Novel 2-Arylbenzofuran Derivatives from *Artocarpus petelotii*

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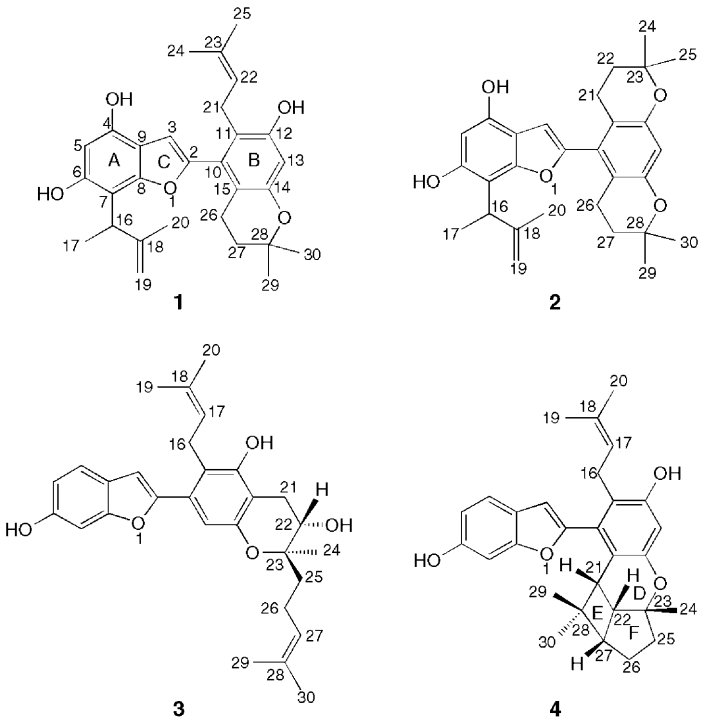
Further phytochemical investigations on the root barks of *Artocarpus petelotii* GAGNEP afforded four novel isoprenylated 2-arylbenzofuran derivatives, namely artopetelins D–G (**1**–**4**). Their structures were elucidated by spectroscopic methods, mainly by 2D-NMR techniques. The biogenetic origins of artopetelins F and G (**3** and **4**) were also postulated.

Introduction. – In the course of searching for bioactive isoprenylated phenols from Chinese Moraceous plants [1], we have investigated the chemical constituents of *Artocarpus petelotii* GAGNEP and reported the isolation of three 2-arylbenzofurans, artopetelins A–C [2]. A re-examination of the EtOH extract of the root barks of this plant provided four novel isoprenylated 2-arylbenzofuran derivatives, artopetelins D–G (**1**–**4**). To the best of our knowledge, compounds **1** and **2** are the first two 2-arylbenzofurans with isoprenoid substituents in the form of 1,2-dimethylallyl (=1,2-dimethylprop-2-enyl) groups. Compound **3** is the first 2-arylbenzofuran bearing a 3-hydroxy-2-methyl-2-(4-methylpent-3-enyl)chroman moiety, and compound **4** is the first 2-arylbenzofuran containing a special four- and five-membered-ring moiety. The origins of **4** and **3** could be biosynthetically traced back to artopetelins A (**5**) and B (**6**), respectively [2]. In this paper, we describe the isolation, structural elucidation, and biosynthetic pathway of these compounds.

Results and Discussion. – Artopetelin D (**1**), a pale-yellow, amorphous powder, had a molecular formula $C_{29}H_{34}O_5$, as deduced from HR-EI-MS (M^+ at m/z 462.2406). The UV absorptions at λ_{max} 204 and 291 nm suggested the presence of a 2-arylbenzofuran skeleton [2][3]. The IR spectrum exhibited absorptions for OH groups (3396 cm^{-1}) and aromatic rings (1600, 1506 cm^{-1}). From the ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*), HMQC, and HMBC data, the planar structure of artopetelin D (**1**) was elucidated as 7-(1,2-dimethylprop-2-enyl)-2-[3,4-dihydro-7-hydroxy-2,2-dimethyl-6-(3-methylbut-2-enyl)-2*H*-1-benzopyran-5-yl]-1-benzofuran-4,6-diol. The configuration at C(16) remains to be determined.

