ARTONINS Q, R, S, T, AND U, FIVE NEW ISOPRENYLATED PHENOLS FROM THE BARK OF *ARTOCARPUS HETEROPHYLLUS* LAMK.#,[1]

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Abstract - Five new isoprenylated phenols, artonins Q (**1**), R (**2**), S (**3**), T (**4**), and U (**5**), were isolated from the bark of *Artocarpus heterophyllus* Lamk., an Indonesian moraceous plant. The structures of artonins Q, R, S, T, and U were shown to be **1**, **2**, **3**, **4**, and **5**, respectively, on the basis of spectroscopic data and chemical evidence.

In our continuing studies on the phenolic compounds of moraceous plants, we reported a series of isoprenoid-substituted phenolic compounds isolated from *Artocarpus heterophyllus*,[2-5] *A. communis*,[6] *A. rigida*,[7,8] and *Antiaris toxicaria*.[9-11] Previously, we reported the structures of artonins A - D, and I - L from the root bark of *A. heterophyllus*.[2-5] Further extension of studies on the components of *A. heterophyllus* led to the isolation of five new isoprenylated phenols, artonins Q (**1**), R (**2**), S (**3**), T (**4**), and U (**5**). This paper deals with characterization of these new phenols.

Artonin Q (**1**) is a yellow crystalline powder, mp 57 - 59 °C, $[\alpha]_D$ 0°, $C_{31}H_{30}O_8$, and gave a brown color with methanolic ferric chloride. The uv spectrum was similar to that of 1,3-dihydroxyxanthone, indicating that **1** is a xanthone derivative.[12] The ir spectrum disclosed absorption bands due to hydroxyl, cyclic ketone, ester carbonyl, and conjugated carbonyl moieties. The ^1H nmr spectrum of **1** showed the signals of the following

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#This paper is dedicated to Dr. Arnold Brossi, Scientist Emeritus NIH, on the occasion of his 70th birthday.

