ARTONOLS A, B, C, D, AND E, FIVE NEW ISOPRENYLATED PHENOLS FROM THE BARK OF *ARTOCARPUS COMMUNIS* FORST.[1]

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Abstract - Five new isoprenylated phenols, artonols A (**1**), B (**2**), C (**3**), D (**4**), and E (**5**) were isolated from the bark of *Artocarpus communis* Forst. (Moraceae), along with four known compounds, artonin E (**6**), cycloartobiloxanthone (**7**), artonin K (**8**), and artobiloxanthone (**9**). The structures of artonols A, B, C, D, and E were shown to be **1** - **5**, respectively, on the basis of spectroscopic data. Artonols A (**1**) and B (**2**) have unique structures. These compounds are biogenetically assumed to be derivatives from the flavone derivatives having the dihydrobenzoxanthone skeleton, such as artobiloxanthone (**9**).

In the previous papers, we reported the structure determination of isoprenylated flavonoids from Indonesian moraceous plants, *Artocarpus heterophyllus*,[2-7] *A. rigida*,[8,9] and *A. communis*,[10] and a Sri Lankan moraceous plant, *A. altilis*.[11] Some of these flavonoids showed potent inhibitory activity against the action of arachidonate 5-lipoxygenase from porcine leukocytes.[12] Artonin E (**6**)[10] obtained from *A. communis* was the most potent inhibitor of arachidonate 5-lipoxygenase (IC_{50} 0.36 μM). On the constituents of *Artocarpus communis*, many kinds of isoprenylated flavonoids have been isolated by our group and other two groups.[13,14] In our continuous studies on the isoprenylated flavonoids from the plants, we isolated five new isoprenylated phenols, named artonols A (**1**), B (**2**), C (**3**), D (**4**), and E (**5**), along with four known isoprenylated flavones, artonin E (**6**), cycloartobiloxanthone (**7**),[15] artonin K (**8**),[5] and artobiloxanthone (**9**),[15] from the acetone extract (Figures 1 and 2).

Artonol A (**1**), orange prisms, mp 189 - 196 °C, $[\alpha]_D$ 0°, exhibited positive ferric chloride reaction. The molecular formula of **1** was determined by HRMS to be $C_{21}H_{20}O_5$. The IR spectrum of **1** disclosed the

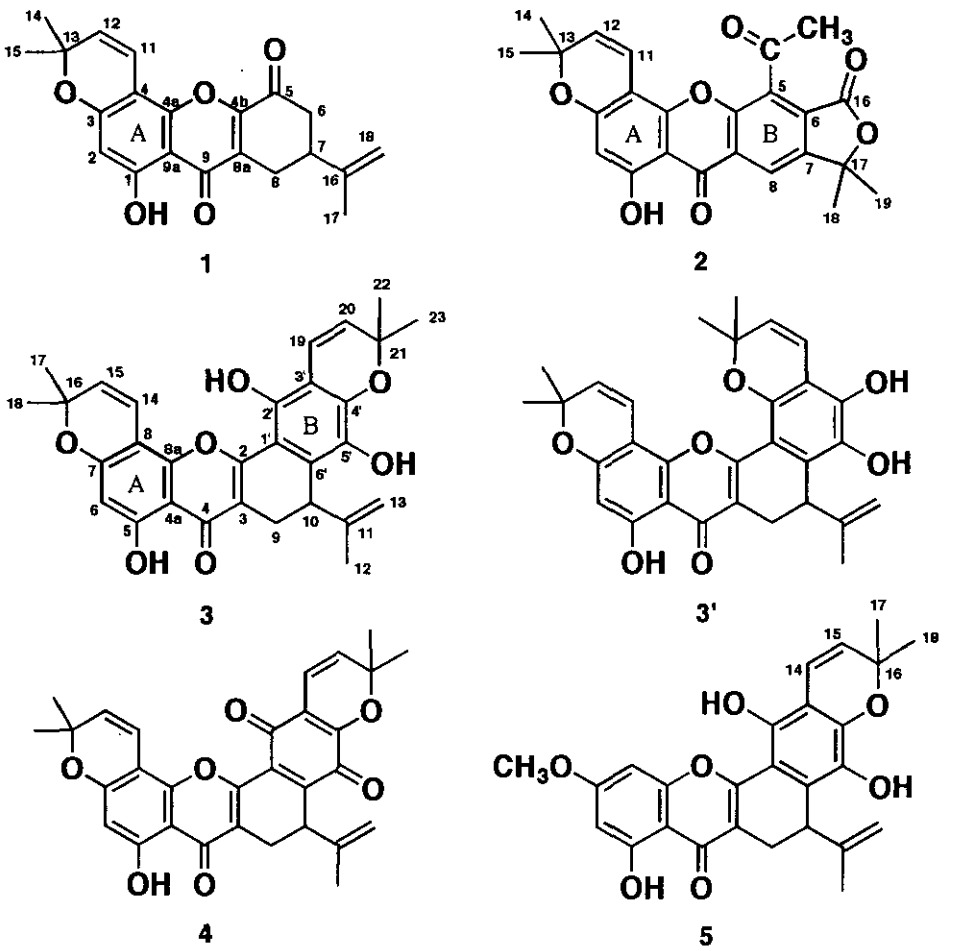

Figure 1 Structures of artonols A(1), B(2), C(3), D(4), and E(5)

