New Cytotoxic Coumarins and Prenylated Benzophenone Derivatives from the Bark of *Ochrocarpos punctatus* from the Madagascar Rainforest[1]

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Bioassay-guided fractionation of a CH_2Cl_2−MeOH extract of the bark of *Ochrocarpos punctatus* resulted in the isolation of seven new coumarins, ochrocarpins A−G (**1**−**7**), three new benzophenone derivatives, ochrocarpinones A−C (**8**−**10**), and five known coumarins, mammea A/AC cyclo F (**11**), mammea A/AD cyclo D (**12**), mammea A/AB cyclo F (**13**), mammea A/AA cyclo F (**14**), mammea A/AB cyclo D (**15**), and 15,16-dihydro-16-hydroperoxyplukenetione (**16**). The structures of compounds **1**−**10** were established on the basis of extensive 1D and 2D NMR spectroscopic data interpretation. All compounds exhibited cytotoxicity against the A2780 ovarian cancer cell line.

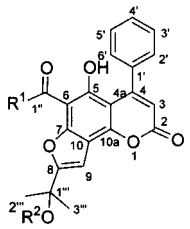
In our continuing search for bioactive metabolites from the Suriname and Madagascar rainforests as part of an International Cooperative Biodiversity Group (ICBG) program[2] we obtained a sample of a cytotoxic extract of the plant *Ochrocarpos punctatus* H. Perrier (Clusiaceae),[3] collected at Ampijoroa, Madagascar, from the National Cancer Institute. The plant was a small tree 7−8 m tall with yellow latex and white flowers.

The genus *Ochrocarpos* Noronha ex Thouars was treated by Perrier[4] as consisting of about 30 species of trees occurring in tropical Africa, Madagascar, and tropical Asia. Modern students studying the family Clusiaceae do not recognize the genus and place its constituent species in the genera *Garcinia* L. or *Mammea* L. in Madagascar[5] or in *Mammea* L. in Malaya.[6] The Clusiaceae of Madagascar have not been treated in their entirety since Perrier's 1951 work, and many of the combinations have not been published for Madagascar. While the species from which the compounds described in this paper were isolated is clearly a member of *Mammea*, there is no combination available in that genus, so it is referred to by its older name in *Ochrocarpos* in this study.

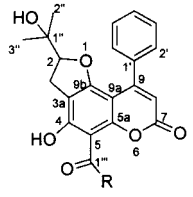
Earlier studies of the genus *Ochrocarpos* resulted in the isolation of xanthones,[7] coumarins,[8−10] biflavones, meso-inositol, and vitexin.[11] The crude extract after extensive chromatography followed by reversed-phase HPLC yielded seven new coumarins, ochrocarpins A−G (**1**−**7**), and three new benzophenones, ochrocarpinones A−C (**8**−**10**), in addition to the six known compounds **11**−**16**.

Results and Discussion

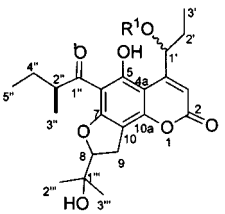
Initial liquid−liquid partition of the crude extract indicated that the cytotoxic activity was concentrated in the *n*-hexane- and $CHCl_3$-soluble portions of *n*-hexane−aqueous MeOH and $CHCl_3$−aqueous MeOH partitions. Chromatography of the *n*-hexane-soluble fraction on a Sephadex LH-20 column followed by normal-phase preparative TLC and then by reversed-phase HPLC furnished seven new coumarins, ochrocarpins A−G (**1**−**7**) as well as the five known compounds **11**−**15**. The structures of the five known compounds were identified as mammea A/AC cyclo F (**11**), mammea A/AD cyclo D (**12**), mammea A/AB cyclo F (**13**), mammea A/AA cyclo F (**14**), and mammea A/AB cyclo D (**15**), by comparison of their spectral data with values reported in the literature.[12−14]



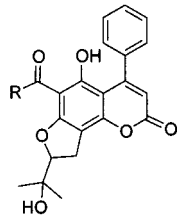
1 R^1 = $CH(CH_3)CH_2CH_3$, R^2 = H
2 R^1 = $CH_2CH(CH_3)_2$, R^2 = H
3 R^1 = $CH(CH_3)_2$, R^2 = H
4 R^1 = $CH(CH_3)CH_2CH_3$, R^2 = CH_3



5 R = $CH(CH_3)_2$
18 R = $CH_2CH(CH_3)_2$



6 R^1 = ⋯$COCH_3$
7 R^1 = —$COCH_3$
20 R^1 = ⋯H
22 R^1 = —H



11 R = $CH_2CH_2CH_3$
13 R = $CH(CH_3)CH_2CH_3$
14 R = $CH_2CH(CH_3)_2$

Ochrocarpin A (**1**) was isolated as a colorless viscous liquid whose molecular formula was established as $C_{25}H_{24}O_6$ from HRFABMS and ^{13}C NMR spectral data. The UV spectrum of **1** showed maxima at 236, 285, and 332 nm, similar to those of 5,7-dioxygenated coumarins.[15] Compound **1** gave a green coloration with methanolic ferric chloride, indicating the presence of a phenolic hydroxyl group, and this assignment was supported by observation of an absorption at 3445 cm^{-1} in its IR spectrum. The ^1H NMR spectrum of **1** showed the presence of a phenolic hydroxyl group as a singlet at δ 14.78, strongly chelated

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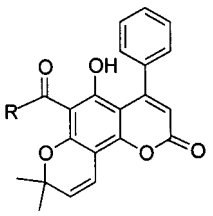
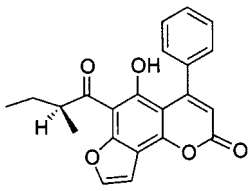


12 R = $CH(CH_3)_2$
15 R = $CH(CH_3)CH_2CH_3$



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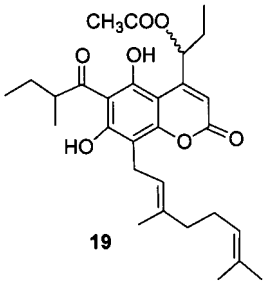

