Abietanes and a Novel 20-Norabietanoid from *Plectranthus cyaneus* (Lamiaceae)

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Antioxidative-activity-guided fractionation of extracts of the aerial parts of the title plant yielded the two novel abietanoid diterpenoids 11,20-dihydroxysugiol (=11,12,20-trihydroxyabieta-8,11,13-trien-7-one; **3**) and 1,11-epoxy-6,12-dihydroxy-20-norabieta-1(10),5,8,11,13-pentaen-7-one (**4**) in addition to 11-hydroxysugiol (=12-*O*-demethylcryptojaponol=11,12-dihydroxyabieta-8,11,13-trien-7-one; **2**) and the main constituent carnosolon (=6,20-epoxy-6,11,12-trihydroxyabieta-8,11,13-trien-7-one; **1**). The structures were established on the basis of spectroscopic, chiroptic, and X-ray crystallographic evidence.

1. Introduction. – In continuation of our current program concerning the isolation, synthesis, and chemical transformations of biologically active constituents of African and Asian medicinal plants of the *Lamiaceae* species of the genera *Coleus*, *Plectranthus*, and *Solenostemon* [1–5], we investigated *Plectranthus cyaneus* GÜRKE[2]). Antioxidant-activity-guided fractionation [7–9] of the air-dried plant material (see *Exper. Part*) afforded the main constituent carnosolon (**1**) as well as 11-hydroxysugiol (**2**), the novel 11,20-dihydroxysugiol (**3**), and the 1,11-epoxy-20-norabietanoid **4**. In addition, 5-hydroxy-4′,6,7-trimethoxyflavone (=salvigenin or scutellarein 4′,6,7-trimethyl ether; **6**) was isolated and characterized[3]).

2. Results and Discusssion. – The predominant constituent of *Plectranthus cyaneus* was identified by spectroscopic and further physical data as carnosolon (**1**), a 6,20-epoxyabietanoid that was first isolated from *Coleus carnosus* HASSK. [10][4]). Comparison of the data with those of an authentic sample fully confirmed this finding

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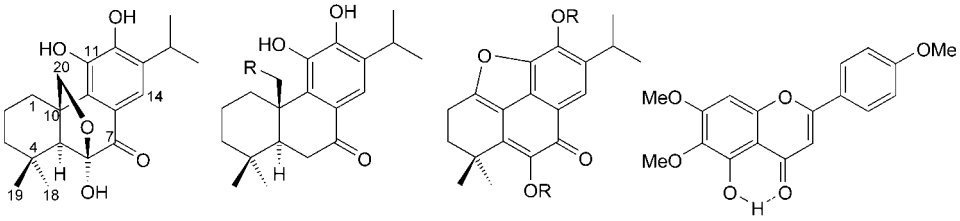
[2]) *Plectranthus cyaneus* GÜRKE is native of East Africa [6]; it was originally obtained as seedlings (Kew Gardens 1985). The plant was propagated in Zurich and later cultivated in the open field. Living plants are kept at the Institute of Organic Chemistry, University of Zurich.

[3]) According to the activity-guided separation, the substances are antioxidants. Qualitative comparison on TLC with other phenols and catechols isolated by us from *Plectranthus* species [1][2] showed the abietanoids to have very similar activity and to be almost as efficient as the commercial antioxidant 2,6-di(*tert*-butyl)-4-methylphenol (BHT) [1][2]. However, since the compounds did not exhibit significantly enhanced activity, no quantitative testing was performed. As stated earlier [2], the dominant structural element seems to be the catechol (=benzene-1,2-diol) moiety, whereas the functional groups have little influence.

[4]) This is only the second account on the occurrence of carnosolon (**1**). It is noteworthy that both plant species contain unusually high amounts of **1** (*P. cyaneus*, 0.57%, and *C. carnosus*, 0.13% [10], per air-dried weight).