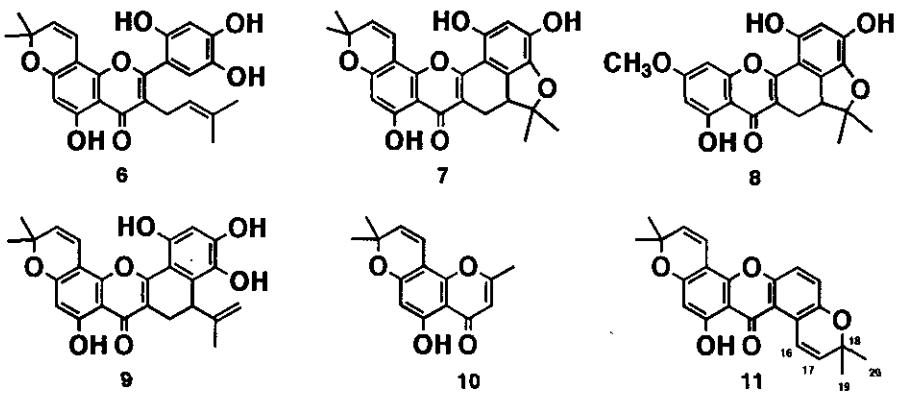

Figure 2 Structures of known compounds (6 - 9) and the related compounds

absorption bands due to hydroxyl, conjugated carbonyl, and benzene ring moieties. The UV spectrum of **1** exhibited the absorption maxima at 236.2, 279.4, and 334.7 nm, and was similar to that of allopteroxylin (**10**),[16] indicating that **1** is a chromone derivative. The UV spectrum of **1** showed a remarkable bathochromic shift upon addition of aluminum chloride. The ^{1}H NMR spectrum ($CDCl_3$) showed the signals of the following protons; protons in a 2,2-dimethylpyran ring, δ 1.47 (6H, s), 5.59, 6.82 (each 1H, d, J = 10.1 Hz); an aromatic proton, δ 6.28 (1H, s); a proton in a hydrogen-bonded hydroxyl group, δ 12.35 (1H, s); protons in an isopropenyl group, δ 1.83 (3H, s), 4.85, 4.92 (each 1H, br s); five aliphatic protons, δ 2.61 (1H, dd, J = 10.3 and 17.4 Hz), 2.68 (1H, dd, J = 11.5 and 15.6 Hz), 2.81 (1H, m), 2.88 (1H, ddd, J = 1.8, 3.4, and 15.6 Hz), 3.15 (1H, ddd, J = 1.8, 4.0, and 17.4 Hz). The ^{13}C NMR spectrum indicated the presence of twenty-one carbons (Table 1). In the ^{13}C NMR spectrum of **1**, two carbonyl carbon signals were observed at δ 182.4 and 192.0 ppm. One of them (δ 182.4) could be assigned to the C-9 carbonyl carbon in the chromone skeleton[17] and the other (δ 192.0) was attributable to a cyclic ketone. Angular type of the 2,2-dimethylpyran ring structure in the A ring of **1** was revealed with the aid of the HMBC spectrum (Figure 3). In the ^{13}C NMR spectrum of **1**, the chemical shifts of all the carbon atoms of pyranochromone moiety except the carbon atom of C-8a were similar to those of the relevant carbon atoms of cudraxanthone A (**11**).[18] From the above results, the partial structure was proposed for the structure of artonol A (Figure 3).

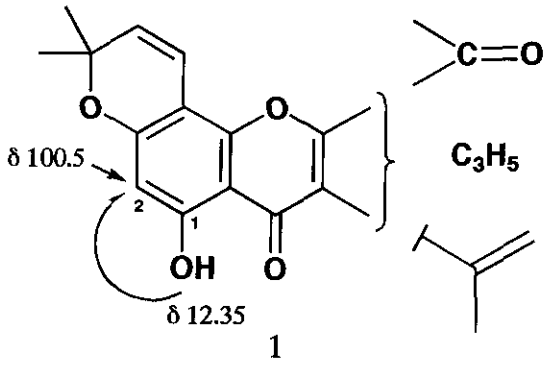

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Figure 3 Partial structure of 1 and HMBC spectrum

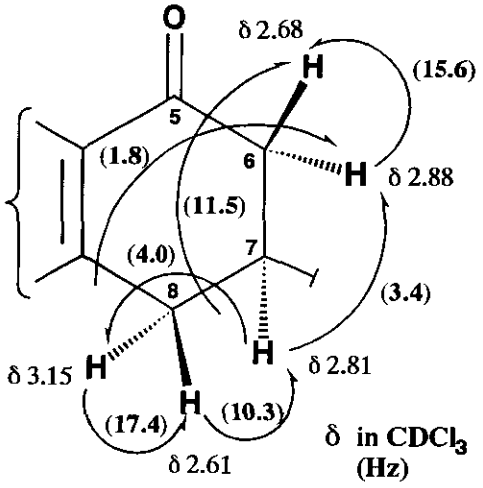


Figure 4 ^{1}H NMR spectrum of C_3H_5 moiety of 1

The structure of C_3H_5 moiety was confirmed, as described in Figure 4 by the ^1H-^1H COSY and ^1H-^{13}C COSY spectra along with the consideration of the coupling constants among the five aliphatic protons. Furthermore the structure of isopropenylcyclohexenone moiety was confirmed by the HMBC spectra of **1** (Figure 5). In the HMBC spectrum, one of the methylene protons at δ 3.15 (C-8-H) shows long-range correlation with the carbonyl carbon at δ 182.4 (C-9). From the above results, the structure of artonol A was represented by the formula (**1**).