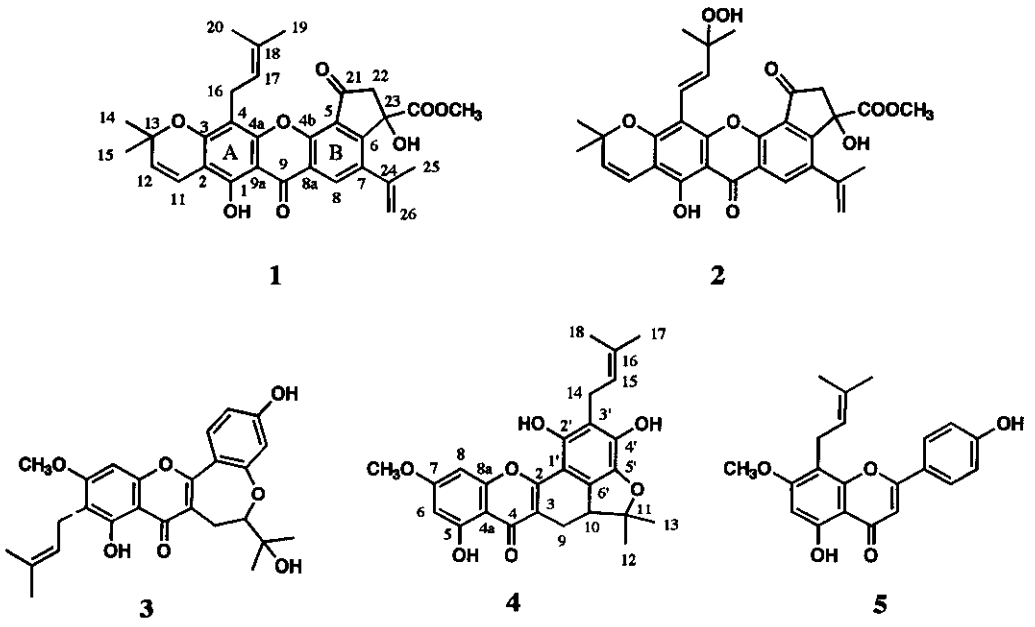


Figure 1

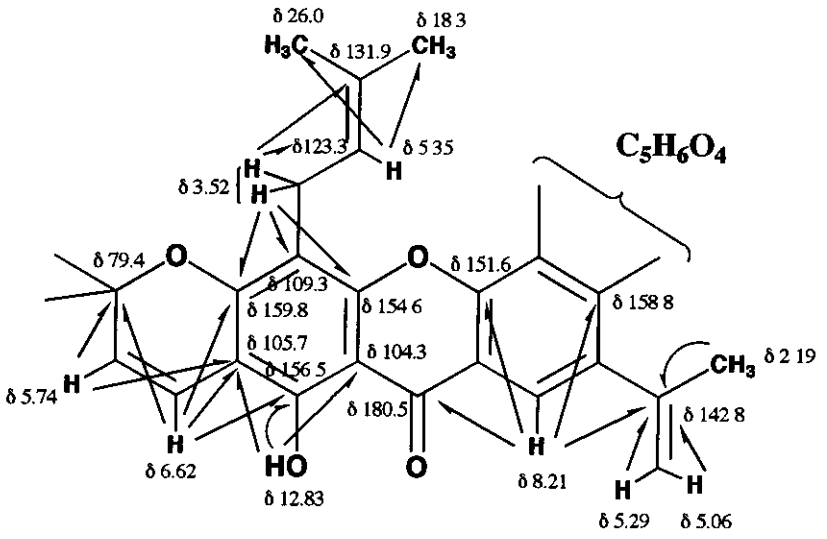


Figure 2 **Partial structure (1a) on the basis of HMBC spectrum (J_{CCH} = 6 Hz)**

Table 1 ^{13}C Nmr Chemical Shifts (ppm) of **1** and **2**

Carbon	**1**	correlated proton	**2**
1	156.5		157.1
2	105.7		105.9
3	159.8		159.9
4	109.3		106.4
4a	154.6		154.5
4b	151.6		151.3
5	126.1		126.1
6	158.8		159.2
7	138.9		139.2
8	132.5	8.21 (s)	132.7
8a	122.0		122.0
9	180.5		180.8
9a	104.3		104.5
11	115.8	6.62 (d, J=10)	115.8
12	128.9	5.74 (d, J=10)	129.2
13	79.4		80.0
14	28.6	1.50 (3H, br s)	28.6
15	28.6	1.51 (3H, br s)	28.6
16	22.0	3.52 (2H, br d, J=7)	118.0
17	123.3	5.35 (m)	139.6
18	131.9		83.1
19	18.3	1.85 (3H, br s)	25.2
20	26.0	1.64 (3H, br s)	25.2
21	197.4		198.2
22	53.3	2.98, 3.28 (each 1H, d, J=18)	53.4
23	77.7		77.7
24	142.8		142.7
25	25.2	2.19 (3H, br s)	25.2
26	117.9	5.06, 5.29 (each 1H br s)	117.7
$-\underline{C}OOCH_3$	174.2		174.1
$-COO\underline{C}H_3$	53.3	3.75 (3H, s)	53.3

measured in acetone-d_6

protons: protons in a 3,3-dimethylallyl (prenyl) group, δ 1.64, 1.85 (each 3H, s), 3.52 (2H, br d, J = 7 Hz), 5.35 (1H, m); protons in a 2,2-dimethylpyran ring, δ 1.50, 1.51 (each 3H, s), 5.74, 6.62 (each 1H, d, J = 10 Hz); protons in an isopropenyl group, δ 2.19 (3H, br s), 5.06, 5.29 (each 1H, br s); an aromatic proton, δ 8.21 (1H, s); a proton in a hydrogen-bonded hydroxyl group, δ 12.83 (1H, s); isolated methylene protons, δ 2.98, 3.28 (each 1H, d, J = 18 Hz); a proton in a hydroxyl group, δ 5.52 (1H, br s); protons in a methoxyl group, δ 3.75 (3H, s). The ^{13}C nmr spectrum showed the signals of 31 carbon atoms. The analyses of the ^{1}H nmr spectrum of **1** were further supported with the aid of ^{1}H - ^{13}C shift correlated spectroscopy (COSY) (Table 1). In the ^{13}C nmr spectrum of **1**, three carbonyl carbon signals were observed at δ 174.2, 180.5, and 197.4 ppm

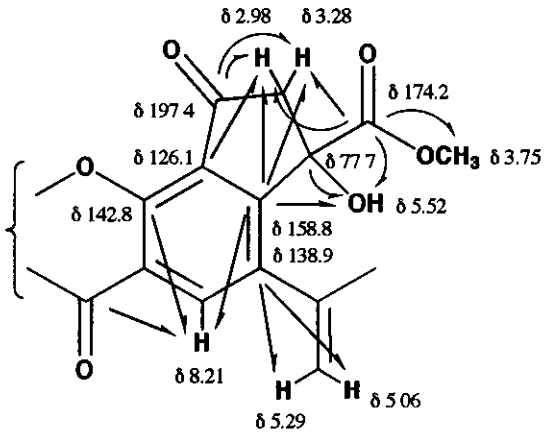


Figure 3 ^{13}C-^{1}H **Long-range correlation spectroscopy (COLOC,** J_{CCH} **= 8 Hz)**