1 **2** R = H **4** R = H **6**
3 R = OH **5** R = Ac

and established compound **1** to be 6,20-epoxy-6,11,12-trihydroxyabieta-8,11,13-trien-7-one.

The spectroscopic, chiroptic, and further physical data of compound **2** are in full accord with those published for 12-*O*-demethylcryptojaponol (**2**) [11][12]. This abietanoid was first isolated as a genuine natural compound from *Salvia phlomoides* [11] but it has been reported earlier as a partial synthetic product [13][14]. Therefore, constituent **2** is 11,12-dihydroxyabieta-8,11,13-trien-7-one (=11-hydroxysugiol, =6-*O*-demethylcryptojaponol).

Compound **3** was isolated as colorless needles. According to the MS and ^{1}H- and ^{13}C-NMR spectra, its molecular formula is $C_{20}H_{28}O_4$. The UV and NMR spectroscopic features are very similar to those of **2** (see *Exper. Part* and *Tables 1* and *2*), the only striking difference being the absence of a low-field angular Me group in the ^{1}H-NMR spectrum, which is replaced by a CH_2OH moiety.

Moreover, the presence of carnosolon (**1**) strongly indicates a biogenetic relationship. An independent determination of the absolute configuration was not performed. However, due to the co-occurrence of the known abietanoids **1** and **2** and since we had never isolated an *ent*-abietanoid from *Coleus*, *Plectranthus*, or *Solenostemon* species, we assigned the normal abietane configuration to **3**. This conclusion is further corroborated by the positive optical rotation of the diterpenoids **1**–**3**. As a consequence, the novel diterpenoid **3** is 11,12,20-trihydroxyabieta-8,11,13-trien-7-one (=11,20-dihydroxysugiol).

The CH_2OH moiety of **3** appears as an *AB* system at δ 4.06 and 4.61 (^2J = 9.5 Hz) in the ^{1}H-NMR and the corresponding C-signal at δ 65.5 in the ^{13}C-NMR. It was concluded that this group is located at C(10) for the following reasons: the low-field signal of **2** at δ 1.40 (*s*) is attributed to Me(20), and the high-field signals for the geminal Me(18) an Me(19) at C(4) remain unchanged in **3** at δ 0.94 and 0.97 (each *s*).

The minor compound **4**, isolated as yellow prisms, is optically inactive. Its molecular formula was determined to be $C_{19}H_{20}O_4$ from MS (*m/z* 312) and ^{1}H- and ^{13}C-NMR data. The UV spectrum of **4** (λ_{max} 363 nm) and prominent IR absorptions (1625, 1590 cm^{-1}) indicate the presence of an extensively conjugated carbonyl chromophore.

The ^{1}H-NMR spectrum of **4** (*Table 1*) reveals an isopropyl group at δ 1.33 (*d*, ^3J = 6.8 Hz) and (3.54 *sept.*, ^3J = 6.8 Hz) and a deshielded aromatic H-atom at δ 7.93 (*s*), similar to the compounds **1**–**3**. This finding strongly points to a 7-oxoabietane skeleton for **4**. However, the ^{1}H-NMR spectrum is quite sparse and would suggest that rings A and B are significantly different from those of **1**–**3**. Furthermore, only the signals of two angular Me

Table 1. *^{1}H-NMR Data* (600 MHz, $CDCl_3$) *for* **1**–**4**. δ(H) in ppm, J in Hz. Trivial numbering (see **1**).