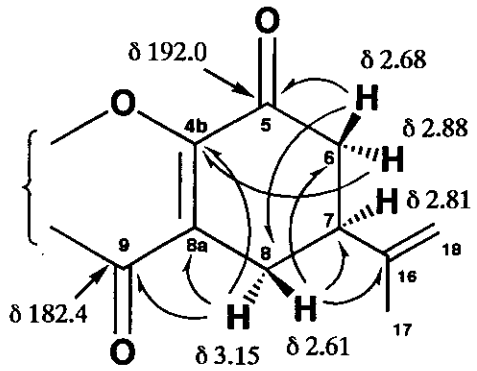
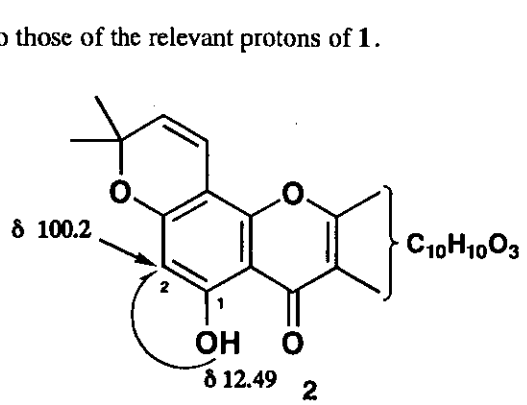


Figure 5 HMBC spectrum of isopropenylcyclohexenone moiety of 1 (δ in $CDCl_3$)

Artonol B (**2**), orange needles, mp 189 - 196 °C, $[\alpha]_D$ 0°, exhibited positive ferric chloride reaction. The molecular formula of **2** was determined by HRMS to be $C_{24}H_{20}O_7$. The IR spectrum of **2** disclosed the absorption bands due to hydroxyl, conjugated carbonyl, and benzene ring moieties. The UV spectrum exhibited the absorption maxima at 246.2, 284.0, 337.8 and 404.6 nm, which was similar to those of xanthones.[18] The ^1H NMR spectrum ($CDCl_3$) showed the following protons; protons in a 2,2-dimethylpyran ring, δ 1.50 (6H, s), 5.63, 6.60 (each 1H, d, J = 10.1 Hz); protons in two methyl groups, δ 1.76 (6H, s); protons in an acetyl group, δ 2.81 (3H, s); two aromatic protons, δ 6.31 (1H, s), 8.30 (1H, s); a proton in a hydrogen-bonded hydroxyl group, δ 12.49 (1H, s). The chemical shifts and coupling patterns of the protons of the pyranochromone moiety were similar to those of the relevant protons of **1**.



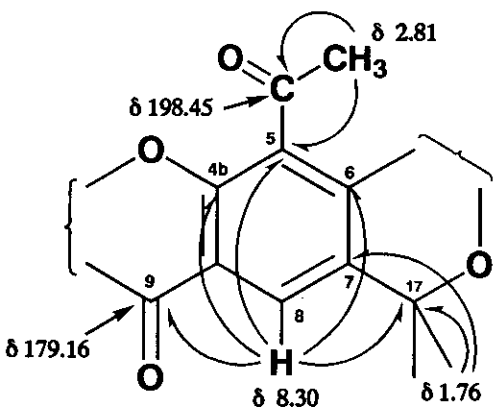


Figure 6 Partial structures and HMBC spectrum of 2 (δ in $CDCl_3$)

Table 1 ^{1}H and ^{13}C NMR chemical shifts (δ) of compounds (**1**, **2**, and **11**)

carbon	**1**	correlated proton	**2**	correlated proton	**11**
1	161.6	12.35 (s, OH)	163.2	12.49 (s, OH)	163.4
2	100.5	6.28 (s)	100.2	6.31 (s)	99.1
3	160.6		162.3		160.6
4	101.7		101.4		100.4
4a	151.0		151.3		154.6
4b	150.3		151.1		149.4
5	192.0		130.2		117.6
6	43.5	2.68 (dd, *J* = 11.5 and 15.6 Hz) 2.88 (ddd, *J* = 1.8, 3.4 and 15.6 Hz)	126.5		124.2
7	40.5	2.81 (m)	148.6		151.8
8	25.6	2.61 (dd, *J* = 10.3 and 17.4 Hz) 3.15 (ddd, *J* = 1.8, 4.0, and 17.4 Hz)	119.2	8.30 (s)	115.6
8a	127.5		125.2		119.0
9	182.4		179.2		181.5
9a	106.1		103.6		104.4
11	114.2	6.82 (d, *J* = 10.1 Hz)	114.2	6.60 (d, *J* = 10.1 Hz)	115.1
12	127.5	5.59 (d, *J* = 10.1 Hz)	128.2	5.63 (d, *J* = 10.1 Hz)	126.8
13	78.9		79.1		78.1
14	28.3	1.47 (3H, s)	28.5	1.50 (3H, s)	28.3
15	28.3	1.47 (3H, s)	28.5	1.50 (3H, s)	28.3
16	145.2		166.7		120.8
17	20.7	1.83 (3H, s)	86.6		132.8
18	111.9	4.85 (br s), 4.92 (br s)	27.6	1.76 (3H, s)	75.6
19			27.6	1.76 (3H, s)	27.4
20					27.4
-$\underline{C}OCH_3$			198.5		
-CO$\underline{C}H_3$			32.3	2.81 (3H, s)	