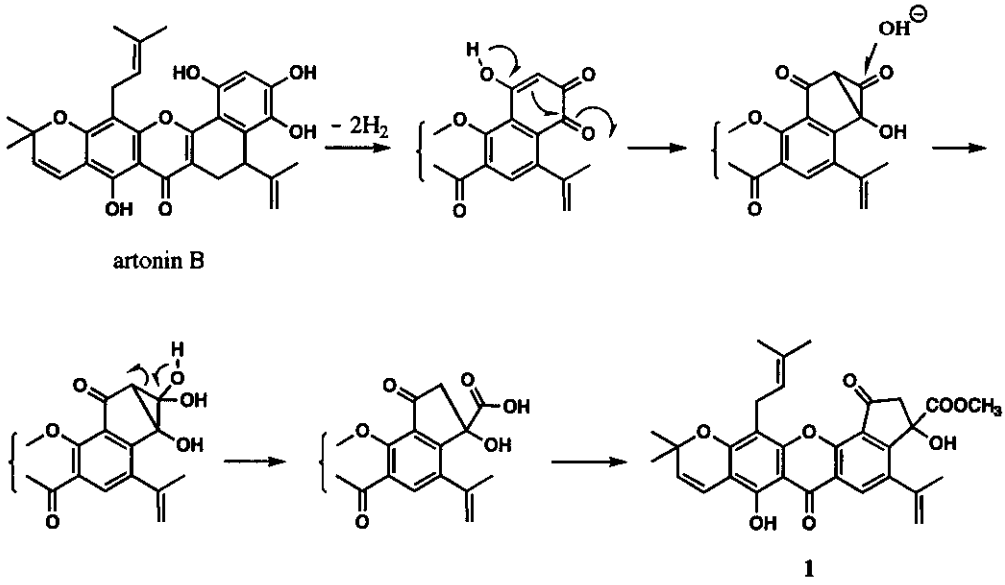


Figure 4 A hypothesis of the formation of artonin Q (1) through the oxidation of artonin B

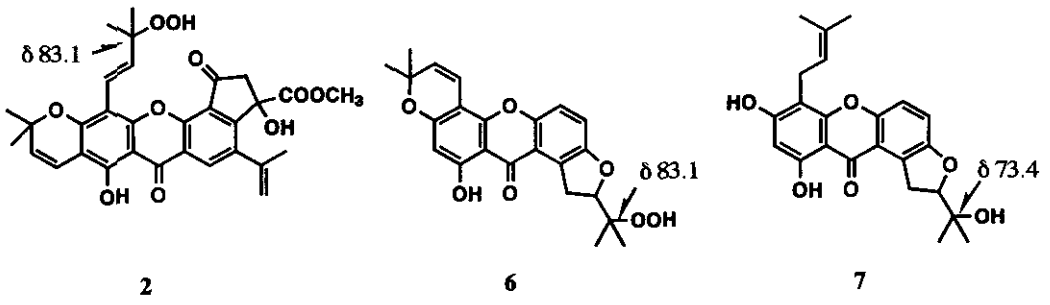
(Table 1). One of them (δ 180.5 ppm) could be assigned to the C-9 carbonyl carbon in a xanthone skeleton[13] and the others were attributable to an ester carbonyl carbon (δ 174.2 ppm) and a cyclic ketone (δ 197.4 ppm). A linear type of 2,2-dimethylpyran ring structure in the A ring of **1** and the location of the prenyl group were revealed with the aid of the ^{1}H-detected heteronuclear multiple bond connectivity (HMBC) spectrum. As can be seen in Figure 2, the quaternary carbon at δ 105.7 (C-2) shows long-range correlations with the olefinic proton at δ 5.74 (12-H) and the proton in the hydrogen-bonded hydroxyl group at δ 12.83 (C-1-OH), while the quaternary carbon at δ 159.8 (C-3) shows long-range correlations with the methylene protons at δ 3.52 (16-H x 2) and the olefinic proton at δ 6.62 (11-H). The location of the isopropenyl group at the C-7 position on the B ring of the xanthone skeleton was supported from the following results. In the HMBC spectrum, the aromatic proton at δ 8.21 (8-H) shows long-range correlations with the quaternary carbons at δ 142.8 (C-24), 151.6 (C-4b), 158.8 (C-6), and 180.5 (C-9). Therefore the signal at δ 8.21 could be assigned to the proton at C-8 position. The quaternary carbon at δ 142.8 shows long-range correlation with the aromatic proton at δ 8.21 as well as the methyl protons at δ 2.19 (24-CH_3) and the terminal methylene protons at δ 5.06 and 5.29 (24 =CH_2) (Figure 2). From these results, the partial structure A (**1a**) was proposed for the structure of artonin Q. In order to obtain detailed information about the structure of the substituent, $C_5H_6O_4$, on the B ring, we measured the ^{1}H-^{13}C long-range COSY (COLOC) spectrum (Figure 3). The proton in the hydroxyl group at δ 5.52 (exchangeable with D_2O) shows long-range correlations with the quaternary carbons at δ 77.7 (C-23) and 158.8 (C-6) as well as the ester carbonyl carbon at δ 174.2. The assignment of the carbon at δ 158.8 was confirmed by the observation of a long-range correlation with the aromatic proton at δ 8.21 (8-H). The quaternary carbon at δ 77.7 and the ester carbonyl carbon at δ 174.2 show long-range correlation with the isolated methylene protons at δ 2.98 and 3.28 (22-H). The isolated methylene protons show long-range correlations with the cyclic carbonyl carbon at δ 197.4 (Figure 3). The location of the methoxyl group in the substituent was confirmed with the aid of HMBC spectrum. The methoxyl protons show a long-range correlation with the carbonyl carbon at δ 174.2, while they show no long-range correlation with other carbons. Therefore the methyl ester moiety was located in the substituent. From the above results, the structure of artonin Q was represented by the formula (**1**).

