COMPONENTS OF THE BARK OF ARTOCARPUS RIGIDA BL. 2.*,[1] STRUCTURES OF FOUR NEW ISOPRENYLATED FLAVONE DERIVATIVES ARTONINS M, N, O, AND P

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Abstract —— Four new isoprenylated flavone derivatives, artonins M (**1**), N (**2**), O (**3**), and P (**4**), were isolated from the bark of Artocarpus rigida Bl., an Indonesian moraceous plant. The structures of artonins M, N, O, and P were determined to be formulae **1**, **2**, **3**, and **4**, respectively, on the basis of spectroscopic studies and chemical evidence.

In our continuing studies on the phenolic compounds of moraceous plants, we reported on the structure of isoprenoid-substituted phenolic components isolated from Indonesian moraceous plants, Artocarpus heterophyllus,[2-5] A. communis,[6] A. rigida,[7] and Antiaris toxicaria.[8-10] Previously, we reported the structure of artonins G and H from the bark of A. rigida.[7] Further extension of studies on the components of the bark of A. rigida led to the isolation of four new flavone derivatives, artonins M (**1**), N (**2**), O (**3**), and P (**4**). This paper deals with the characterization

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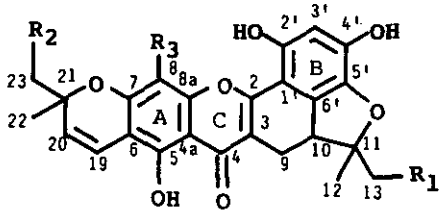
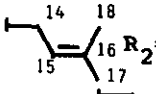
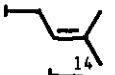
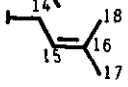
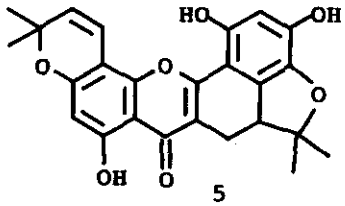
*This paper is dedicated to Prof. Edward C. Taylor on the occasion of his 70th birthday.



1 : R_1=  R_2=R_3=H

1': R_1=H R_2=  R_3=H

6 : R_1=R_2=H R_3= 



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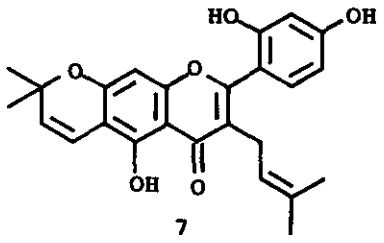

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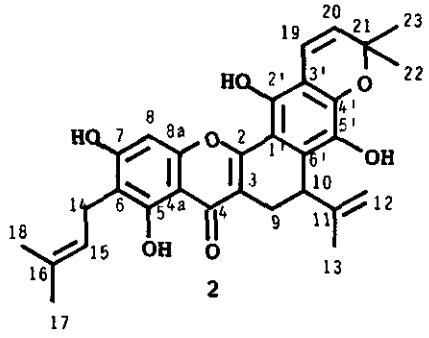

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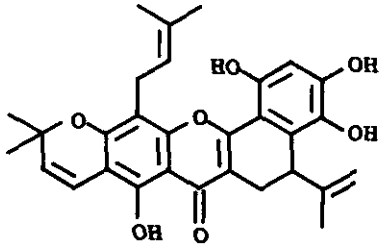

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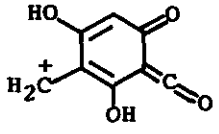

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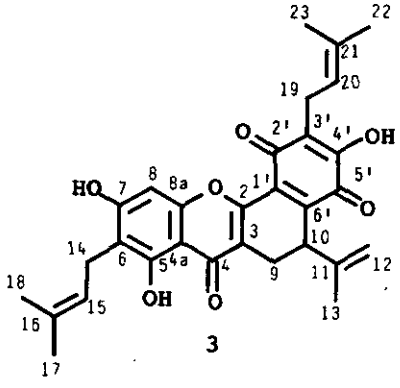
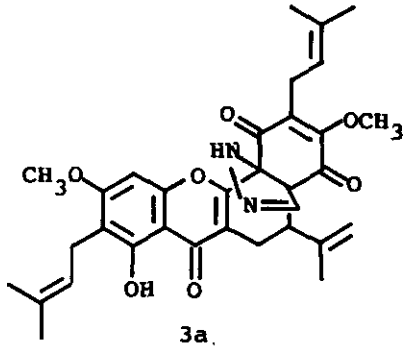


