Paeciloquinones A, B, C, D, E and F: New Potent Inhibitors of Protein Tyrosine Kinase Produced by *Paecilomyces carneus*

II. Characterization and Structure Determination

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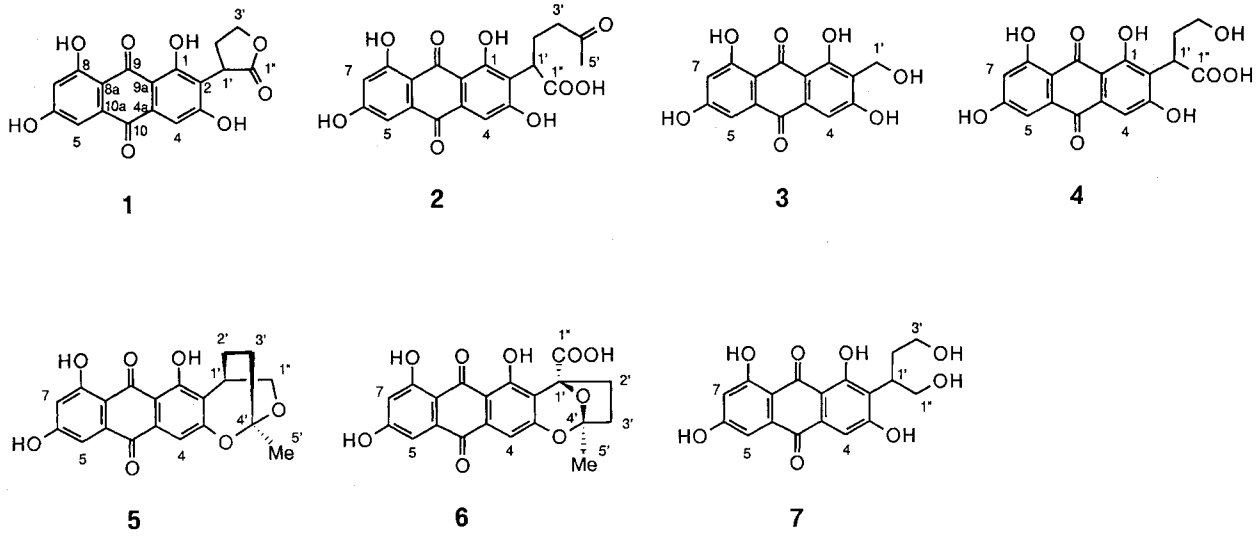
Paeciloquinones A to F and versiconol have been isolated as inhibitors of protein tyrosine kinases from the culture broth of the fungus *Paecilomyces carneus* P-177. The structures of the new anthraquinones were determined by spectroscopic methods, mainly ^{1}H NMR and ^{13}C NMR. The substitution pattern was established by investigation of the respective methylated derivatives.

In our search for naturally occurring inhibitors of the v-abl protein tyrosine kinase among secondary metabolites from microorganisms, a series of new inhibitors, named paeciloquinones, was isolated from cultures of the fungus *Paecilomyces carneus* P-177. In the preceding paper[1] we described the fermentation, isolation and biological properties of the paeciloquinones. Here we will present the structure elucidation and the physicochemical properties of these compounds.

As reported in the preceding paper the *Paecilomyces carneus* strain P177 produced 7 different metabolites. According to their UV and visible spectra these 7 components were closely related. One product could be identified as versiconol (**7**), a fungal metabolite which had previously been isolated from a strain of *Aspergillus versicolor*[2] and from cultures of an *Aspergillus parasiticus* treated with dichlorvos[3]. The physico-chemical characteristics of **7**, particularly the ^{13}C NMR data (Table 2) were in good agreement with the published ones[3]. For the determination of the structures of the new paeciloquinones the study of the methylated derivatives (Scheme 1) proved to be very useful. Unlike the acidic parent compounds **2**, and **6**, the more volatile methyl esters did not eliminate water during MS fragmentation and gave unequivocal EI-MS . Furthermore ^{1}H NOE experiments with the methylated derivatives proved to be very helpful for the assignment of the position of the side-chains.

