Tribenzylbutyrolactones and Dibenzyldiphenyl-4,5,6,7-tetrahydrobenzofuranones from *Kyrtuthrix maculans*

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Ten novel compounds, maculalactones B−K (**2**−**11**), have been isolated from the marine cyanobacterium *Kyrtuthrix maculans*. Their structures, which involve either three benzyl groups substituted on a butyrolactone ring or two benzyl and two phenyl groups substituted on a 4,5,6,7-tetrahydrobenzofuranone nucleus, were determined by 2D NMR spectroscopy. Some speculation is made concerning the biogenesis of these two novel classes of natural products.

A preliminary investigation of the chemistry of the epilithic-encrusting cyanobacterium *Kyrtuthrix maculans* Umezaki (Mastigocladaceae),[1−6] collected in Hong Kong by the present authors, described maculalactone A **(1)**,[7] which was isolated following gradient column chromatography of a CH_2Cl_2 extract. We now report the isolation of 10 additional novel compounds, maculalactones B−K (**2**−**11**), belonging to two new structural classes, from a full-scale study employing both gradient column chromatography and HPLC as purification procedures.

Results and Discussion

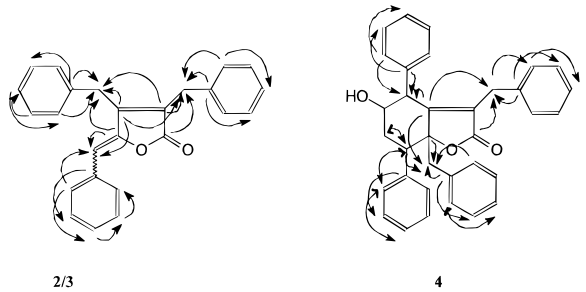
The molecular formulas of isomeric compounds maculalactone B **(2)** and maculalactone C **(3)** were both established as $C_{25}H_{20}O_2$ by HREIMS. ^{13}C-NMR/DEPT spectra for both compounds showed only 19 distinct carbon resonances, six of which (methines) were of double intensity, consistent with the presence of three benzyl groups. The carbon skeletons of **2** and **3** were established by the 2D NMR experiments HSQC and HMBC (full ^{13}C- and ^{1}H-NMR assignments from HSQC experiments are given in Table 1; connections through 2- and 3-bonds observed in HMBC are shown in Figure 1). ^{1}H−^{1}H COSY experiments (not shown) were sometimes useful in confirming assignments of protons in the three benzyl groups.

Geometrical isomerism about the 5−1c double bond for compounds **2** and **3** was most easily demonstrated by NOESY experiments (Figure 2). Thus, H-1c in compound **2** correlated with the methylene H-1b protons (B-benzyl substituent), whereas in compound **3** it was H-3c/7c of the C-benzyl group that correlated with H-1b. Consequently, **2** is the (*Z*)-isomer and **3** is the (*E*)-isomer. It was also interesting to compare the ^{1}H chemical shifts for protons in the B- and C-benzyl substituents of compounds **2** and **3**. In compound **2**, H-1c is strongly shielded (ca. 1 ppm) because it lies in the shielding region of the B-benzyl group; whereas, in compound **3**, H-1c points away from the B-benzyl group and has a normal value for an alkene proton involved in conjugation; consequent juxtaposition of the B- and C-rings in compound **3** resulted in protons in both rings acquiring strong upfield shifts (0.1−0.7 ppm) when compared with **2**. ^{13}C chemical shifts followed the same trend as for ^{1}H in these two series of compounds. This

