Aesculaxanthin, a New Carotenoid Isolated from Pollens of *Aesculus hippocastanum*

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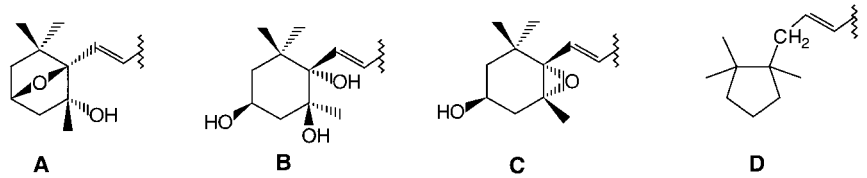
From the pollens of *Aesculus hippocastanum*, a new apocarotenoid was isolated as the main carotenoid and, based on the spectroscopic data, identified as (all-*E*,3*R*)-3-hydroxy-6′-apo-*β*-caroten-6′-al (**4**, *aesculaxanthin*). In addition, (all-*E*)-lutein (**3**) and (all-*E*)-*β*-citraurin (**5**) were isolated. Furthermore, **6** (*aesculaxanthol*) was prepared by reduction of **4** with $NaBH_4$ and tentatively identified as natural carotenoid.

Introduction. – During our investigations of different varieties of paprika (*Capsicum annuum*), some novel carotenoids were identified such as cucurbitaxanthins A and B, capsanthin-3,6-epoxide, and cycloviolaxanthin containing the 7-oxabicyclo[2.2.1]heptyl end group **A** [1], and 5,6-diepikarpoxanthin, 5,6-diepicapsokarpoxanthin with the (3*S*,5*S*,6*S*)-3,5,6-trihydroxy-5,6-dihydro-*β*-end group **B** [2]. These compounds may be formed from antheraxanthin and violaxanthin containing the (3*S*,5*R*,6*S*)-5,6-epoxy-5,6-dihydro-*β*-end group **C**, and their occurrence may be connected with the biosynthesis of *κ*-end group **D** which has not been clarified in detail yet. In the biosynthesis of the 3,6-epoxy-end group **A** from the 3-hydroxy-5,6-epoxy-end group **C**, compounds with the 3,5,6-trihydroxy-end group **B** may occur as intermediates.

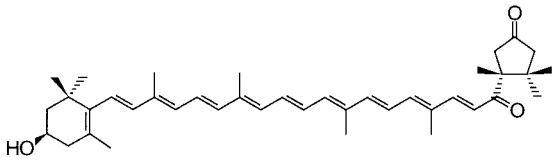


A **B** **C** **D**

As a continuation of our work related to the biosynthesis of carotenoids, we aimed at investigating other natural sources containing carotenoids with the *κ*-end group, especially at the isolation and identification of carotenoids containing the 3,5,6-trihydroxy-5,6-dihydro-*β*- or the 3,6-epoxy-end group.

Based on UV/VIS spectra, the chemical and chromatographic properties, the occurrence of various carotenoids with the *κ*-end group, especially capsanthone (**1**), in the anthers of the flowers of different species of *Aesculus* (horse chestnut) has been postulated long time ago [3][4]. Further investigations were carried out on the carotenoid composition of leaves in various phases of growth, floral buds in various stages of development, and of flowers of *Aesculus parviflora* and *A. rubicunda* [5]. As

main pigments, capsanthin (**2**) and capsanthone (**1**), capsorubin, zeaxanthin, and β-carotene were postulated, accompanied by small amounts of cryptoxanthin, lutein (**3**), cryptocapsin, cryptocapsone, and capsanthin monoepoxide [3]. In the present paper, we report on the re-investigation of the carotenoid composition of the pollens of *Aesculus hippocastanum*.