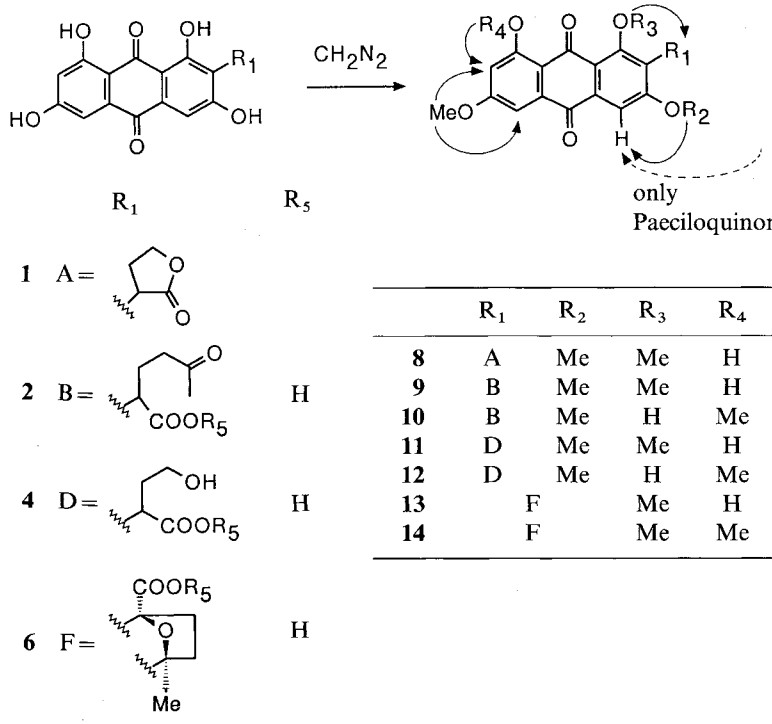
The NOE experiments were recorded as difference spectra. The correlation of the shifts of the protonated

Fig. 1. Chemical structures of paeciloquinones A (**1**), B (**2**), C (**3**), D (**4**), E (**5**), F (**6**) and of versiconol (**7**) isolated from *Paecilomyces carneus*.



Structures **5** and **6** represent the relative configuration of centers 1′ and 4′.

Scheme 1. Methylation products of paeciloquinones A (**1**), B (**2**), D (**4**) and F (**6**).



	R_1	R_2	R_3	R_4	R_5
8	A	Me	Me	H	
9	B	Me	Me	H	Me
10	B	Me	H	Me	Me
11	D	Me	Me	H	Me
12	D	Me	H	Me	Me
13	F		Me	H	Me
14	F		Me	Me	Me

The arrows indicated the NOE effects observed from the methyl groups. Moiety **6** represents the relative configuration.

Table 1. ^{1}H NMR chemical shifts of **1** to **6**.

Paeciloquinone	**1** A	**2** B	**3** C	**4** D[a]	**5** E	**6** F
1-OH	12.80 s br*	12.71 s*	12.66 s*		12.6 br	12.68 b*
3-OH/6-OH	11.5 br	11.3~4 br				12.0/11.4 b*
4	7.20 s	7.23 s	7.21 s	6.90 s br	6.83 s	7.02 s
5	7.11 d	7.12 d	7.12 d	7.08 d	6.96 d	7.12 d
7	6.59 d	6.59 d	6.59 d	6.53 d	6.47 d	6.59 d
8-OH	12.18 s br*	12.14 s*	12.20 s*	12.4 b*	11.95 br	
1′	4.48 m	3.95 dd	4.54 s	4.07 dd	3.48 m br	
2′	2.43 m	2.28/1.88 m		2.15/1.90 m	2.13/1.91 m	2.6/2.3 m*
3′	4.35 m	2.4/2.28 m		3.34 m	2.28/2.22 m	2.6/2.3 m*
5′		2.00 s			1.46 s	1.72 s
1″					4.16/4.05 dd/dt	13.36 b

Chemical shifts given in ppm. Solvent: DMSO-d_6. Temperature: ambient except for [a] at 60°C. Assignments with asterisks may be interchanged.

^{13}C atoms of **5** and **6** with those of the attached protons has been made with a PFG-HSQC (pulsed field gradient heteronuclear single quantum coherence) experiment[4]. Multiple bond connectivities between protons and carbons[5] have been used to assign all the carbon signals of **5** and **6**. A pulsed field gradient version of the original pulse sequence was applied[6].

