Polyoxygenated Cyclohexene Derivatives from *Uvaria rufa*

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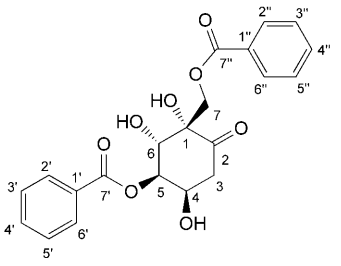
Four new polyoxygenated cyclohexene derivatives, uvarirufone A (**1**) and uvarirufols A–C (**2**–**4**), along with ten related known compounds, were isolated from the EtOH extract of the aerial parts of *Uvaria rufa* BL. Their structures and absolute configurations were determined by in-depth spectroscopic and spectrometric methods in combination with molecular modeling.

Introduction. – The genus *Uvaria* (Annonaceae) is widely distributed over the tropical zone of Asia, Africa, and Australia [1], with *ca.* 10 species occurring in Southern China. Phytochemical investigation of this genus has led to the isolation of a number of polyoxygenated cyclohexene derivatives [1][2], some of which show interesting biological properties such as antileukemic and antimalarial activities [3], as well as inhibition of nucleoside transport [4].

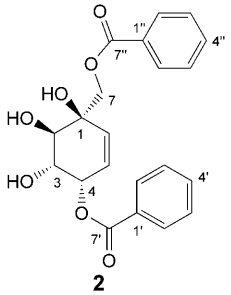
In China, *Uvaria rufa* BL. grows mainly in the Provinces Hainan, Guangdong, and Yunnan, as well as in some other countries in Southern Asia [5]. The species growing in Thailand has been studied some time ago, and several flavonoids were reported [6]. However, *U. rufa* growing in China has not previously been investigated phytochemically.

Herein, we report the isolation and characterization of four new polyoxygenated cyclohexene derivatives, uvarirufone A (**1**) and uvarirufols A–C (**2**–**4**), along with ten known compounds, tonkinenin A (**5**) [7], 2-*O*-benzoyl-3-*O*-debenzoylzeylenone (**6**) [8], uvarigranol B (**7**) [9], zeylenol (**8**) [10], uvarigranol F (**9**) [11], 1-epizeylenol (**10**) [12], grandifloracin (**11**) [4], grandiflorone (**12**) [4], 1,6-desoxypipoxide (**13**) [13], and tingtanoxide (**14**) [14].

Results and Discussion. – Uvarirufone A (**1**), obtained as a colorless amorphous powder, has the molecular formula $C_{21}H_{20}O_8$, as determined by HR-EI-MS (*m*/*z* 278.0795 ([*M* – BzOH]$^+$)) and positive-mode ESI-MS (*m*/*z* 423 ([*M* + Na]$^+$)). All the 21 C-atoms were resolved in the ^{13}C-NMR (DEPT) spectrum (see *Table 1* in the *Exper. Part*), including one CH_2, 14 CH, and six quaternary C-atoms. The IR spectrum of **1** showed the presence of monosubstituted phenyl rings (1601, 1586, 1500, and 712) [10], as well as ester (1728) and keto (1703 cm^{-1}) functions. The presence of two benzoyl (Bz) groups was evident from the ^{1}H-NMR signals at δ(H) 7.41–8.09 (10 H) (see *Table 2* in the *Exper. Part*) and the corresponding resonances in the ^{13}C-NMR spectrum,



1



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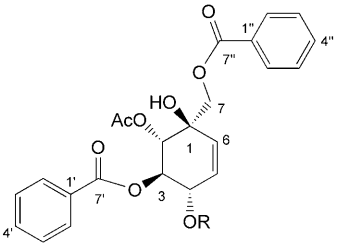
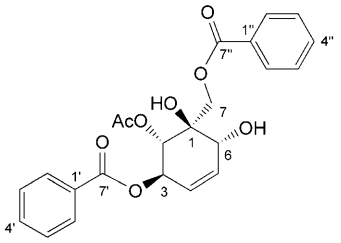


3 R = H
3a R = Bz



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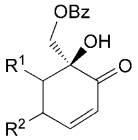
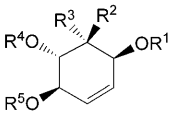
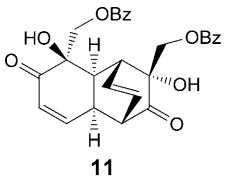