The ^{1}H-NMR spectrum of **1** showed signals of three OH groups at δ(H) 8.46, 8.17, and 7.91 (3*s*), three downfield *s* at δ(H) 6.68, 6.40, and 6.37 (3*s*, 1 H each), a prenyl group at 5.13 (br. *t*, J=6.8 Hz, 1 H), 3.29 (br. *d*, J=6.8 Hz, 2 H), and 1.56 and 1.45 (2 br. *s*, 3 H each), and a 3,4-dihydro-2,2-dimethylpyran moiety at 2.56 (*dt*, J=7.0, 17.0 Hz, 1 H), 2.42 (*dt*, J=6.5, 17.0 Hz, 1 H), 1.68 (overlapped, 2 H),



and 1.29 (*s*, 6 H). Furthermore, a 1,2-dimethylallyl group was inferred from the following ^{1}H- and ^{13}C-NMR (HMQC) data: δ(H) 4.88 and 4.78 (2 br. *s*, 1 H each), 4.04 (*q*, J=7.0 Hz, 1 H), 1.67 (br. *s*, 3 H), and 1.51 (*d*, J=7.0 Hz, 3 H), as well as δ(C) 36.9 (C(16))[1]), 18.2 (C(17)), 149.8 (C(18)), 109.6 (C(19)), and 22.9 (C(20)). Interpretation of the HMQC and HMBC spectra of **1** revealed the substitution pattern and fully assigned all ^{1}H- and ^{13}C-NMR signals. The prenyl group was located at C(11) on the basis of HMBC correlations between CH_2(21) (δ(H) 3.29) and C(10) (δ(C) 133.2), C(11) (122.1), and C(12) (155.4) (*Fig. 1*). The signal at δ(H) 8.17 was assigned to OH–C(12), as shown in *Fig. 1*. The 3,4-dihydro-2,2-dimethylpyran moiety was fused at C(14) and C(15), as established by HMBC correlations of CH_2(26) at δ(H) 2.56 and 2.42 with C(10) (δ(C) 133.2), C(14) (153.8), and C(15) (114.0). The position of the 1,2-dimethylallyl side chain was corroborated by the HMBC couplings between Me(17) (δ(H) 1.51) and C(7) (δ(C) 107.8), as well as by those between H–C(16) (δ(H) 4.04) and C(6) (δ(C) 153.9), C(7) (107.8), and C(8) (156.9). The remaining two OH groups at δ(H) 8.46 and 7.91 were connected to C(4) and C(6), respectively, supported by the HMBC cross-peaks shown in *Fig. 1*.

Artopetelin E (**2**), a pale-yellow, amorphous powder, was shown to have a molecular formula $C_{29}H_{34}O_5$ by HR-EI-MS (M^+ at m/z 462.2400). Its ^{1}H- and ^{13}C-NMR data resembled those of **1** (*Tables 1* and *2*), except for signals due to the symmetrical ring *B* fused to two 3,4-dihydro-2,2-dimethyl-2*H*-pyran moieties. The planar structure of artopetelin E (**2**) was elucidated as 7-(1,2-dimethylprop-2-enyl)-2-(3,4,7,8-tetrahydro-2,2,8,8-tetramethyl-2*H*,6*H*-benzo[1,2-*b*:5,4-*b*′]dipyran-5-yl)benzofuran-4,6-diol. Similarly to compound **1**, the configuration at C(16) remains to be determined.

