**); 10 mm of intermediate zone; 15 mm pale yellow (*Zone 5*; **4**); 6 mm of intermediate zone; 20 mm yellow (*Zone 6*, **2**). For further purification, the fractions were submitted to repeated CC ($CaCO_3$, benzene/hexane 3:7), and after development, the carotenoids were crystallized from benzene/hexane 1:4 to give from the photoisomerization 40 mg of **1**, 4.0 mg of **2**, 4.1 mg of **3**, 2.0 mg of **4**, 2.2 mg of **5** and 1.0 mg of a mixture of (di-*Z*)-isomers. From the thermal isomerization, 4.0 mg of **4** and 4.1 mg of **5** were obtained.

5. *(9Z)-Cucurbitaxanthin A* (**2**). M.p. 54–56°. UV/VIS (benzene): 482, 453, 430, 339; $\%A_{cis\text{-peak}}/A_{max} = 8.87$ (*Fig. 1,a*). CD (EPA, r.t.): 200 (−4.33), 216.5 (+6.41), 239 (−3.84), 276 (+0.49), 331.5 (−1.96), 440 (−0.64), 472 (−1.00). CD (EPA, −180°): 200 (−14.93), 217.5 (+27.44), 243 (−17.76), 279.5 (+5.89), 328 (−6.00), 344 (−7.12), 365.5 (+0.17), 380 (+1.20), 403 (+2.70), 426 (+5.10), 452.5 (+7.81), 485 (+7.93) (*Fig. 2*). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.90 (*s*, Me(17)); 1.08 (*s*, Me(16′)); 1.08 (*s*, Me(17′)); 1.23 (*s*, Me(18)); 1.32 (br., OH−C(3′)); 1.45 (*s*, Me(16)); 1.49 (*t*, $J_{gem} = J(2'eq,3') = 12.0$, H_{eq}−C(2′)); 1.63 (*d*, $J_{gem} = 11.3$, H_{eq}−C(2)); 1.70 (*d*, $J_{gem} = 12.0$, H_{eq}−C(4)); 1.74 (*s*, Me(18′)); 1.78 (*ddd*, $J(2'ax,4'ax) = 2.1$, $J(2'ax,3') = 5.7$, $J_{gem} = 12.0$, H_{ax}−C(2′)); 1.87 (*ddd*, $J(2ax,4ax) = 2.3$, $J(2ax,3) = 5.9$, $J_{gem} = 11.3$, H_{ax}−C(2)); 1.96 (*s*, Me(19)); 1.97 (*s*, Me(20)); 1.97 (*s*, Me(19′)); 1.97 (*s*, Me(20′)); 2.02 (*m*, $J_{gem} = 5.9$, H_{eq}−C(4′)); 2.07 (*m*, H_{ax}−C(4)); 2.39 (*dd*, $J(4'ax,3') = 4.5$, $J_{gem} = 16.0$, H_{ax}−C(4′)); 4.00 (*m*, H−C(3′)); 4.43 (*t*, $J(3,2ax) = J(3,4ax) = 5.9$, H−C(3)); 5.78 (*d*, $J(7,8) = 15.8$, H−C(7)); 6.07 (*d*, $J(10,11) = 11.4$, H−C(10)); 6.11 (*d*, $J(7',8') = 16.0$, H−C(7′)); 6.12 (*d*, $J(8',7') = 16.0$, H−C(8′)); 6.16 (*d*, $J(10',11') = 11.4$, H−C(10′)); 6.25 (*m*, H−C(14)); 6.25 (*m*, H−C(14′)); 6.29 (*d*, $J(12,11) = 14.8$, H−C(12)); 6.63 (*d*, $J(12',11') = 14.8$, H−C(12′)); 6.63 (*m*, H−C(15)); 6.36 (*m*, H−C(15′)); 6.65 (*m*, $J(11',10') = 11.4$, H−C(11′)); 6.79 (*dd*, $J(11,10) = 11.4$, $J(11,12) = 14.8$, H−C(11)). EI-MS: 584 (68, M^+), 566 (8, $[M - H_2O]^+$), 504 (14, $[M$ − methylcyclopentadiene$]^+$, 492 (10, $[M$ − toluene$]^+$), 299 (15), 286 (40), 221 (33), 181 (34), 160 (68), 145 (30), 119 (29), 105 (25), 91 (35), 55 (20), 44 (36), 43 (32), 28 (100).