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to the carbonyl function of an acyl group as in disparfuran B (**17**) isolated from *Calophyllum dispar*.[15] The ^{1}H NMR spectrum of **1** also showed the presence of a singlet at δ 6.14 characteristic for H-3 of a 4-substituted coumarin, a 2-methyl-1-oxobutyl substituent [δ_H 0.97, 3H, t, J = 7.2 Hz (H-5″); 1.24, 3H, d, J = 6.6 Hz (H-3″); 1.52, 1H, m (H_β-4″); 1.88, 1H, m (H_α-4″); and 3.78, 1H, m (H-2″), and δ_C 208.6 (C-1″), 45.7 (C-2″), 16.3 (C-3″), 26.5 (C-4″), and 11.8 (C-5″)], a second olefinic singlet at δ 6.96, and two methyl groups as a six-proton singlet at δ 1.72. The location of the 2-methyl-1-oxobutyl group was fixed at C-6 on the basis of the HMBC correlations 5-OH/C-10, C-6 and H-2″/C-1″, C-3″, C-6. The substituent at C-4 was identified as a phenyl group from its five aromatic signals [δ_H 7.37, 2H, m, (H-2′ and H-6) and 7.43, 3H, m (H-3′, H-4′, and H-5′)], and its location was supported by the HMBC correlations H-3/C-2, C-4, C-1′ and H-2′ or H-6′/C-4, C-1′, C-3′, or C-5′. HMBC correlations were also observed for the olefinic proton at δ 6.96 with C-8 and C-10, while the two methyl groups observed at δ 1.72 were correlated with the oxygenated quaternary carbon at C-1‴ and with the C-8 carbon. This indicated the presence of a 1-hydroxy-1-methylethyl side chain at C-8, similar to those of the previously isolated compounds **11**, **13**, and **14**. A close comparison of the ^{1}H NMR data of **1** with those of **17** indicated that the two compounds were identical except for the presence of the 1-hydroxy-1-methylethyl chain at the C-8 position in **1**, confirming the structure further. The ^{13}C NMR values for all the carbons were assigned on the basis of HMQC and HMBC spectra and were in good agreement with the structure. The stereochemistry at C-2″ in the 2-methyl-1-oxobutyl substituent of **1** was tentatively assigned as *S* because the sign of rotation of **1** and **17** were the same; the absolute stereochemistry of **17** has previously been assigned by synthesis. On the basis of the above spectral data the structure of **1** was established as 5-hydroxy-8-(1-hydroxy-1-methylethyl)-6-(2-methyl-1-oxobutyl)-4-phenyl-2*H*-furo[2′,3′:5,6]benzo[1,2-*b*]pyran-2-one.

Table 1. ^{1}H NMR Data for Compounds **1**−**5**[a] ($CDCl_3$, 500 MHz)

position	**1**	**2**	**3**	**4**	**5**
2					4.50 t 9.1
3	6.14 s	6.13 s	6.14 s	6.14 s	H_α 3.06 dd 10.0, 15.2
					H_β 2.93 dd 8.4, 15.5
4-OH					14.24 s
5-OH	14.78 s	14.68 s	14.57 s	14.96 s	
8					6.07 s
9	6.96 s	6.96 s	6.95 s	6.96 s	
2′, 6′	7.37 m	7.34 m	7.35 m	7.29 m	7.34 m
3′, 5′	7.43 m	7.42 m	7.42 m	7.38 m	7.42 m
4′	7.43 m	7.42 m	7.42 m	7.38 m	7.42 m
2″	3.78 m	3.17 m	3.84 m	3.78 m	1.01 s
3″	1.24 d 6.6	2.24 m	1.17 d 6.5	1.24 d 6.6	0.93 s
4″	H_α 1.88 m	1.06 d 6.6	1.17 d 6.5	H_α 1.86 m	
	H_β 1.52 m			H_β 1.54 m	
5″	0.97 t 7.2	1.06 d 6.6		0.96 t 7.1	
2‴	1.72 s	1.72 s	1.71 s	1.84 s	4.12 m
3‴	1.72 s	1.72 s	1.71 s	1.84 s	1.29 d 6.5
4‴					1.29 d 6.5
OCH_3				3.74 s	

[a] Assignments made on the basis of COSY and HMBC and comparison with the literature data.[12−14]

The molecular formula of ochrocarpin B (**2**) was also determined to be $C_{25}H_{24}O_6$ by HRFABMS. The ^{1}H NMR spectrum of **2** was almost identical to that of **1**, except for the difference in the signals of the acyl side chain at C-6. The presence of a 3-methyl-1-oxobutyl acyl side chain in **2** was evident from the ^{1}H NMR values of δ 1.06 [6H, d, J = 6.6 Hz (H-4″ and H-5″), 2.24 [1H, m (H-3″)] and 3.17 [2H, m (H-2″)] and ^{13}C NMR values of δ 208.6 (C-1″), 52.3 (C-2″), 25.6 (C-3″), and 22.4 (C-4″and 5″). The ^{1}H NMR spectral data of the side chain at C-6 in **2** were almost identical with those of the known compound **14**, supporting their identical nature. This was further supported by the COSY (H3″/H-4″ or H-5″and H-2″/H-3″) and HMBC (H-4″ or H-5″/C-3″, C-2″; H-3″/C-2″, C-1″, C-4″, or C-5″, H-2″/C-3″, C-1″, C-6) correlations. On the basis of the above spectral data the structure of **2** was confirmed as 5-hydroxy-8-(1-hydroxy-1-methylethyl)-6-(3-methyl-1-oxobutyl)-4-phenyl-2*H*-furo[2′,3′:5,6]benzo[1,2-*b*]pyran-2-one.

Ochrocarpin C (**3**) was also obtained as a colorless liquid, and its molecular formula was deduced as $C_{24}H_{22}O_6$ by HRFABMS. Its UV and IR spectra indicated the presence of a phenolic hydroxyl group and a 5,7-dioxygenated coumarin moiety in its structure, as observed for **1** and **2**. The ^{1}H NMR spectrum of **3** was almost identical to that of **1** and **2** (Table 1), differing only in the nature of the acyl substituents at the C-6 position. The presence of a 1-oxo-2-methylpropyl side chain in **3** could be deduced from the signals at δ_H 1.17 [6H, d, J = 6.5 Hz (H-3″ and H-4″)] and 3.84 [1H, m (H-2″)] and δ_C 208.7 (C-1″), 39.6 (C-2″), and 18.8 (C-3″ and C-4″). Comparison of the ^{1}H NMR values of the 1-oxo-2-methylpropyl side chain of **3** with those of the side chain of **12** confirmed the structural assignment. The ^{13}C NMR values of **3** were assigned for all the carbons on the basis of HMQC and HMBC spectra as well as by comparison with those of **1**. Thus, the structure of **3** was established as 5-hydroxy-8-(1-hydroxy-1-methylethyl)-6-(2-methyl-1-oxopropyl)-4-phenyl-2*H*-furo[2′,3′:5,6]benzo[1,2-*b*]pyran-2-one.

Table 2. ^{13}C NMR Data for Compounds **1**−**5**[a] ($CDCl_3$, 125 MHz)

carbon	1	2	3	4	5
2	159.4	159.2	159.4	159.1	92.7
3	114.3	114.2	114.3	114.2	27.0
3a					110.0
4	156.9	156.7	156.8	156.7	164.2
4a	103.1				
5	163.3	163.1	163.7	163.4	161.9
5a					157.9
6	103.4	104.2	104.9	103.8	
7	155.5	155.4	155.4	155.6	159.4
8	162.4	162.3	162.4	159.0	114.2
9	98.6	98.4	98.5	98.2	155.0
9a					99.2
9b					161.9
10	110.4	109.7	110.4	110.6	
10a	153.4	153.1	153.2	153.2	
1′	139.1	139.0	139.0	139.1	138.2
2′, 6′	127.2	127.2	127.3	127.2	127.4
3′, 5′	127.8	127.8	127.8	127.7	127.8
4′	128.4	128.4	128.5	128.2	129.0
1″	208.6	208.6	208.7	208.6	71.7
2″	45.7	52.3	39.6	45.6	23.3
3″	16.3	25.6	18.8	16.2	23.3
4″	26.5	22.4	18.8	26.4	
5″	11.8	22.4		11.6	
1‴	69.1	69.2	69.1	79.4	204.5
2‴	28.8	28.8	28.8	29.2	40.4
3‴	28.8	28.8	28.8	29.2	19.4
4‴					19.4
OCH_3				57.8	