Table 1. ^{13}C and ^{1}H Assignments of Tribenzylbutyrolactones **2** and **3**

		δ_C		δ_H[b]	
atom	mult[a]	**2**	**3**	**2**	**3**
2	C	170.31	169.72		
3	C	127.86	133.02		
4	C	150.79	148.25		
5	C	148.21	149.27		
1a	CH_2	29.81	29.82	3.75 (s)	3.66 (s)
2a	C	137.44	137.21		
3a/7a	CH	128.62	128.70	7.18 (d, 6.9)	7.16 (m)
4a/6a	CH	128.73	128.67	7.24 (m)	7.23 (m)
5a	CH	126.70	126.70	7.20 (m)	7.19 (m)
1b	CH_2	30.59	31.48	3.93 (s)	3.67 (s)
2b	C	136.62	136.17		
3b/7b	CH	128.18	127.66	7.11 (d, 7.0)	6.60 (dd, 7.8, 2.7)
4b/6b	CH	128.94	128.39	7.27 (m)	7.11 (m)
5b	CH	127.04	126.45	7.24 (m)	7.11 (m)
1c	CH	110.46	115.30	5.97 (s)	6.84 (s)
2c	C	133.01	132.62		
3c/7c	CH	130.50	129.25	7.71 (d, 7.5)	7.01 (d, 7.9)
4c/6c	CH	128.73	128.22	7.35 (dd, 7.5, 7.5)	7.16 (m)
5c	CH	128.83	128.15	7.29 (m)	7.24 (m)

[a] Multiplicity established from DEPT. [b] Multiplicity and coupling constants (in Hz) indicated in parentheses.



2/3 4

Figure 1. Two- and three-bond carbon−proton correlations for compounds **2**/**3** and **4**, as established by HMBC (indicated by arrows from ^{13}C to ^{1}H)

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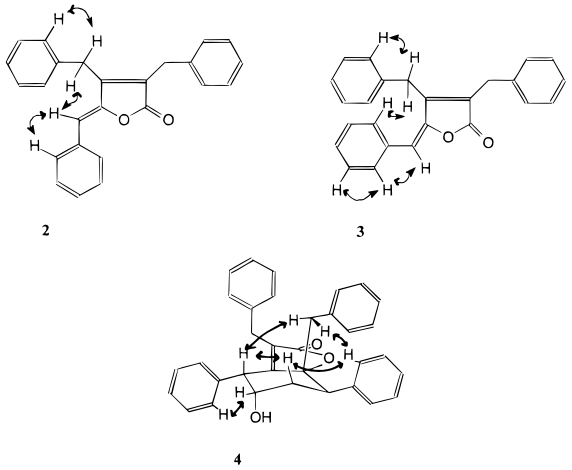
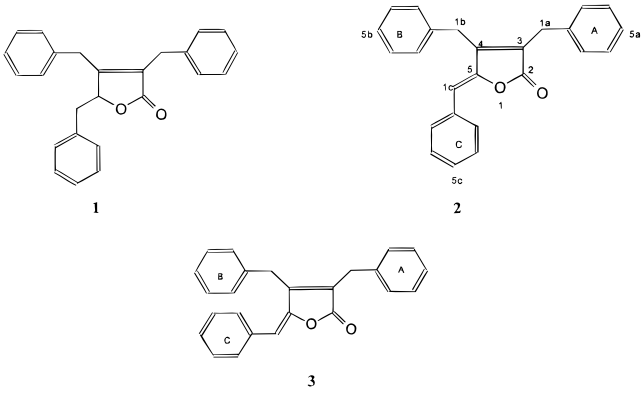


Figure 2. Critical NOESY correlations for assigning stereochemistry in compounds **2**−**4** (indicated by double-headed arrows). Relative stereochemistry **only** shown for compound **4**.

may be a consequence of a favorable-stacking interaction between the B- and C-rings in the *E* isomer, which results in protons in both rings lying in the shielding region of the other. In this connection, it was interesting to note that **3** is apparently the thermodynamically more stable isomer. After three weeks standing in $CDCl_3$, compound **2** underwent ca. 50% conversion to **3**, but a solution of **3** remained unchanged. The increased stability of compound **3** may be associated with the possibility of π-stacking in the *E* isomer, which is geometrically disallowed for the *Z* isomer (**2**).