	R^1	R^2
5	α-OH	α-OBz
6	β-OBz	α-OH



	R^1	R^2	R^3	R^4	R^5
7	H	CH_2OBz	OH	Ac	Bz
8	H	CH_2OBz	OH	H	Bz
9	Bz	CH_2OH	OH	H	Bz
10	H	OH	CH_2OBz	H	Bz



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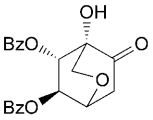

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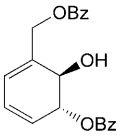

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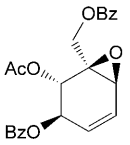

14

Ac = Acetyl, Bz = benzyol

and corroborated by the typical EI-MS fragment ions at *m/z* 77, 105, and 122 ([BzOH]$^+$). A total of 17 H-atoms were observed in the ^{1}H-NMR spectrum, and the missing three ones were considered to be exchangeable protons. One keto group at δ(C) 205.2 and six signals in the range 42.3–79.0 were observed, implying that **1** was probably a polyoxygenated methylcyclohexanone derivative [7][8].

The planar structure[1]) of **1** was determined by means of 2D-NMR techniques, especially ^{1}H,^{1}H-COSY and HMBC experiments (*Fig. 1*). In the ^{1}H,^{1}H-COSY spectrum, the spin system $CH_2CH(O)CH(O)CH(O)$ was revealed by the correlation pairs CH_2–C(3)/H–C(4), H–C(4)/H–C(5), and H–C(5)/H–C(6). For a methylcyclohexanone

[1]) Arbitrary atom numbering; for systematic names, see *Exper. Part.*

skeleton, the oxygenated quaternary C-atom at δ(C) 79.0 was only assignable to C(1) [15]. The keto C=O group at δ(C) 205.2 was located at C(2), on the basis of the multiple HMBC correlations between CH_2–C(3) and both C(1) and C(2), and between H–C(4) and C(2). The HMBC correlations between CH_2–C(7) and both C(1) and C(6), and between H–C(5) and C(1) allowed the attachment of C(6) and C(7) to C(1), respectively. The two BzO groups were linked to C(5) and C(7), as inferred from the strong HMBC correlations H–C(5)/C(7′) and CH_2–C(7)/C(7″), respectively.

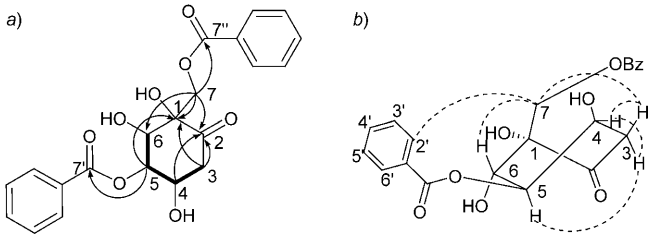

Fig. 1. a) *^{1}H,^{1}H-COSY* (▬) *and selected HMBC* (H → C) *correlations of* **1**. b) *Key NOESY* (···) *correlations of* **1**.

The relative configuration of the cyclohexanone ring was established with the aid of a NOESY spectrum (*Fig. 1*). The NOESY correlations of H_α–C(3)/H–C(5) and H_a–C(7)/H_β–C(3) indicated that the cyclohexanone ring adopted a 'twist-boat' conformation. Thus, H–C(5) and CH_2–C(7) were arbitrarily assigned α- and β-configuration, respectively. Correlations of H–C(4) with both H_α–C(3) and H_β–C(3) in the NOESY spectrum implied that they were present in a gauche relationship, suggesting that H–C(4) was α-oriented. H–C(6) was assigned β-orientation based on the NOESY correlation between CH_2–C(7) and H–C(6). A 3D structure of **1** (*Fig. 2*), generated by molecular modeling (CS Chem 3D Prom, Version 9.0) using the MM2 force field, was consistent with the proposed relative configuration and conformation determined from the NOESY data.