6. *(9′Z)-Cucurbitaxanthin A* (**3**). M.p. 56–58°. UV/VIS (benzene): 481, 452, 432, 339; $\%A_{cis\text{-peak}}/A_{max} = 8.78$ (*Fig. 1,a*). CD (EPA, r.t.): 200 (−1.63), 202.5 (−2.09), 209 (−1.68), 221 (−0.84), 235 (−1.30), 283.5 (+0.48), 337 (−0.10), 370 (+0.10), 442 (−0.27), 474 (−0.29), 510 (+0.10). CD (EPA, −180°): 201.5 (−2.20), 215.5 (−0.53), 217 (−0.46), 240 (−5.22), 279.5 (+2.37), 330 (−0.80), 344.5 (−1.07), 385.5 (+1.30), 401 (+2.37), 426 (+4.09), 450 (+4.92), 483 (+4.36) (*Fig. 2*). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.88 (*s*, Me(17)); 1.09 (*s*, Me(16′)); 1.10 (*s*, Me(17′)); 1.22 (*s*, Me(18)); 1.32 (br., OH−C(3′)); 1.44 (*s*, Me(16)); 1.50 (*t*, $J_{gem} = 11.9$, H_{eq}−C(2′)); 1.62 (*d*, $J_{gem} = 11.4$, H_{eq}−C(2)); 1.68 (*d*, $J_{gem} = 12.1$, H_{eq}−C(4)); 1.78 (*s*, Me(18′)); 1.80 (*m*, H_{ax}−C(2′)); 1.85 (*ddd*, $J(2ax,4ax) = 2.1$, $J(2ax,3) = 5.8$, $J_{gem} = 11.4$, H_{ax}−C(2)); 1.95 (*s*, Me(19)); 1.97 (*s*, Me(20)); 1.97 (*s*, Me(19′)); 1.97 (*s*, Me(20′)); 2.07 (*m*, H_{ax}−C(4)); 2.07 (*dd*, $J(4'eq,3') = 5.7$, $J_{gem} = 17.0$, H_{eq}−C(4′)); 2.42

(*dd*, *J*(4′eq,3′) = 5.7, H_{ax}–C(4′)); 4.03 (*m*, H–C(3′)); 4.40 (*t*, *J*(3,2ax) = *J*(3,4ax) = 6.0, H–C(3)); 5.74 (*d*, *J*(7,8) = 16.0, H–C(7)); 6.07 (*d*, *J*(10′,11′) = 11.6, H–C(10′)); 6.13 (*d*, *J*(7′,8′) = 15.9, H–C(7′)); 6.20 (*d*, *J*(10,11) = 11.0, H–C(10)); 6.25 (*m*, H–C(14)); 6.25 (*m*, H–C(14′)); 6.30 (*d*, *J*(12′,11′) = 15.0, H–C(12′)); 6.36 (*d*, *J*(12,11) = 15.0, H–C(12)); 6.38 (*d*, *J*(7,8) = 16.0, H–C(8)); 6.62 (*m*, *J*(10,11) = 11.0, H–C(11)); 6.62 (*m*, H–C(15)); 6.62 (*m*, H–C(15′)); 6.67 (*d*, *J*(8′,7′) = 15.9, H–C(8′)); 6.74 (*dd*, *J*(11′,10′) = 11.6, *J*(11′,12′) = 15.0, H–C(11′)). EI-MS: 584 (77, M^+), 566 (7, $[M - H_2O]^+$), 504 (12, [*M* – methylcyclopentadiene]$^+$), 492 (9, [*M* – toluene]$^+$), 299 (17), 286 (44), 221 (36), 181 (36), 160 (76), 145 (131), 119 (31), 105 (26), 91 (40), 55 (18), 43 (31), 28 (100).