	1	**2**	**3**	**4**
H_{ax}–C(1)	2.21 (*td*, J = 13.5, 5.5)	1.51 (*td*, J = 13.8, 3.5)	1.58–1.53 (*m*)[c])	
H_{eq}–C(1)	2.80 (*d*br.*t*, J = 13.5, 3)	3.11 (*dt*, J = 13.8, 3.5)	3.32 (*d*br.*t*, J = 13.5, 3)	–
H_{ax}–C(2)	1.79 (*qt*, J = 13.5, 3)	1.78 (*qt*, J = 13.8, 3.5)	1.75 (*qt*, J = 13.6, 3)	3.00 (*t*, J = 6.0)
H_{eq}–C(2)	1.69 (*m*, *dquint.*-like, J = 13.5, 5.5, 3)	1.61 (*dquint.*, J = 13.8, 3.5)	1.68 (*dquint.*-like, J = 13.6, 3)	
H_{ax}–C(3)	1.24 (*td*, J = 13.5, 3)	1.28 (*td*, J = 13.8, 3.5)	1.28 (*td*-like, J = 13.6, 3)	2.07 (*t*, J = 6.0)
H_{eq}–C(3)	1.43 (*d*br.*t*, J = 13.5, 3)	1.50 (*m*)[b])	1.58–1.53 (*m*[c]))	
H–C(5)	1.72 (*s*)	1.87 (*dd*, J = 14.2, 3.2)	1.99 (*dd*, J = 15.2, 2.5)	–
H_{ax}–C(6)	–	2.53 (*dd*, J = 17.5, 14.2)	2.38 (*dd*, J = 17.4, 15.2)	–
H_{eq}–C(6)	–	2.62 (*dd*, J = 17.5, 3.2)	2.61 (*dd*, J = 17.4, 2.5)	–
H–C(14)	7.77 (*s*)	7.63 (*s*)	7.74 (*s*)	7.93 (*s*)
H–C(15)	3.07 (*sept.*, J = 6.8)	3.08 (*sept.*, J = 7.0)	3.25 (*sept.*, J = 7.0)	3.54 (*sept.*, J = 6.8)
Me(16)	1.28 (*d*, J = 6.8)[a])	1.24 (*d*, J = 7.0)[a])	1.25 (*d*, J = 7.0)[a])	1.33 (*d*, J = 6.8)
Me(17)	1.29 (*d*, J = 6.8)[a])	1.27 (*d*, J = 7.0)[a])	1.27 (*d*, J = 7.0)[a])	1.33 (*d*, J = 6.8)
Me(18)	1.13 (*s*)	0.92 (*s*)	0.94 (*s*)	1.46 (*s*)
Me(19)	1.41 (*s*)	0.97 (*s*)	0.97 (*s*)	1.46 (*s*)
H_a–C(20)	3.48 (*d*, J = 7.8)	1.40 (*s*)	4.06 (*d*, J = 9.5)	–
H_b–C(20)	4.38 (*d*, J = 7.8)		4.61 (*d*, J = 9.5)	
OH	5.24 (*s*), 5.74, 5.90 (br. *s*)	5.81, 6.13 (br. *s*)	1.55, 6.57, 8.45 (br. *s*)	5.80, 7.40 (br. *s*)

[a]) Assignments interchangable. [b]) Not resolved, partially hidden under H_{ax}–C(1). [c]) Not resolved.

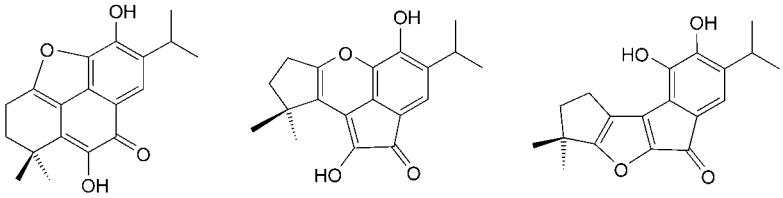
Table 2. *^{13}C-NMR Data* (150.9 MHz, $CDCl_3$) *for* **1**–**4**. δ(C) in ppm. Trivial numbering (see **1**).