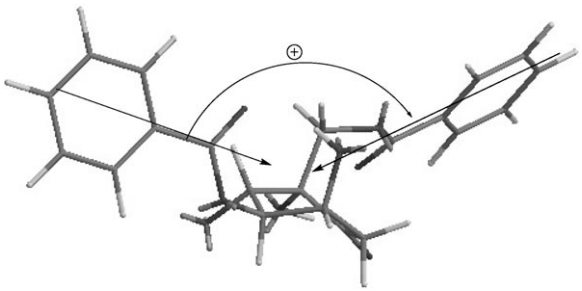

Fig. 2. *Computer model and chiral analysis of* **1**

The CD spectrum of **1** showed a split *Cotton* effect (*Fig. 3*) at 236 nm ($\Delta\varepsilon = +13.6$) and 219 nm ($\Delta\varepsilon = -2.15$), centered at 228 nm, corresponding to the UV maximum of the two BzO groups. This behavior results from dipole–dipole interaction of the elec-

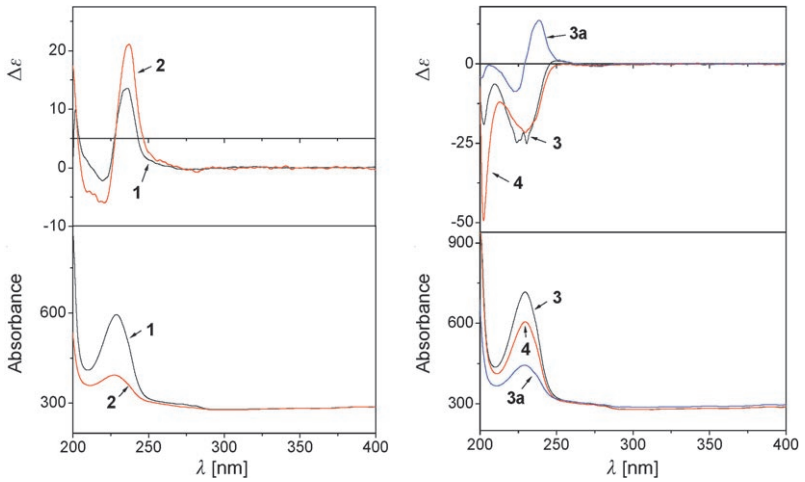

Fig. 3. *CD and UV Spectra of* a) **1** *and* **2**, *and of* b) **3**, **3a**, *and* **4**

tronic transition moments of the two benzoate chromophores [15], indicating that they are oriented in a clockwise manner (*Fig. 2*). The absolute configuration of **1** was, hence, (1*S*,4*R*,5*R*,6*S*).

The HR-EI mass spectrum of uvarirufol A (**2**) showed the $[M+H-H_2O]^+$ ion at *m*/*z* 367.1191, in accord with the molecular formula $C_{21}H_{20}O_7$ [11][14][16]. The ^{1}H-NMR spectrum of **2** (*Table 2*) was identical with that of the known compound piperenol B isolated from *Piper cubeb* [15]. 1D- and 2D-NMR spectroscopic analyses (*Fig. 4*) indicated that both compounds had the same planar structure and relative configuration. However, the optical rotation of **2** ($[\alpha]_D^{20}=-37.6$) differed from that of piperenol B ($[\alpha]_D^{20}=+50$) [15], suggesting that these two compounds are enantiomers.

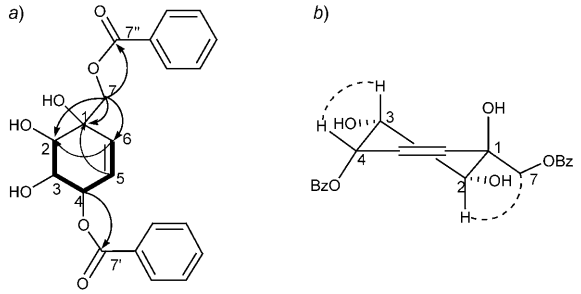

Fig. 4. a) *^{1}H,^{1}H-COSY* (▬) *and selected HMBC* (H → C) *correlations of* **2**. b) *Key ROESY* (···) *correlations of* **2**.

Compound **2** showed a split *Cotton* effect at 237 nm ($\Delta\varepsilon=+21.1$) and 221 nm ($\Delta\varepsilon=-6.0$), centered at 228 nm, corresponding to the exciton coupling of two benzoate chromophores (see *Fig. 3*). In contrast, piperenol B exhibited a strong negative exciton coupling at 237 and 215 nm, which further supported opposite absolute configurations.