Structure of Paeciloquinone A (**1**)

The HR-MS of **1** gives the molecular formula as $C_{18}H_{12}O_8$. The ^{1}H NMR spectrum of **1** (Table 1) displays the following structural fragments: one singlet aromatic signal, two aromatic signals with meta couplings, two phenolic hydrogen signals at 12.8 and 12.1 ppm possibly sharpened by hydrogen bridges, approximately two very broad phenolic hydrogen signals and, according to the chemical shift, a CH–CH_2–CH_2–O moiety. Comparison of the ^{13}C NMR data with those of versiconol[3] (Table 2) showed very good correlation for the carbons of the anthraquinone ring except for the connecting carbon atom 2 and clarified that part of the molecule. A ^{13}C NMR signal at 176 ppm indicated an ester or acid moiety and an additional ring system had to be in the side chain according to the elementary

Table 2. ^{13}C NMR chemical shifts of **1**, **2** and **4** to **7**.

Paeciloquinone	**1** A	**2** B	**4** D[a]	**5** E	**6** F[b]	**7** Versiconol
1	161.7 s	161.8 s	162.5 s*	160.0 s	160.0 s	163.0
2	117.7 s	119.9 s	118.8 s	125.0 s	120.5 s	123.1
3	162.7 s	≈163 s	≈171 s*	161.9 s	160.1 s	163.4
4	108.0 d	108.0 d	113.2 d	110.1 d	109.7 d	108.6 d*
4a	133.1 s	132.6 s	132.5 s	132.4 s	136.6 s*	132.2
5	108.7 d	108.9 d	108.0 d	108.4 d	110.2 d	108.6 d
6	165.1 s	165.3 s	163.8 s	165.7 s	166.9 s*	165.0
7	107.8 d	108.3 d	108.0 d	108.0 d	109.2 d	108.0 d*
8	164.2 s	164.1 s	164.3 s	164.3 s	166.4 s*	164.2
8a	≈108.7 s	108.3 s	109.0 s	109.2 s	110.4 s	108.2
9	188.7 s	188.8 s	186.9 s	188.4 s	191.0 s	189.0
9a	108.3 s	108.6 s	108.3 s	109.1 s	120.5 s	108.8
10	181.2 s	181.3 s	182.0 s	180.9 s	182.4 s	181.3
10a	134.9 s	134.9 s	135.0 s	134.9 s	135.6 s*	135.0
1′	34.6 d	38.3 d	40.9 d	27.6 d	85.8 s	35.3 d
2′	27.1 t	22.7 t	33.9 t	24.2 t	38.8 t	32.7 t
3′	66.7 t	40.3 t	59.6 t	31.6 t	38.4 t	60.0 t
4′		207.8 s		105.1 s	110.6 s	
5′		29.7 q		28.4 q	23.6 q	
1″	176.7 s	173.7 s	175.6 s	68.9 t	168.1 s[c]	62.9 t

Chemical shifts given in ppm. Solvent: DMSO-d_6 except for [b] in CD_3OD. Temperature: ambient except for [a] at 60°C. [c]: value in DMSO-d_6; in CD_3OD the signal could not be detected. Assignments with asterisks may be interchanged.

Table 3. ^{1}H NMR chemical shifts of the methylated derivatives **8** to **14**.

	8	**9**	**10**	**11**	**12**	**13**	**14**
4	7.65	7.62	7.31	7.64	7.33	7.46	7.36
5	7.28	7.27	7.42	7.28	7.44	7.26	7.30
7	6.70	6.70	6.79	6.70	6.80	6.69	6.79
1-OMe	3.88	3.85		3.90		3.82*	3.80*
3-OMe	4.00	3.96	3.93	3.97	3.95		
6-OMe	3.91	3.91	3.98*	3.92	3.98*	3.90*	3.93*
8-OMe			3.97*		3.97*		3.93*
1′	4.42	4.15	4.15	4.35	4.33		
2′	2.5	2.46/1.90	2.42/1.94	2.48/1.86	2.42/1.90	2.80/2.40	2.77/2.4
3′	4.54/4.38	2.46/2.28	2.42/2.30	3.60/3.41	3.58/3.40	2.40/2.23	2.4/2.20
5′		2.03	2.01			1.76	1.74
COOMe		3.60	3.60	3.61	3.60	3.81	3.80*