	1	**2**	**3**	**4**
C(1)	29.6	35.6	31.1	147.5
C(2)	18.4	19.0	18.9	22.1
C(3)	41.2	41.1	41.0	42.7
C(4)	32.2	33.4	33.6	35.8
C(5)	58.2	50.3	51.1	123.5
C(6)	105.1	36.8	35.0	162.5
C(7)	192.6	199.6	197.6	181.8
C(8)	121.5	125.2	124.5	129.0
C(9)	137.4	138.8	135.3	114.8
C(10)	51.4	40.2	45.3	116.5
C(11)	140.2	141.2	141.4	146.2
C(12)	147.7	146.6	150.4	142.9
C(13)	133.0	131.9	132.3	138.8
C(14)	120.0	118.1	120.0	122.4
C(15)	27.2	27.3	27.5	28.9
C(16)	22.28[a])	22.3[a])	22.6[a])	23.2
C(17)	22.33[a])	22.5[a])	22.5[a])	23.2
C(18)	33.6	33.0	33.5	26.5
C(19)	22.0	21.5	22.3	26.5
C(20)	72.0	18.6	65.5	–

[a]) Assignments interchangable.

groups at δ 1.46 (*s*, 6 H), two mutually coupled CH_2 groups at δ 2.07 and 3.00 (each *t*, $^3J = 6.0$), and 2 OH groups at δ 5.80, 7.40 (each br. *s*) are present. The ^{13}C-NMR spectrum (*Table 2*) confirms the conclusions drawn from the ^{1}H-NMR data. Furthermore, it shows the presence of a C=O group at δ 181.8 and of ten olefinic C-atoms. Six of them can be assigned to the 11,12-dioxy-substituted aromatic ring C in an abietane, whereas the signals at δ 116.5, 123.5, 147.5, and 162.5 (quaternary C-atoms) cannot be assigned easily.

Comparison with the spectra of compounds **1**–**3** suggests that, in **4**, C(1), C(5), C(6), and C(10) are olefinic C-atoms and that C(20) is probably lacking. Thus, a norditerpenoid structure becomes evident, as assumed from the molecular formula, and, taking into account the double-bond equivalents deduced from it, compound **4** must be tetracyclic. Extensive interpretation of the connectivities and correlations in a complete set of 2D NMR experiments (COSY, NOESY, HSQC, HMBC) finally led to the structures **4**, **4′**, and **4″**, which remained indistinguishable despite of all the modern NMR methods. The latter two seem rather peculiar and would not explain the observed IR carbonyl absorptions; hence, the biogenetically most-obvious proposal, **4**, was



4 **4'** **4"**

preferred. However, since we had encountered many unexpected modifications of the abietane skeleton within the scope of our work on the constituents of lamiaceae (*abeo*-, seco-, and spirocyclopropane structures, see *e.g.*, [15]), structures **4′** and **4″** could not be precluded *a priori*.

Mild acetylation of **4** gave the monoacetate **5** (*m/z* 354; δ(H) 2.40 (*s*, MeCO)), which ruled out structure **4″**, because it would furnish an 11,12-di-*O*-acetyl derivative under the applied conditions. Finally, structure **4** was confirmed by an X-ray crystallographic analysis of derivative **5**, as shown in the *Figure*. Hence, the novel compound is 1,11-epoxy-6,12-dihydroxy-20-norabieta-1(10),5,8,11,13-pentaen-7-one (**4**).

Compound **4** is supposed to be biogenetically derived from carnosolon (**1**), the crucial step being the oxidative removal of C(20) (see *Scheme*). Either *retro*-aldol reaction or oxidative decarboxylation yields a 6,7,11,12-tetrahydroxy intermediate. After benzylic oxidation, it undergoes intramolecular addition of OH–C(11) to C(1) and dehydration to the metabolite **4**. Oxidation of C(1) in abietanoids is very rare and seems to take place only in 20-nor compounds at the benzylic position. The first known compounds with this structural feature were arucadiol [16][17] and miltionone I [18].

The flavonoid **6** was characterized fully by spectroscopic methods and was found to be identical in every respect with 5-hydroxy-4′,6,7-trimethoxyflavone (=salvigenin or scutellarein 4′,6,7-trimethyl ether) [19–21].