Uvarirufol B (**3**) was shown to have the molecular formula $C_{23}H_{22}O_8$, as determined by HR-EI-MS (*m/z* 409.1292 ($[M+H-H_2O]^+$). ^{13}C- and ^{1}H-NMR Spectroscopic analyses (see *Tables 1* and *2*, resp., in the *Exper. Part*) indicated two BzO groups, one AcO function, one disubstituted C=C bond, three oxygenated CH, one oxygenated CH_2, and one oxygenated quaternary C-atom – characteristic of a polysubstituted methylcyclohexene derivative. In the ^{1}H,^{1}H-COSY spectrum of **3**, the spin system CH(O)CH(O)-CH(O)CH=CH was revealed by the correlations H–C(2)/H–C(3), H–C(3)/H–C(4), H–C(4)/H–C(5), and H–C(5)/H–C(6). HMBC correlations from both H–C(2) and H–C(5) to C(1) allowed the linkage of C(6) and C(2) to C(1) to construct the cyclohexene ring. The oxygenated CH_2 was located at C(1), on the basis of the HMBC correlations of CH_2–C(7) to C(1), C(2), and C(6). The two BzO groups were placed at C(3) and C(7), according to the HMBC correlations H–C(3)/C(7′) and CH_2–C(7)/C(7″), respectively (*Fig. 5*). The AcO group was located at C(2), on the basis of the HMBC correlation between H–C(2) and the acetyl C=O group.

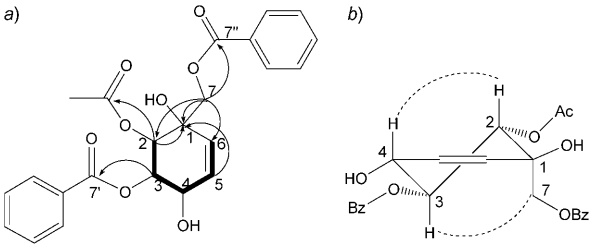

Fig. 5. a) *^{1}H,^{1}H-COSY* (▬) *and selected HMBC* (H → C) *correlations of* **3**. b) *Key ROESY* (···) *correlations of* **3**.

In the cyclohexene ring of **3**, strong ROESY correlations for CH_2–C(7)/H–C(3) and H–C(2)/H–C(4) showed that two correlating pairs were in a 1,3-diaxial relationship on the cyclohexene ring (*Fig. 5*), which, in turn, adopted a 'half-chair' conformation. The *J*(2,3) value of 11.1 Hz also indicated that H–C(2) and H–C(3) were in axial positions. The relative configuration of **3** was, thus, determined as depicted in *Fig. 5*.

The CD spectrum of **3** displayed very complex *Cotton* effects at 230 nm ($\Delta\varepsilon = -24.5$), 228 nm (−21.7), and 224 nm (−24.8), and it was very difficult to assign the corresponding chromophores. To determine the absolute configuration of **3**, we, thus, esterified **3** to **3a** by introducing a BzO group in 4-position. The CD spectrum of **3a** exhibited a positive *Cotton* effect at 239 nm ($\Delta\varepsilon = +13.7$), and a negative one at 222 nm ($\Delta\varepsilon = -8.7$), centered at the UV maximum of 229 nm. These effects are caused by the electronic transition dipole of the two vicinal BzO groups at C(3) and C(4), indicating that the two chromophores are oriented in a clockwise manner (*Fig. 6*). Hence, the absolute configuration of **3** was established as (1*R*,2*S*,3*R*,4*S*).

Uvarirufol C (**4**) has the molecular formula $C_{23}H_{22}O_8$, as determined by HR-EI-MS (*m/z* 409.1277 ($[M+H-H_2O]^+$)). Comparison of the ^{1}H- and ^{13}C-NMR data of **4** with those of the known compounds uvarigranol B (**7**) [9] and 1-epizeylenol 6- acetate [12] indicated that they share the same planar structure, and this was confirmed by ^{1}H,^{1}H-COSY and HMBC experiments (*Fig. 7*). The main difference was the configuration at