Although artonin Q seems to be a unique xanthone derivative, the compound is biogenetically assumed to be a derivative from artonin B[2] through the oxidative reaction as shown in Figure 4.

Artonin R (**2**) is a yellow crystalline powder, mp 173 °C, $[\alpha]_D$ 0°, exhibited positive ferric chloride reaction, and gave the EI-ms spectrum which showed the dehydrated molecular ion peak at *m/z* 544. The ^{13}C nmr spectrum

indicated the presence of 31 carbons. The uv spectrum was similar to that of **1**. The ir spectrum disclosed absorption bands due to hydroxyl, cyclic ketone, ester carbonyl, and conjugated carbonyl moieties. The ^{1}H nmr spectrum of **2** showed the signals of the following protons: protons in a 2,2-dimethylpyran ring, δ 1.57, 1.58 (each 3H, s), 5.86, 6.75 (each 1H, d, J = 10 Hz); protons in an isopropenyl group, δ 2.19 (3H, br s), 5.04, 5.29 (each 1H, br s); an aromatic proton, δ 8.26 (1H, s); a proton in a hydrogen-bonded hydroxyl group, δ 13.20 (1H, s); isolated methylene protons, δ 3.02, 3.31 (each 1H, d, J = 18 Hz); protons in two hydroxyl groups, δ 5.57 (1H, br s), 10.12 (1H, s); two methyl protons, δ 1.56 (6H, br s); two olefinic protons, δ 7.21, 7.26 (each 1H, d, J = 17 Hz). The ^{13}C nmr spectrum of **2** was analysed by comparing with that of **1**. The chemical shifts of all the carbons except those of the C-4 and the five carbons of the moiety located at the position were similar to the relevant carbons of **1** (Table 1). Presence of hydroperoxide group in the moiety was supported from the following results. The chemical shifts of the quaternary carbon in the moiety (δ 83.1 ppm) was more similar to that of the relevant carbon of cudraxanthone O[14] (**6**, δ 83.1 ppm) than that of cudraxanthone J[15] (**7**, δ 73.4 ppm) (Figure 5). Furthermore the deoxygenated compound (**2a**) which showed the molecular ion peak at *m/z* 546 in the EI-ms spectrum was obtained by treatment with triphenylphosphine. Finaly, the compound (**2**) was derived from **1** by photo-sensitized oxidation using methylene blue. These results and the nmr data described above suggested the molecular formula of **2** to be $C_{31}H_{30}O_{10}$ and the structure of artonin R was represented by the formula (**2**).