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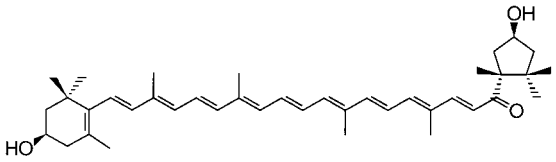

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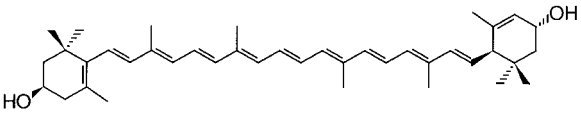

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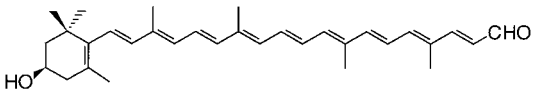

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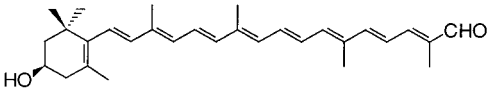

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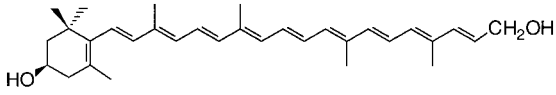

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Results and Discussion. – For the isolation of the main carotenoids, 250 g of pollen of *Aesculus hippocastanum* were extracted with MeOH and Et_2O, and then the extract was saponified. After precipitation of the main carotenoids (20 mg of crystals), repeated column chromatography (see *Exper. Part*) gave 1.8 mg of **4**, 0.8 of mg lutein (**3**), and 0.5 mg of β-citraurin (**5**).

The UV/VIS spectrum of **4** (488 nm in benzene) with no spectral fine structure is in accordance with a decaene chromophore conjugated to a C=O group. Reduction of **4**

with $NaBH_4$ gave **6**, whose UV/VIS spectrum exhibited, as expected, a fine spectral structure and a hypsochromic shift (485, 455, and 433 nm in benzene). In the EI-MS of **4**, the signal for the molecular ion was observed at *m/z* 458 (100, M^+) which corresponds to $C_{32}H_{42}O_2$. Acetylation of **4** gave a compound which exhibited in the EI-MS a molecular ion at *m/z* 500 (100, M^+) corresponding to a monoacetate of **4**. These data indicated that **4** corresponds to a 6′-apo-β-carotenal containing one primary or secondary OH group.

Based on the NMR and CD data, **4** was identified as (all-*E*,3*R*)-3-hydroxy-6′-apo-β-caroten-6′-al, and we propose for this new carotenoid the name *aesculaxanthin*. Accordingly, carotenoid **6**, which has been obtained by reduction of **4**, was identified as (all-*E*,3*R*)-6′-apo-β-carotene-3,6′-diol (*aesculaxanthol*). The HPLC comparison of the natural extract with semisynthetic **6** gave an indication that aesculaxanthol (**6**) occurs also naturally in small amounts in *A. hippocastanum*. ^{1}H-NMR and ^{1}H,^{1}H-COSY experiments allowed complete ^{1}H-signal assignments, and the δ(H) and *J*(H,H) values were identical with the corresponding data from the literature [6]. ^{13}C Chemical shifts were assigned using ^{1}H-decoupled ^{13}C-NMR, inverse HMQC, and HMBC experiments. In the case of **6**, the ^{13}C experiment was not accessible due to the small sample size, and certain ^{13}C chemical-shift values could not be assigned unambiguously or are lacking. However, the chemical-shift values of the identified ^{13}C resonances, given in the *Exper. Part*, are in full agreement with reference data [7]. Aesculaxanthin (**4**) exhibited a conservative CD spectrum with prominent maxima of alternative signs at 202 (+), 222 (−), 250 (+) 295 (−), and 366 (+) nm (EPA, −180°), and, based on the comparison with the data of **5**, the (3*R*)-configuration of **4** and **6** was established.

In addition, the NMR data of **3** were consistent with those of (all-*E*)-lutein, and of **5** with (all-*E*)-β-citraurin. The CD spectra of **3** were consistent with those reported in the literature for (all-*E*,3*R*,3′*R*,6′*R*)-lutein [8], and those of **5** for (all-*E*,3*R*)-β-citraurin [8].