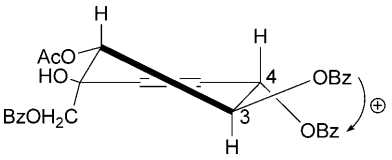

Fig. 6. *Exciton coupling in* **3a**

C(1) and C(6), as judged from ^{1}H-NMR signals for H–C(2) and H–C(6). In the NOESY spectrum of **4** (*Fig. 7*), the correlations for CH_2–C(7)/H–C(3) and H–C(2)/H–C(6) suggested that the H-atoms in each pair were in a 1,3-diaxial relationship on the cyclohexene ring, which, in turn, adopted a 'half-chair' conformation. CH_2–C(7) and H–C(3) were arbitrarily assigned as α-oriented; thus, H–C(2) and H–C(6) were β-oriented. A J(2,3) value of 8.2 Hz (literature value: 7.6 Hz [12]) further showed that H–C(2) and H–C(3) were in axial positions.

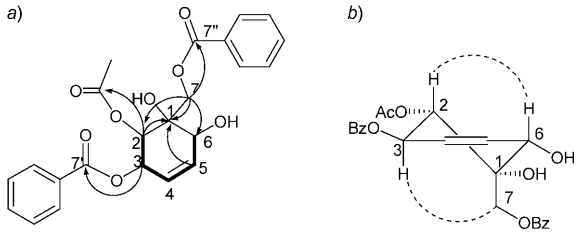

Fig. 7. a) *^{1}H,^{1}H-COSY* (▬) *and selected HMBC* (H → C) *correlations of* **4**. b) *Key NOESY* (···) *correlations of* **4**.

The absolute configuration of **4** was determined by CD analysis. The CD spectrum of **4** exhibited a negative *Cotton* effect at 230 nm ($\Delta\varepsilon = -21.6$) due to exciton coupling between the BzO group at C(3) and the nearby C=C bond (allylic benzoate; *Fig. 8*) [17]. Thus, the absolute configuration of **4** was identified as (1*S*,2*S*,3*R*,6*R*).

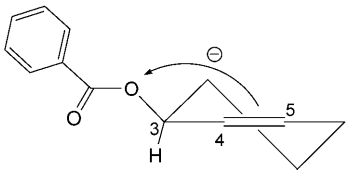

Fig. 8. *Exciton coupling in* **4**

The known compounds were identified as tonkinenin A (**5**), 2-*O*-benzoyl-3-*O*-debenzoylzeylenol (**6**), uvarigranol B (**7**), zeylenol (**8**), uvarigranol F (**9**), 1-epizeylenol (**10**), grandifloracin (**11**), grandiflorone (**12**), 1,6-desoxypipoxide (**13**), and tingtanoxide (**14**), on the basis of their EI-MS, ^{1}H- and ^{13}C-NMR data.

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Experimental Part

General. All solvents were of anal. grade (*Shanghai Chemical Plant*, Shanghai, P. R. China). Column chromatography (CC): silica gel (200–300 mesh), silica gel *H60*, *C18* reversed-phase (RP) silica gel (250 mesh; *Merck*), and *MCI* gel (*CHP20P*, 75–150 μm; *Mitsubishi Chemical Industries, Ltd.*). TLC: precoated silica gel GF_{254} plates (*Qingdao Haiyang Chemical Plant*, Qingdao, P. R. China). UV Spectra: *Hitachi U-2010*. Optical rotation: *Perkin-Elmer-341* polarimeter. CD spectra: *JASCO J-810* instrument; λ in nm ($\Delta\varepsilon$ in mdeg). IR spectra: *Perkin-Elmer-577* spectrometer; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker AM-400* spectrometer; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. EI-MS (70 eV) and ESI-MS: *Finnigan MAT-95* and *Finnigan LCQ-DECA* instruments, resp; in *m*/*z* (rel.%).

Plant Material. The aerial parts of *Uvaria rufa* BL. were collected from Hainan Island, China, and were authenticated by Prof. *Shi-Man Huang*, Hainan University. A voucher specimen (Uv-rufa-2004-1Y) has been deposited at the Shanghai Institute of Materia Medica.