[a] Assignments made on the basis of HMQC and HMBC and comparison with literature data.[12−14]

Ochrocarpin D (**4**) was isolated as a colorless oil, with the molecular formula of $C_{26}H_{26}O_6$. The ^1H NMR spectrum of **4** was almost identical to that of **1**, except for the presence of additional signals at δ 3.74 and 57.8 in the ^1H and ^{13}C NMR spectral data, respectively. The HMBC spectrum of **4**, which showed correlations OMe/C-1‴, C-2‴, C-3‴; H-9/C-8, C-10, C-1‴, coupled with the mass spectrum of **4**, which showed a molecular ion peak 14 mass units greater than **1**, indicated the presence of a methoxyl group at the C-1‴ position. The ^{13}C NMR values for all the carbons were assigned and are given in Table 2. Thus, the structure of **4** was established as 5-hydroxy-8-(1-methoxy-1-methylethyl)-6-(2-methyl-1-oxobutyl)-4-phenyl-2*H*-furo-[2′,3′:5,6]benzo[1,2-*b*]pyran-2-one.

Ochrocarpin E (**5**) was isolated as a colorless viscous liquid, and its molecular formula was deduced as $C_{24}H_{24}O_6$ by HRFABMS. The ^1H NMR spectrum of **5** (Table 1) showed the presence of a coumarin moiety substituted by a chelated hydroxyl group, a phenyl ring at C-4, a 1-oxo-2-methylpropyl side chain, and two methyl singlets similar to those of **3**. The ^1H NMR spectrum also showed the presence of a triplet at δ 4.50 (1H, J = 9.1 Hz, H-2) and two doublets of doublets at δ 3.06 (1H, J = 10.0, 15.2 Hz, H-3α) and 2.93 (1H, J = 8.4, 15.5 Hz, H-3β) in **5** instead of the olefinic proton in **1** at C-9 of the furan ring. This information, together with the mass spectral data of **5**, which showed a molecular ion 2 mass units higher than that of **3**, indicated that the furan ring has been reduced to a dihydrofuran system in **5**, as was also observed for the known coumarins **11**, **13**, and **14**. From the HMBC correlations of **5** (Figure 2), it was clear that the dihydrofuran ring was located between C-3a and C-9b, and the phenolic hydroxyl group and the 1-oxo-2-methylpropyl side chains were placed at C-4 and C-9, respectively. A close comparison of the ^1H and ^{13}C NMR values of **5** with those of mammea A/BA cyclo F (**18**), isolated earlier from *Calophyllum dispar*,[15] confirmed the structure further. On the basis of the above spectral data, the structure of **5** was assigned as 2,3-dihydro-4-hydroxy-2-(1-hydroxy-1-methylethyl)-5-(2-methyl-1-oxopropyl)-9-phenyl-7*H*-furo[2′,3′:3,4]-benzo[1,2-*b*]pyran-2-one.

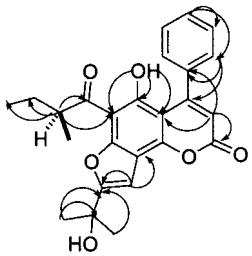


Figure 1. Selected HMBC correlations for **1**.

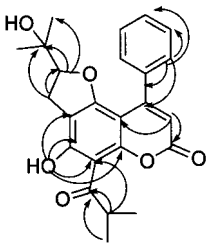


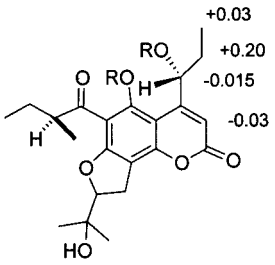
Figure 2. Selected HMBC correlations for **5**.

Table 3. NMR Data for Compounds **6** and **7**[a] ($CDCl_3$)

	6		7	
position	^1H	^{13}C	^1H	^{13}C
2		159.4		159.6
3	6.22 s	106.2	6.24 s	106.5
4		155.9		156.4
4a		97.3		97.2
5		163.6		163.6
6		104.9		104.8
7		161.4		161.4
8	4.93 t 9.1	93.3	4.89 t 8.9	93.3
9	3.15 m	26.9	3.18 br d 9.8	26.8
10		110.4		110.6
10a		157.3		157.3
1′	6.29 dd 3.8, 8.7	72.7	6.49 dd 3.6, 8.9	72.6
2′	1.75 m	28.3	1.70 m	28.8
3′	1.04 t 7.2	9.8	0.99 t 7.5	10.3
1″		210.6		210.6
2″	3.86 m	46.9	3.86 m	46.9
3″	1.23 d 6.5	16.7	1.23 d 6.4	16.7
4″ H_α	1.87 m	26.2	1.88 m	26.3
4″ H_β	1.48 m		1.47 m	
5″	0.97 t 7.5	11.8	0.96 t 7.2	11.9
1‴		71.7		71.8
2‴	1.28 s	24.9	1.23 s	24.3
3‴	1.38 s	27.2	1.38 s	27.2
OH-5	14.21 s		14.23 s	
$OCOCH_3$	2.14 s	21.0	2.16 s	21.0
$OCOCH_3$		170.3		170.7

[a] Assignments made on the basis of COSY and HMBC and comparison with literature data.[8,12−14]

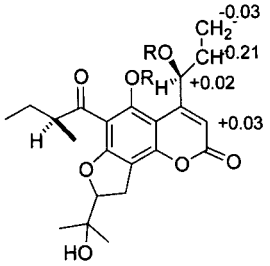
Ochrocarpin F (**6**) was isolated as a colorless liquid and was deduced to have the composition $C_{24}H_{30}O_8$ by HR-FABMS and ^{13}C NMR spectral data. The ^1H NMR spectrum of **6** (Table 3) was similar to that of **13** except for the difference in the substitution at the C-4 position. The ^1H NMR spectrum of the side chain at C-4 in **6** showed signals at δ 6.29 [1H, dd, J = 3.8, 8.7 Hz (H-1′)], 1.75 (2H, m, H-2′), 2.14 (3H, s, $OCOCH_3$), and 1.04 [3H, t, J = 7.2 Hz, H-3′)], similar to the side chain observed in surangin B (**19**) isolated from *Mammea longifolia*.[8] This was further supported by COSY (H-1′/H-2′ and H-2′/H-3′) and HMBC (H-1′/C-4, C-2′, C-3′, C-OAc; H-2/C-1′, C-3′, C-4) correlations. The ^{13}C NMR values for all the carbons were assigned on



21*R* R = (*R*)-(-)-MPA

21*S* R = (*S*)-(+)-MPA

Figure 3. Difference in the δ^{RS} ($\delta^R - \delta^S$) values for the (*R*)- and (*S*)-MPA esters **21*R*** and **21*S*** in $CDCl_3$.