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

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

	1[a][b])	**2**[c][d])	**3**[b][c])	**4**[b][c])
H–C(3)	6.68 (*s*)	6.66 (*s*)	6.78 (*d*, $J=0.8$)	6.59 (*d*, $J=0.8$)
H–C(4)	–	–	7.42 (*d*, $J=8.4$)	7.44 (*d*, $J=8.4$)
H–C(5)	6.37 (*s*)	6.23 (*s*)	6.82 (*dd*, $J=2.0, 8.4$)	6.83 (*dd*, $J=2.0, 8.4$)
H–C(7)	–	–	6.99 (br. *d*, $J=2.0$)	6.98 (br. *d*, $J=2.0$)
H–C(13)	6.40 (*s*)	6.38 (*s*)	–	6.56 (*s*)
H–C(15)	–	–	6.74 (*s*)	–
H–C(16) or CH_2(16)	4.04 (*q*, $J=7.0$)	4.00 (*q*, $J=7.0$)	3.56 (br. *d*, $J=6.5$)	3.19 (br. *d*, $J=6.9$)
Me(17) or H–C(17)	1.51 (*d*, $J=7.0$)	1.49 (*d*, $J=7.0$)	5.16–5.19 (*m*)	5.13 (br. *t*, $J=6.9$)
CH_2(19) or Me(19)	4.88 (br. *s*), 4.78 (br. *s*)	5.23 (br. *s*), 5.16 (br. *s*)	1.68 (br. *s*)	1.39 (br. *s*)
Me(20)	1.67 (br. *s*)	1.77 (*s*)	1.66 (br. *s*)	1.55 (*d*, $J=1.0$)
CH_2(21) or H–C(21)	3.29 (br. *d*, $J=6.8$)	2.62 (*t*, $J=6.8$)	2.66 (*dd*, $J=8.1, 16.8, H_\alpha$), 3.04 (*dd*, $J=5.7, 16.8, H_\beta$)	3.05 (*d*, $J=9.7, H_\beta$)
H–C(22)	5.13 (br. *t*, $J=6.8$)	–	3.94 (*dt*, $J=5.7, 8.1, H_\beta$)	2.50 (*t*, $J=9.7, H_\beta$)
CH_2(22)	–	1.71 (*t*, $J=6.8$)	–	–
Me(24)	1.45 (br. *s*)	1.33 (*s*)	1.24 (*s*)	1.25 (*s*)
Me(25) or CH_2(25)	1.56 (br. *s*)	1.33 (*s*)	1.70–1.76 (*m*)	1.96–2.00 (*m*, H_α), 1.56–1.62 (*m*, H_β)
CH_2(26)	2.56 (*dt*, $J=7.0, 17.0$), 2.42 (*dt*, $J=6.5, 17.0$)	2.62 (*t*, $J=6.8$)	2.20–2.24 (*m*)	1.71–1.75 (*m*, H_α), 1.62–1.66 (*m*, H_β)
CH_2(27) or H–C(27)	1.68 (overlapped)	1.71 (*t*, $J=6.8$)	5.16–5.19 (*m*)	2.30–2.35 (*m*, H_β)
Me(29)	1.29 (*s*)	1.33 (*s*)	1.62 (br. *s*)	0.85 (*s*)
Me(30)	1.29 (*s*)	1.33 (*s*)	1.66 (br. *s*)	0.59 (*s*)
OH–C(4)	8.46 (*s*)	4.97 (br. *s*)	–	–
OH–C(6)	7.91 (*s*)	5.83 (*s*)	8.40 (*s*)	8.35 (*s*)
OH–C(12)	8.17 (*s*)	–	7.25 (*s*)	8.25 (*s*)
OH–C(22)	–	–	4.21 (*d*, $J=5.7$)	–

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

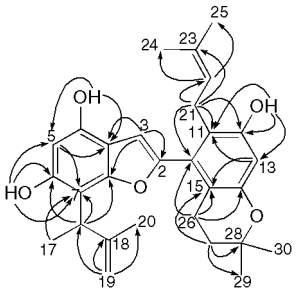


Fig. 1. *Selected HMBC correlations of compound* **1**

The symmetrical benzodipyran moiety of **2** gave rise to the following NMR signals: δ(H) 2.62 and 1.71 (2*t*, $J=6.8$ Hz, 4 H each) and 1.33 (*s*, 12 H), as well as δ(C) 21.1 (C(21), C(26)), 33.1 (C(22), C(27)), 73.7 (C(23), C(28)), and 26.8 (C(24), C(25), C(29), C(30)). In the HMBC spectrum, CH_2(21)

Table 2. *^{13}C-NMR Data of* **1**–**4**. δ in ppm. Arbitrary atom numbering.