Extraction and Isolation. U. rufa (2 kg) was extracted with 95% EtOH at r.t. After solvent evaporation, a green-dark residue (282 g) resulted, which was partitioned between AcOEt and H_2O. The org. and aq. layers were concentrated to afford an AcOEt-soluble fraction (86 g) and a water-soluble fraction (190 g). The AcOEt-soluble extract was subjected to column chromatography (CC) (SiO_2; petroleum ether (PE)/Me_2CO 50:1 → 1:1): *Fr. 1–4*. *Fr. 3* (24.4 g) was subjected to CC (*MCI* gel; MeOH/H_2O 6:4 → 9:1): *Fr. 3a–3f*. *Fr. 3a* was subjected to CC (SiO_2; PE/AcOEt 5:1) to afford a major compound, which was further purified by CC (SiO_2; PE/Me_2CO 4:1) to yield **11** (60 mg). *Fr. 3b* was subjected to CC (SiO_2; PE/AcOEt 5:1 → 1:1): *Fr. 3b.1–Fr. 3b.5*. *Fr. 3b.1* and *Fr. 3b.2* were subjected to CC (SiO_2; PE/Me_2CO 4:1) to afford **5** (652 mg) and **7** (53 mg), resp. *Fr. 3b.3* was separated by CC (SiO_2; PE/Me_2CO 5:1): *Fr. 3b.3.1* and *Fr. 3b.3.2*. *Fr. 3b.3.1* was further chromatographed (SiO_2; $CHCl_3$/MeOH 200:1) to give two compounds, which were each separated by CC (SiO_2; hexane/AcOEt 2:1) to yield **3** (12 mg) and **6** (16 mg), resp. *Fr. 3b.3.2* was purified by CC (SiO_2; $CHCl_3$/MeOH 200:1) to yield **1** (251 mg). *Fr. 3b.4* was subjected to CC (SiO_2; 1. PE/Me_2CO 4:1; 2. $CHCl_3$/MeOH 100:1) to provide **8** (213 mg) and **9** (15 mg) in turn. *Fr. 3b.5* was chromatographed (SiO_2; PE/Me_2CO 3:1) to afford **2** (62 mg). *Fr.*

Table 1. *^{13}C-NMR Data of* **1**–**4**. Arbitrary atom numbering; recorded at 125 MHz; δ in ppm.

	1[a])	**2**[a])	**3**[a])	**4**[b])
C(1)	79.0	71.6	74.1	75.7
C(2)	205.2	68.7	75.5	75.3
C(3)	42.3	68.5	76.5	72.7
C(4)	67.0	69.1	71.3	127.0
C(5)	73.5	127.0	130.2	131.8
C(6)	70.7	134.2	129.7	63.3
C(7)	64.6	67.0	66.6	65.0
C(1′)	129.2	129.6	129.0	130.6
C(2′,6′)	129.8	129.7	129.9	130.3
C(3′,5′)	128.6	128.4	128.6	129.4
C(4′)	133.6	133.2	133.7	134.2
C(7′)	166.3	166.3	167.3	166.3
C(1″)	129.2	129.6	129.4	130.7
C(2″,6″)	129.7	129.6	129.9	130.5
C(3″,5″)	128.4	128.4	128.6	129.4
C(4″)	133.4	133.2	133.4	134.1
C(7″)	166.4	166.3	166.4	166.5
*C*OMe	–	–	171.5	170.4
CO*Me*	–	–	20.7	20.7

[a]) Solvent: $CDCl_3$. [b]) Solvent: (D_6)acetone.

3e was subjected to CC (SiO_2; PE/AcOEt 7:1) to afford **10** (112 mg). *Fr. 3f* was separated by CC (SiO_2; PE/AcOEt 7:1): *Fr. 3f.1* and *Fr. 3f.2*. *Fr. 3f.1* was further separated by CC (SiO_2; $CHCl_3$/MeOH 500:1) to yield **4** (33 mg) and **13** (136 mg). *Fr. 3f.2* was purified by CC (SiO_2; PE/Me_2CO 6:1) to give two major fractions, which were further purified by CC (SiO_2; $CHCl_3$/MeOH 400:1) to yield **12** (18 mg) and **14** (8 mg), resp.