measured in $CDCl_3$

The ^{13}C NMR spectrum indicated the presence of twenty-four carbons. In the ^{13}C NMR spectrum of **2**, the chemical shifts of all the carbon atoms of the pyranochromone moiety were similar to those of the relevant carbons of **1** and cudraxanthone A (**11**) (Table 1). The assignments of the following proton signals, δ 1.76 (6H, s), 2.81 (3H, s), and 8.30 (1H, s), were carried out by using the ^{1}H-^{13}C COSY and HMBC spectra (Figure 6). The aromatic proton signal at δ 8.30 showed the correlation with that of the aromatic carbon at δ 119.2 (C-8), and showed the long-range correlation with the five carbon signals [δ 86.6 (C-17), 126.5 (C-6), 130.2 (C-5),[19] 151.1 (C-4b), 179.2 (C-9)] (Figure 6). These results confirmed that the proton signal at δ 8.30 was assigned to the proton at C-8 position as well as the presence of the xanthone skeleton in the structure of **2**. The location of an acetyl group was confirmed by the following results.

The proton signal at δ 2.81 (3H, s) showed the correlation with the carbon signal at δ 32.3 and the long-range correlation with the carbonyl carbon signal at δ 198.45 and the aromatic carbon signal at δ 130.2 (C-5). The signal at δ 1.76 (6H, s) showed the correlation with the carbon at δ 27.6 (C-18, 19) and the long-range correlation with the oxygenated quaternary carbon at δ 86.8 (C-17) along with the aromatic carbon at δ 148.6 (C-7) (Figure 6). From these results and the

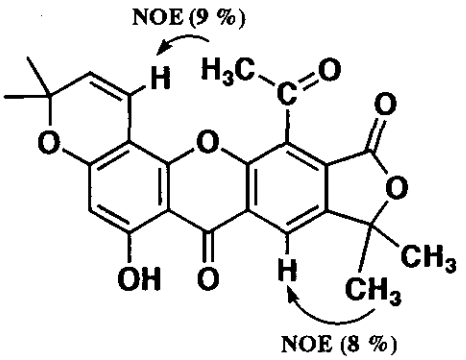


Figure 7 NOE experiment of 2

presence of lactone carbonyl carbon at δ 166.7, the α,β-unsaturated γ-lactone partial structure was suggested. The further confirmation of the locations of the acetyl group and the *gem*-dimethyl group on the α,β-unsaturated γ-lactone ring was obtained from the NOE experiment described in Figure 7. From the above results, the formula (**2**) was proposed for the structure of artonol B.

Artonols A and B have unique structures. Biogenetically these two compounds seems to be the derivatives from the dihydrobenzoxanthone derivative, such as artobiloxanthone (**9**), as follows : the compound (**1**) is assumed to be derived from dihydrobenzoxanthone hydrate (**9'**) through the *retro* Diels-Alder reaction as shown in Figure 8. On the other hand, the compound (**2**) is assumed to be derived from xanthone derivative having a five-membered cyclic ketone ring (**9"**) through the oxidative reaction as shown in Figure 9.

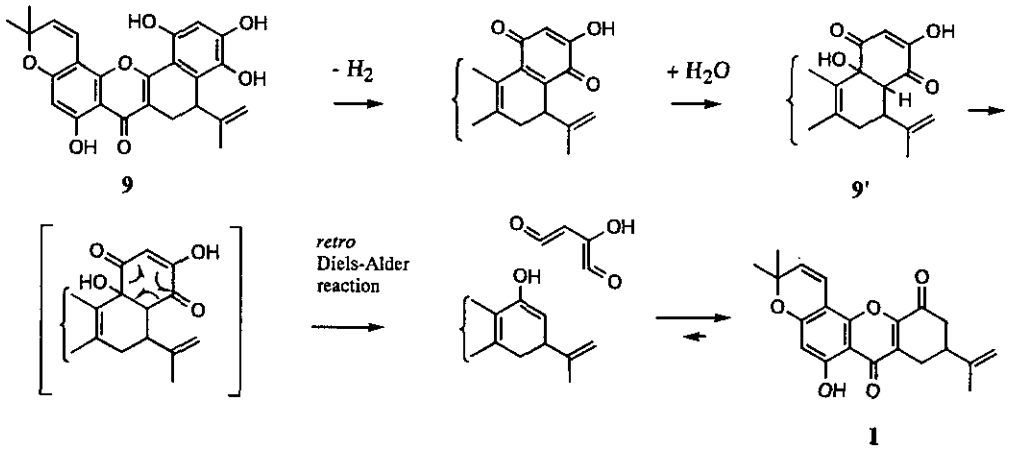


Figure 8 Hypothesis of biogenetic route to artonol A (1)