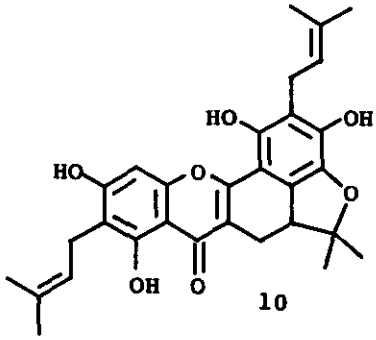
3

CH_2N_2

$(C_2H_5)_2O$



3a



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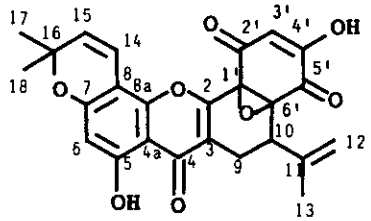

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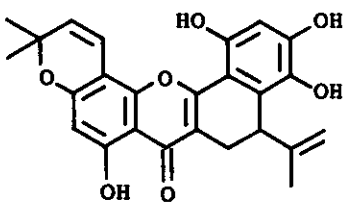

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Table 1 ^{13}C Nmr chemical shifts (ppm)

	1	5	6	7	2	10	3	4	11
C-2	161.6	161.5	161.5	162.8	160.8	161.6	156.6	159.3	161.7
C-3	113.0	112.7	112.5	121.7	112.1	112.7	118.1	116.5	111.4
C-4	181.3	181.4	181.7	183.2	181.0	181.1	181.2	181.4	181.2
C-4a	106.1	104.9	105.0	105.6	104.8	104.7	105.6	105.5	105.5
C-5	159.7	162.6	154.5	160.0	160.1	160.1	159.9	162.3	162.6
C-6	106.1	99.9	108.3	105.7	112.5	112.5	112.7	100.3	99.8
C-7	157.3	159.5	157.0	158.1	162.0	161.9	162.9	160.2	159.5
C-8	95.7	101.9	105.8	95.2	94.3	94.3	94.3	102.4	102.3
C-8a	156.9	152.0	155.3	157.2	155.3	155.1	156.4	153.0	152.3
C-1'	105.5	105.4	105.3	112.7	107.2	104.2	132.2	57.5	107.1
C-2'	151.3	151.5	151.5	157.3	145.4	148.1	183.7	184.5	150.9
C-3'	105.7	105.5	105.3	103.8	110.4	118.4	122.0	109.9	103.7
C-4'	147.3	147.0	147.0	161.6	145.3	144.7	152.9	169.5	145.3
C-5'	138.1	137.9	137.9	108.0	137.3	138.3	182.6	195.1	136.7
C-6'	133.2	133.6	133.6	132.2	128.6	129.0	145.0	68.3	129.9
C-9	21.0	20.3	20.4	24.6	21.9	20.7	22.8	19.8	22.3
C-10	45.9	47.5	47.6	122.5	37.8	47.2	36.3	36.6	38.1
C-11	96.0	93.7	93.7	132.2	145.4	94.0	142.3	144.0	151.5
C-12	23.7	22.8	22.8	25.8	111.8	22.9	112.9	112.9	111.9
C-13	42.3	28.4	28.3	17.7	22.4	28.3	21.8	23.5	21.9
C-14	21.9	116.0	22.0	115.9	22.1	22.1	21.9	116.1	116.1
C-15	124.9	127.8	123.6	129.1	123.3	123.6	123.0	128.1	127.8
C-16	132.4	78.7	131.7	78.6	131.6	131.5	133.3	79.2	78.7
C-17	25.8	28.3	25.8	28.3	25.9	25.8	25.8	28.4	28.2
C-18	17.8	28.3	18.1	28.3	17.9	17.9	18.0	28.6	28.5
C-19	116.0		116.4		117.3	23.2	22.0		
C-20	129.2		128.8		129.7	123.9	121.3		
C-21	78.6		78.4		78.3	131.3	131.8		
C-22	28.4		28.3		28.0	25.8	25.8		
C-23	28.4		28.3		28.0	17.9	18.0		

measured in acetone-d_6

of the four new compounds.