Chemical shifts given in ppm. Solvent: CD_2Cl_2. Temperature: ambient. Assignments with asterisks may be interchanged.

composition. This part was clarified by spectroscopic examination of the trimethyl derivative **8** (Scheme 1, Table 3): Upon irradiation of the 1-methyl group a NOE of 7% was observed on the 1′-methine proton defining the linkage of C-2 to C-1′. No further connectivities are hence possible apart from the 5-membered lactone ring of structure **1**. In the anthraquinone moiety NOE's of more than 20% from 3-methyl to H-4 and from 6-methyl to H-5 and H-7 were observed. As compound **1** shows no CD curve and as racemization of center 1′ during the slightly acidic workup is unlikely, **1** appears to represent a relatively rare case of a racemic natural product[7]. Since versiconol (**7**) is chiral, **1** might be biosynthesized as one enantiomer and racemization of the slightly acidic center 1′ might occur during the fermentation, when the compounds are exposed to the broth with pH 8.

Structure of Paeciloquinone B (**2**)

The IR spectrum of **2** indicates a carboxylic acid function. Although the HREI-MS gives an molecular formula of $C_{20}H_{14}O_8$, FAB-MS and elementary analysis clarify the actual formula as $C_{20}H_{16}O_9$. The ^{1}H NMR and ^{13}C NMR spectra document the following structural fragments: A substituted anthraquinone ring as in **1**, a singlet methyl group, a CH_2–CH_2–CH moiety and two carbonyl signals which are attributed to a ketone and an acid function. Selective reduction of the ketone by $LiAlH_4$ (data not shown) leads to a mixture of

diastereoisomers where the methyl groups are split into doublets supporting the methyl ketone. Analysis of the COSY reveals the side chain 1′ to 5′ of the starting material **2**. Structure **2** is supported by the methylated compound **9** where proton 1′ upon irradiation of the 1-methyl group at 3.86 ppm gives rise to a NOE of 10%. A fully coupled ^{13}C NMR spectrum confirms the proposed structure. Compound **2** shows no signal in the CD spectrum and is therefore also racemic at C-1′.

Structure of Paeciloquinone C (3)

Molecular formula and ^{1}H NMR of paeciloquinone C lead to structure **3** in a straightforward way: The singlet at 4.54 ppm corresponds to a CH_2–OH moiety which is linked to C-2 of the anthraquinone ring system. The structurally simple compound **3** has already been described as a synthetic intermediate by Japanese researchers[8].

Structure of Paeciloquinone D (4)

The molecular formula $C_{18}H_{14}O_9$ for **4** was deduced from the FAB-MS and high-resolution EI-MS. This elementary composition and the similarity of the ^{1}H NMR and ^{13}C NMR data suggest that paeciloquinone D is an analogue to paeciloquinone A with an opened lactone ring. Methylation leads to derivative **11** which has four additional methyl groups according to EI-MS and ^{1}H NMR, one methyl ester (3.6 ppm) and three methoxy groups. The methyl ether protons show the expected NOE effects on the aromatic protons and upon irradiation of the 1-methyl group, the 1′-methine proton gives rise to a NOE of 11% corroborating structure **4**. Both compounds **1** and **4** are genuine products of *Paecilomyces carneus* and not artifacts, as the peaks of both compounds were detected directly in the culture filtrates by HPLC. Just as the related compound **1**, paeciloquinone D shows no CD curve and is therefore racemic at center 1′.

Structure of Paeciloquinone E (5)

From HREI-MS the molecular formula of **5** was determined as $C_{20}H_{16}O_7$. The ^{1}H NMR spectrum displays the usual aromatic protons of the substituted anthraquinone ring system, a CH_2–CH_2–CH–CH_2–O moiety and a singlet methyl group. Since no additional carbonyl groups or double bonds were observed in ^{13}C NMR, two additional ring systems must be present according to the elemental composition. Analysis of the ^{13}C NMR data shows in addition to the above structural elements a quaternary carbon at 105 ppm suggesting a ketal or a semiketal function. According to its chemical shift, the methyl group displaying a singlet signal must be linked directly to this group.