Artonin S (**3**), pale yellow needles, mp 236 - 238 °C, $[\alpha]_D$ +10°, $C_{26}H_{28}O_7$, showed positive reaction to methanolic ferric chloride reaction and magnesium-hydrochloric acid test, and gave the EI-ms spectrum which showed the molecular ion peak at *m/z* 452. The uv spectrum was similar to that of chaplasin[16] (**8**). The ir spectrum disclosed absorption bands due to hydroxyl and conjugated carbonyl groups. The ^{1}H nmr spectrum of **3** showed the signals for the following protons: protons in a 3,3-dimethylallyl group, δ 1.63, 1.78 (each 3H, s), 3.33 (2H, br d, J = 7 Hz), 5.21 (1H, m); protons in a methoxyl group, δ 3.98 (3H, s); a proton in a hydrogen-bonded hydroxyl group, δ 13.24 (1H, s); an aromatic proton, δ 6.76 (1H, s); ABX type aromatic protons, δ 6.67 (1H, d, J = 2 Hz), 6.73 (1H, dd, J = 2 and 9 Hz), 8.00 (1H, d, J = 9 Hz); AMX type aliphatic protons, δ 2.61 (1H, dd, J = 10 and 16 Hz), 3.54 (1H, dd, J = 2 and 16 Hz), 4.01 (1H, dd, J =2 and 10 Hz); two methyl protons, δ 1.34, 1.37 (each 3H, s). The chemical shift of the aromatic proton (δ 6.76) was similar to that of the 8-H of **8** (δ 6.79), and furthermore, **3** exhibited positive reaction to Gibbs test. The chemical shifts and the coupling patterns of the aliphatic protons and the two methyl groups were similar to the relevant protons of **8**.



2 6 7

Figure 5

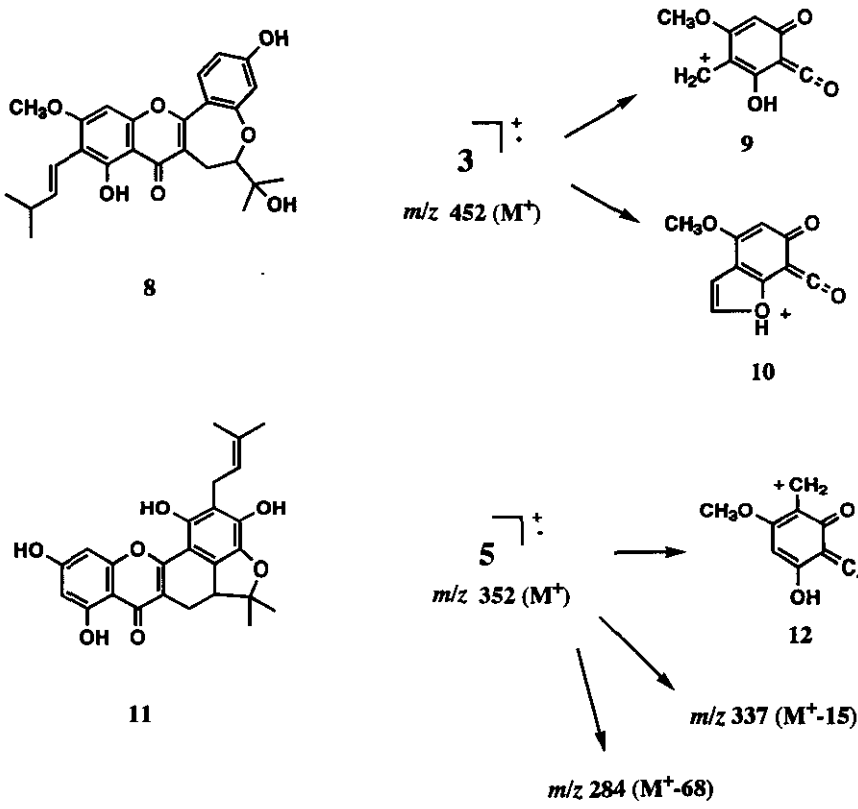


Figure 6

Table 2 ^{13}C Nmr Chemical Shifts (ppm) of **4** and **11**

carbon	**4**	**11**	carbon	**4**	**11**
2	161.8	161.2	13	22.4	22.4
3	111.5	111.3	14	22.5	22.5
4	179.7	179.6	15	123.0	123.2
4a	103.8	103.2	16	130.0	129.9
5	160.7	160.4	17	17.7	17.7
6	97.8	98.7	18	25.4	25.4
7	164.4	163.4	1'	104.1	104.2
8	92.8	94.3	2'	146.9	146.9
8a	156.1	156.2	3'	118.4	118.6
9	19.4	19.5	4'	144.0	143.8
10	45.8	46.0	5'	137.0	137.1
11	92.7	92.7	6'	128.2	128.2
12	27.8	27.8	$-OCH_3$	55.8	

measured in DMSO-*d6*

The EI-ms of **3** showed the fragment ions at *m/z* 179 (**9**) and 191 (**10**) (Figure 6). From the above results, the structure of artonin S was represented by the formula (**3**).