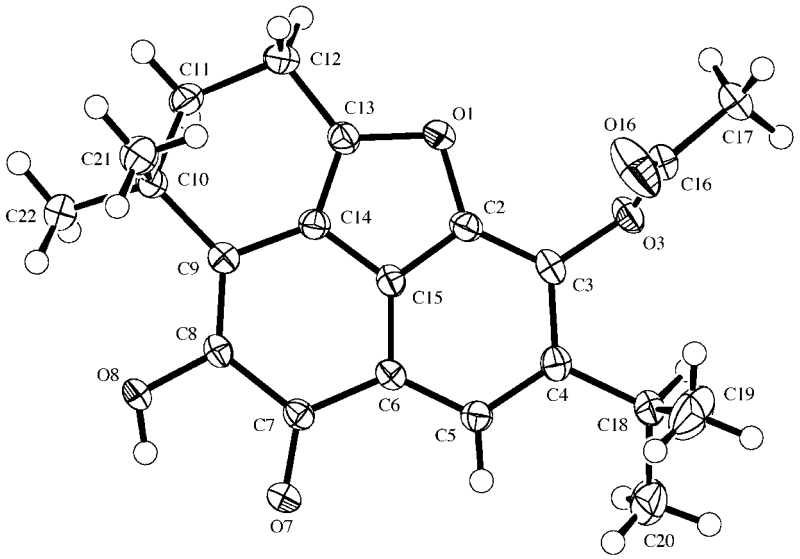
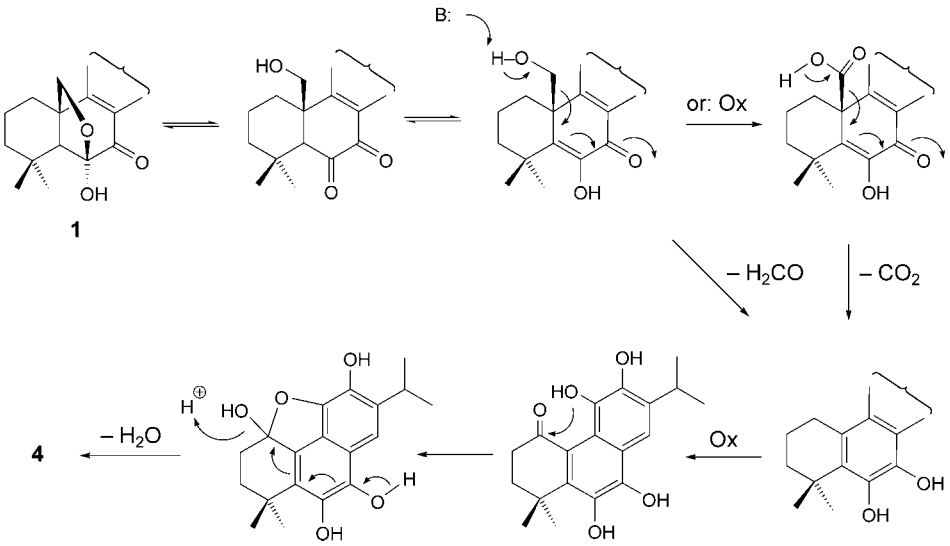


Figure. *Molecular structure of derivative* **5**. Arbitrary atom numbering; 50% probability ellipsoids.

Experimental Part

1. *General*. Antioxidants were detected on TLC (*Merck 60F$_{254}$* silica gel plates) according to [7] (linoleic acid/β-carotene, orange spots) and [9] (2,2-diphenyl-1-picrylhydrazyl radical, violet spots). Qualitative comparison with known catechols and BHT [1][2] was performed on TLC by dissolving aliquots of the