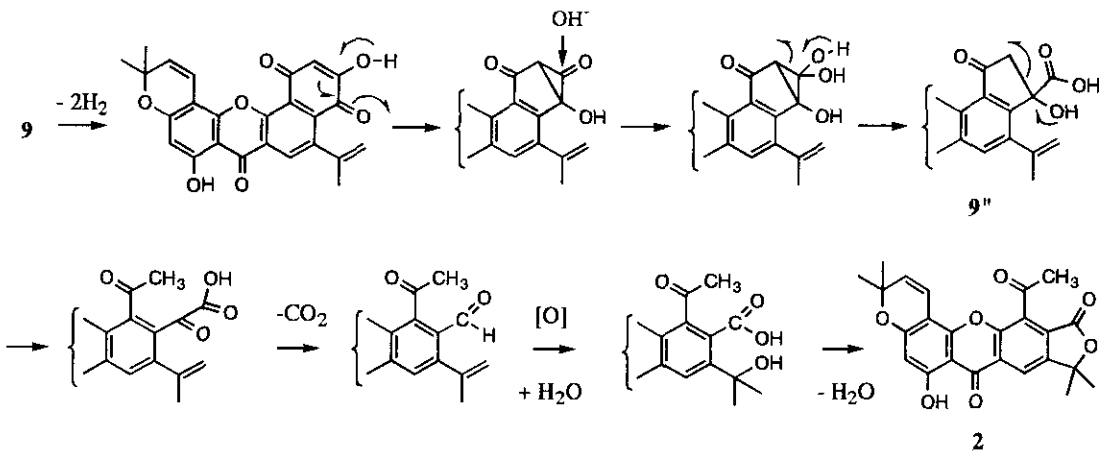


Figure 9 Hypothesis of biogenetic route of artonol B (2)

Artonol C (**3**), yellow needles, mp 182 - 184 °C, $[\alpha]_D$ 0°, exhibited positive ferric chloride reaction. The molecular formula of **3** was determined by HRMS to be $C_{30}H_{28}O_7$. The UV spectrum exhibited the absorption maxima at 236.8, 281.2, 345.0, and 386.4 nm, which was similar to that of artobiloxanthone (**9**). The ^{1}H NMR spectrum (acetone-d_6) showed the signals of the following protons; protons in two 2,2-dimethylpyran rings, δ 1.45, 1.47 (each 3H, s, C-16-CH_3 x 2), 5.75 (1H, d, J = 10 Hz, C-15-H), 6.79 (1H, d, J = 10 Hz, C-14-H); δ 1.47 (6H, s, C-21-CH_3 x 2), 5.78 (1H, d, J = 10 Hz, C-20-H), 6.82 (1H, d, J = 10 Hz, C-19-H); ABX type aliphatic protons, δ 2.45 (1H, dd, J = 6 and 16 Hz), 3.40 (1H, dd, J = 2 and 16 Hz), 3.98 (1H, br d, J = 6 Hz); protons in an isopropenyl group, δ 1.78 (3H, s), 4.32, 4.65 (each 1H, br s); an aromatic proton, δ 6.15 (1H, s); a proton in a hydrogen-bonded hydroxyl group, δ 13.29 (1H, s). The chemical shifts and coupling patterns of all the proton signals except those of a set of 2,2-dimethylpyran ring protons were similar to those of the relevant protons of artobiloxanthone (**9**).[15] In the ^{13}C NMR spectrum of **3**, the chemical shifts of all the carbon atoms except those of a set of 2,2-dimethylpyran ring and the B ring carbon atoms, along with the C-11 carbon atom were similar to those of the relevant carbon atoms of artobiloxanthone (**9**) (Table 2). From these results, two possible structures (**3**) and(**3'**) (Figure 1) were suggested. To discriminate the structures, the following experiment was carried out. The UV spectrum of **3** showed no bathochromic shift upon addition of boric acid and sodium acetate. This result supports that artonol C has no *ortho*-diphenol structure.[20] From these results, the formula (**3**) was proposed for the structure of artonol C.

Artonol D (**4**), reddish needles, mp 130 °C, exhibited positive ferric chloride reaction. The molecular formula of **4** was determined by HRMS to be $C_{30}H_{26}O_7$. The UV spectrum exhibited the absorption maxima at 234.6, 265.2, and 337.0 nm. The ^{1}H NMR spectrum (acetone-d_6) showed the following protons; protons in two 2,2-dimethylpyran rings, δ 1.46, 1.51 (each 3H, s, C-16-CH_3 x 2), 5.79 (1H, d, J = 10 Hz, C-15-H), 6.95 (1H, d, J = 10 Hz, C-14-H); δ 1.51, 1.52 (each 3H, s, C-21-CH_3 x 2), 5.91 (1H, d, J = 10 Hz, C-20-H), 6.56 (1H, d, J = 10 Hz, C-19-H); ABX type aliphatic protons, δ 2.71 (1H, dd, J = 6 and 16 Hz), 3.36 (1H, dd, J = 1 and 16 Hz), 3.86 (1H, br d, J = 6 Hz); protons in an isopropenyl group, δ 1.83 (3H, s), 4.69, 4.78 (each 1H, br s); an aromatic proton, δ 6.19 (1H, s); a proton in a hydrogen-bonded hydroxyl group, δ 12.77 (1H, s). While the coupling patterns of all the proton signals of **4** were similar to the relevant protons of **3**, chemical shifts were different slightly. From the above results, it was suggested that artonol D is a *p*-quinoidal structure of **3**. To confirm the structure, the following experiments were carried out. The UV spectrum of **4** showed the bathochromic shift upon addition of sodium hydrosulfite[21] and the resultant spectrum was similar to that of **3**. Furthermore artonol D (**4**) was derived from **3** by treatment with ammonium cerium (IV) nitrate (CAN).[22] (Figure 10). In the ^{13}C NMR of **4**, three carbonyl carbon signals were observed at δ 180.3 (C-5'), 180.8 (C-2'), and 181.4 (C-4) (Table 2). These chemical shifts (δ 180.3, 180.8) were similar to those of the relevant carbons of artonin O[9] and the oxidative product of artomunoxanthone[23] both having a *p*-quinoidal structure in the B ring. Further confirmation of the *p*-quinoidal partial structure was obtained by comparison of the ^{1}H NMR spectrum of **4** with that of **3**. In the spectrum of **4**, the olefinic protons (C-14-H, 15-H), the isopropenyl protons, and the ABX type aliphatic protons shifted to lower (or higher) magnetic field than the relevant protons of **3**. The similar results were observed in the spectra of the model compounds.[24] From the above results, the formula (**4**) was proposed for the structure of artonol D.