Long range ^{1}H-^{13}C connectivities were used to confirm the structure. Those cross peaks proving the structure of the proposed bicyclic ring system and its attachment to the anthraquinone chromophore were of particular interest. Cross peaks from H-1′ to carbon atoms 1, 2 and 3 identify the bond between carbons 1′ and 2. Long range couplings from both protons H-1″ to the quaternary carbon 4′ are in support of a cyclic ether link between these two carbons. Finally the protons 5′ display a four bond connectivity to the aromatic C-3, in addition to the link to C-4′. According to the CD spectrum in methanol compound **5** is chiral. However, the absolute configuration drawn in Fig. 1 is arbitrary.

Structure of Paeciloquinone F (6)

Paeciloquinone F was produced by *Paecilomyces carneus* if peanut meal was added to the fermentation medium or by increasing the fermentation temperature from 28° to 33°. HRFAB-MS points to a molecular formula of $C_{20}H_{14}O_9$. The ^{1}H NMR and ^{13}C NMR data disclose the following structural fragments in addition to the usual substituted anthraquinone ring system: a C–CH_2–CH_2–C moiety, a singlet methyl group and three quaternary carbons at 86, 110 and 168 ppm. The latter has to be part of an aliphatic acid function, as shown in the IR spectrum (1720 cm^{-1}) and by the methylated derivatives **13** and **14** where methyl esters are formed. These derivatives provide the following additional information: The oxygen at the aromatic carbon 3 cannot be methylated by CH_2N_2 and must consequently be part of a cyclic ether system. According to the elementary composition two ring systems should be present apart from the anthraquinone moiety and two oxygens should be part of those rings. An epoxide ring can be excluded since the compound is stable towards diluted H_2SO_4 at room temperature. For derivative **13** and **14** as well as for paeciloquinone F itself a weak but reproducible NOE effect of 3% is observed on H-4 upon irradiation of the methyl group at 1.7 ppm disclosing their spatial closeness.

Long range couplings in CD_3OD were used to define the structure of side chain 1′ to 5′. The following long range connectivities are particularly worth mentioning: from H-2′ to C-1′ and to the aromatic C-2, from H-3′ to C-1′, C-2′ and C-4′, from H-5′ to C-3, C-3′ and C-4′ and from H-4 to C-4′. No cross peaks involving C-1″ were observed. As in compound **5**, a four bond connectivity from H-5′ to the aromatic C-3 confirms the

3-4'-ether bond.

The chemical shifts of the quaternary carbon atoms 1' and 4' were estimated by comparison to averufin[9] taking into consideration the structural differences between the two compounds (substitution and ring strain). The NOE of 3% on the proton at 2.1 ppm upon irradiation of the 1-methyl group of **13** in C_6D_6 is much weaker than in the other compounds of this series and therefore well in range for the proposed structure. All this evidence supports the proposed assignment of structure **6** to paeciloquinone F. According to the CD spectrum in methanol the compound **6** is chiral. However, the assigned absolute configuration of **6** is arbitrary.

Experimental

The following instruments were used in this study: mass spectrometer CEC-121 B, VG 70-4SE (for HREI-MS), MAT-90; NMR: Varian VXR-400 S and Varian Unity 500, UV/VIS spectrophotometer Perkin Elmer Lamda 5, FT-IR spectrophotometer Bruker IFS-48. All ^{1}H-NMR were recorded at 400 MHz and all ^{13}C NMR at 100 MHz except where stated. Semipreparative HPLC was performed with a Beckman 110B solvent delivery module, a Kratos SF769 detector and a silica gel column Nucleosil 100-5, 100 Å, 5 μm 16 × 250 mm.

Preparation of **8**

To a stirred suspension of paeciloquinone A (25 mg) in methanol (2 ml) an etheral solution of CH_2N_2 was added (5 ml)[10]. The clear solution was stirred for 7 minutes and the solvent was removed by a stream of nitrogen. The pure product was obtained by semipreparative silica gel HPLC (CH_2Cl_2, saturated with water; 8 ml/minutes; 300 nm; 5 runs; Rt 4.7 minutes): 5 mg; MP >210°C.