	1[a][b]	**2**[c][d]	**3**[b][c]	**4**[b][c]		**1**[a][b]	**2**[c][d]	**3**[b][c]	**4**[b][c]
C(2)	152.1	151.4	155.9	154.1	C(16)	36.9	36.8	27.1	27.6
C(3)	104.3	103.5	105.7	107.7	C(17)	18.2	17.6	125.3	125.4
C(4)	150.0	147.4	122.2	122.1	C(18)	149.8	150.2	132.2	130.6
C(5)	99.1	99.0	113.4	113.2	C(19)	109.6	111.2	18.5	18.2
C(6)	153.9	153.0	157.0	156.6	C(20)	22.9	22.6	26.2	26.2
C(7)	107.8	105.9	98.8	98.9	C(21)	27.3	21.1	28.2	39.4
C(8)	156.9	155.0	156.9	157.0	C(22)	125.7	33.1	68.4	41.7
C(9)	112.7	111.1	123.0	122.7	C(23)	130.5	73.7	79.3	84.8
C(10)	133.2	130.4	130.8	132.7	C(24)	18.3	26.8	18.5	26.0[e]
C(11)	122.1	113.4	119.1	123.3	C(25)	26.2	26.8	39.1	41.8
C(12)	155.4	153.4	154.8	155.4	C(26)	21.9	21.1	22.7	26.1[e]
C(13)	105.7	106.5	110.5	107.8	C(27)	34.0	33.1	125.9	47.8
C(14)	153.8	153.4	153.2	153.9	C(28)	74.5	73.7	132.2	41.0
C(15)	114.0	113.4	110.1	119.2	C(29)	27.1	26.8	18.1	34.0
					C(30)	27.1	26.8	26.2	19.7

[a]) At 125 MHz. [b]) In (D_6)acetone. [c]) At 100 MHz. [d]) In $CDCl_3$. [e]) Signals may be exchangeable.

and CH_2(26)) at δ(H) 2.62 were correlated with C(10) (δ(C) 130.4), C(11) and C(15) (113.4), C(12) and C(14) (153.4), C(22) and C(27) (33.1), and C(23) and C(28) (73.7), and CH_2(22) and CH_2(27) at δ(H) 1.71 were coupled with C(11) and C(15) as well as with C(24), C(25), C(29), and C(30), indicating fusion of the two pyrane rings at C(11) and C(12) and at C(14) and C(15). Other HMBC correlations were in agreement with the constitution of **2**.

Artopetelin F (**3**), a pale-yellow, amorphous powder, was deduced to have a molecular formula $C_{29}H_{34}O_5$ by HR-EI-MS (M^+ at m/z 462.2409). The UV and IR data showed that **3** was a derivative of 2-arylbenzofuran. The structure of artopetelin F (**3**) was elucidated as *rel*-(2*R*,3*S*)-3,4-dihydro-7-(6-hydroxybenzofuran-2-yl)-2-methyl-6-(3-methylbut-2-enyl)-2-(4-methylpent-3-enyl)-2*H*-1-benzopyran-3,5-diol.

The ^{1}H-NMR spectrum of **3** contained signals of two phenolic OH groups at δ(H) 8.40 and 7.25 (2*s*, 1 H each), an *ABX* spin system (ring *A*) at 7.42 (*d*, *J* = 8.4 Hz, 1 H), 6.99 (br. *d*, *J* = 2.0 Hz, 1 H), and 6.82 (*dd*, *J* = 2.0, 8.4 Hz, 1 H), an aromatic *s* at 6.74 (*s*, 1 H), and a furan olefinic proton at 6.78 (*d*, *J* = 0.8 Hz, 1 H). Furthermore, signals for a prenyl group and a 3-hydroxy-2-methyl-2-(4-methylpent-3-enyl)chroman moiety [4] were observed in the ^{1}H-NMR spectrum: δ(H) 5.16–5.19 (*m*, 2 H), 4.21 (*d*, *J* = 5.7 Hz, 1 H), 3.94 (*dt*, *J* = 5.7, 8.1 Hz, 1 H), 3.56 (br. *d*, *J* = 6.5 Hz, 2 H), 3.04 (*dd*, *J* = 5.7, 16.8 Hz, 1 H), 2.66 (*dd*, *J* = 8.1, 16.8 Hz, 1 H), 2.20–2.24 and 1.70–1.76 (2*m*, 2 H each), 1.68 and 1.62 (2 br. *s*, 3 H each), 1.66 (br. *s*, 6 H), and 1.24 (*s*, 3 H). Analysis of the HMBC spectrum of **3** placed the two phenolic OH and prenyl substituents at the 6-, 12-, and 11-position, respectively (*Fig. 2*). In addition, the HMBC correlations from CH_2(21) at δ(H) 2.66 and 3.04 to C(12) (δ(C) 154.8), C(13) (110.5), C(14) (153.2), C(22) (68.4), and C(23) (79.3), as well as those from OH–C(22) at 4.21 to C(21) (28.2), and C(23) (79.3), indicated that the dihydro-3-hydroxy-2*H*-pyran ring was attached at C(13) and C(14). This geranyl-derived pyrane moiety was further confirmed by the long-range correlations from CH_2(25) at δ(H) 1.70–1.76 to C(26) (δ(C) 22.7), from CH_2(26) at δ(H) 2.20–2.24 to C(23) (79.3) and C(28) (132.2), and from Me(24) at δ(H) 1.24 to C(22) (68.4) and C(25) (39.1). The relative configuration of **3** was established on the basis of the NOESY spectrum. The NOE cross-peaks of H–C(22) at δ(H) 3.94 with CH_2(25) and CH_2(26) suggested the *syn*-periplanar relationship between H–C(22) and the 4-methylpent-3-enyl side chain, shown in β-configuration, whereas Me(24) and OH–C(22) were α-oriented.