HPLC separation of a more polar fraction isolated from gradient column chromatography yielded the dibenzyldiphenyl-4,5,6,7-tetrahydrobenzofuranone, maculalactone D **(4)**. HREIMS of **4** demonstrated the molecular formula $C_{34}H_{30}O_3$, and ^{13}C-NMR/DEPT spectra now showed 26 distinct carbons, eight of which (aromatic methines) were of double intensity. The suggestion that compound **4** contained four benzene groups was confirmed by HSQC (Tables 2 and 3), HMBC (Figure 1), and ^{1}H−^{1}H COSY, from which it was possible to deduce a planar structure consisting of a 4,5,6,7-tetrahydrobenzofuran-2-one nucleus substituted by two phenyl groups at the 4 and 7 positions and by two benzyl groups at the 3 and 8 positions. The stereochemistry for the hydroxy group and C-phenyl substituent was determined from coupling constants observed in the ^{1}H-NMR spectrum of **4**. Thus, the H-7 was clearly axial [since H-7 showed a large coupling to one of the H-6 protons (14 Hz), meaning that the C-phenyl group must be equatorial]. The hydroxyl group should be axial because the appearance of H-5 as a broad signal, with no clearly resolved couplings to the 6-methylene protons, indicated that this proton is equatorial. It was also possible to confirm these conclusions and establish the relative stereochemistry of the B-phenyl and D-benzyl substituents in **4** from NOESY experiments (Figure 2); however, the absolute stereochemistry of compound **4** and the other dibenzyldiphenyl-4,5,6,7-tetrahydrobenzofuranones **5**−**11** remains unknown. Strong upfield shifts observed for protons in the A-benzyl group (0.2−1 ppm) in **4** may be the result of shielding by the equatorial B-phenyl group.

Maculalactone E **(5)**, the 4-hydroxy analogue of **4**, gave a molecular ion corresponding to $C_{34}H_{30}O_4$ in HREIMS and showed a similar pattern of correlations to **4** in its 2D NMR spectra. Significant changes in ^{13}C chemical shift (ca. 5 ppm) (Table 2) for positions 6 and 1b of **5** were noted as compared to **4**, in addition to the gross changes at position 4 itself. These changes were consistent with the introduction of an axial hydroxyl group at the 4 position. Apart from the absence of H-4 (Table 3), NOESY correlations for **5** remained substantially the same as for **4**.

Maculalactone F **(6)** can be viewed as arising by oxidation of the secondary alcohol group in **5**. IR demonstrated the presence of a new aliphatic carbonyl group (1728 cm^{-1}) in addition to the carbonyl of the unsaturated lactone (1757 cm^{-1}). ^{13}C NMR confirmed the new C═O group at 207.69, and HMBC correlations through two or three bonds to protons H-6α/6β and 4-OH unambiguously located the new functional group at C-5. NOESY correlations of **6** were similar to those of **4**, except that H-1d correlated with both H-6β and H-2b/6b, and consequently, the configuration of C-4 must be inverted. Large shifts in the ^{1}H-NMR resonances for the A-ring of **6** were consistent with this conclusion.

Maculalactone G **(7)** is an epoxide derivative of alkene **5** as shown by its molecular ion in HREIMS ($C_{34}H_{30}O_5$), the replacement of the two quaternary alkene carbons in **5** (δ_C 131.22, 161.04) by two quaternary epoxide signals in **7** (δ_C 62.10, 70.95), and an increase in wavenumber (40 cm^{-1}) for the C═O stretching absorbance in **7** when compared with **5**, as a result of removal of conjugation to the double bond.