Uvarirufone A (=*{(1S,2S,3R,4R)-1,2,4-Trihydroxy-6-oxo-3-[(benzoyl)oxy]cyclohexyl}methyl Benzoate*; **1**). Colorless powder. M.p. 146–147°. UV (MeOH): 228 (5.53), 273 (4.53). $[\alpha]_D^{20} = +57.1$ ($c = 0.3$, MeOH). CD (MeOH): 236 (+3.6), 219 (−2.15). IR (KBr): 3458, 2922, 1728, 1703, 1601, 1586, 1500, 1452, 1329, 1282, 1117, 1072, 1026, 712. ^{1}H-NMR: see *Table 2*. ^{13}C-NMR: see *Table 1*. ESI-MS (pos.): 401 ($[M+H]^+$), 423 ($[M+Na]^+$). EI-MS: 278 (2.3, $[M-BzOH]^+$), 122 (13.9), 105 (100), 77 (81.6). HR-EI-MS: 278.0795 ($[M-BzOH]^+$, $C_{14}H_{14}O_6^+$; calc. 278.0790).

Uvarirufol A (=*{(1R,4S,5R,6R)-1,5,6-Trihydroxy-4-[(benzoyl)oxy]cyclohex-2-en-1-yl}methyl Benzoate*; **2**). Oil. UV (MeOH): 228 (4.77), 273 (3.56). $[\alpha]_D^{20} = -37.6$ ($c = 0.425$, $CHCl_3$). CD (MeOH): 237 (+21.1), 221 (−6.0). IR (KBr): 3444, 2922, 1716, 1601, 1583, 1493, 1452, 1356, 1315, 1275, 1178, 1113, 1026, 935, 831, 764, 708. ^{1}H-NMR: see *Table 2*. ^{13}C-NMR: see *Table 1*. EI-MS: 367 (0.24, $[M+H-H_2O]^+$), 262 (0.5, $[M-BzOH]^+$), 127 (22.0), 105 (100), 77 (17.9). HR-EI-MS: 367.1191 ($[M+H-H_2O]^+$, $C_{21}H_{19}O_6^+$; calc. 367.1182).

Uvarirufol B (=*{(1R,4S,5R,6S)-6-Acetoxy-1,4-dihydroxy-5-[(benzoyl)oxy]cyclohex-2-en-1-yl}-methyl Benzoate*; **3**). Oil. UV (MeOH): 228 (4.06), 278 (3.56). $[\alpha]_D^{20} = -178$ ($c = 0.065$, $CHCl_3$). CD (MeOH): 230 (−24.5), 228 (−21.7), 224 (−24.8). IR (KBr): 3444, 2922, 1755, 1724, 1608, 1587, 1498, 1452, 1377, 1273, 1113, 1070, 1028, 711. ^{1}H-NMR: see *Table 2*. ^{13}C-NMR: see *Table 1*. EI-MS: 409 (0.22, $[M+H-H_2O]^+$), 304 (0.16, $[M-BzOH]^+$), 127 (20.4), 105 (100), 77 (14.7). HR-EI-MS: 409.1292 ($[M+H-H_2O]^+$, $C_{23}H_{21}O_7^+$; calc. 409.1287).

4-O-Benzoyluvarirufol B (**3a**). A soln. of **3** (1 mg), benzoic acid (0.5 mg), dicyclohexylcarbodiimide (DCC; 1 mg), and 4-(dimethylamino)pyridine (DMAP; 0.1 mg) in anh. CH_2Cl_2 (1 ml) was stirred at r.t. for 4 h [18]. The solvent was evaporated under reduced pressure, and the crude product was purified by prep. TLC (SiO_2; $CHCl_3$/MeOH 300:1) to yield **3a** (0.5 mg). CD (MeOH): 239 (+13.7), 222 (−8.7). ^{1}H-

Table 2. *^{1}H-NMR Data of* **1**–**4**. Arbitrary atom numbering; δ in ppm, J in Hz.