Artonin M (**1**), yellow plates, mp 240-249 °C (decomp.), $[\alpha]_D$ 0°, $C_{30}H_{30}O_7$, gave a brown color with methanolic ferric chloride reaction and showed a positive reaction to magnesium-hydrochloric acid (Mg-HCl) and Gibbs tests. The ultraviolet spectrum (uv) of **1** was similar to those of cycloartobiloxanthone[11] (**5**) and artonin A[2] (**6**), which have a partial structure of dihydro-1-oxaacenaphthene skeleton in the molecule. In the ^1H nucler magnetic resonance spectrum (nmr) of **1**, the proton signals ascribable to a hydrogen-bonded hydroxyl group [δ 13.12 (1H, s)], two aromatic protons [δ 6.36 (1H, s), 6.46 (1H, d, J = 0.7 Hz)], a 2,2-dimethylpyran ring [δ 1.45, 1.46 (each 3H, s), 5.75 (1H, d, J = 10 Hz), 6.67 (1H, dd, J = 0.7 and 10 Hz)], and a 4-methylpent-3-enyl moiety [δ 1.65, 1.69 (each 3H, br s), 1.99, 2.22 (each 2H, m), 5.21 (1H, m)] were observed. In addition to the above signals, a methyl signal [δ 1.34 (3H, s)] and a characteristic ABX type signals of a 2,2-disubstituted dihydro-1-oxaacenaphthene moiety [δ 2.40 (1H, t, J = 15 Hz), 3.21 (1H, dd, J = 6 and 15 Hz), 3.48 (1H, dd, J = 6 and 15 Hz)] were observed. The chemical shift values and the coupling constants of the ABX type protons were in good agreement with the corresponding protons of 2,2-dimethyl-dihydro-1-oxaacenaphthene partial structure of **5** and **6**, suggesting **1** to be a congener of these compounds. Comparison of the ^{13}C nmr spectrum of **1** with the spectra of **5** and **6** indicated that **1** has a dihydro-1-oxaacenaphthene partial structure in the molecule as well as the same oxygenated pattern as those of **5** and **6** (Table 1). Furthermore, a linear type-fused 2,2-dimethylpyran ring structure in the A ring of **1** was revealed by the comparison of the ^{13}C nmr spectrum of **1** with that of cudraflavone B[12] (**7**) (Table 1). From the above data, two possible structures (**1** and **1'**) were proposed for artonin M. In the ^{13}C nmr of **1**, the chemical shifts of the carbons at C-10 and 11 position were differ from those of the relevant carbons of **5** and **6**, indicating that these carbons were affected by the substituent at C-11. Thus, the structure of artonin M

was concluded to be formula **1**.

Artonin N (**2**), yellow needles, mp 223-230°C (decomp.), exhibited the molecular ion peak at m/z 502 in its EI-ms and the molecular formula $C_{30}H_{30}O_7$ for **2** was established by high-resolution ms. The positive color reaction for flavone derivative and the uv spectum suggested that **2** is a flavone derivative analogous to artonin B[2] (**8**). The ^1H nmr spectrum of **2** exhibited a hydrogen-bonded hydroxyl group at δ 13.45 (1H, s), an aromatic proton signal at δ 6.62 (1H, s), proton signals due to a 3,3-dimethylallyl group at δ 1.64, 1.76 (each 3H, br s), 3.35 (2H, br d, J = 7 Hz), and 5.27 (1H, m), proton signals due to a 2,2-dimethylpyran ring at δ 1.45, 1.47 (each 3H, s), 5.75, 6.76 (each 1H, d, J = 10 Hz), proton signals due to an isopropenyl group at δ 1.77 (3H, br s), 4.30, 4.64 (each 1H, br s), and an ABC type aliphatic signals at δ 2.45 (1H, dd, J = 6 and 16 Hz), 3.40 (1H, dd, J = 1 and 16 Hz), and 3.98 (1H, br d, J = 6 Hz). Of these, the chemical shifts and the coupling constants of an ABC type aliphatic protons and of protons due to an isopropenyl group were essentially the same as those of the relevant protons of artonin B (**8**), indicating that **2** has the same partial structure as **8**. The presence of a 3,3-dimethylallyl group in the A ring was shown by the fragment ion at m/z 165 (**9**) due to retro Diels-Alder cleavage of the C ring in the EI-ms, and this was substantiated by comparing the ^{13}C nmr spectrum of **2** with that of artonin G[7] (**10**) (Table 1). This indicated that a 2,2-dimethylpyran ring locates in the B ring, and two possible structures, whether the oxygen function participated in the ring is of C-2' or C-4' position, were proposed. On the other hand, the absence of ortho dihydroxyl groups in the molecule was revealed by the fact that no bathochromic shift was observed upon addition of NaOAc + H_3BO_3 in the uv spectrum.[13] From the above data, the formula **2** was proposed for artonin N.