Maculalactone H **(8)** had undergone both epoxidation at the conjugated alkene and hydroxylation at the 1d position as shown by the appearance of new resonances in the NMR spectrum of **8** (δ_C 75.68, δ_H 5.43) replacing those of the 1d-methylene group. Complete assignment of all proton resonances by 2D NMR as previously (Table 3) allowed determination of the relative stereochemistry of the epoxide in **7** and **8**, since NOESY correlations were observed between protons of the A-benzyl substituent and the 4-OH group, which also correlated with H-1d (other correlations were as for Figure 2).

Maculalactone I **(9)** would appear to arise by nucleophilic attack of the 1d-hydroxyl group of **8** at the 9-position of the epoxide to form an oxetane, whereas maculalactone J **(10)** may be produced by attack at the 3 position to produce a tetrahydrofuran ring. The relative stereochemistry of both **9** and **10** was shown to

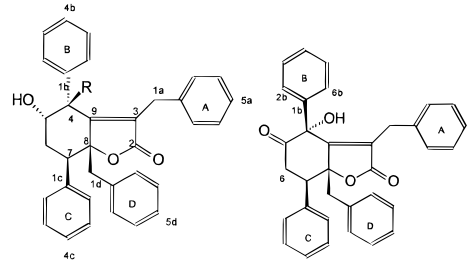
Table 2. ^{13}C-NMR Assignments for Dibenzyldiphenyl-4,5,6,7-tetrahydrobenzofuranones **4**−**11**

		compound							
atom	mult[a]	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
2	C	173.15	172.74	171.96	171.18	172.31	175.96	173.55	175.91
3	C	129.60	131.22	132.21	62.10	61.52	74.65	86.91	77.10
4	C	48.90[b]	77.73	83.54	75.57	73.80	74.33	74.17	78.95
5	CH	70.02	74.17	207.69[c]	77.91	75.87	71.63	77.51	203.56[c]
6	CH_2	36.15	31.40	40.81	32.28	31.46	29.10	29.04	37.95
7	CH	49.07	49.77	49.76	41.37	38.39	39.05	32.45	42.80
8	C	89.13	91.64	87.46	86.73	87.70	89.31	92.68	86.71
9	C	161.78	161.04	160.93	70.95	70.63	90.79	87.81	92.18
1a	CH_2	28.58	29.23	30.11	28.14	28.59	36.73	30.98	37.91
2a	C	137.93	137.56	139.00	134.26	134.42	131.97	134.09	131.85
3a/7a	CH	127.69	127.41	128.56	129.57	129.82	132.01	130.66	131.93
4a/6a	CH	127.91	127.88	128.34	127.81	127.96	128.21	127.66	128.32
5a	CH	125.61	125.50	125.91	126.34	126.63	127.51	126.30	127.68
1b	C	136.52	141.29	139.82	139.34	139.21	142.41	143.08	135.60
2b/6b	CH	128.57	128.14	127.64	128.34	*d*	127.64	*d*	129.38
3b/5b	CH	128.56	128.14	129.32	128.24	*d*	128.43	*d*	127.94
4b	CH	127.53	128.90	129.34	128.90	*d*	128.43	128.39	128.28
1c	C	137.76	138.38	135.53	138.01	137.03	136.93	136.33	136.42
2c/6c	CH	129.32	129.53	129.04	129.33	128.77	128.92	128.25	128.74
3c/5c	CH	128.39	128.37	128.56	129.33	127.48	128.78	129.80	128.82
4c	CH	127.66	127.59	128.24	127.30	126.69	127.84	126.90	128.31
1d	CH_2	36.80	38.66	36.34	38.16	75.68[e]	86.01[e]	80.70[e]	85.27[e]
2d	C	134.26	135.73	132.35	134.00	137.78	133.71	135.58	133.70
3d/7d	CH	129.96	131.22	130.76	132.53	129.80	125.78	128.59	126.61
4d/6d	CH	128.56	127.88	127.75	128.07	127.60	127.94	127.03	128.32
5d	CH	127.38	126.68	126.88	127.09	126.63	128.21	127.23	128.60

[a] Multiplicity established from DEPT. [b] CH in **4**. [c] C in **6** and **11**. [d] Not assigned. [e] CH in **8**, **9**, **10** and **11**.