Scheme



individual compounds and estimation of the intensities of the colored spots. Column chromatography (CC): silica gel *60* (40–63 μm, *Merck* Art. Nr. *109385*). M.p.: *Mettler FP 5/52*; not corrected. $[\alpha]_D$: *Perkin-Elmer 241-MC* polarimeter with thermostat *B. Braun Thermomix 1441*; 10-cm cell. UV: *Perkin-Elmer Lambda-9* UV/VIS/NIR spectrophotometer; λ_{max} (log ε) in nm. IR: *Perkin-Elmer 1600*-FT-IR spectrometer, $\tilde{\nu}_{max}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR: *Bruker ARX-300* (300 and 75.4 MHz, resp.) and *AMX-600* or *DRX-600* (600 and 150.9 MHz, resp.); chemical shifts δ in ppm rel. to Me_4Si (= 0 ppm), coupling constants *J* in Hz, assignments based on ^{1}H,^{1}H-COSY, DEPT90, DEPT135, ^{13}C,^{1}H-COSY (HSQC), and ^{13}C,^{1}H long-range HMBC experiments. MS: *Varian MAT 112s* or *Varian MAT 90* for electron impact (EI; 70 eV); *Varian MAT 7011* or *Finnigan MAT SSQ 700* for chemical ionization (CI) with NH_3; *Finnigan MAT TSQ 7000*, for electrospray ionization (ESI); in *m/z* (% rel. int.).

2. *Extraction and Isolation.* Air-dried leaves of *P. cyaneus* (800 g) were extracted at r.t. with Et_2O (2 h, twice) and then re-extracted with Et_2O/Me_2CO 1:1 (2 h). The extract was evaporated at 35° and partitioned between benzene/hexane 1:1 and 85% MeOH/H_2O. The polar phase was evaporated to yield a greenish residue (16.4 g) that was subjected to CC (*Sephadex LH-20*, gradient elution with hexane/CH_2Cl_2 1:6 → CH_2Cl_2/Me_2CO 4:1 → 1:1, → Me_2CO): nine fractions. *Frs. 2* (4.50 g), *4* (1.01 g), and *5* (5.52 g) exhibited significant antioxidative acitvity and were investigated further. CC (silica gel, hexane → CH_2Cl_2) of *Fr. 2* gave crystalline **6** (127 mg). Repeated CC (silica gel, hexane/Me_2CO 25:1, hexane/Et_2O 5:1) of *Fr. 4* afforded **2** (26 mg), **3** (31 mg), and **4** (7 mg). CC (silica gel, hexane/Me_2CO 15:1) of *Fr. 5* yielded carnosolon (**1**; 4.52 g).

3. *Carnosolon* (= *6,20-Epoxy-6,11,12-trihydroxyabieta-8,11,13-trien-7-one* = *(4a*R*,10*S*,10a*S*)-1,2,3,4,10,10a-Hexahydro-5,6,10-trihydroxy-1,1-dimethyl-7-(1-methylethyl)-9*H*-10,4a-(epoxymethano)phenanthren-9-one*; **1**). Colorless needles (Et_2O/hexane). M.p. 182°. $[\alpha]_D^{20} = +58$ ($c = 1.0$, $CHCl_3$). UV (EtOH): 237 (4.09), 295 (3.99). IR (KBr): 3455, 3422, 3195 (br.), 2980, 2950, 2927, 2895, 2865, 2845, 1685, 1607, 1560, 1462, 1365, 1299, 1279, 1227, 1197, 1177, 1145, 1000. ^{1}H-NMR; *Table 1*. ^{13}C-NMR; *Table 2*. CI-MS: 364 (10, $[M + NH_4]^+$), 347 (100, $[M + H]^+$), 315 (8, $[M + H - MeOH]^+$). EI-MS: 346 (79, $M^{+\bullet}$), 328 (38, $[M - H_2O]^+$), 300 (35, $[M - H_2O - CO]^+$), 285 (38, $[M - H_2O - MeCO]^+$).