Data of **8**: orange crystals from MeOH, MP >210°C, EI-MS: *m/z* 398 (100, M^+), 381 (29), 380 (23), 369 (70), 339 (35), 337 (22), 325 (33), 323 (38), 312 (24), 311 (49), 43 (25). ^{1}H NMR: see Table 3

Preparation of **9** and **10**

10 ml of an etheral solution of CH_2N_2 was added to a stirred suspension of paeciloquinone B (30 mg) in methanol (3 ml). The clear solution was stirred for 30 minutes and the solvent was removed by a stream of nitrogen. The pure products were obtained by semipreparative silica gel HPLC (CH_2Cl_2-2-PrOH, 99.5:0.5, saturated with water; 8 ml/minutes; 295 nm; 4 runs) to give 6.3 mg of 1,3,6-trimethoxy-paeciloquinone B methyl ester **9** (Rt 3.7 minutes; MP 160~163°C) and 6.5 mg of 3,6,8-trimethoxy-paeciloquinone B methyl ester **10** (Rt 5.3 minutes; MP >210°C).

Data of **9**: orange crystals, MP 160~163°C. EI-MS: *m/z* 456 (30, M^+), 424 (86), 367 (57), 339 (100) 45 (57), 43 (88). ^{1}H NMR: see Table 3.

Data of **10**: orange crystals, MP >210°C. EI-MS: *m/z* 456 (8, M^+), 424 (49), 367 (100), 354 (29), 339 (33). ^{1}H NMR: see Table 3.

Preparation of **11** and **12**

To a stirred suspension of paeciloquinone D (8.7 mg) in methanol (1 ml) an etheral solution of CH_2N_2 was added (5 ml). After stirring during 30 minutes the solvent was removed by a stream of nitrogen. The pure products were obtained by semipreparative silica gel HPLC (CH_2Cl_2-2-PrOH, 98.8:1.2, saturated with water; 8 ml/minutes; 285 nm; 2 runs) to give 1.6 mg of 1,3,6-trimethoxy-paeciloquinone D methyl ester **11** (Rt 5.8 minutes; MP 124~130°C) and 1.7 mg of 3,6,8-trimethoxy-paeciloquinone D methyl ester **12** (Rt 8.0 minutes; MP 173~176°C).

Data of **11**: orange crystals, MP 124~130°C. EI-MS: *m/z* 399 (40, $M-CH_3O$), 398 (79), 340 (24), 339 (100), 45 (32). ^{1}H NMR: see Table 3.

Data of **12**: orange crystals, MP 173~176°C. EI-MS: *m/z* 399 (20, $M-CH_3O$), 398 (78), 383 (24), 369 (37), 367 (40), 354 (51), 341 (57), 339 (100), 313 (45), 43 (82). ^{1}H NMR: see Table 3.

Preparation of **13** and **14**

To a stirred suspension of paeciloquinone F (20 mg) in methanol (2 ml) an etheral solution of CH_2N_2 was added (10 ml). Stirring of the clear red solution was terminated after 15 minutes and the solvent was removed by a stream of nitrogen. The pure products were obtained by semipreparative silica gel HPLC (CH_2Cl_2-heptane, 80:20, saturated with water; 8 ml/minute; 285 nm; 8 runs) to give 6.4 mg of 1,6-dimethoxy-paeciloquinone F methyl ester **13** (Rt 3.6 minutes) and 4.4 mg of 1,6,8-trimethoxy-paeciloquinone F methyl ester **14** (Rt 6.6 minutes; MP >210°C).

Data of **13**: EI-MS: *m/z* 440 (58, M^+), 381 (74), 43 (100). ^{1}H NMR: see Table 3.

Data of **14**: orange crystals from MeOH, MP >210°C. EI-MS: *m/z* 454 (54, M^+), 411 (58), 395 (100), 365 (72), 351 (61). ^{1}H NMR: see Table 3.

Data of **1**: yellow crystals from MeOH, MP >350°C. HREI-MS Found: *m/z* 356.051 Cacld for $C_{18}H_{12}O_8$: 356.053, EI-MS: *m/z* 356 (80, M^+), 338 (100), 325 (24), 312 (30), 311 (24), 310 (53), 297 (88), 44 (30). UV λ_{max}^{MeOH} nm (ε) 203 (18,000), 222 (27,300), 262 (16,100), 294 (20,200), 314 (21,300), 470 (6,570). FT-IR (CH_2Cl_2) cm^{-1} 3300 br, 2920, 1730, 1690, 1670, 1625, 1600, 1480, 1450, 1430, 1400, 1330, 1290, 1260, 1230, 1200, 1180, 1130, 1100, 1030, 1000, 850, 770, 720, 620. ^{1}H NMR: see Table 1. ^{13}C NMR: see Table 2.