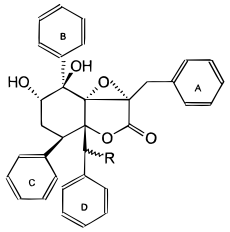
be consistent with such epoxide cleavage of **8**, and the chirality of the new stereocenter at 1d was confirmed for both compounds by observation of NOESY correlations between H-1d and the phenyl 2c/6c protons in addition to those commented on above. Two-dimensional NMR analysis demonstrated compound **11** to be the 5-keto analogue of the secondary alcohol **9**.

Both the tribenzylbutyrolactones (**1**−**3**) and the dibenzyldiphenyl-4,5,6,7-tetrahydrobenzofuranones (**4**−**11**) are new classes of natural products. When comparing the skeletons of the two classes, it seems reasonable to propose that the second class is derived from the first one by incorporation of a phenylpropanoid (C_6−C_3) unit. A common feature in the oxygenation pattern of compounds **4**−**11** is the appearance of either a hydroxy or carbonyl substituent at C-5, which suggests that the biogenetic phenylpropanoid unit is oxygenated at the terminal aliphatic carbon (cinnamate is one possibility). Conceivably, the tribenzylbutyrolactones could themselves also be formed by condensation of three such biogenetic phenylpropanoid equivalents, accompanied by loss of two carbons, in which case both the tribenzylbutyrolactones and the dibenzyldiphenyl-4,5,6,7-tetrahydrobenzofuranones from *Kyrtuthrix maculans* could be biogenetically classified as lignans. However, there is no literature precedent for such a loss of a C_2 unit in this class of compounds,[8−12] and an alternative proposition is that these two new structural classes arise from condensation of two or three phenylpropanoid units with a benzyl or benzoyl (C_6−C_1) unit.

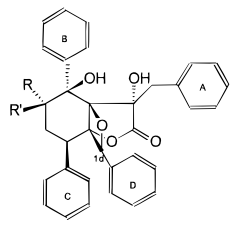


4 R = H
5 R = OH

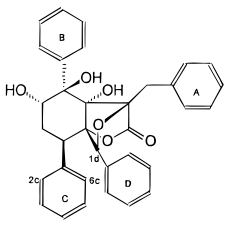
6



7 R = H
8 R= OH



9 R = OH, R' = H
11 R + R' = O



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Experimental Section

General Experimental Procedures. Chemical shifts are expressed in ppm (δ) relative to TMS as internal standard. All NMR experiments were run on a Bruker DRX 500 instrument. Due to extensive overlap in the aromatic region, HSQC and HMBC spectra were recorded with high digital resolution (4096 data points in F_2 and 1024 data points in F_1). HRMS were recorded in EI mode at 70 eV on a Finnigan-MAT 95 MS spectrometer. IR spectra were recorded in $CHCl_3$

Table 3. ^{1}H-NMR Assignments[a] for Dibenzyldiphenyl-4,5,6,7-tetrahydrobenzofuranones **4**−**11**