23*R* R = (*R*)-(-)-MPA

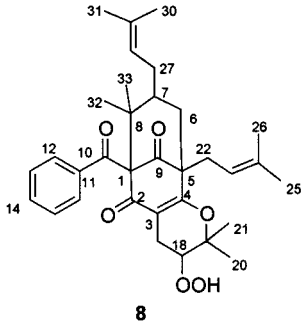
23*S* R = (*S*)-(+)-MPA

Figure 4. Difference in the δ^{RS} ($\delta^R - \delta^S$) values for the (*R*)- and (*S*)-MPA esters **23*R*** and **23*S*** in $CDCl_3$.

the basis of HMQC and HMBC and are given in Table 3. The stereochemistry at C-1′ in **6** was established by converting the secondary acetate to the corresponding alcohol (**20**) by treatment with methanolic K_2CO_3. The secondary alcohol (**20**) was then converted to the corresponding methoxyphenylacetate (MPA) ester as described by Latypov et al.[16] Acylation of **20** with (*R*)-(−)- and (*S*)-(+)-methoxyphenyl acetic acid (MPAA) yielded the (*R*)-ester (**21*R***) and the (*S*)-ester (**21*S***). The chemical shift differences ($\Delta^{RS} = \delta^R - \delta^S$) of the individual protons of **21*R*** and **21*S*** are shown in Figure 3. The systematic arrangement of negative and positive values indicated that the absolute configuration of C-1′ is *S*, as indicated in the structures of **6** and **20**. On the basis of the above spectral and chemical evidence, **6** was confirmed as 8,9-dihydro-5-hydroxy-8-(1-hydroxy-1-methylethyl)-6-(2-methyl-1-oxobutyl)-4-(1*S*-acetoxypropyl)-2*H*-furo[2′,3′:5,6]benzo[1,2-*b*]pyran-2-one.

The molecular formula of ochrocarpin G (**7**) was deduced as $C_{24}H_{30}O_8$ by HRFABMS, identical to that of **6**. The ^1H NMR data of **7** were very similar to that of **6** except for differences in the proton values for the C-1′, C-2′, and C-3′ positions (Table 3). On the basis of HMQC and HMQC spectral data, the ^{13}C NMR values for all the carbons in **7** were assigned, and it was found that the ^{13}C NMR values for compounds **6** and **7** were almost identical. This suggested that **7** is an isomer of **6** at the C-1′ position. To confirm the stereochemistry at C-1′, **7** was converted to the corresponding MPA esters as described for **6**. The chemical shift differences (Δ^{RS}) of the individual protons of **23*R*** and **23*S*** are shown in Figure 4. From the systematic arrangement of positive and negative Δ^{RS} values, the absolute configuration at C-1′ was established as *R*. Thus **7** was established as 8,9-dihydro-5-hydroxy-8-(1-hydroxy-1-methylethyl)-6-(2-methyl-1-oxobutyl)-4-(1*R*-acetyloxypropyl)-2*H*-furo[2′,3′:5,6]benzo[1,2-*b*]pyran-2-one.

Column chromatography of the $CHCl_3$-soluble fraction over Sephadex LH-20 followed by a reversed-phase HPLC yielded three new benzophenone derivatives, ochrocarpinones A−C (**8**−**10**), together with the known 15,16-dihydro-16-hydroperoxyplukenetione (**16**).



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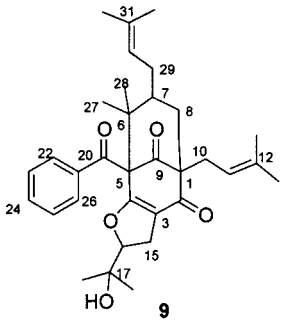

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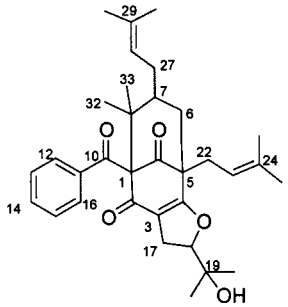

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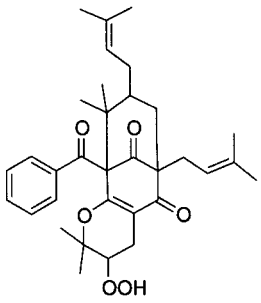

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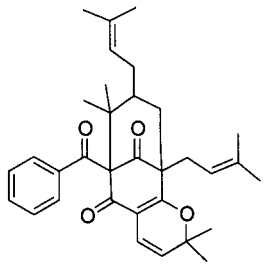

24

The molecular formula of ochrocarpinone A (**8**) was assigned as $C_{33}H_{42}O_6$ by HRFABMS and ^{13}C NMR spectral data; this composition requires 13 degrees of unsaturation. The ^1H and ^{13}C NMR data (Table 4) indicated the presence of a benzoyl group, two additional carbonyl groups, one of which was a part of an enone system, and two isopentenyl groups. The absence of any additional olefinic carbons required the presence of three additional rings in the structure. A close comparison of the spectral data of **8** with those of 15,16-dihydro-16-hydroperoxyplukenetione (**16**), isolated earlier from *Clusia havetiodes*,[17] indicated that the compounds had very similar structures. In particular, the presence of a substituted bicyclo[3.3.1]nonane moiety and a 2,2-dimethyl-3-hydroperoxy-2*H*-dihydropyran ring was indicated in the structure of **8**. Compound **8** gave a positive peroxide test with FeSCN,[18] which indicated the presence of a peroxide group in its structure as in **16**. The HMBC correlations H-6/C-17, C-9, C-7, C-5, C-4; H-22/C-23, C-5, C-9, C-4, C-6; and H-17/C-18, C-4, C-3, C-2 (Figure 5) required that the dihydropyran ring be placed between C-3 and C-4 as in plukenetione G (**24**),[19] isolated previously from *Clusia plukenetii*. Thus, the structure of **8** was assigned as 17,18-dihydro-18-hydroperoxyplukenetione G.

Table 4. NMR Data for Compounds **8**−**10**[a] ($CDCl_3$)