7. *Mixture of (di-*Z*)-Isomers.* UV/VIS (benzene): 475, 447, 425, 337; $\%A_{cis\text{-peak}}/A_{max} = 31.54$.

8. *(13*Z*)-Cucurbitaxanthin A* (**4**). M.p. 46–48°. UV/VIS (benzene): 479.5, 451.5, 427, 339; $\%A_{cis\text{-peak}}/A_{max} = 37.74$ (*Fig. 1,b*). CD (EPA, r.t.): 200 (–2.00), 215.5 (+2.60), 241.5 (–4.09), 281 (+4.55), 331.5 (–4.40), 417 (+0.27). CD (EPA, –180°): 200 (–4.80), 217 (+10.67), 243 (–17.76), 281 (+19.29), 330.5 (–15.42), 344.5 (–20.60), 387 (+2.06), 404 (+4.80), 425.5 (+8.35), 452 (+11.30), 481 (+8.55) (*Fig. 2*). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.89 (*s*, Me(17)); 1.08 (*s*, Me(16′)); 1.08 (*s*, Me(17′)); 1.22 (*s*, Me(18)); 1.34 (br., OH–C(3′)); 1.44 (*s*, Me(16)); 1.48 (*t*, $J_{gem} = J$(2′eq,3′) = 12.0, H_{eq}–C(2′)); 1.61 (*d*, J_{gem} = 11.4, H_{eq}–C(2)); 1.68 (*d*, J_{gem} = 12.1, H_{eq}–C(4)); 1.74 (*s*, Me(18′)); 1.77 (*ddd*, *J*(2′ax,4′ax) = 2.0, *J*(2′ax,3′) = 3.4, J_{gem} = 12.0, H_{ax}–C(2′)); 1.84 (*ddd*, *J*(2ax,4ax) = 2.1, *J*(2ax,3) = 5.8, J_{gem} = 11.4, H_{ax}–C(2)); 1.96 (*s*, Me(19)); 1.97 (*s*, Me(19′)); 1.97 (*s*, Me(20′)); 1.99 (*s*, Me(20)); 2.02 (*m*, H_{eq}–C(4′)); 2.06 (*m*, H_{ax}–C(4)); 2.39 (*dd*, *J*(4′ax,3′) = 5.3, J_{gem} = 17.0, H_{ax}–C(4′)); 4.01 (*m*, H–C(3′)); 4.41 (*t*, *J*(3,2ax) = *J*(3,4ax) = 5.8, H–C(3)); 5.76 (*d*, *J*(7,8) = 16.1, H–C(7)); 6.09 (*m*, *J*(7′,8′) = 16.0, H–C(7′)); 6.11 (*m*, H–C(14)); 6.11 (*m*, H–C(8′)); 6.16 (*d*, *J*(10′,11′) = 11.7, H–C(10′)); 6.24 (*m*, H–C(10)); 6.27 (*m*, H–C(14′)); 6.37 (*d*, *J*(12′,11′) = 14.8, H–C(12′)); 6.39 (*d*, *J*(8,7) = 16.1, H–C(8)); 6.56 (*dd*, *J*(15′,15) = 12.1, H–C(15′)); 6.62 (*dd*, *J*(11,10) = 11.5, *J*(11,12) = 14.5, H–C(11)); 6.65 (*dd*, *J*(11′,10′) = 11.7, *J*(11′,12′) = 14.8, H–C(11′)); 6.80 (*dd*, *J*(15,15′) = 12.1, H–C(15)); 6.87 (*d*, *J*(12,11) = 14.5, H–C(12)). EI-MS: 584 (100, M^+), 566 (10, $[M - H_2O]^+$), 504 (16, [*M* – methylcyclopentadiene]$^+$), 492 (13, [*M* – toluene]$^+$), 299 (23), 286 (59), 221 (46), 181 (46), 160 (96), 145 (42), 119 (39), 105 (36), 91 (59), 55 (33), 43 (60), 28 (91).