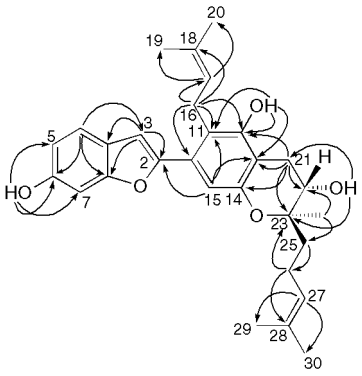


Fig. 2. *Selected HMBC correlations of compound* **3**

Artopetelin G (**4**), a white, amorphous powder, had a molecular formula $C_{29}H_{32}O_4$, as determined by HR-EI-MS (M^+ at m/z 444.2291). A comparison of the NMR data of compounds **3** and **4** showed that **4** had a 6,12-dihydroxy-11-(3-methylbut-2-enyl)-2-arylbenzofuran[1]) moiety identical to that of **3**. However, the ^{1}H- and ^{13}C-NMR data suggested the presence of a tricyclic moiety (rings *D*–*F*) in consideration of 14 degrees of unsaturation. The ^{1}H,^{1}H-COSY, HMQC, and HMBC data (*Fig. 3*) established the constitution of rings *D*–*F*, and the NOESY data suggested the relative configuration. A 3D structure of **4**, generated by MM2 computer modeling is shown in *Fig. 4*. Hence, the structure of artopetelin G (**4**) was elucidated as *rel*-(1a*R*,3a*S*,8b*S*,8c*S*)-1a,2,3,3a,8b,8c-hexahydro-8-(6-hydroxybenzofuran-2-yl)-1,1,3a-trimethyl-7-(3-methylbut-2-enyl)-1*H*-4-oxabenzo[*f*]cyclobut[*cd*]inden-6-ol.

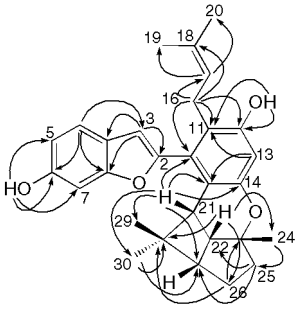


Fig. 3. *Selected HMBC correlations of compound* **4**

The tricyclic moiety of **4** gave rise to the following NMR signals: δ(H) 3.05 (*d*, J = 9.7 Hz, 1 H), 2.50 (*t*, J = 9.7 Hz, 1 H), 2.30–2.35, 1.96–2.00, 1.71–1.75, 1.62–1.66 and 1.56–1.62 (5*m*, 1 H each), and 1.25, 0.85 and 0.59 (3*s*, each 3 H), as well as δ(C) 39.4 (C(21)), 41.7 (C(22)), 84.8 (C(23)), 26.0 (C(24)), 41.8 (C(25)), 26.1 (C(26)), 47.8 (C(27)), 41.0 (C(28)), 34.0 (C(29)), and 19.7 (C(30)). The HMBC correlations from H–C(21) at δ(H) 3.05 to C(10) (δ(C) 132.7), C(14) (153.9), and C(15) (119.2) indicated that C(21) was directly bonded to C(15) (*Fig. 3*). Further HMBC correlations were observed from H–C(21) to C(23), C(27), C(28), C(29), and C(30), from H–C(22) at δ(H) 2.50 to C(24), C(26), C(27), and C(28), from Me(29) and Me(30) at δ(H) 0.85 and 0.59 to C(21), C(27), and C(28), and from Me(24) at δ(H) 1.25 to C(22) and C(25). In the ^{1}H,^{1}H-COSY plot, H–C(21) was correlated with H–C(22), and the latter was coupled with H–C(27) at δ(H) 2.30–2.35. These data suggested a dihydro-2-methyl-2*H*-pyran ring (ring *D*) fused at C(14) and C(15) and a four-membered ring (*E*) moiety attached at C(21) and C(22).