4. *11-Hydroxysugiol* (= *12*-O*-Demethylcryptojaponol* = *11,12-Dihydroxyabieta-8,11,13-trien-7-one* = *(4a*-S*,10a*S*)-2,3,4,4a,10,10a-Hexahydro-5,6-dihydroxy-1,1,4a-trimethyl-7-(1-methylethyl)-phenanthren-9(1*H*)-one;* **2**). Pale yellow needles (CH_2Cl_2/hexane). M.p. 194–196°. $[\alpha]_D^{20} = +21$ ($c = 1.0$, MeOH). UV (EtOH): 234 (4.08), 288 (3.97), 363 (sh, 3.26). IR (KBr): 3465, 3180, 2960, 2923, 2855, 1637, 1579, 1460, 1443, 1324, 1271, 1260, 1241, 1210, 1176, 1142, 1102, 991. ^{1}H-NMR (300 MHz, C_6D_5N): 8.24 (*s*, H–C(14)); 3.92 (br. *d*, $^2J = 12$, H_{eq}–C(1)); 3.69 (*quint.*, $^3J = 7$, H–C(15)), 3.02 (*dd*, $^2J = 17$, $^3J(6ax,5) = 4$, H_{ax}–C(6)); 2.78 (*dd*, $^2J = 17$,

^3J(6eq,5) = 14, H_{eq}–C(6)); 1.96 (*dd*, ^3J(5,6ax) = 14, ^3J(5,6eq) = 4, H–C(5)); 1.83 (*qt*-like, $^2J \approx {}^3J$(2ax,1ax) ≈ ^3J(2ax,3ax) ≈ 12, ^3J(2ax,1eq) ≈ ^3J(2ax,3eq) ≈ 4, H_{ax}–C(2)); 1.61 (*s*, Me(20)); 1.33 (6H, *d*, ^3J = 7, Me(16), Me(17)); 0.93 (*s*, Me(19)); 0.88 (*s*, Me(18)). ^{1}H-NMR ($CDCl_3$): *Table 1*. ^{13}C-NMR; *Table 2*. EI-MS: 316 (28, $M^{+\bullet}$), 301 (5, $[M - Me]^+$), 245 (8), 3 (41).

5. *11,20-Dihydroxysugiol (=11,12,20-Trihydroxyabieta-8,11,13-trien-7-one = (4a*R*,10a*S*)-2,3,4,4a,10,10a-Hexahydro-5,6-dihydroxy-4a-(hydroxymethyl)-1,1-dimethyl-7-(1-methylethyl)phenanthren-9(1*H*)-one;* **3**). Colorless needles (Me_2CO/hexane). M.p. 240–242°. $[\alpha]_D^{20} = +31$ (*c* = 0.5, MeOH). UV (EtOH): 237 (4.10), 293 (4.01). IR (KBr): 3485, 3322, 2960, 2925, 2870, 1698, 1649, 1587, 1555, 1465, 1436, 1390, 1364, 1300, 1268, 1246, 1205, 1195, 1150, 1110, 1012, 979. ^{1}H-NMR (300 MHz, C_6D_5N): 8.26 (*s*, H–C(14)); 4.41 (*d*, ^2J = 10, H_a–C(20)); 4.78 (*d*, ^2J = 10, H_b–C(20)); 3.82 (br. *d*, ^2J = 13, H–C(1)); 3.70 (*quint.*, ^3J = 7, H–C(15)); 2.82 (*m*, CH_2(6)); 2.04 (*dd*, ^3J (5,6ax) = 13, ^3J (5,6eq) = 4, H–C(5)); 1.83 (*qt*-like, $^2J \approx {}^3J$(2ax,1ax) ≈ ^3J(2ax,3ax) ≈ 12, ^3J(2ax,1eq) ≈ ^3J(2ax,3eq) ≈ 4, H_{ax}–C(2)); 1.38 (*d*, ^3J = 7, Me(16), Me(17)); 0.91 (*s*, Me(19)); 0.87 (*s*, Me(18)). ^{1}H-NMR ($CDCl_3$): *Table 1*. ^{13}C-NMR: *Table 2*. EI-MS: 332 (18, $M^{+\bullet}$), 301 (43, $[M - CH_2OH]^+$), 283 (5, $[M - CH_2OH - H_2O]^+$), 285 (30, $[M - Me]^+$).