In our present investigations of the pollen of *A. hippocastanum*, no carotenoids with the κ-end group has been isolated which is in contrast to earlier reports [3–5]. This may be explained by the fact that the structure proposal in the earlier investigations were based solely on the UV/VIS spectra, and the chemical and chromatographic behavior. Because capsanthone (**1**) and the new apocarotenoid aesculaxanthin (**4**) possess the same chromophore and similar polarity, we conclude that the carotenoid wrongly identified as capsanthone (**1**) is identical to aesculaxanthin (**4**).

This study, on the part of Hungarian authors, was supported by a grant from *OTKA T 023096* (*Hungarian National Research Foundation*). The financial support of the Swiss group by *F. Hoffmann-La Roche Ltd.*, Basel, and that of the *Swiss National Science Foundation* is gratefully acknowledged. We thank Mrs. *É. Nyers*, Mrs. *S. Hanzel*, and Mrs. *A. Bognár* for their skillful assistance; and Dr. *F. Müller* and Mrs. *J. Kohler* (*F. Hoffmann-La Roche Ltd.*, Basel) for recording the CD spectra.

Experimental Part

1. *General*. UV/VIS: *Beckman DU-65*. CD: *Jobin-Yvon Dichrograph-6* in EPA (Et_2O/isopentane/EtOH 5:5:2) at r.t. and −180°. NMR: *Bruker DRX 400* (^{1}H: 400.14 MHz, ^{13}C: 100.61 MHz), solvent: $CDCl_3$, 20°, δ in ppm (relative to the solvent signal), *J* in Hz. MS: *Varian MA-CH 7A*; *m/z* (rel. intensity in %).

2. *Isolation*. The pollen of *Aesculus hippocastanum* (250 g) were extracted with MeOH. The mixture was allowed to stand in MeOH for dehydration. After 20 h, the mixture was filtered and the filter cake extracted

repeatedly with MeOH and finally with Et_2O. The two MeOH extracts were combined, transferred to a separatory funnel, diluted with Et_2O, washed free from MeOH with H_2O, dried (Na_2SO_4), and evaporated *in vacuo* to *ca.* 1/2 of the volume. The Et_2O extract was washed free from MeOH, evaporated *in vacuo* to *ca.* 1/2 of the volume and combined with the MeOH extract. The combined extract was saponified with 30% KOH/MeOH at r.t. for 18 h. After saponification, the Et_2O soln. was washed free from alkali. The soln. was evaporated to dryness, and the residue was dissolved in benzene, and, upon addition of hexane, 20 mg of crystals were precipitated.

The crystalline product (20 mg) was submitted to CC: 3 column 6×30 cm, $CaCO_3$ (*Biogal*, Hungary), benzene/hexane 30 : 70 and 40 : 60. The picture after development: 3 mm yellow (zone *1*, unidentified); 3 mm pink (zone *2*, unidentified); 5 mm yellow (zone *3*, **3**); 15 mm pink (zone *4*, **4**); 3 mm orange (zone *5*, **5**); 6 mm yellow (zone *6*, β-cryptoxanthin and β-carotene). After processing, zone *5* was crystallized (benzene/hexane) to give 0.5 mg of β-citraurin.

The zone containing **4** was subsequently submitted to a second CC: 1 column 6×30 cm, $CaCO_3$ (*Biogal*, Hungary), 1% acetone in hexane. The picture after development: 1 mm pale-yellow (unknown), 1 mm pink (unknown), 25 mm red (**4**). After desorption, **4** was crystallized (benzene/hexane) to give 1.8 mg of red crystals, with a purity of 97%.

The zone containing lutein was submitted to a second CC: 1 column 6×30 cm, $CaCO_3$ (*Biogal*, Hungary), 1% acetone in hexane. The picture after development: 2 mm pale-yellow (unidentified), 10 mm yellow (**3**), 1 mm pink (unidentified). After processing, lutein was crystallized from benzene by addition of hexane; yield: 1 mg of crystals.

2. *Reduction of* **4** *with* $NaBH_4$. A soln. of 1.8 mg of **4** in 10 ml benzene was treated with an excess of $NaBH_4$ in benzene/96% EtOH 1 : 1 at 20° for 1 h. After the usual workup [6], the dried residue was submitted to CC: 1 column 5×30 cm, $CaCO_3$ (*Biogal*, Hungary), 40% hexane in benzene. The picture after development: 2 mm lemon yellow ((*Z*)-**6**), 30 mm yellow (**6**). After the processing, **6** was crystallized from benzene by addition of hexane; yield: 1.2 mg of crystals.