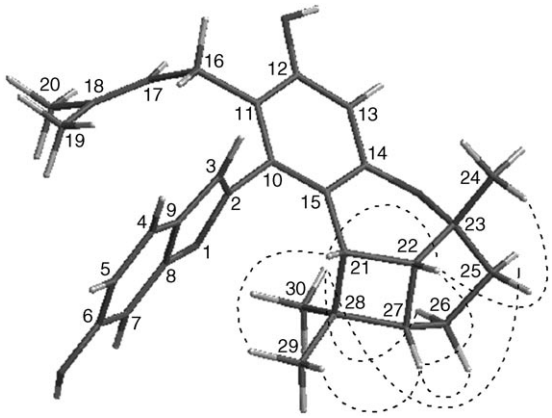
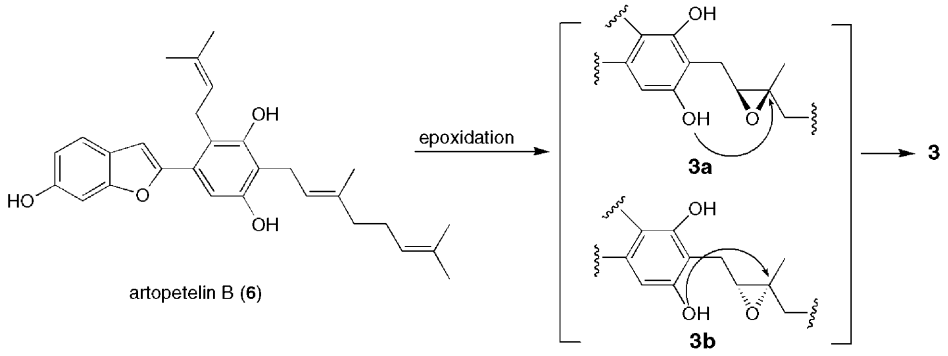


Fig. 4. *Selected NOESY correlations of compound* **4**

Scheme 1. *Proposed Biogenetic Pathway for Compound* **3**

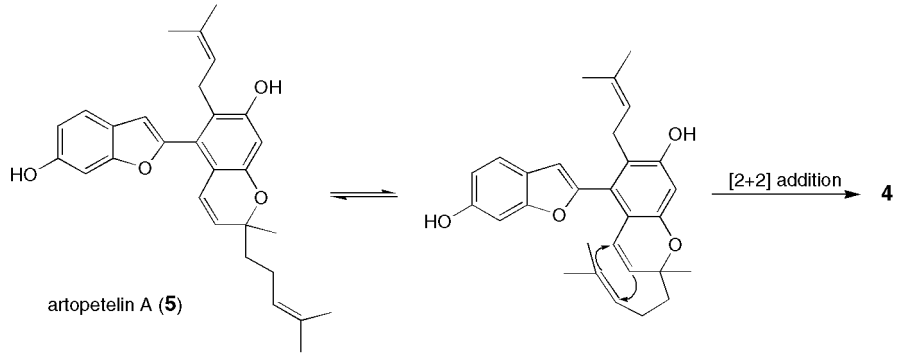


Furthermore, the ^{1}H,^{1}H-COSY cross-peaks between H–C(27) and H–C(26) at δ(H) 1.62–1.66, and between H–C(26) at 1.71–1.75 and CH_2(25) at 1.56–1.62 and 1.96–2.00 established the connectivities in ring *F*, which were confirmed by the HMBC correlations from CH_2(26) to C(23) and C(28) and from CH_2(25) to C(22), C(23), C(24), and C(27). The relative configuration of **4** was established by NOESY cross-peaks of H–C(21) with H–C(22) and Me(29), of H–C(22) with H–C(27) and Me(24), and of H–C(27) with Me(29) (*Fig. 4*), indicating the relative β-orientations of H–C(21), H–C(22), Me(24), and H–C(27).