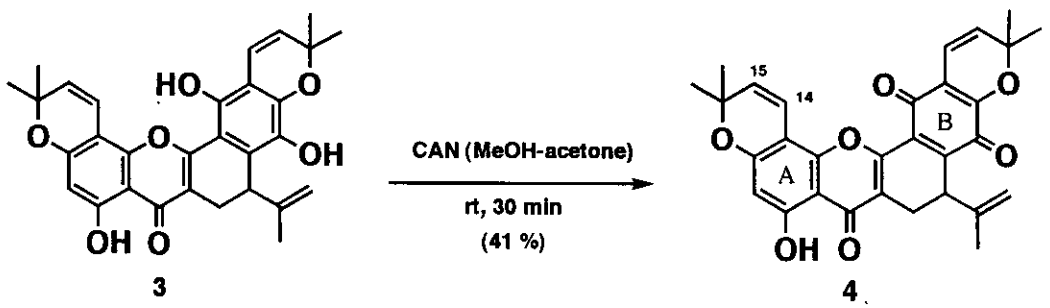


Figure 10 Formation of artonol D (4) from artonol C (3)

Table 2 ^{13}C NMR chemical shifts (δ) of compounds (**3**, **4***, **5**, and **9**)

carbon	3	4*	5	9	carbon	3	4*	5	9
2	161.2	156.9	161.3	161.7	9	22.2	21.9	22.3	22.3
3	111.9	117.8	112.3	111.4	10	38.0	36.3	37.7	38.1
4	181.2	181.4	181.0	181.2	11	145.3	142.5	145.4	151.5
4a	105.8	106.1	107.0	105.5	12	22.0	21.8	21.9	21.9
5	162.6	162.4	162.8	162.6	13	111.8	113.1	112.3	111.9
6	100.1	100.4	98.9	99.8	14	115.6	115.7	117.2	116.1
7	159.6	160.5	166.2	159.5	15	128.4	128.5	129.8	127.8
8	101.9	102.3	93.4	102.3	16	78.7	78.3	78.3	78.7
8a	152.0	152.6	157.4	152.3	17	28.2	28.1	28.0	28.2
1'	105.5	133.7	105.6	107.1	18	28.3	28.2	28.0	28.5
2'	145.0	180.8	145.3	150.9	19	117.2	115.4		
3'	110.8	117.3	110.4	103.7	20	129.1	131.9		
4'	145.0	151.1	145.4	145.3	21	78.2	81.2		
5'	137.4	180.3	137.3	136.7	22	28.0	28.5		
6'	129.9	130.1	129.8	129.9	23	28.0	28.6		
-OCH_3			56.4						

measured in acetone-d_6
*measured on **4** derived from **3**

Artonol E (**5**), pale yellow needles, mp 224 - 227°C, exhibited positive ferric chloride reaction. The molecular formula of **5** was determined by HRMS to be $C_{26}H_{24}O_7$. The UV spectrum exhibited the absorption maxima at 211.2, 270.6, and 377.2 nm, which was similar to those of artonol C (**3**). The ^1H NMR spectrum (acetone-d_6) showed the signals of the following protons; protons in a 2,2-dimethylpyran ring, δ 1.46, 1.48 (each 3H, s), 5.76, 6.77 (each 1H, d, J = 10 Hz); ABX type aliphatic protons, δ 2.47 (1 H, dd, J = 6 and 16 Hz), 3.40 (1H, dd, J = 2 and 16 Hz), 4.00 (1H, br d, J = 6 Hz); protons in an isopropenyl group, δ 1.77 (3H, s), 4.31, 4.65 (each 1H, br s); two *meta*-coupled aromatic protons, δ 6.33, 6.83 (each 1H, d, J = 2 Hz); protons in a methoxyl group, δ 3.92 (3H, s); a proton in a hydrogen-bonded hydroxyl group, δ 13.13 (1H, s). The chemical shifts and coupling patterns of all the proton signals except those of two *meta*-coupled aromatic protons as well as the

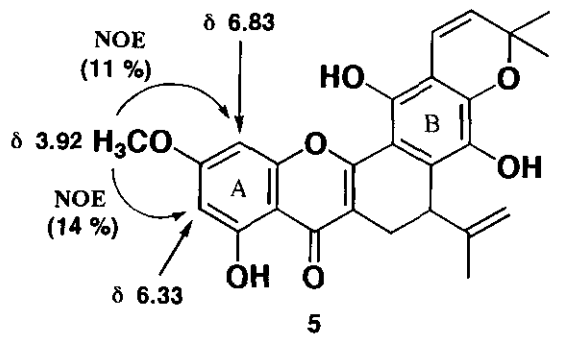


Figure 11 NOE experiment of 5

methoxyl protons were similar to those of the relevant protons of artonol C (**3**). In the ^{13}C NMR spectrum of **5**, the chemical shifts of all the carbon atoms except those of a methoxyl group and the A ring carbons were similar to those of the relevant carbons of artonol C (**3**). Furthermore the location of the methoxyl group was obtained by the NOE experiment described in Figure 11. From the above results, the formula (**5**) was proposed for the structure of artonol E.