Data of **2**: orange crystals from water, MP 240~260°C dec.

Anal Calcd for $C_{20}H_{16}O_9 \cdot \frac{1}{2}H_2O$:
C 58.69, H 4.19, O 37.12
Found: C 58.73, H 4.11, O 36.88

HREI-MS Found: *m/z* 382.067 Cacld for $C_{20}H_{14}O_8$

($M-H_2O$): 382.065 FAB-MS: 401 ($M+H$). UV λ_{max}^{MeOH} nm (ε) 204 (20,700), 223 (30,300), 262 (15,900), 296 (31,000), 314 (21,300), 462 (9,400). FT-IR (KBr) cm^{-1} 3410, 1760, 1680, 1630, 1600, 1580, 1470, 1440, 1410, 1320, 1260, 1210, 1200, 1170, 1090, 1050, 870, 775, 625. ^1H NMR: see Table 1. ^{13}C NMR: see Table 2.

Data of **3**: orange solid from MeOH, MP >300°C. HRFAB-MS (negative mode) Found: *m/z* 301.0315 Cacld for $C_{15}H_9O_7$ ($M-H^-$): 301.0348. FT-IR (KBr) cm^{-1} 3410 br., 2930, 1610, 1445, 1400, 1310, 1270, 1200, 1170, 1120, 1090, 1040, 775, 625. ^1H NMR: see Table 1. ^{13}C NMR: see Table 2.

Data of **4**: orange crystals from MeOH, MP >300°C. FAB-MS: 375 ($M+H$). HREI-MS Found: *m/z* 356.0518. Cacld for $C_{18}H_{12}O_8$ ($M-H_2O$): 356.0532. EI-MS: *m/z* 356 (27, $M-H_2O$), 338 (49), 326 (20), 312 (70), 311 (24), 310 (35), 309 (20), 298 (36), 297 (100; $C_{16}H_9O_6$), 284 (52), 69 (45), 55 (36). FT-IR (CH_2Cl_2) cm^{-1} 3430 br., 2990, 2950, 1670, 1620, 1600, 1570, 1480, 1440, 1390, 1330, 1290, 1270, 1210, 1170, 1130, 1090, 1050, 1020, 775. ^1H NMR: see Table 1. ^{13}C NMR: see Table 2.

Data of **5**: orange crystals from MeOH, MP 212~214°C. HREI-MS Found: *m/z* 368.0907 Cacld for $C_{20}H_{16}O_7$: 368.0896. EI-MS: *m/z* 368 (14, M^+), 311 (28), 310 (100, $C_{17}H_{10}O_6$), 297 (24), 43 (22). FT-IR (KBr) cm^{-1} 3380, 2940, 1670, 1620, 1570, 1470, 1400, 1310, 1260, 1190, 1160, 1110, 1080, 1050, 1020, 860, 830, 770. ^1H NMR (500 MHz; DMSO-d_6): see Table 1. ^{13}C NMR (120 MHz; DMSO-d_6): see Table 2. CD-spectrum (MeOH): nm (θ) 442 (−360), 397 (−400), 330 (930), 295 (−720), 250 (−950), 224 (−3000).

Data of **6**: yellow crystals from CH_2Cl_2/EtOH, MP 201~205°C. HRFAB-MS (neg. mode) Found: 397.0553. Cacld for $C_{20}H_{13}O_9$ ($M-H^-$) 397.0560. UV λ_{max}^{MeOH} nm (ε) 454 (8,900), 293 (26,000), 266 (16,000), 224 (29,000). FT-IR (KBr) cm^{-1} 3400 br., 3330, 3080, 2960, 1720, 1670, 1620, 1570, 1440, 1390, 1310, 1280, 1230, 1200, 1190, 1170, 1070, 870, 790, 780. ^1H NMR: see Table 1. ^{13}C NMR (120 MHz; CD_3OD): see Table 2. CD-spectrum (MeOH): nm (θ) 453 (+170), 433 (+210), 410 (+250), 327 (+44), 243 (−1500), 220 (+340).

Data of **7**: CD-spectrum (MeOH): nm (θ) 459 (−210), 442 (−200), 394 (−510), 325 (710), 291 (−210), 270 (590), 228 (−2300).

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