3. *Aesculaxanthin* ((*all*-E,3R)-*3-Hydroxy-6′-apo-β-caroten-6′-al*, **4**): 1.8 mg. M.p. 168–170°. UV/VIS (benzene): 488. CD (EPA, r.t.): 204 (+ 12.99), 224 (+ 8.45), 243 (+ 10.97), 293 (− 1.23), 346 (+ 4.94), 498 (− 2.24). CD (EPA, − 180°): 202 (+ 11.11), 222 (+ 1.04), 250 (+ 2.26), 295 (− 18.16), 366 (+ 7.71), 497 (− 2.85), 509 (− 2.17), 523 (− 2.77). ^{1}H-NMR ($CDCl_3$)[1]): 1.074 (*s*, Me(16,17)); 1.38 (br., OH); 1.48 (Ψt, J(2ax, 2eq) = J(2ax, 3) = 12.0, H_{ax}–C(2)); 1.736 (*s*, Me(18)); 1.77 (*ddd*, J(2eq, 2ax) = 12.0, J(2eq, 3) = 3.5, J(2eq, 4eq) = 2.1, H_{eq}–C(2)); 1.976 (*s*, Me(20′))*; 1.977 (*s*, Me(19′))*; 1.979 (*s*, Me(19))*; 1.992 (*s*, Me(20)); 2.05 (*dd*, J(4ax, 4eq) = 16.9, J(4ax, 3) = 9.8, H_{ax}–C(4)); 2.39 (*ddd*, J(4eq, 4ax) = 16.9, J(4ax, 3) = 5.5, J(4eq, 2eq) = 2.1, H_{eq}–C(4)); 4.00 (*m*, H–C(3)); 6.11 (*AB*, J(7, 8) ≈ 17, H–C(7)); 6.16 (*AB*, J(8, 7) ≈ 17, H–C(8)); 6.16 (*d*, J(10, 11) = 11.3, H–C(10)); 6.18 (*dd*, J(7′, 6′) = 7.8, J(7′, 8′) = 15.4, H–C(7′)); 6.27 (*d*, J(14, 15) = 11.4, H–C(14)); 6.37 (*d*, J(12, 11) = 14.9, H–C(12)); 6.39 (*d*, J(14′, 15′) = 11.0, H–C(14′)); 6.59 (*m*, H–C(11′)); 6.60 (*m*, H–C(10′)); 6.61 (*m*, H–C(12′)); 6.63 (*dd*, J(15′, 14′) = 11.0, J(15′, 15) ≈ 15, H–C(15′)); 6.69 (*dd*, J(11, 10) = 11.3, J(11, 12) = 14.9, H–C(11)); 6.73 (*dd*, J(15, 14) = 11.4, J(15, 15′) ≈ 15, H–C(15)); 7.17 (*d*, J(8′, 7′) = 15.4, H–C(8′)); 9.58 (*d*, J(6′, 7′) = 7.8, H–C(6′)). ^{13}C-NMR ($CDCl_3$)[1]): 12.73 (C(20))*; 12.78 (C(19, 19′))*; 12.89 (C(20′)); 21.61 (C(18)); 28.73 (C(16)); 30.25 (C(17)); 37.12 (C(1)); 42.56 (C(4)); 48.43 (C(2)); 65.07 (C(3)); 123.70 (C(11′)); 125.74 (C(11)); 125.98 (C(7)); 126.31 (C(5)); 126.98 (C(7′)); 129.55 (C(15′)); 131.17 (C(10)); 132.16 (C(15)); 132.26 (C(14)); 135.75 (C(9)); 136.02 (C(9′, 14′)); 136.31 (C(13)); 137.29 (C(12)); 137.72 (C(13′)); 137.98 (C(6)); 138.40 (C(8)); 141.44 (C(10′)); 143.42 (C(12′)); 156.80 (C(8′)); 193.74 (C(6′)). EI-MS: 458 (100, M^+), 440 (2, $[M - H_2O]^+$), 352 (4), 209 (15), 145 (51), 119 (45), 105 (35).