A possible biosynthetic pathway for artopetelin F (**3**) is proposed in *Scheme 1*. Two isomers, **3a** and **3b**, produced by epoxidation of artopetelin B (**6**) would be transformed into a racemic mixture **3** by intramolecular cyclization, which would explain why $[\alpha]_D$ of **3** is 0. The origin of artopetelin G (**4**) could be assumed biosynthetically from an intramolecular [2+2] addition of artopetelin A (**5**) (*Scheme 2*).

Financial support from the *National Natural Science Foundation of China* (30572247) is gratefully acknowledged.

Scheme 2. *Proposed Biogenetic Pathway for Compound* **4**



Experimental Part

General. Column chromatography (CC): silica gel *H* (10–40 μm and 200–300 mesh; *Yantai Institute of Chemical Technology*, China), and *Chromatorex RP-18* gel (20–45 μm; *Fuji Silysia Chemical, Ltd.*, Kasugai, Japan). Prep. and anal. TLC: precoated silica gel GF_{254} plates (10–40 μm; *Yantai Institute of Chemical Technology*, China). Optical rotation: *Jasco-P1030* polarimeter. UV Spectra: *Shimadzu-UV-2401PC* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Nicolet-Avatar-360* spectrometer; KBr pellets; in cm^{-1}. NMR Spectra: *Bruker-DRX-400* and *-500* instruments; chemical shifts δ in ppm rel. to residual solvent peaks of (D_6)acetone (δ(H) 2.04, δ(C) 206.0) and $CDCl_3$ (δ(H) 7.26, δ(C) 77.0). EI-MS (70 eV): *Finnigan-MAT-95* mass spectrometer; in *m/z* (rel. %). Computer modeling: *Chem 3D Pro*, Vs. 8.0.3, *Cambridge Soft*, Cambridge, MA, USA.

Plant Material. The root barks of *A. petelotii* GAGNEP were collected in Xishuangbanna, Yunnan, P. R. China, in July 1998, and air-dried. The plant was identified by Prof. *Han-Dong Sun*, Kunming Institute of Botany, and a voucher specimen (TCM 98-07-02 Hou) was deposited in the Herbarium of the Department of Pharmacognosy, School of Pharmacy, Fudan University.

Extraction and Isolation. The dried and powdered root barks (6.4 kg) of *A. petelotii* were percolated with 95% EtOH (60 l) at r.t. The filtrate was evaporated to give a residue (800 g), which was suspended in H_2O (2 l) and extracted successively with petroleum ether (4×800 ml) and AcOEt (4×800 ml). The AcOEt extract (110 g after evaporation) was subjected to CC (SiO_2, petroleum ether/acetone 8:2 → 2:8): *Fractions A–I*. *Fr. B* (1.5 g) was separated by CC (SiO_2, petroleum ether/i-PrOH 30:1): *Fr. B1–8*. *Fr. B5* was purified by CC (1. *RP-18*, MeOH/H_2O 8.5:1.5; 2. SiO_2, petroleum ether/AcOEt 8:1), then by prep. TLC (SiO_2, $CHCl_3$/Et_2O 50:3): **3** (3 mg). *Fr. B6* was fractionated by CC (*RP-18*, MeOH/H_2O 70 → 85%), followed by prep. TLC (SiO_2, petroleum ether/AcOEt 12:13), then by CC (SiO_2, $CHCl_3$/AcOEt 50:4): **2** (3 mg). *Fr. E* (3.0 g) was subjected to CC (SiO_2, petroleum ether/i-PrOH 20:1 → 8:1): *Fr. E1–9*. *Fr. E5* was purified by CC (SiO_2, $CHCl_3$/AcOEt 25:1 → 4:1): *Fr. E5.1–5.6*. *Fr. E5.4* was separated by CC (*RP-18*, MeOH/H_2O 7:3), then by prep. TLC (SiO_2, petroleum ether/AcOEt 1:1): **1** (25 mg). *Fr. E5.5* was fractionated by CC (*RP-18*, MeOH/H_2O 7.5:2.5), then by prep. TLC (SiO_2, petroleum ether/AcOEt 17:8), followed by CC (SiO_2, benzene/acetone 50:3): **4** (2 mg).