	1[a])[b])	**2**[a])[b])	**2**[c])[d])	**3**[a])[c])	**4**[b])[c])
H–C(2)	–	4.22 (*d*, *J* = 10.4)	4.28 (*d*, *J* = 10.2)	5.47 (*d*, *J* = 11.1)	5.67 (*d*, *J* = 8.2)
CH_2(3) or H–C(3)	3.05 (*dd*, *J* = 4.7, 13.9, H_α), 3.01 (*dd*, *J* = 8.6, 13.9, H_β)	4.21 (*dd*, *J* = 2.9, 10.4)	4.16 (*dd*, *J* = 4.0, 10.2)	5.56 (*dd*, *J* = 7.0, 11.1)	5.97 (*ddd*, *J* = 1.2, 2.6, 8.2)
H–C(4)	4.48–4.51 (*m*)	5.70 (*dd*, *J* = 2.9, 5.5)	5.67 (*dd*, *J* = 4.0, 4.6)	4.57–4.58 (*m*)	6.06 (*dd*, *J* = 10.4, 1.2)
H–C(5)	5.74 (*dd*, *J* = 3.0, 5.9)	6.13 (*dd*, *J* = 5.5, 9.9)	6.08 (*dd*, *J* = 4.6, 9.8)	5.89 (*dd*, *J* = 2.3, 10.3)	6.04 (*dd*, *J* = 10.4, 2.7)
H–C(6)	4.32 (*d*, *J* = 5.9)	6.03 (*d*, *J* = 9.9)	6.04 (*d*, *J* = 9.8)	5.79 (br. *d*, *J* = 0.3)	5.16 (br. *d*, *J* = 2.7)
CH_2(7)	4.46 (*d*, *J* = 11.5), 4.96 (*d*, *J* = 11.5)	4.37 (*d*, *J* = 10.8), 4.48 (*d*, *J* = 10.8)	4.35 (*d*, *J* = 10.5), 4.42 (*d*, *J* = 10.5)	4.42 (*d*, *J* = 11.5), 4.58 (*d*, *J* = 11.5)	4.70 (*d*, *J* = 11.8), 4.78 (*d*, *J* = 11.8)
H–C(2′,6′)	8.08–8.10 (*m*)	7.91–7.93 (*m*)	7.96–7.99 (*m*)	8.01 (*d*, *J* = 8.2)	7.97–7.99 (*m*)
H–C(3′,5′)	7.44–7.47 (*m*)	7.29–7.32 (*m*)	7.44–7.48 (*m*)	7.44–7.47 (*m*)	7.50–7.53 (*m*)
H–C(4′)	7.57–7.60 (*m*)	7.50–7.54 (*m*)	7.60–7.65 (*m*)	7.58–7.61 (*m*)	7.63–7.67 (*m*)
H–C(2″,6″)	7.94–7.96 (*m*)	7.96–7.98 (*m*)	8.01–8.03 (*m*)	8.12 (*d*, *J* = 8.2)	8.12–8.14 (*m*)
H–C(3″,5″)	7.39–7.42 (*m*)	7.24–7.27 (*m*)	7.27–7.31 (*m*)	7.47–7.50 (*m*)	7.53–7.57 (*m*)
H–C(4″)	7.54–7.57 (*m*)	7.48–7.51 (*m*)	7.53–7.57 (*m*)	7.58–7.61 (*m*)	7.65–7.69 (*m*)
AcO	–	–	–	1.98 (*s*)	1.98 (*s*)

[a]) Solvent: $CDCl_3$. [b]) At 500 MHz. [c]) Solvent: (D_6)acetone. [d]) At 400 MHz.

NMR (400 MHz, $CDCl_3$); 1.97 (*s*, AcO); 4.43 (*d*, *J* = 11.4, H–C(7)); 4.67 (*d*, *J* = 11.4, H–C(7)); 5.51 (*d*, *J* = 11.3, H–C(2)); 5.92 (*m*, H–C(5), H–C(6)); 5.96 (br. *d*, *J* = 7.9, H–C(4)); 6.26 (*dd*, *J* = 11.3, 7.9, H–C(3)); 7.38–8.21 (*m*, 15 arom. H).

Uvarirufol C (=*[(1*S*,2*R*,5*R*,6*S*)-6-Acetoxy-1,2-dihydroxy-5-[(benzoyl)oxy]cyclohex-3-en-1-yl]-methyl Benzoate*; **4**). Colorless solid. M.p. 87–88°. UV (MeOH): 229 (5.35), 273 (4.23). $[\alpha]_D^{20} = -254$ ($c = 0.07$, $CHCl_3$). CD (MeOH): 230 (−21.6). IR (KBr): 3481, 2925, 1755, 1711, 1599, 1578, 1482, 1452, 1280, 1226, 1111, 713. ^{1}H-NMR: see *Table 2*. ^{13}C-NMR: see *Table 1*. EI-MS: 409 (8.7, $[M+H-H_2O]^+$), 163 (9.8), 105 (100), 77 (16.3). HR-EI-MS: 409.1277 ($[M+H-H_2O]^+$, $C_{23}H_{21}O_7^+$; calc. 409.1287).

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