EXPERIMENTAL

Abbreviations: s = singlet, d = doublet, dd = double doublet, ddd = double double doublet, t = triplet, m = multiplet, br = broad, sh = shoulder. The general procedures followed and instruments used are described in our previous papers.[2-11]

Plant material: The bark of *Artocarpus communis* Forst. (Moraceae) was collected in the Botanical Garden of Bogor, Indonesia, in February 1988, and was identified by the members of Botanical Garden of Bogor.

Isolation of Artonols A (**1**), B (**2**), C(**3**), D(**4**), and E(**5**) from the bark

The dried bark of *A. communis* Forst. (1 Kg) was extracted with *n*-hexane (8 L) at rt for 3 days and such was repeated two more times. The residue was extracted successively with benzene (8 L x 3) and acetone (8 L x 3) as descried above. Evaporation of the *n*-hexane, benzene, and acetone solutions to dryness yield 15 g, 7 g, and 45 g of residue, respectively.[11] The acetone extract (19 g) was chromatographed on silica gel (200 g) with benzene (frs. 1 - 5), benzene : acetone = 9 : 1 (frs. 6 - 10), 4 : 1 (frs. 11 - 15), 2 : 1 (frs. 16 - 21), 1 : 1 (frs. 22 - 27), and acetone (frs. 28 - 30), each fraction (eluted volume of 300 mL) monitored by TLC. The combined fraction (frs. 1 - 6, 0.9 g) was rechromatographed on silica gel (100 g) with *n*-hexane : acetone = 19 : 1 (frs. 1'- 6'), 9 : 1 (frs. 7'- 13'), and acetone (frs. 14'), each fraction (eluted volume of 200 mL) monitored by TLC. The combined fraction (frs. 1' and 2') was purified by preparative TLC [silica gel, solvent; *n*-hexane : acetone = 7 : 3, chloroform : *n*-hexane = 7 : 3] to give artonol A (**1**, 7.1 mg). The combined fraction (frs. 7' and 8') was purified by preparative TLC (silica gel, solvent; *n*-hexane : acetone = 7 : 3, *n*-hexane : ethyl acetate = 7 : 3] to give artonol B (**2**, 7.3 mg), and artonol D (**4**, 1.0 mg). The combined fraction (frs. 9' and 10') was purified by preparative TLC (silica gel, solvent; *n*-hexane : acetone = 7 : 3) to give artonol C (**3**, 25 mg) and artonol E (**5**, 6.9 mg). The fraction 11 (1.1 g) was purified by repeated recrystallization from benzene to give artonin E (**6**, 883 mg). The mother liquor of frs. 11 and frs. 12 - 15 (2.0 g) were combined, which was rechromatographed on silica gel (100 g) with benzene : chloroform = 3 : 1, 3 : 2, 2 : 3, and chloroform, each fraction (frs. 1"- 48", eluted volume of 100 mL) monitored by TLC. The fraction with benzene : chloroform = 2 : 3 (frs. 21"- 30") was fractionated by preparative TLC (silica gel, solvent; *n*-hexane : acetone = 3 : 2) to give cycloartobiloxanthone (**7**, 11 mg) and artonin K (**8**, 3 mg). The combined fraction 16 - 21 (0.8 g) was fractionated by gel filtration (Sephadex LH-20, solvent; MeOH) followed by preparative HPLC (solvent; *n*-hexane : ethyl acetate = 3 : 2, column; Senshu Pak SSC-silica 4251-N, 1ϕ cm x 25 cm, detector; UV 254 nm) to give artobiloxanthone (**9**, 20 mg).

Artonol A (**1**)

Compound (**1**) was recrystallized from acetone to give orange prisms, mp 189 - 196 °C. $FeCl_3$ test : positive (brown). $[\alpha]_D$ 0° (c = 0.10, MeOH). FABMS : *m/z* 353 (MH^+). HRMS : *m/z* 353.1458 (MH^+, $C_{21}H_{21}O_5$ requires 353.1389). IR νmax (KBr) cm^{-1} : 3400 (br), 2950 (sh), 2900, 2860, 1700, 1650, 1580, 1480. UV λmax (MeOH) nm (log ε) : 337.4 (3.57), 279.4 (4.31), 236.2 (4.45). UV λmax (MeOH + $AlCl_3$) nm (log ε) : 458.2 (3.28), 286.4 (4.42), 240.6 (4.45).

Artonol B (2)

Compound (**2**) was recrystallized from benzene to give orange needles, mp 267 - 273 °C. $FeCl_3$ test : positive (brown). $[\alpha]_D$ 0° (c = 0.10, MeOH). FABMS : *m/z* 421 (MH^+). HRMS : *m/z* 421.1248 (MH^+, $C_{24}H_{21}O_7$ requires 421.1287). IR νmax (KBr) cm^{-1} : 3400 (br), 1773, 1710, 1650, 1640, 1580, 1480. UV λmax (MeOH) nm (log ε) : 404.6 (3.10), 337.8 (3.50), 284.0 (3.99), 246.2 (4.10). UV λmax (MeOH + $AlCl_3$) nm (log ε) : 482.6 (3.22), 357.2 (3.66), 289.8 (4.12), 242.4 (4.10).