4. *Aesculaxanthol* ((*all*-E,3R)-*6′Apo-β-carotene-3,6′-diol*, **6**): 1.2 mg. M.p. 144–146°. UV/VIS (benzene): 485, 455, 433. CD (EPA, r.t.): 203 (− 0.46), 215 (− 0.42), 222 (− 0.19), 243 (+ 0.37), 299 (+ 0.09), 432 (+ 0.22). CD (EPA, − 180°): 200 (− 0.63), 215 (− 0.46), 241 (+ 1.02), 279 (− 1.94), 363 (+ 0.06). ^{1}H-NMR: 1.073 (*s*, Me(16, 17)); 1.32 (*t*, J(OH, 6′) = 6.0, HO–C(6′)); 1.36 (*d*, J(OH, 3) = 4.9, HO–C(3)); 1.48 (Ψt, J(2ax, 2eq) = J(2ax, 3) = 12.0, H_{ax}–C(2)); 1.735 (*s*, Me(18)); 1.77 (*ddd*, J(2eq, 2ax) = 12.0, J(2eq, 3) ≈ 3.3, J(2eq, 4eq) = 2.1, H_{eq}–C(2)); 1.930 (*s*, Me(19′)); 1.97 (*s*, Me(19, 20, 20′)); 2.04 (*dd*, J(4ax, 4eq) = 16.6, J(4a, 3) = 9.7, H_{ax}–C(4)); 2.39 (*ddm*, J(4eq, 4ax) = 16.6, J(4ax, 3) ≈ 5.3, H_{eq}–C(4)); 4.00 (*m*, H–C(3)); 4.25 (Ψt, J(6′, 7′) = J(6′, OH) = 6.2, H–C(6′)); 5.86 (*dt*, J(7′, 6′) = 6.1, J(7′, 8′) = 15.6, H–C(7′)); 6.09 (*AB*, J(8, 7) = 16.3, H–C(8)); 6.14 (*AB*, J(7, 8) = 16.3, H–C(7)); 6.15 (*d*, J(10, 11) = 11.2, H–C(10)); 6.19 (*d*, J(10′, 11′) = 11.3, H–C(10′)); 6.21–6.31 (*AA′BB′*, H–C(14, 14′)); 6.35 (*d*, J(8′, 7′) = 15.6, H–C(8′)); 6.36

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[1]) *: Assignments may be interchanged.

(*d*, *J*(12, 11) = 14.9, H–C(12)); 6.37 (*d*, *J*(12′, 11′) = 14.9, H–C(12′)); 6.58–6.68 (*AA′BB′*, H–C(15, 15′)); 6.60 (*dd*, *J*(11′, 12′) = 14.9, *J*(11′, 10′) = 11.3, H–C(11′)); 6.65 (*dd*, *J*(11, 10) = 11.2, *J*(11, 12) = 14.9, H–C(11)). ^{13}C-NMR ($CDCl_3$): 12.44 (C(20)); 12.62 (C(19, 20′)); 12.67 (C(19′)); 21.28 (C(18)); 28.41 (C(16)); 29.97 (C(17)); 36.90 (C(1)); 42.36 (C(4)); 48.22 (C(2)); 63.78 (C(6′)); 64.88 (C(3)); 124.64 (C(11′)); 124.82 (C(11)); 125.44 (C(7)); 125.9 (C(5)); *ca.* 130.5[2] (C(15, 15′)); 131.16 (C(10)); *ca.* 132.3 (C(10′)); 132.44 (C(14, 14′)); 134.18 (C(9′)); 136.18 (C(8′)); 137.56 (C(6)); *ca.* 137.9 (C(12)); 137.94 (C(12′)); *ca.* 138.3 (C(8)). EI-MS: 460 (100, M^+), 368 (43), 354 (20), 211 (14), 145 (38), 119 (39), 105 (25).