	8		**9**		**10**	
position	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1		79.2		60.3		79.2
2		188.2		193.3		188.0
3		118.4		115.6		117.6
4		175.6		172.4		176.2
5		55.6		69.4		55.9
6	2.16 m	39.8		48.2	2.15 m	39.6
7	1.49 m	43.4	1.50 m	42.8	1.52 m	43.8
8		47.8	2.10 m	39.3		48.1
9		207.2		205.1		206.5
10		193.8	2.68 m	30.4		193.4
11		136.8	5.04 t 7.2	120.7		136.7
12	7.54 d 8.0	128.2		133.7	7.52 d 8.1	128.4
13	7.26 dd 8.1, 8.0	128.0	1.67 s	25.9	7.26 dd, 7.8, 8.1	128.1
14	7.40 t 8.1	132.2	1.70 s	17.9	7.40 t 8.0	132.2
15	7.26 dd 8.1, 8.0	128.0	3.10 dd 14.8, 10.6 3.04 dd 15.2, 8.8	26.0	7.26 dd 7.8, 8.1	128.1
16	7.54 d 8.0	128.2	4.63 dd 12.0, 8.0	90.3	7.52 d 8.1	128.4
17	3.03 dd 15.0, 10.5 2.94 dd 15.2, 8.5	26.9		71.2	3.00 dd 15.0, 10.5 2.92 dd 15.2, 8.6	26.2
18	4.84 dd 11.5, 7.6	93.6	1.24 s	23.9	4.82 dd 10.8, 7.5	92.6
19		71.8	1.38 s	26.8		72.1
20	1.13 s	27.0		193.7	1.23 s	26.8
21	1.24 s	23.7		136.9	1.29 s	23.7
22	2.52 m	27.2	7.46 d 8.0	128.4	2.53 m	27.6
23	5.03 t 8.1	120.5	7.25 dd 7.6, 8.1	128.2	5.08 t 7.8	118.4
24		134.9	7.38 t 8.1	132.2		135.4
25	1.71 s	18.2	7.25 dd 7.6, 8.1	128.2	1.65 s	18.2
26	1.81 s	26.0	7.46 d 8.0	128.4	1.70 s	25.8
27	2.0 m	29.2	1.16 s	23.2	1.98 m	28.9
28	4.98 t 7.6	122.6	1.39 s	16.5	4.97 t 8.0	122.6
29		133.7	2.11 m	26.9		133.9
30	1.69 s	18.0	4.96 t 7.2	122.4	1.68 s	17.9
31	1.58 s	26.1		137.9	1.56 s	25.2
32	1.35 s	23.8	1.64 s	25.8	1.13 s	23.8
33	1.47 s	15.9	1.67 s	18.2	1.39 s	15.9

[a] Assignments made on the basis of COSY and HMBC and comparison with the literature data.[17,19]

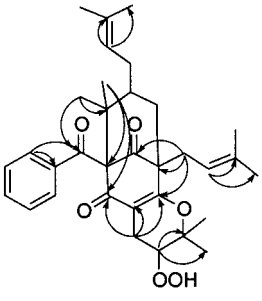

Figure 5. Selected HMBC correlations for **8**.

Ochrocarpinone B (**9**) was isolated as a viscous liquid, whose molecular formula was assigned as $C_{33}H_{42}O_5$ by HRFABMS; it gave a negative test for peroxides, but an IR absorption at 3502 cm^{-1} supported the presence of a hydroxyl group. The NMR spectra of **9** (Table 4) indicated that it also contained a benzoyl group, two additional carbonyl groups, one of which one was part of an enone ring, and two isopentenyl groups. These spectra also indicated the presence of a 2-(1-hydroxy-1-methylethyl)-

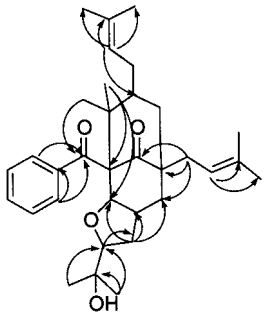

Figure 6. Selected HMBC correlations for **9**.

dihydrofuran ring (as in **6** and **7**) in place of the dihydropyran ring of **8**, **16**, and **24**. From the cross-peaks observed in the HMBC spectrum (Figure 6), it was inferred that the 2-(1-hydroxy-1-methylethyl)dihydrofuran ring was located at C-3, C-4. The structure was thus confirmed as that of **9**, with the stereochemistry undetermined.

The molecular formula of ochrocarpinone C (**10**) was also established as $C_{33}H_{42}O_5$ by HRFABMS. A close comparison of the ^{1}H and ^{13}C NMR data of **10** with that of **9** (Table 4) indicated the close similarity of the two compounds, which differed only in the position of the 2-(1-hydroxy-1-methylethyl)dihydrofuran ring. The HMBC spectrum, which showed the correlations H-6/C-17, C-9, C-7, C-5, C-4 and H-22/C-23, C-5, C-9, C-4, required the location of the 2-(1-hydroxy-1-methylethyl)dihydrofuran ring at C-3 and C-4 as in **10**.

It should be noted that none of the new coumarins (**1**−**7**) gave any significant $[\alpha]_D$ values. The same observation has been made for a number of coumarins isolated from the genus *Mammea*.[15] Since the known compound **13** was available in sufficient quantity, we thus determined its enantiomeric purity using *R*-(−)-α-acetoxyphenylacetic acid as the chiral solvating agent as reported earlier for compound **14**.[15] The ^{1}H NMR spectrum of **13** in $CDCl_3$ with 0.3 M *R*-(−)-α-acetoxyphenylacetic acid showed that the signals for the furan part of **13** at C-8 were doubled, indicating the racemic nature of the compound and confirming the reported evidence.[15] Due to the small amounts of compounds isolated, this experiment with the chiral reagent could not be carried out with compounds **5**−**7**, but it is assumed that these compounds are also racemic at the C-8 position of their respective furan moieties. By reasonable inference it is likely that the benzophenones **9** and **10** also have racemic dihydrofuran moieties.

In view of the confusion previously noted surrounding the correct placement of species formerly assigned to *Ochrocarpos*, it is interesting to note that the presence of coumarins in the extract may indicate a relationship with *Calophyllum*[20] and *Mammea*,[21] while the presence of benzophenones indicates a relationship to *Garcinia*.[22] This would support the close relationship of the three genera *Calophyllum, Mammea,* and *Garcinia,* the latter two of which contain the species formerly assigned to *Ochrocarpos*.[23]

The isolated compounds were tested for cytotoxicity against A2780 ovarian cancer cells. As shown in Table 5, all the isolated compounds (**1**−**16**) were found to be weakly cytotoxic, with IC_{50} values ranging between 3.2 and 11.4 μg/mL.

Experimental Section

General Experimental Procedures. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter. IR and UV spectra were measured on MIDAC M-series FTIR and Shi-

Table 5. Cytotoxicities of Compounds **1**−**16**[a]

compound	IC_{50}, μg/mL
1	5.2 ± 0.4
2	3.8 ± 0.3
3	3.7 ± 0.5
4	6.3 ± 0.3
5	4.9 ± 0.1
6	8.9 ± 0.6
7	8.6 ± 0.3
8	6.9 ± 0.3
9	7.4 ± 0.2
10	8.2 ± 0.3
11	4.4 ± 0.5
12	10.8 ± 0.5
13	8.2 ± 0.1
14	6.4 ± 0.6
15	4.5 ± 0.3
16	8.4 ± 0.6

[a] The concentration of compound that inhibited 50% (IC_{50}) of the growth of the A2780 mammalian cell line according to the procedure described.[1,19]

madzu UV-1201 spectrophotometers, respectively. NMR spectra were obtained on a JEOL Eclipse 500 spectrometer. The HR mass were obtained on a JEOL HX-110 instrument. The chemical shifts are given in ppm with TMS (tetramethylsilane) as internal reference, and coupling constants are reported in Hz. Sephadex LH-20 and reversed-phase Si gel (LRP-2, 200 μm) were used for column chromatography. Reversed-phase HPLC was performed on a Shimadzu LC-10AT instrument with an ODS C-18 column (250 × 10 mm).