Artonol C (3)

Compound (**3**) was recrystallized from MeOH - benzene to give yellow needles, mp 182 - 184 °C. $FeCl_3$ test : positive (green). Mg - HCl test : positive (red). $[\alpha]_D$ 0° (c = 0.10, MeOH). FABMS : *m/z* 501 (MH^+). HRMS : *m/z* 501.1977 (MH^+, $C_{30}H_{29}O_7$ requires 501.1913). IR νmax (KBr) cm^{-1} : 3530, 1660, 1570, 1450. UV λmax (MeOH) nm (log ε) : 386.4 (4.11), 345.0 (3.90), 281.2 (4.44), 236.8 (4.36). UV λmax (MeOH + $AlCl_3$) nm (log ε) : 434.6 (4.12), 380.6 (4.01), 284.6 (4.42), 252.2 (4.37). UV λmax (MeOH + AcONa + H_3BO_3) : no shift.

Artonol D (4)

Compound (**4**) was recrystallized from acetone to give reddish needles, mp 130 °C. $FeCl_3$ test : positive (green). FABMS : *m/z* 499 (MH^+). HRMS : *m/z* 499.1802 (MH^+, $C_{30}H_{27}O_7$ requires 499.1757). IR νmax (KBr) cm^{-1} : 3850, 2900, 1700, 1650, 1640, 1580, 1460. UV λmax (MeOH) nm (log ε) : 337.0 (3.84), 265.2 (4.43), 234.6 (4.33). UV λmax (MeOH + $AlCl_3$) nm (log ε) : 356.6 (3.86), 269.6 (4.40), 230.3 (4.32). UV λmax (MeOH + $Na_2S_2O_4$) nm (log ε) : 384.4 (4.01), 273.4 (4.43), 210.4 (4.87).

Artonol E (5)

Compound (**5**) was recrystallized from ethyl acetate to give yellow needles, mp 224 - 227 °C. $FeCl_3$ test : positive (brown). Mg - HCl test : positive (red). FABMS : *m/z* 449 (MH^+). HRMS : *m/z* 449.1595 (MH^+, $C_{26}H_{25}O_7$ requires 449.1601). IR νmax (KBr) cm^{-1} : 3550, 1650, 1570, 1440, 1370. UV λmax (MeOH) nm (log ε) : 377.2 (4.09), 270.6 (4.26), 211.2 (4.31). UV λmax (MeOH + $AlCl_3$) nm (log ε) : 421.4 (4.22), 276.4 (4.25), 211.6 84.35). UV λmax (MeOH + AcONa + H_3BO_3) : no shift.

Formation of artonol D (4) from artonol C (3)

To a solution of **3** (8.0 mg) in acetone (5 mL), the methanolic solution of ammonium cerium (IV) nitrate (5.0 mg, 9.1 x 10^{-3} mmol) was added. The mixture was stirred for 30 min at rt and treated as usual. The reaction product was purified by preparative TLC (silica gel, solvent; *n*-hexane : acetone = 2 : 1) to give **4** (3.25 mg, 40.7 %). Compound (**4**) was identified with artonol D by comparing the physical and spectral data of **4**.

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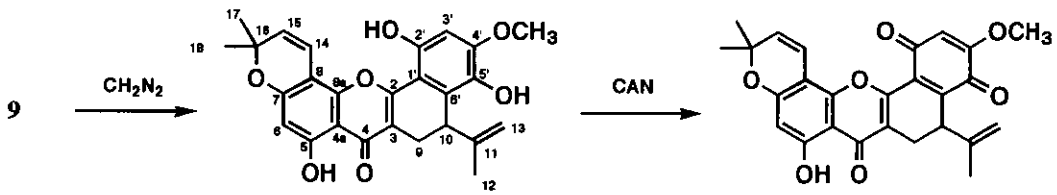
24. The model compounds (**9a** and **9b**) were derived from artobiloxanthone (**9**) as described below.

The ^{1}H NMR spectra of the model compounds are as follows : **9a**, δ (acetone-d_6) 1.43, 1.45 (each 3H, s, C-16-CH_3 x2), 1.76 (3H, s, C-11-CH_3), 2.42 (1H, dd, J = 8 and 16 Hz, C-9-H), 3.40 (1H, br d, J = 16 Hz, C-9-H), 3.90 (3H, s, -OCH_3), 4.00 (1H, br d, J = 8 Hz, C-10-H), 4.30, 4.63 (1H, br s, C-11-CH_2), 5.65 (1H, d, J = 10 Hz, C-15-H), 6.10 (1H, s, C-6-H), 6.62 (1H, s, C-3'-H), 6.86 (1H, d, J = 10 Hz, C-14-H), 13.17 (1H, s, C-5-OH); **9b**, δ (acetone-d_6) 1.46, 1.51 (each 3H, s, C-16-CH_3 x2), 1.83 (3H, s, C-11-CH_3), 2.73 (1H, dd, J = 8 and 16 Hz, C-9-H), 3.36 (1H, dd, J = 1.6 and 16 Hz, C-9-H), 3.86 (1H, br d, J = 8 Hz, C-10-H), 3.91 (3H, s, -OCH_3), 4.64, 4.78 (1H, br s, C-11-CH_2), 5.78 (1H, d, J = 10 Hz, C-15-H), 6.17 (1H, s, C-3'-H), 6.19 (1H, d, J = 0.6 Hz, C-6-H), 6.94 (1H, dd, J = 0.6 and 10 Hz, C-14-H), 12.75 (1H, s, C-5-OH).



9a **9b**

The compound (**9a**), artomunoxanthone, has been isolated from *A. communis* by W. L. Shieh *et al.* (see ref. 23). The compound (**9b**) has been also reported as an oxidative product of **9a** in the literature.

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