atom	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
4	4.14 (br s)							
5	4.90 (br s)	4.62 (br s)		4.05 (br s)	3.99 (br s)	4.73 (br s)	4.00 (br s)	
6β	2.54 (ddd, 14.6, 13.8, 2.1)	3.18 (ddd, 14.2, 14.0, 2.1)	3.62 (dd, 15.0, 15.0)	3.09 (ddd, 14.3, 13.8, 2.8)	3.06 (ddd, 14.2, 14.0, 3.3)	3.27 (dd, 14.0, 13.8)	2.96[c]	3.53 (dd, 17.6, 8.4)
6α	2.29 (ddd, 14.6, 3.9, 3.0)	2.02 (m)	3.26 (dd, 15.0, 3.6)	2.19 (ddd, 14.3, 3.0, 3.0)	2.41 (ddd, 14.2, 3.2, 3.0)	2.18 (ddd, 14.0, 5.6, 4.6)	2.41 (m)	3.05 (dd, 17.6, 7.6)
7	3.51 (dd, 13.8, 3.9)	3.43 (dd, 14.0, 4.2)	3.43 (dd, 15.0, 3.6),	3.99 (d, ca. 14)	4.04 (dd, 14.0, 3.2)	3.60 (dd, 13.8, 5.6)	3.90 (dd, 13.8, 3.7)	4.05 (dd, 8.4, 7.6)
1a	2.84 (d, 15.7)	2.97 (d, 16.0)	4.20 (d, 14.7)	2.01 (d, 15.0)	2.96 (d, 14.6)	3.21 (d, 14.4)	3.51 (d, 15.5)	2.94 (d, 14.3)
	2.79 (d, 15.7)	2.44 (d, 16.0)	3.97 (d, 14.7)	1.88 (d, 15.0)	2.46 (d, 14.6)	2.97 (d, 14.4)	2.98 (d, 15.5)	2.56 (d, 14.3)
3a/7a	6.22 (d, 7.1)	6.00 (d, 7.7)	6.79 (d, 6.4)	6.61 (d, 6.3)	6.91 (m)	6.67 (d, 7.2)	6.94[c]	6.99 (m)
4a/6a	6.96 (m)	6.92 (dd, 7.4, 7.4)	7.13 (m)	7.02 (m)	7.11 (m)	7.19 (m)	6.98[c]	7.24 (m)
5a	6.99 (m)	6.98 (t, 7.3)	7.14 (m)	7.02 (m)	*b*	7.17 (m)	7.00 (m)	7.24 (m)
2b/6b	7.23 (m)	7.40 (m)	6.87 (d, 7.4)	8.08 (d, 6.9)	8.08 (br d)	7.93 (d, 7.3)	7.98 (m)	7.66 (d, 7.0)
3b/5b	7.13 (m)	7.40 (m)	7.25 (dd, 7.5, 7.5)	7.42 (m)	7.47 (m)	7.49 (dd, 6.6, 6.6)	7.35[c]	7.42 (m)
4b	7.19 (m)	7.20 (t, 7.4)	7.40 (m)	7.36 (m)	*b*	7.44 (m)	7.34[c]	7.40 (m)
2c/6c	7.47 (d, 7.4)	7.52 (d, 7.6)	7.40 (m)	7.35 (m)	7.09 (m)	7.44 (m)	7.20[c]	7.39 (m)
3c/5c	7.41 (dd, 7.3, 7.3)	7.41 (m)	7.40 (m)	7.35 (m)	6.93 (m)	7.35 (m)	6.96[c]	7.40 (m)
4c	7.35 (m)	7.34 (m)	7.38 (m)	7.30 (m)	6.93 (m)	7.35 (m)	6.98 (m)	7.40 (m)
1d	3.05 (d, 15.0)	3.64 (d, 13.5)	2.92 (d, 14.3)	3.99 (d, ca. 14)	5.43 (s)	6.01 (s)	6.09 (s)	6.01 (s)
	2.88 (d, 15.0)	2.67 (d, 13.5)	2.56 (d, 14.3)	2.67 (d, 13.9)				
3d/7d	7.16 (m)	7.38 (m)	6.14 (d, 7.4)	7.33 (m)	6.91 (m)	6.29 (d, 7.6)	6.71 (d, 7.5)	6.75 (dd, 7.0, 2.0)
4d/6d	7.28 (m)	7.27 (m)	6.94 (dd, 7.5, 7.5)	7.16 (m)	6.89 (m)	7.06 (dd, 7.7, 7.7)	6.86 (dd, 7.5, 7.5)	7.24 (m)
5d	7.29 (m)	7.28 (m)	7.12 (m)	7.12 (m)	7.08 (m)	7.14 (m)	6.93[c]	7.26 (m)
3-OH						4.59 (br s, exch. D_2O)		2.45 (br s, exch. D_2O)
9-OH							5.48 (br s, exch. D_2O)	
4-OH		2.29 (br s)	4.29 (s)	2.96 (br s)	4.54 (br s, exch. D_2O)	4.44 (br s, exch. D_2O)	2.51 (br s, exch. D_2O)	4.01 (br s, exch. D_2O)
5-OH	2.32 (br s)	1.85 (br s)		2.84 (br s)	2.30 (br s, exch. D_2O)	4.93 (br s, exch. D_2O)	2.66 (br s, exch. D_2O)	
1d-OH					1.88 (br s, exch. D_2O)			