Cytotoxic Bioassays. The A-2780 ovarian cancer cell line assay was performed at Virginia Polytechnic and State University as previously reported.[1,24]

Plant Material. The bark of *Ochrocarpos punctatus* H. Perr. (Clusiaceae = Guttiferae) was collected at the Station Forestiere d'Ampijoroa, piste vers jardin botanique, elev. 200 m, 16°18′40″ S, 46°48′00″ E, in the province of Mahajanga in Madagascar on March 9, 1996, by P.-J. Rakotomalaza, K. Sikes, C. Rasolomanana, S. Andrianasolo, and F. R. Andriantsiferana. The voucher (*Rakotomalaza et al. 639*) is deposited at the Missouri Botanical Garden (MO), with duplicate specimens deposited at the Parc Botanique and Zoologique de Tsimbazaza (TAN), Centre National D'Application et des Recherches Pharmaceutiques (CNARP), and the Muséum National d'Histoire Naturelle in Paris (P), and it was identified by Roy E. Gereau of the Missouri Botanical Garden. The plant was a small tree 7−8 m tall with yellow latex and white flowers. The forestry station at Ampijoroa is a protected parcel of semideciduous forest in Madagascar's western floristic province.

Extract Preparation. Field-dried plant was ground in a hammermill, then extracted by overnight percolation at room temperature with a 1:1 mixture of reagent-grade CH_2Cl_2−MeOH. The solvent was withdrawn quickly by suction, and the specimen was covered with 100% MeOH. After 30 min the MeOH wash was drained into the same flask as the CH_2Cl_2−MeOH extract, and the combined organic solvent extracts were evaporated on a rotary evaporator below 40 °C to give a thick concentrate, which was transferred into a glass bottle for storage. The bottle was dried overnight under high vacuum to give the dried CH_2Cl_2−MeOH extract N092783.

Isolation of Bioactive Compounds. The crude extract (1.9 g) was suspended in aqueous MeOH (MeOH−H_2O, 9:1, 200 mL) and extracted with *n*-hexane (3 × 200 mL). The aqueous layer was then diluted to 60% MeOH (v/v) with H_2O and extracted with $CHCl_3$ (3 × 200 mL). The aqueous layer was concentrated, and the residue was suspended in H_2O (25 mL) and extracted with *n*-BuOH (3 × 25 mL). The *n*-hexane extract was fractionated over Sephadex LH-20 using *n*-hexane−EtOAc (100:0 to 0:100) to furnish seven fractions (A−G), of which fractions C−E were found to be active. Fraction C on preparative TLC over RP C_{18} using MeOH−H_2O (90:10) yielded seven fractions, C-1 to C-7. Fraction C-1 on reversed-phase HPLC with the mobile phase CH_3CN−H_2O (75:25) furnished the three new coumarins **2** (1.2 mg), **3** (0.8 mg), and **5** (0.75 mg) and the five known compounds **11** (1.3 mg), **12** (1.1 mg), **13** (4.6 mg), **14** (0.8 mg), and **15** (1.0 mg). Fractionation of D on preparative TLC over RP C_{18} using MeOH−H_2O (90:10) followed by reversed-phase HPLC with the mobile phase CH_3CN−H_2O (70:30) furnished the two new coumarins **1** (1.5 mg) and **4** (0.65 mg). Similarly fraction E on preparative TLC over RP C_{18} using MeOH−H_2O (80:20) followed by reversed-phase HPLC with the mobile phase CH_3CN−H_2O (70:30) furnished the two new coumarins **6** (2.6 mg) and **7** (2.4 mg).

The $CHCl_3$-soluble portion was fractionated over Sephadex LH-20, eluted with *n*-hexane−EtOAc (100:0 to 0:100) to furnish nine fractions (A−I), of which fractions C and I were found to be active. Fraction C on preparative TLC over RP C_{18} using MeOH−H_2O (80:20) followed by reversed-phase HPLC with the mobile phase CH_3CN−H_2O (75:25) furnished the new benzophenone **8** (1.5 mg) and the known compound **16** (1.1 mg). Similarly fraction I on preparative TLC over RP C_{18} using MeOH−H_2O (70:30) followed by reversed-phase HPLC with the mobile phase CH_3CN−H_2O (70:20) furnished the two new benzophenones **9** (1.8 mg) and **10** (1.6 mg). The structures of the six known compounds **11**−**16** were identified by comparison of their spectral data with the literature values.[8−10]

Ochrocarpin A (1): viscous liquid; $[\alpha]_D$ −0.28° (*c* 0.32, $CHCl_3$); UV (MeOH); λ_{max} (log ε) 236 (3.76), 285 (3.88), 332 (3.49); IR ($CHCl_3$) ν_{max} 3445, 1730, 1715, 1612, 755, 702 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; HRFABMS *m*/*z* 421.1662 $[M + H]^+$ (calcd for $C_{25}H_{25}O_6$, 421.1651).

Ochrocarpin B (2): viscous liquid; $[\alpha]_D$ +0.12° (*c* 0.45, $CHCl_3$); UV (MeOH); λ_{max} (log ε) 234 (3.42), 287 (3.48), 338 (3.69); IR ($CHCl_3$) ν_{max} 3440, 1732, 1713, 1625, 755, 700 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; HRFABMS *m*/*z* 421.1637 $[M + H]^+$ (calcd for $C_{25}H_{25}O_6$, 421.1651).

Ochrocarpin C (3): viscous liquid; $[\alpha]_D$ +0.21° (*c* 0.38, $CHCl_3$); UV (MeOH); λ_{max} (log ε) 229 (3.56), 285 (3.83), 339 (3.46); IR ($CHCl_3$) ν_{max} 3442, 1728, 1715, 1609, 753, 702 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; HRFABMS *m*/*z* 407.1492 $[M + H]^+$ (calcd for $C_{24}H_{23}O_6$, 407.1495).

Ochrocarpin D (4): viscous liquid; $[\alpha]_D$ −0.48° (*c* 0.52, $CHCl_3$); UV (MeOH); λ_{max} (log ε) 235 (3.75), 285 (3.78), 326 (3.39); IR ($CHCl_3$) ν_{max} 3440, 1732, 1715, 1610, 755, 700 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; HRFABMS *m*/*z* 435.1801 $[M + H]^+$ (calcd for $C_{26}H_{27}O_6$, 435.1808).

Ochrocarpin E (5): viscous liquid; $[\alpha]_D$ −0.06° (*c* 0.46, $CHCl_3$); UV (MeOH); λ_{max} (log ε) 236 (3.64), 280 (3.79), 334 (3.52); IR ($CHCl_3$) ν_{max} 3445, 1735, 1710, 1615, 755, 705 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; HRFABMS *m*/*z* 409.1635 $[M + H]^+$ (calcd for $C_{24}H_{25}O_6$, 409.1651).

Ochrocarpin F (6): viscous liquid; $[\alpha]_D$ −0.16° (*c* 0.64, $CHCl_3$); UV (MeOH); λ_{max} (log ε) 224 (4.32), 288 (3.96), 334 (4.49); IR ($CHCl_3$) ν_{max} 3345, 1740, 1715, 1612, 1215, 1150, 1030, 955, 934 cm^{-1}; ^1H and ^{13}C NMR, see Table 3; HRFABMS *m*/*z* 447.2019 $[M + H]^+$ (calcd for $C_{24}H_{31}O_8$, 447.2019).