9. *(13′*Z*)-Cucurbitaxanthin A* (**5**). M.p. 57–59°. UV/VIS (benzene): 480, 451.5, 429, 339; $\%A_{cis\text{-peak}}/A_{max} = 43.48$ (*Fig. 1,b*). CD (EPA, r.t.): 201 (–3.24), 216.5 (+3.07), 242 (–2.54), 282.5 (+1.74), 331 (–3.71), 412 (+0.41). CD (EPA, –180°): 200 (–6.27), 216.5 (+9.67), 242.5 (–11.12), 282 (+9.02), 331.5 (–13.63), 343.5 (–17.90), 383 (+2.25), 402 (+4.60), 426.5 (+7.98), 451.5 (+9.90), 482 (+7.55) (*Fig. 2*). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.89 (*s*, Me(17)); 1.08 (*s*, Me(16′)); 1.08 (*s*, Me(17′)); 1.22 (*s*, Me(18)); 1.32 (br., OH–C(3′)); 1.44 (*s*, Me(16)); 1.50 (*t*, $J_{gem} = J$(2′eq,3′) = 11.9, H_{eq}–C(2′)); 1.62 (*d*, J_{gem} = 11.5, H_{eq}–C(2)); 1.68 (*d*, J_{gem} = 12.1, H_{eq}–C(4)); 1.75 (*s*, H–C(18′)); 1.79 (*m*, *J*(2′ax,4′ax) = 2.1, J_{gem} = 11.9, H_{ax}–C(2′)); 1.85 (*ddd*, *J*(2ax,4ax) = 2.0, *J*(2ax,3) = 6.0, J_{gem} = 11.5, H_{eq}–C(2)); 1.95 (*s*, Me(19)); 1.96 (*s*, Me(20)); 1.98 (*s*, Me(19′)); 2.00 (*s*, Me(20′)); 2.03 (*m*, H_{eq}–C(4′)); 2.06 (*m*, H_{ax}–C(4)); 2.40 (*dd*, *J*(4′ax,3′) = 5.4, J_{gem} = 17.1, H_{eq}–C(4′)); 4.01 (*m*, H–C(3′)); 4.40 (*t*, *J*(3,2ax) = *J*(3,4ax) = 5.9, H–C(3)); 5.75 (*d*, *J*(7,8) = 16.0, H–C(7)); 6.11 (*d*, *J*(14′,15′) = 11.9, H–C(14′)); 6.13 (*m*, H–C(7′)); 6.15 (*m*, H–C(8′)); 6.20 (*d*, *J*(10,11) = 11.4, H–C(10)); 6.21 (*d*, *J*(10′,11′) = 11.5, H–C(10′)); 6.24 (*d*, *J*(14,15) = 11.8, H–C(14)); 6.36 (*d*, *J*(12,11) = 15.0, H–C(12)); 6.38 (*d*, *J*(8,7) = 16.0, H–C(8)); 6.56 (*dd*, *J*(15,14) = 11.8, *J*(15,15′) = 14.0, H–C(15)); 6.60 (*m*, H–C(11)); 6.65 (*dd*, *J*(11′,10′) = 11.5, *J*(11′,12′) = 14.9, H–C(11′)); 6.80 (*dd*, *J*(15′,14′) = 11.9, *J*(15′,15) = 14.0, H–C(15′)); 6.89 (*d*, *J*(12′,11′) = 14.9, H–C(12′)). EI-MS: 584 (44, M^+), 566 (7, $[M - H_2O]^+$), 504 (9, [*M* – methylcyclopentadiene]$^+$), 492 (8, [*M* – toluene]$^+$), 299 (14), 286 (25), 221 (27), 181 (35), 160 (40), 145 (29), 119 (27), 105 (25), 91 (36), 55 (52), 43 (100), 28 (58).