Artonin T (**4**), yellow needles, mp 252 °C, $[\alpha]_D$ 0°, $C_{26}H_{26}O_7$, showed positive reactions to methanolic ferric chloride reaction and magnesium-hydrochloric acid test, and gave the EI-ms spectrum which showed the molecular ion peak at *m/z* 450. The uv spectrum was similar to that of artonin J[5] (**11**). The ir spectrum disclosed absorption bands due to hydroxyl and conjugated ketone groups. The ^1H nmr spectrum of **4** showed the signals for the following protons: protons in a 3,3-dimethylallyl group, δ 1.62, 1.72 (each 3H, s), 3.28 (2H, br d, J = 7 Hz), 5.16 (1H, m); *meta*-coupled aromatic protons, δ 6.35, 6.90 (each 1H, d, J = 2 Hz); two methyl protons, δ 1.28, 1.63 (each 3H, s); ABX type signals, δ 2.30 (1H, t, J = 15 Hz), 3.13 (1H, dd, J = 7 and 15 Hz), 3.41 (1H, dd, J = 7 and 15 Hz); protons in a methoxyl group, δ 3.85 (3H, s). The chemical shifts and coupling patterns of all the proton signals except a methoxyl group were similar to those of the relevant signals of artonin J (**11**). The ^{13}C nmr spectrum of **4** was analysed by comparing with that of **11**. The chemical shifts of all the carbons except those of C-6, C-7, and C-8 were similar to those of the relevant carbons of **11** (Table 2). Final proof for the location of the methoxyl group was confirmed by the difference NOE experiment, where irradiation of the methoxyl signal (δ 3.85) increased the intensities of 6-H (δ 6.35) and 8-H (δ 6.90). From the above results, the structure of artonin T was represented by the formula (**4**).

Artonin U (**5**), *yellow needles, mp* 238 - 239 °C, $C_{21}H_{20}O_5$, showed positive methanolic ferric chloride reaction and magnesium-hydrochloric acid test, and gave the EI-ms spectrum which showed the molecular ion peak at *m/z* 352. The ^{1}H nmr spectrum of **5** showed the signals for the following protons: protons in a 3,3-dimethylallyl group, δ 1.66, 1.82 (each 3H, s), 3.53 (2H, br d, *J* = 7 Hz), 5.24 (1H, m); an aromatic proton, δ 6.47 (1H, s); an olefinic proton, δ 6.66 (1H, s); aromatic A_2B_2 signals, δ 7.05, 7.96 (each 2H, d, *J* = 9 Hz); a proton in hydrogen-bonded hydroxyl group, δ 13.09 (1H, s); protons in a methoxyl group, δ 3.97 (3H, s). From the above results, **5** was considered to be 8-prenylapigenin monomethyl ether or 6-prenylapigenin monomethyl ether. Compound (**5**) showed the fragment ion at *m/z* 179 (**12**), which supported the location of the methoxyl group at C-7 (Figure 6). The location of the prenyl group was supported by the fragmentation patterns in EI-ms. Takayama *et al.*[17] reported that the 6-prenylflavones showed the characteristic fragment ions such as [M^+-55] and [M^+-43], while the 8-prenylflavones showed the ions such as [M^+-15] and [M^+-68]. Compound (**5**) showed the fragment ions at *m/z* 337 [M^+-15] and 284 [M^+-68]. Furthermore, compound (**5**) was identified with the 8-prenyl-7-*O*-methylapigenin derived from 8-prenylapigenin. From the above results, the structure of artonin U was represented by the formula (**5**).

EXPERIMENTAL

Abbreviations: s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet, br = broad, sh = shoulder, infl = inflection. The general procedures followed and the instruments used in our previous papers.[2-5]

Plant material: Bark of *A. heterophyllus* was collected in the Botanical Garden of Bogor, Indonesia, in March 1988, and was identified by the members of Botanical Garden of Bogor.

Isolation of Artonins Q (**1**), R (**2**), S (**3**), T (**4**), and U (**5**)