[a] Multiplicity and coupling constants (in Hz) indicated in parentheses. [b] Not assigned. [c] Multiplicity obscured by compound **8** present in mixture.

on a BIO-RAD FT S-7 IR spectrometer. Column chromatography was performed using Si gel 60−200 μM (Merck). HPLC separations were performed using a Varaian chromatograph equipped with RI star 9040 and UV 9050 detectors and a Intersil PREP−SIL 20-mm × 25-cm column, flow rate 8 mL/min.

Biological Material. *K. maculans* was collected from rocks in the mid-high intertidal zone from the shores in the vicinity of Swire Institute of Marine Science, Cape d'Aguilar, Hong Kong Island, in June 1996. Taxonomic verification was made by Dr. Williams, and type specimens of *K. maculans* are lodged at the Swire Institute of Marine Science (SML.B20, SML.B21).[1]

Extraction and Isolation. The sample (570 g) was surface dried on filter paper and then extracted with CH_2Cl_2 over several days. The organic extract was then dried and evaporated under reduced pressure to yield a pale yellow gum (2.99 g; 0.52% w/w). Compounds **1**−**11** were isolated by column chromatography using hexane and EtOAc (TLC plates used to monitor the column were visualized using *p*-anisaldehyde). In most cases, further purification was required by HPLC, using EtOAc−hexane: **1** (120 mg) (R_f 0.36 in 20% EtOAc−hexane; t_R 10.9 min in 20% EtOAc−hexane); **2** (6.9 mg) (R_f 0.42 in 15% EtOAc−hexane; t_R 14.5 min in 15% EtOAc−hexane); **3** (8.8 mg) (R_f 0.42 in 15% EtOAc−hexane; t_R 13.2 min in 15% EtOAc−hexane); **4** (5.7 mg) (R_f 0.42 in 30% EtOAc−hexane; t_R 9.8 min in 25% EtOAc−hexane); **5** (15.4 mg) (R_f 0.44 in 30% EtOAc−hexane; t_R 17.9 min in 25% EtOAc−hexane); **6** (11.8 mg) (R_f 0.40 in 20% EtOAc−hexane; t_R 14.2 min in 20% EtOAc−hexane); **7** (27.3 mg) (R_f 0.44 in 30% EtOAc−hexane; t_R 17.2 min in 25% EtOAc−hexane); **8** (19.2 mg) (R_f 0.44 in 30% EtOAc−hexane; t_R 15.8 min in 25% EtOAc−hexane); **9** (7.2 mg) (R_f 0.44 in 30% EtOAc−hexane; t_R 18.4 min in 25% EtOAc−hexane); **10** (as a mixture with **8** 13.8 mg); **11** (5.7 mg) (R_f 0.40 in 20% EtOAc−hexane; t_R 13.2 min in 20% EtOAc−hexane).

Maculalactone A (1). Data have already been described by Tsui et al.[7]

Maculalactone B (2): oil; IR ($CHCl_3$) ν_{max} 3026, 2930, 2862, 1757 cm^{-1}; ^{1}H NMR and ^{13}C NMR, see Table 1; HREIMS *m/z* 352.1466 (100) (calcd for $C_{25}H_{20}O_2$, 352.1463), 261 (10).