5. *β-Citraurin* (*(all-*E*,3*R*)-3-Hydroxy-8′-apo-β-caroten-8′-al*, **5**): 0.5 mg. UV/VIS (benzene): 4.69. CD (EPA, r.t.): 203 (– 0.20), 209 (– 0.07), 214 (– 0.08), 239 (+ 0.13), 338 (+ 0.01). CD (EPA, – 180°): 200 (– 0.645), 217 (– 0.13), 239 (+ 0.59), 279 (– 1.15), 345 (0.02). ^{1}H-NMR: 1.08 (*s*, Me(16, 17)); 1.36 (br, OH); 1.48 (*Ψt*, *J*(2ax, 2eq) = 12.1, *J*(2ax, 3) ≈ 11.9, H_{ax}–C(2)); 1.74 (*s*, Me(18)); 1.77 (*ddd*, *J*(2eq, 2ax) = 12.1, *J*(2eq, 3) = 3.6, *J*(2eq, 4eq) = 2.1, H_{eq}–C(2)); 1.90 (*d*, *J*(19′, 10′) = 1.2, Me(19′)); 1.98 (*s*, Me(19)); 2.00 (*s*, Me(20, 20′)); 2.05 (*dd*, *J*(4ax, 4eq) = 16.7, *J*(4ax, 3) = 9.2, H_{ax}–C(4)); 2.39 (*ddd*, *J*(4eq, 4ax) = 16.7, *J*(4ax, 3) = 5.5, *J*(4eq, 2eq) = 2.1, H_{eq}–C(4)); 4.00 (*m*, H–C(3)); 6.13 (*AB*, H–C(7)); 6.13 (*AB*, H–C(8)); 6.16 (*d*, *J*(10, 11) = 11.9, H–C(10)); 6.28 (*d*, *J*(14, 15) = 11.7, H–C(14)); 6.37 (*d*, *J*(12, 11) = 14.9, H–C(12)); 6.45 (*d*, *J*(14′, 15′) = 11.7, H–C(14′)); 6.64 (*dd*, *J*(15′, 14′) = 11.7, *J*(15′, 15) = 14.1, H–C(15′)); 6.66 (*d*, *J*(11′, 12′) = 14.9, *J*(11′, 10′) = 10.6, H–C(11′)); 6.69 (*dd*, *J*(11, 10) = 11.9, *J*(11, 12) = 14.9, H–C(11)); 6.74 (*d*, *J*(12′, 11′) = 14.9, H–C(12′)); 6.77 (*dd*, *J*(15, 14) = 11.7; *J*(15, 15′) = 14.1, H–C(15)); 6.94 (*dd*, *J*(10′, 11′) = 10.6, *J*(10′, 19′) = 1.2, H–C(10′)); 9.45 (*s*, H–C(8′)). ^{13}C-NMR ($CDCl_3$): 9.66 (C(19′)); 12.71 (C(20′)); 12.80 (C(19)); 12.93 (C(20)); 21.62 (C(18)); 28.73 (C(16)); 30.26 (C(17)); 37.13 (C(1)); 42.57 (C(4)); 48.44 (C(2)); 65.08 (C(3)); 122.71 (C(11′)); 126.12 (C(11)); 126.02 (C(7)); 126.36 (C(5)); 129.27 (C(15′)); 131.13 (C(10)); 132.09 (C(14)); 132.95 (C(15)); 135.25 (C(13′)); 136.52 (C(9)); 136.74 (C(9′)); 137.20 (C(12)); 137.52 (C(14′)); 137.72 (C(6)); 138.39 (C(8)); 138.53 (C(13)); 145.92 (C(12′)); 149.29 (C(10′)); 194.55 (C(8′)).