Artopetelin D (=*7-(1,2-Dimethylprop-2-enyl)-2-[3,4-dihydro-7-hydroxy-2,2-dimethyl-6-(3-methylbut-2-enyl)-2*H*-1-benzopyran-5-yl]-1-benzofuran-4,6-diol*; **1**): Yield 25 mg. Pale-yellow, amorphous powder. $[\alpha]_D^{20} = +0.7$ ($c = 0.15$, acetone). UV (MeOH): 204 (4.52), 291 (3.95). IR (KBr): 3396, 2975, 2931, 1699, 1615, 1600, 1506, 1435, 1371, 1326, 1266, 1161, 1138, 1120, 1036, 961, 738. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 462 (100, M^+), 447 (24), 419 (33), 407 (25), 363 (14), 335 (4), 321 (3), 293 (3), 269 (7), 256 (14), 207 (15), 196 (7), 101 (8), 59 (19). HR-EI-MS: 462.2406 (M^+, $C_{29}H_{34}O_5^+$; calc. 462.2406).

Artopetelin E (=*7-(1,2-Dimethylprop-2-enyl)-2-(3,4,7,8-tetrahydro-2,2,8,8-tetramethyl-2*H,*6*H*-benzo[1,2-b:5,4-b′]dipyran-5-yl)benzofuran-4,6-diol*; **2**): Yield 3 mg. Pale-yellow, amorphous powder. $[\alpha]_D^{20} = +7.9$ ($c = 0.19$, acetone). UV (MeOH): 206 (4.38), 248 (sh, 3.94), 297 (4.00). IR (KBr): 3385,

2973, 2925, 1701, 1617, 1600, 1508, 1454, 1383, 1369, 1323, 1292, 1156, 1119, 1037, 922, 738. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 462 (100, M^+), 445 (33), 419 (7), 407 (48), 389 (5), 363 (5), 351 (16), 255 (3), 213 (10), 196 (7), 167 (5), 149 (8), 59 (16). HR-EI-MS: 462.2400 (M^+, $C_{29}H_{34}O_5^+$; calc. 462.2406).

Artopetelin F (=rel-*(2*R*,3*S*)-3,4-Dihydro-7-(6-hydroxybenzofuran-2-yl)-2-methyl-6-(3-methylbut-2-enyl)-2-(4-methylpent-3-enyl)-2*H*-1-benzopyran-3,5-diol*; **3**): Yield 3 mg. Pale-yellow, amorphous powder. $[\alpha]_D^{20} = 0$ ($c = 0.20$, acetone). UV (MeOH): 216 (4.38), 313 (4.22). IR (KBr): 3386, 2924, 1623, 1568, 1489, 1446, 1383, 1290, 1145, 1114, 1075, 972, 831, 738. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 462 (77, M^+), 445 (45), 418 (12), 377 (12), 361 (42), 340 (15), 323 (47), 305 (49), 279 (68), 267 (100), 251 (17), 239 (23), 211 (12), 201 (18), 181 (10), 165 (23), 152 (13), 123 (17), 69 (85). HR-EI-MS: 462.2409 (M^+, $C_{29}H_{34}O_5^+$; calc. 462.2406).

Artopetelin G (=rel-*(1a*R*,3a*S*,8b*S*,8c*S*)-1a,2,3,3a,8b,8c-Hexahydro-8-(6-hydroxybenzofuran-2-yl)-1,1,3a-trimethyl-7-(3-methylbut-2-enyl)-1*H*-4-oxabenzo[*f*]cyclobut[*cd*]inden-6-ol*; **4**): Yield 2 mg. White, amorphous powder. $[\alpha]_D^{20} = +3.5$ ($c = 0.20$, acetone). UV (MeOH): 215 (4.49), 298 (4.18). IR (KBr): 3384, 2950, 2860, 1625, 1597, 1489, 1446, 1375, 1289, 1265, 1217, 1145, 1114, 967, 739. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 444 (12, M^+), 429 (5), 400 (3), 361 (100), 317 (22), 305 (16), 277 (8), 249 (2), 149 (4), 101 (2), 81 (3), 69 (4), 57 (5). HR-EI-MS: 444.2291 (M^+, $C_{29}H_{32}O_4^+$; calc. 444.2301).

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Received January 17, 2006