The dried bark of *A. heterophyllus* (20 Kg) was extracted with methanol (200 l x 3) at room temperature for 3 days. Evaporation of the methanol under reduced pressure yielded 1.1 Kg of residue. The residue (1.1 Kg) was extracted with benzene (3 l x 3) and acetone (3 l x 3) at room temperature for 3 days. The benzene and acetone solutions were evaporated to give 420 g and 365 g of residue, respectively. The benzene extract (200 g) was chromatographed over silica gel (1200 g) using *n*-hexane, benzene, benzene-ethyl acetate (99 : 1, 97 : 3, 95 : 5, 9 : 1, and 4 : 1), and then acetone to prepare frs. 1 - 157. Each fraction (500 ml) was monitored by tlc. The fraction eluted with benzene - ethyl acetate (*95 : 5*, frs. *25 - 30, 0.7 g*) was crystallized from acetone to give artonin S (*3, 15* mg). The mother liquor of 3 was fractionated by preparative tlc [silica gel, n-hexane - acetone (7 : 1)] followed by preparative hplc [solvent, *n*-hexane - ethyl acetate (1 : 1), column, Senshu Pak SSC Silica 4251-N, 10 ϕ x 250 mm, detector, uv 254 nm] to give artonin Q (**1**, 20 mg), and artonin R (**2**, 3 mg). The fraction eluted with benzene - ethyl acetate (95 : 5, frs. 46 - 51, 2.1 g) was rechromatographed over silica gel (70 g) with *n*-hexane containing increasing amount of acetone as an eluent (frs. 1' - 47', eluted volume 200 ml each). The fraction eluted with *n*-hexane - acetone (9 : 1, frs. 16' - 25', 0.7 g) was fractionated by preparative tlc [*n*-hexane - acetone = 3 : 2)] followed by preparative hplc [solvent, *n*-hexane - ethyl acetate (4 : 1), column, Senshu Pak SSC Silica 4251-N, 10 ϕ x 250 mm, detector, uv 254 nm] to give artonin T (**4**, 2 mg). The fraction eluted with benzene - ethyl acetate (95 : 5,

frs. 52 - 59, 1.7 g) was rechromatographed over silica gel (40 g) with *n*-hexane containing increasing amount of acetone as an eluent (frs. 1" - 21", eluted volume 100 ml each). The fraction eluted with *n*-hexane - acetone (7 : 1, frs. 5" - 6", 0.1 g) was fractionated by preparative tlc [*n*-hexane - acetone (3 : 1), chloroform - acetone (10 : 1)] to give artonin U (**5**, 1 mg).

Artonin Q (**1**)

Compound (**1**) was obtained as a yellow crystalline powder from *n*-hexane - ether, mp 57 - 59 ℃. $FeCl_3$ test: positive (brown). $[\alpha]_D$ 0° (c = 0.27, $CHCl_3$). EI-ms: *m/z* (rel. int.) 530 (M^+, 52 %), 515 (100), 487 (21), 475 (14), 455 (7). HR-ms: *m/z* 530.1901 (M^+, $C_{31}H_{30}O_8$ requires 530.1941), *m/z* 515.1693 ($C_{30}H_{27}O_8$ requires 515.1706), *m/z* 487.1393 ($C_{28}H_{23}O_8$ requires 487.1393). Ir ν_{max}^{KBr} cm^{-1}: 3600 - 3300 (br), 1750 - 1710 (br), 1650, 1600, 1470, 1440. Uv λ_{max}^{MeOH} nm (log ε): 390 (infl 3.61), 350 (infl 3.95), 302 (4.44), 250 (sh 4.42), 225 (4.40), 205 (4.49). Uv $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 450 (infl 3.39), 373 (4.03), 310 (4.44), 250 (sh 4.42), 225 (4.40), 205 (4.49).

Artonin R (**2**)

Compound (**2**) was obtained as a yellow crstalline powder from *n*-hexane - ether, mp 173 ℃. $FeCl_3$ test: positive (brown). $[\alpha]_D$ 0° (c = 0.10, $CHCl_3$). EI-ms: *m/z* (rel. int.) 544 ($M^+ - H_2O$, 3 %), 529 ($M^+ - O_2H$, 3), 489 (21), 487 (10), 475 (13). Ir ν_{max}^{KBr} cm^{-1}: 3600 - 3300 (br), 1780 - 1710 (br), 1650, 1600, 1550, 1540, 1470, 1440. Uv λ_{max}^{MeOH} nm (log ε): 400 (infl 2.92), 350 (infl 3.32), 298 (3.80), 226 (3.87), 202 (3.90).

Artonin S (**3**)

Compound (**3**) was recrystallized from ethyl acetate to give pale yellow needles, mp 236 - 238 ℃. $[\alpha]_D^{25}$ + 10° (*c* = 0.20, MeOH). $FeCl_3$ test: positive (brown). Mg - HCl test : positive (red). Gibbs test : positive. EI-ms: *m/z* (rel. int.) 452 (M^+, 49 %), 437 (4), 409 (40), 397 (100), 391 (56), 379 (14), 179 (4), 191 (2). HR-ms: *m/z* 452.1855 (M^+, $C_{26}H_{28}O_7$ requires 452.1835), *m/z* 409.1285 ($C_{23}H_{21}O_7$ requires 409.1287). Ir ν_{max}^{KBr} cm^{-1}: 3500 - 3300 (br), 1650 (sh), 1600, 1580 (sh). Uv λ_{max}^{EtOH} nm (log ε): 341 (3.87), 272 (3.88), 215 (sh 4.21). Uv $\lambda_{max}^{EtOH+AlCl_3}$ nm (log ε): 363 (3.97), 296 (sh 3.86), 284 (3.93), 216 (sh 4.41).