6. *1,11-Epoxy-6,12-dihydroxy-20-norabieta-1(10),5,8,11,13-pentaen-7-one (=2,3-Dihydro-5,9-dihydroxy-1,1-dimethyl-6-(1-methylethyl)phenanthro[4,5-*bcd*]furan-8(1*H*)-one;* **4**). Yellow prisms (CH_2Cl_2/hexane). M.p. 188°. UV (Et_2O): 248 (4.01), 253 (4.00), 269 (3.60), 315 (sh, 3.76), 335 (4.00), 363 (4.08), 385 (sh, 3.76). IR (KBr): 3339, 3210, 2950, 2920, 2870, 1660, 1625, 1590, 1559, 1520, 1480, 1381, 1340, 1307, 1246, 1211, 1181, 1137, 1112, 1086, 945, 910, 848, 796, 777, 700. ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. ES-IMS: 313 (100, $[M + H]^+$). EI-MS: 312 (56, M^+), 297 (100, $[M - Me]^+$), 282 (4), 281 (6), 269 (5), 254 (3), 141 (17).

7. *5-(Acetyloxy)-2,3-dihydro-9-hydroxy-1,1-dimethyl-6-(1-methylethyl)phenanthro[4,5-*bcd*]furan-8(1*H*)-one* (**5**). Compound **4** (1 mg) was stirred in Ac_2O (2 ml) and anh. NaOAc (3 mg) at r.t. overnight. After usual workup, the residue was chromatographed on TLC (SiO_2, hexane/AcOEt 2:1). Recrystallizations from hexane (twice) yielded **5** (0.6 mg). Yellowish prisms. M.p. 201°. ^{1}H-NMR ($CDCl_3$; trivial numbering (see **1**)): 7.91 (*s*, H–C(14)); 3.21 (*quint.*, ^3J = 6.9, H–C(15)); 2.93 (*t*, ^3J = 6.0, CH_2(2)); 2.40 (*s*, COMe), 1.99 (*t*, ^3J = 6.0, CH_2(3)); 1.39 (*s*, Me(18), Me(19)); 1.23 (*d*, ^3J = 6.9, Me(16), Me(17)). ESI-MS: 355 (100, $[M + H]^+$).

8. *X-Ray Crystallographic Analysis of* **5**. $C_{21}H_{22}O_5$, M_r 354.4. Yellow prisms. Monoclinic, space group $P2_1/c$; *a* = 11.790(2), *b* = 10.117(3), *c* = 16.234(3) Å, β = 111.23(1)°, *V* = 1805.0(7) Å^3, *Z* = 4, D_x = 1.304 g cm^{-3}, μ = 0.0924 mm^{-1}, *T* = 173 K; *Rigaku-AFC-5R* diffractometer, Mo$K\alpha$ radiation, λ 0.71073 Å, no absorption correction, structure solved by direct methods with SIR-92 [22] and refined with teXsan [23]. The non-H-atoms were refined anisotropically; the hydroxy H-atom was placed in the position indicated by a difference *Fourier* map, and its position was allowed to refine; all other H-atoms were fixed in geometrically calculated positions. Of the 4531 measured reflections ($2\theta < 55°$), 4143 were unique, and 2859 reflections ($I > 2\sigma(I)$) were used for the least-squares refinement on *F* of 240 parameters. Final *R* = 0.0469, R_w = 0.0420, g.f. = 1.769, Δ_{max}/σ = 0.0004, $\Delta\rho_{max}$ = 0.27 e Å^{-3}. CCDC-233199 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

9. *5-Hydroxy-4′,6,7-trimethoxyflavone* (=*5-Hydroxy-6,7-dimethoxy-2-(methoxyphenyl)-4*H*-1-benzofuran-4-one*; **6**). Colorless prisms (Me_2CO/CH_2Cl_2/hexane). M.p. 185–187°. UV, IR, ^{1}H-NMR, EI-MS and further physical data: in full agreement with the reported values [19][20].

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