10. *(all-*E*)-Cucurbitaxanthin A* (= *(all-*E*,3*S*,5*R*,6*R*,3′*R*)-3,6-Epoxy-5,6-dihydro-β,β-carotene-5,3′-diol*; **1**): M.p. 160–162°. UV/VIS (benzene): 487, 457, 434 (*Fig. 1*). CD, NMR and MS: see [3].

REFERENCES

[1] J. Szabolcs, 'Plant Carotenoids', in 'Carotenoids, Chemistry and Biology', Eds. N. I. Krinsky, M. M. Mathews-Roth, and R. F. Taylor, Plenum Press, New York, 1989, pp. 39–58.

[2] P. Molnár, 'Structure Elucidation of Mono- and Di-*cis*-carotenoids, Isolation of New Carotenoids and Kinetics of (*E*/*Z*)-Isomerization', Ph.D. Thesis, Pécs, 1988.

[3] P. Molnár, J. Deli, Z. Matus, G. Tóth, A. Steck, *Helv. Chim. Acta* **1996**, *79*, 1444.

[4] K. E. B. Parkes, G. Pattenden, M. Baranyai, P. Molnár, J. Szabolcs, G. Tóth, *Tetrahedron Lett.* **1986**, *27*, 2535.

[5] T. Matsuno, Y. Tani, T. Maoka, K. Matsuno, T. Komori, *Phytochemistry* **1986**, *25*, 2837.

[6] J. Deli, P. Molnár, Z. Matus, G. Tóth, A. Steck, *Helv. Chim. Acta* **1996**, *79*, 1435.

[7] L. Zechmeister, '*Cis-Trans* Isomeric Carotenoids, Vitamins A and Arylpolyenes', Springer Verlag, Wien, 1962.
[8] J. A. Haugan, S. Liaaen-Jensen, *Phytochemistry* **1992**, *31*, 1359.
[9] U. Hengartner, K. Bernhard, K. Meyer, G. Englert, E. Glinz, *Helv. Chim. Acta* **1992**, *75*, 1848.
[10] J. A. Haugan, S. Liaaen-Jensen, *Tetrahedron Lett*. **1994**, *35*, 2245.
[11] T. Refven, A. Strand, B. Kjeldstad, J. A. Haugan, S. Liaaen-Jensen, *Acta Chem. Scand.* **1999**, *53*, 114.
[12] P. Molnár, J. Szabolcs, *J. Chem. Soc., Perkin Trans. 2* **1993**, 261.
[13] P. Molnár, T. Körtvélyesi, Z. Matus, J. Szabolcs, *J. Chem. Res. (S)* **1997**, *4*, 120.
[14] G. Englert, in 'Carotenoids', Eds. G. Britton, S. Liaaen-Jensen, and H. Pfander, Birkhäuser Verlag, Basel, 1995, Vol. 1B, pp. 147–260.
[15] A. Bax, 'Two-Dimensional Nuclear Magnetic Resonance in Liquids', Delft University Press, Delft, 1982, p. 50.
[16] R. Buchecker, K. Noack, in 'Carotenoids', Eds. G. Britton, S. Liaaen-Jensen, and H. Pfander, Birkhäuser Verlag, Basel, 1995, Vol. 1B, pp. 63–116.
[17] C. R. Enzell, S. Back, in 'Carotenoids', Eds. G. Britton, S. Liaaen-Jensen, and H. Pfander, Birkhäuser Verlag, Basel, 1995, Vol. 1B, pp. 261–320.
[18] P. Molnár, J. Szabolcs, *Acta Chim. Acad. Sci. Hung*. **1979**, *99*, 155.

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