Hydrolysis of Ochrocarpin F (6). Ochrocarpin F (**6**, 1.0 mg) was suspended in 10% methanolic K_2CO_3 (5 mL) and the reaction mixture refluxed for 6 h. TLC showed the absence of the starting material. The reaction mixture was then concentrated, water (3 mL) was added, and the solution was acidified with 1 N HCl and extracted with CH_2Cl_2 (3 × 5 mL). The combined CH_2Cl_2 extracts were concentrated and purified by normal-phase preparative TLC (*n*-hexanes−EtOAc, 75:25) to furnish alcohol **20** (0.7 mg): ^1H NMR ($CDCl_3$) δ 6.49 (1H, s, H-3), 5.33 (1H, dd, *J* = 3.7, 8.9 Hz, H-1′), 1.75 (2H, m, H-2′), 0.94 (3H, t, *J* = 7.2 Hz, H-3′), 3.90 (1H, m, H-2″), 1.23 (3H, d, *J* = 6.5 Hz, H-3″), 1.85 (1H, m, H_α-4″), 1.52 (1H, m, H_β-4″), 0.98 (3H, t, *J* = 7.2 Hz, H-5″), 4.88 (1H, t, *J* = 9.1 Hz, H-8), 3.15 (2H, m, H-9), 1.28 (3H, s, H-2‴), 1.38 (3H, s, H-3‴), 14.17 (1H, s, OH-5); HRFABMS *m*/*z* 405.1912 $[M + H]^+$ (calcd for $C_{22}H_{29}O_7$ 405.1913).

Preparation of the (*R*)-(−)-α-Methoxyphenyl Acetate of 20. Compound **20** (0.3 mg, 0.00075 mmol) was treated with (*R*)-(−)-α-MPAA (1.24 mg, 0.0075 mmol) and 1-[3-(dimethyl-

amino)propyl]-3-ethylcarbodiimide hydrochloride (EDC) (1.44 mg, 0.0075 mmol) in the presence of a catalytic amount of 4-pyrrolidinopyridine in CH_2Cl_2 (0.5 mL), and the mixture was stirred for 24 h at room temperature. The di[(*R*)-(−)-α-methoxyphenyl acetate] (**21*R***, 0.23 mg) was obtained after purification by normal-phase preparative TLC (*n*-hexanes−EtOAc, 75:25): ^{1}H NMR ($CDCl_3$) δ 6.22 (1H, s, H-3), 6.33 (1H, dd, J = 3.8, 8.9 Hz, H-1′), 1.97 (2H, m, H-2′), 1.03 (3H, t, J = 7.4 Hz, H-3′), 3.86 (1H, m, H-2″), 1.21 (3H, d, J = 6.5 Hz, H-3″), 1.85 (1H, m, H$_\alpha$-4″), 1.50 (1H, m, H$_\beta$-4″), 0.98 (3H, t, J = 7.2 Hz, H-5″), 4.93 (1H, t, J = 9.1 Hz, H-8), 3.15 (2H, m, H-9), 1.28 (3H, s, H-2‴), 1.38 (3H, s, H-3‴). The α-methoxyphenylacetic acid part had δ 7.20−7.42 (10H, m, aromatic protons), 4.72 (2H, s), 3.38 (6H, s, 2 × −OCH_3).

Preparation of the (*S*)-(+)-α-Methoxyphenyl Acetate of 20. Compound **20** (0.3 mg, 0.00075 mmol) was treated with (*S*)-(+)-α-MPA (1.24 mg, 0.0075 mmol) and EDC (1.44 mg, 0.0075 mmol) in the presence of a catalytic amount of 4-pyrrolidinopyridine in CH_2Cl_2 (0.5 mL), and the mixture was stirred for 18 h at room temperature. Workup of the reaction product as described above furnished the di[(*S*)-(+)-α-methoxyphenyl acetate] (**21*S***, 0.23 mg): ^{1}H NMR ($CDCl_3$) δ 6.25 (1H, s, H-3), 6.48 (1H, dd, J = 3.8, 8.6 Hz, H-1′), 1.77 (2H, m, H-2′), 1.00 (3H, t, J = 7.5 Hz, H-3′), 3.86 (1H, m, H-2″), 1.24 (3H, d, J = 6.5 Hz, H-3″), 1.87 (1H, m, H$_\alpha$-4″), 1.48 (1H, m, H$_\beta$-4″), 0.96 (3H, t, J = 7.2 Hz, H-5″), 4.89 (1H, t, J = 9.1 Hz, H-8), 3.13 (2H, m, H-9), 1.27 (3H, s, H-2‴), 1.36 (3H, s, H-3‴). The α-methoxyphenylacetic acid part had δ 7.24−7.40 (10H, m, aromatic protons), 4.68 (2H, s), 3.38 (6H, s, 2 × −OCH_3).

Ochrocarpin G (7): viscous liquid; $[\alpha]_D$ −0.12° (*c* 0.42, $CHCl_3$); UV (MeOH); λ_{max} (log ϵ) 226 (3.98), 285 (4.21), 326 (4.24); IR ($CHCl_3$) ν_{max} 3405, 1735, 1708, 1610, 1212, 1146, 1035, 955, 932 cm^{-1}; ^{1}H and ^{13}C NMR, see Table 3; HRFABMS *m*/*z* 447.2036 [M + H]$^+$ (calcd for $C_{24}H_{31}O_8$, 447.2019).

Hydrolysis of Ochrocarpin G (7). Ochrocarpin G (**7**, 0.8 mg) was hydrolyzed as previously described to furnish the alcohol **22** (0.6 mg): ^{1}H NMR ($CDCl_3$) δ 6.49 (1H, s, H-3), 5.46 (1H, dd, J = 3.6, 8.6 Hz, H-1′), 1.78 (2H, m, H-2′), 0.91 (3H, t, J = 7.5 Hz, H-3′), 3.88 (1H, m, H-2″), 1.24 (3H, d, J = 6.6 Hz, H-3″), 1.87 (1H, m, Hα-4″), 1.45 (1H, m, Hβ-4″), 0.96 (3H, t, J = 7.2 Hz, H-5″), 4.88 (1H, t, J = 9.1 Hz, H-8), 3.14 (2H, m, H-9), 1.24 (3H, s, H-2‴), 1.36 (3H, s, H-3‴), 14.15 (1H, s, OH-5); HRFABMS *m*/*z* 405.1923 [M + H]$^+$ (calcd for $C_{22}H_{29}O_7$, 405.1913).