Artonin T (**4**)

Compound (**4**) was recrystallized from acetone to give yellow needles, mp 252 ℃. $FeCl_3$ test: positive (greenish brown). Mg - HCl test : positive (red). $[\alpha]_D$ 0° (c = 0.12, MeOH). EI-ms: *m/z* (rel. int.) 450 (M^+, 100 %), 407 (61), 394 (85), 351 (45), 323 (15), 167 (6). HR-ms: *m/z* 450.1678 (M^+, $C_{26}H_{26}O_7$ requires 450.1679), *m/z* 394.1086 ($C_{22}H_{18}O_7$ requires 394.1053), *m/z* 351.0538 ($C_{19}H_{11}O_7$ requires 351.0504). Ir ν_{max}^{KBr} cm^{-1}: 3560, 3400 - 3100 (br), 1650, 1590, 1550, 1490, 1460 (sh), 1450, 1430 (sh). Uv λ_{max}^{EtOH} nm (log ε): 380 (4.07), 264 (4.10), 209 (4.45). Uv $\lambda_{max}^{EtOH+AlCl_3}$ nm (log ε): 412 (4.08), 274 (4.08), 210 (4.45). Uv $\lambda_{max}^{EtOH+NaOAc}$ nm (log ε): 379 (4.07), 264 (4.10), 209 (4.46).

Artonin U (**5**)

Compound (**5**) was recrystallized from methanol to give yellow needles, mp 238 - 239 ℃. $FeCl_3$ test : positive (brown). Mg-HCl test : positive (orange). Gibbs test : negative. EI-ms: *m/z* (rel. int.) 352 (M^+, 72 %), 337 (100), 297 (13), 284 (63), 179 (12). HR-ms: *m/z* 352.1328 (M^+, $C_{21}H_{20}O_5$ requires 352.1310). Ir ν_{max}^{KBr} cm^{-1}: 3500 - 3300 (br), 1660 (sh), 1590, 1540 (sh). Uv λ_{max}^{MeOH} nm (log ε): 324 (4.26), 272 (4.30), 205 (4.54). Uv $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 398 (4.08), 345 (4.32), 308 (4.27), 280 (4.25), 205 (4.55).

Treatment of Artonin R (**2**) with Triphenylphosphine

A solution of **2** (1 mg) and triphenylphosphine (1 mg) in methanol (1 ml) was kept at room temperature for 10 min. After removal of the solvent, the reaction product was purified by preparative tlc [solvent system, *n*-hexane - ethyl acetate (2 : 1)] to give yellow crystalline powder (**2a**, 0.7 mg).

Compound (**2a**) was obtained as a yellow crystalline powder from *n*-hexane - ether, mp 184 °C. *EI*-ms: *m/z (rel. int.)* 546 (M^+, 17 %), 528 (84), 513 (100), 487 (33). ^{1}H Nmr (acetone-d_6): δ 1.52 (6H, s), 1.55, 1.56 (each 3H, br s), 2.21 (3H, br s), 3.01, 3.31 (each 1H, d, *J* = 18 Hz), 3.62 (1H, br *s*), 3.73 (3H, *s*), 5.03, 5.30 (each 1H, br *s*), 5.56 (1H, br s), 5.85 (1H, d, J = 10 Hz), 6.74 (1H, d, J = 10 Hz), 7.16 (1H, d, J = 17 Hz), 7.46 (1H, d, J = 17 Hz), 8.27 (1H, s), 13.29 (1H, s).

Formation of Artonin R (**2**) from Artonin Q (**1**)

A mixture of **1** (10 mg) and methylene blue (10 mg) in methanol (15 ml) was irradiated in a glass vassel with a 100 W high pressure mercury lamp for 40 h. The reaction product was purified by hplc [solvent system, chloroform - ethyl acetate (12 : 1), column, Senshu Pak SSC Silica 4251-N, 10 ϕ x 250 mm, detector, uv 254 nm] to give **2** (1.2 mg), which was identified with artonin R by comparison of spectral data.

Methylation of 8-Prenylapigenin

A mixture of 8-prenylapigenin (8 mg), dimethyl sulfate (0.005 ml) and potassium carbonate (2 g) in acetone (30 ml) was refluxed for 30 min. The product was purified by preparative tlc [*n*-hexane - acetone (2 : 1)] and hplc [*n*-hexane - ethyl acetate (2 : 1)] to give 8-prenyl-7-*O*-methylapigenin (**5**, 2 mg), which was identified with artonin U by comparison of physical and spectral data.

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