6. *Lutein* (*(all-*E*,3*R*,3′*R*,6′*R*)-β,ε-Carotene-3,3′-diol*, **3**): 1.0 mg. M.p. 165–167°. UV/VIS (benzene): 487, 457, 433. CD (EPA, r.t.): 212 (+ 1.75), 224 (– 0.25), 245 (+ 3.04), 261 (+ 2.67), 285 (– 1.46), 431 (+ 4.29), 469 (+ 4.01). CD (EPA, – 180°): 212 (+ 12.50), 232 (+ 1.89), 249 (+ 5.91), 283 (– 5.86), 307 (– 0.59), 345 (– 2.46), 456 (+ 5.13), 487 (+ 6.08). ^{1}H-NMR ($CDCl_3$): 0.85 (*s*, Me(17′)); 1.00 (*s*, Me(16′)); 1.07 (*s*, Me(16, 17)); 1.37 (*dd*, J_{gem} = 12.9, *J*(2′, 3′) = 6.7, H–C(2′)[3]); 1.48 (*Ψt*, *J*(2ax, 2eq) = *J*(2ax, 3) = 12.1, H_{ax}–C(2)); 1.77 (*ddd*, *J*(2eq, 2ax) = 12.1, *J*(2eq, 3) = 3.0, *J*(2eq, 4eq) = 1.6, H_{eq}–C(2)); 1.63 (*s*, Me(18′)); 1.74 (*s*, Me(18)); 1.84 (*dd*, J_{gem} = 12.9, *J*(2′, 3′) = 6.0, H–C(2)[3]); 1.91 (*s*, Me(19′)); 1.96 (*s*, Me(20, 20′)); 1.97 (*s*, Me(19)); 2.05 (*dd*, *J*(4ax, 4eq) = 16.8, *J*(4ax, 3) = 9.3, H_{ax}–C(4)); 2.39 (*ddd*, *J*(4eq, 4ax) = 16.8, *J*(4eq, 3) = 5.7, *J*(4eq, 2eq) = 1.6, H_{eq}–C(4)); 2.40 (*d*, *J*(6′, 7′) = 9.8, H–C(6′)); 4.00 (*m*, H–C(3)); 4.25 (*m*, H–C(3′)); 5.43 (*dd*, *J*(7′, 6′) = 9.8, *J*(7′, 8′) = 15.3, H–C(7′)); 5.55 (*m*, H–C(4)); 6.11 (*AB*, *J*(7, 8) = 16.3, H–C(7)); 6.14 (*AB*, *J*(8, 7) = 16.3, H–C(8)); 6.14 (*d*, *J*(10′, 11′) = 11.4, H–C(10′)); 6.14 (*d*, *J*(8′, 7′) = 15.3, H–C(8′)); 6.16 (*d*, *J*(10, 11) = 11.4, H–C(10)); 6.25 (*m*, H–C(14, 14′)); 6.35 (*d*, *J*(12′, 11′) = 14.8, H–C(12′)); 6.36 (*d*, *J*(12, 11) = 15.0, H–C(12)); 6.60 (*dd*, *J*(11′, 10′) = 11.4, *J*(11′, 12′) = 14.8, H–C(11′)); 6.63 (*m*, H–C(15, 15′)); 6.64 (*dd*, *J*(11, 10) = 11.4, *J*(11, 12) = 15.0, H–C(11)). ^{13}C-NMR ($CDCl_3$)[4]): 12.7 (C(19, 20, 20′)); 13.0 (C(19′)); 21.6 (C(18)); 22.8 (C(18′)); 24.2 (C(17′)); 28.7 (C(16)); 29.4 (C(16′)); 30.2 (C(17)); 42.5 (C(4)); 44.6 (C(2′)); 48.4 (C(2)); 55.0 (C(6′)); 65.0 (C(3)); 65.9 (C(3′)); 124.5 (C(4′)); 125.0 (C(11, 11′)); 125.7 (C(7)); 128.8 (C(7′)); 130.1 (C(15, 15′)); 131.0 (C(10, 10′)); 132.6 (C(14, 14′)); 137.6 (C(12, 12′)); 137.7 (C(8′)); 138.5 (C(8)). EI-MS: 568 (14, M^+), 550 (2, $[M - H_2O]^+$), 145 (68), 119 (100), 95 (5).

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[2]) Uncertain, due to overlap.

[3]) No assignment to axial or equatorial position.

[4]) Quaternary C signals not identified due to the ^{13}C assignment based on an inverse HMQC spectrum.

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