Preparation of the (*R*)-(−)-α-Methoxyphenyl Acetate of 22. Alcohol **22** (0.3 mg, 0.00075 mmol) was treated with (*R*)-(−)-α-MPAA (1.24 mg, 0.0075 mmol) and EDC (1.44 mg, 0.0075 mmol) in the presence of a catalytic amount of 4-pyrrolidinopyridine in CH_2Cl_2 (0.5 mL), and the mixture was stirred for 24 h at room temperature. The di[(*R*)-(−)-α-methoxyphenyl acetate] (**23*R***, 0.23 mg) was obtained after purification by normal-phase preparative TLC (*n*-hexanes−EtOAc, 70:30): ^{1}H NMR ($CDCl_3$) δ 6.24 (1H, s, H-3), 6.49 (1H, dd, J = 3.6, 8.9 Hz, H-1′), 1.75 (2H, m, H-2′), 1.01 (3H, t, J = 7.2 Hz, H-3′), 3.88 (1H, m, H-2″), 1.23 (3H, d, J = 6.5 Hz, H-3″), 1.87 (1H, m, H$_\alpha$-4″), 1.49 (1H, m, H$_\beta$-4″), 0.98 (3H, t, J = 7.2 Hz, H-5″), 4.87 (1H, t, J = 9.1 Hz, H-8), 3.14 (2H, m, H-9), 1.27 (3H, s, H-2‴), 1.38 (3H, s, H-3‴). The α-methoxyphenylacetic acid part had δ 7.20−7.40 (10H, m, aromatic protons), 4.69 (2H, s), 3.36 (6H, s, 2 × −OCH_3); EIMS *m*/*z* (rel int) 700 [M]$^+$ (12.6), 614 (6.8), 536 (2.6), 535 (13.5), 450 (19.8), 327 (23.4), 309 (8.9), 189 (12.1), 177 (14.6), 105 (100), 91 (12.2), 77 (34), 69 (54.6).

Preparation of the (*S*)-(+)-α-Methoxyphenyl Acetate of 22. Alcohol **22** (0.3 mg, 0.00075 mmol) was treated with (*S*)-(+)-α-MPAA (1.24 mg, 0.0075 mmol) and EDC (1.44 mg, 0.0075 mmol) in the presence of a catalytic amount of 4-pyrrolidinopyridine in CH_2Cl_2 (0.5 mL), and the mixture was stirred for 24 h at room temperature. Workup of the reaction product as described above furnished the di[(*S*)-(+)-α-methoxyphenyl acetate] (**23*S***, 0.23 mg): ^{1}H NMR ($CDCl_3$) δ 6.21 (1H, s, H-3), 6.29 (1H, dd, J = 3.6, 8.8 Hz, H-1′), 1.96 (2H, m, H-2′), 1.04 (3H, t, J = 7.5 Hz, H-3′), 3.86 (1H, m, H-2″), 1.23 (3H, d, J = 6.5 Hz, H-3″), 1.85 (1H, m, H$_\alpha$-4″), 1.48 (1H, m, H$_\beta$-4″), 0.98 (3H, t, J = 7.2 Hz, H-5″), 4.91 (1H, t, J = 9.1 Hz, H-8), 3.16 (2H, m, H-9), 1.27 (3H, s, H-2‴), 1.38 (3H, s, H-3‴). The α-methoxyphenylacetic acid part had δ 7.20−7.38 (10H, m, aromatic protons), 4.70 (2H, s), 3.38 (6H, s, 2 × −OCH_3); EIMS *m*/*z* (rel int) 700 [M]$^+$ (8.4), 614 (10.2), 572 (14.5), 535 (18.4), 450 (21.6), 332 (15.6), 327 (28.9), 309 (6.4), 189 (17.8), 177 (16.4), 105 (100), 91 (23.4), 77 (18.8), 69 (32.6).

Ochrocarpinone A (8): viscous liquid; $[\alpha]_D$ +8.7° (*c* 0.15, $CHCl_3$); UV (MeOH); λ_{max} (log ϵ) 246 (3.86), 275 (4.10); IR ($CHCl_3$) ν_{max} 3608, 1735, 1706, 1690, 1655, 1035, 955 cm^{-1}; ^{1}H and ^{13}C NMR, see Table 4; EIMS *m*/*z* (rel int) 534 [M]$^+$ (1.2), 518 (4.6), 503 (2.6), 465 (3.5), 450 (19.8), 422 (15.2), 381 (28.6), 327 (37.5), 309 (8.9), 189 (14.4), 177 (10.6), 105 (100), 91 (12.2), 77 (55), 69 (74.8); HRFABMS *m*/*z* 535.3067 [M + H]$^+$ (calcd for $C_{33}H_{43}O_6$, 535.3060).

Ochrocarpinone B (9): viscous liquid; $[\alpha]_D$ −3.5° (*c* 0.22, $CHCl_3$); UV (MeOH); λ_{max} (log ϵ) 242 (3.48), 268 (3.91); IR ($CHCl_3$) ν_{max} 3502, 1738, 1712, 1698, 1650, 1028, 949 cm^{-1}; ^{1}H and ^{13}C NMR, see Table 4; CIMS (positive mode) *m*/*z* (rel int) 519 [M + H]$^+$ (21.8), 501 (4.6), 479 (6.8), 451 (29.8), 397 (5.6), 359 (8.6), 327 (17.3), 225 (8.5), 165 (6.4), 105 (43.5), 85 (72.2), 83 (100), 69 (62.8), 57 (95); HRFABMS *m*/*z* 519.3095 [M + H]$^+$ (calcd for $C_{33}H_{43}O_5$, 519.3110).

Ochrocarpinone C (10): viscous liquid; $[\alpha]_D$ +10.2° (*c* 0.18, $CHCl_3$); UV (MeOH); λ_{max} (log ϵ) 245 (3.76), 273 (3.90); IR ($CHCl_3$) ν_{max} 3486, 1732, 1715, 1692, 1642, 1032, 945 cm^{-1}; ^{1}H and ^{13}C NMR, see Table 4; CIMS (positive mode) *m*/*z* (rel int) 519 [M + H]$^+$ (43.5), 501 (8.5), 479 (12.6), 451 (63.6), 397 (8.4), 359 (5.4), 327 (21.2), 225 (2.3), 123 (17.5), 85 (42.6), 83 (68.7), 69 (52.6), 57 (100); HRFABMS *m*/*z* 519.3121 [M + H]$^+$ (calcd for $C_{33}H_{43}O_5$, 519.3110).

Mammea A/AB cyclo F (13): ^{1}H NMR (0.03 M in $CDCl_3$ + 0.3 M *R*-(−)-α-acetoxyphenylacetic acid, 500 MHz) δ_H 5.81 (1H, s, H-3), 14.27 (1H, s, 5-OH), 4.83 (1H, t, J = 9.2 Hz, H-8), 4.82 (1H, t, J = 9.1 Hz, H-8), 3.26 (2H, d, J = 9.2 Hz, H-9), 3.24 (2H, d, J = 9.2 Hz, H-9), 7.37 (2H, m, H-2′ and H-6′), 7.43 (3H, m, H-3′, H-4′, H-5′), 3.55 (1H, m, H-2″), 1.12 (3H, dd, J = 1.9, 7.2 Hz, H-3″), 1.54 (1H, m, H$_\beta$-4″), 1.88 (1H, m, H$_\alpha$-4″), 0.91 (3H, t, J = 7.2 Hz, H-5″), 1.28 (3H, s, H-2‴), 1.27 (3H, s, H-2‴), 1.38 (3H, s, H-3‴), 1.36 (3H, s, H-3‴).

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