Maculalactone C (3): oil; ^{1}H NMR and ^{13}C NMR, see Table 1; HREIMS *m/z* 352.1463 (100) (calcd for $C_{25}H_{20}O_2$, 352.1463), 261 (10).

Maculalactone D (4): oil; $[\alpha]_D$ −47.1 (*c* 0.07, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3500 (br), 3030, 2930, 2856, 1746 cm^{-1}; ^{1}H NMR and ^{13}C NMR, see Tables 2 and 3; HREIMS *m/z* 486.2189 (22) (calcd for $C_{34}H_{30}O_3$, 486.2195), 395 (70), 377 (100).

Maculalactone E (5): oil; $[\alpha]_D$ +84.7 (*c* 0.24, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3578, 3435 (br), 3032, 3013, 1742 cm^{-1}; ^{1}H NMR and ^{13}C NMR, see Tables 2 and 3; HREIMS *m/z* 502.2138 (70) (calcd for $C_{34}H_{30}O_4$, 502.2144), 484 (20), 458 (30), 411 (50), 393 (90), 375 (100), 367 (65), 297 (30).

Maculalactone F (6): oil; IR ($CHCl_3$) ν_{max} 3510 (br), 3032, 2931, 1757, 1728 cm^{-1}; ^{1}H NMR and ^{13}C NMR, see Tables 2 and 3; HREIMS *m/z* 500.1986 (20) (calcd for $C_{34}H_{28}O_4$, 500.1987), 482 (100), 391 (80), 368 (50), 352 (30).

Maculalactone G (7): oil; $[\alpha]_D$ +19.2 (*c* 0.37, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3576, 3375 (br), 3032, 1782 cm^{-1}; ^{1}H NMR and ^{13}C NMR, see Tables 2 and 3; HREIMS *m/z* 518.2088 (8) (calcd for $C_{34}H_{30}O_5$, 518.2093), 466 (8), 427 (30), 375 (40), 367 (100).

Maculalactone H (8): solid (dec 210 °C); $[\alpha]_D$ +43.8 (*c* 0.33, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3323 (br), 3063, 3026, 2930, 1790 cm^{-1}; ^{1}H NMR and ^{13}C NMR, see Tables 2 and 3; HREIMS *m/z* 534.2040 (10) (calcd for $C_{34}H_{30}O_6$, 534.2042), 490 (3), 428 (5), 387 (10), 366 (30), 319 (50), 291 (100).

Maculalactone I (9): oil; $[\alpha]_D$ +52 (*c* 0.08, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3400 (br), 3059, 3022, 1784 cm^{-1}; ^{1}H NMR and ^{13}C NMR, see Tables 2 and 3; HREIMS *m/z* (rel int) 518.2093 $M^+ - H_2O$ (2) (calcd for $C_{34}H_{30}O_5$, 518.2093), 427.1543 (15) (calcd for $C_{27}H_{23}O_5$, 427.1543), 409 (10), 366.1256 (30) (calcd for $C_{25}H_{18}O_3$, 366.1256), 319 (50), 291 (100).

Maculalactone J (10): isolated as a mixture with compound **8**; ^{1}H NMR and ^{13}C NMR, see Tables 2 and 3.

Maculalactone K (11): oil; $[\alpha]_D$ +40.2 (*c* 0.04, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3500 (br), 3026, 2937, 2847, 1788, 1728 cm^{-1}; ^{1}H NMR and ^{13}C NMR, see Tables 2 and 3; HREIMS *m/z* 532.1888 (1) (calcd for $C_{34}H_{28}O_6$, 532.1886), 486 (5), 410 (25), 384 (20), 366 (100), 352 (25), 307 (30), 304 (70).

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