Artonin O (**3**), reddish prisms, mp 200 °C (decomp.), $[\alpha]_D$ 0°, showed a positive reaction to methanolic ferric chloride test and the molecular for-

mula $C_{30}H_{30}O_7$ for **3** was determined by high-resolution ms. The ^1H nmr spectrum of **3** was similar to that of **2** but the signals due to a 2,2-dimethylpyran ring in **2** were replaced by the signals due to a 3,3-dimethylallyl group in **3**. In the ^{13}C nmr spectrum of **3**, three carbonyl carbon signals were observed at δ 181.2, 182.6, and 183.7 ppm (Table 1). One of them can be assigned to the carbonyl carbon in a chromone skeleton and the others are attributable to a quinoidal structure. From the comparison of the ^{13}C nmr spectrum of **3** with that of **2**, the structure of the A and C rings and the partial structure of C-9 to C-13 were thought to be the same as those of **2**, implying that the B ring of **3** is a quinoidal structure (Table 1). In order to confirm this assumption, the long-range selective ^1H decoupling (LSPD) experiments were carried out as follows. The weak irradiation of methylene protons (δ 3.21 ppm) of a 3,3-dimethylallyl group at C-3' converted a triplet signal (J = 4.4 Hz) at δ 183.7 ppm into a singlet signal, a broad triplet signal (J = 8.1 Hz) at δ 122.0 ppm into a broad singlet, and a triplet signal (J = 4.4 Hz) at δ 152.9 ppm into a singlet signal. An analogous irradiation of a methine (δ 3.81 ppm) at C-10 converted a doublet signal (J = 3.7 Hz) at δ 182.6 ppm as well as a doublet signal (J = 4.4 Hz) at δ 132.2 ppm into a singlet signal and a multiplet signal at δ 145.0 ppm into a broad doublet signal (J = 9.5 Hz). From the above data, the structure of the B ring for **3** would be depicted in Figure 1. Further evidence to support this conclusion was obtained by the addition reaction of **3** with diazomethane. Fieser et al.[14] reported that the reaction of *p*-benzoquinone with one mole of diazomethane gives the adduct, a pyrazol and/or a indazol in good yield while *o*-benzoquinone gives much poor results in the same reaction. The reaction of **3** with diazomethane afforded a pyrazol product (**3a**)[15] quantitatively, accompanied by methylation of two hydroxyl groups. This fact substantiated the B ring of **3** to be *p*-benzoquinone structure. Thus, the structure of artonin O was represented by formula **3**.

Artonin P (**4**) was isolated as an unstable reddish amorphous powder. The molecular formula $C_{25}H_{20}O_8$ for **4** was determined by fast-atom bombardment ms (MH^+ m/z 449) and nmr spectroscopic analysis. The ^1H nmr spectrum of **4** exhibited the signals due to a chelated hydroxyl group at δ 12.67, an aromatic proton at δ 6.15 (s), an olefinic proton at δ 5.53 (s), protons in a 2,2-dimethylpyran ring at δ 1.44, 1.48 (each 3H, s), 5.72, 7.11 (each d, J = 10 Hz), an ABX type protons at δ 2.31 (br dd, J = 7 and 16 Hz), 3.05 (br d, J = 16 Hz), 3.63 (br d, J = 7 Hz), and protons in an isopropenyl group at δ 1.82 (3H, br s), 4.53, 4.71 (each br s). These signal pattern was analogous to that of artobiloxanthone[11] (**11**). The ^{13}C nmr spectrum of **4** showed three carbonyl carbon signals resonated at δ 181.4, 184.5 and 195.1 ppm, suggesting that **4** has a quinoidal structure as same as artonin O (**3**) (Table 1). The chemical shifts of the carbons in the A and C rings and of the carbons of C-9 to C-13 of **4** were essentially the same as those of the relevant carbons of **11** (Table 1), indicating that the B ring of **4** is a quinoidal structure. Among the B ring carbons at δ 57.5, 68.3, 109.9, 169.5, 184.5 and 195.1 ppm, the former two carbons were analysed by LSPD experiments. The weak irradiation of C-10-H at δ 3.98 ppm converted a triplet signal (J = 6.6 Hz) at δ 57.5 into a doublet signal (J = 6.6 Hz) and a multiplet signal at δ 68.3 into a broad doublet (J = 8.8 Hz). The irradiation of an olefinic proton at δ 5.53 ppm converted a triplet signal (J ≈ 6.6 Hz) at δ 57.5 ppm into a doublet signal (J = 6.6 Hz). These data and the ABX type signals due to C-9 and C-10 protons which are shielded compared with those of **11** indicated that an epoxide group locates between C-1' and C-6'. On the other hand, the olefinic proton at δ 7.11 ppm in a 2,2-dimethylpyran ring uncommonly appeared in a lower field, suggesting an anisotropic effect of the carbonyl carbon at C-2'. On the basis of the above data, the formula **4** was proposed for artonin P.

EXPERIMENTAL

Abbreviations: s = singlet, d = doublet, dd = double doublet, m = multiplet, sh = shoulder, infl = inflection.

General Procedure: Melting points were measured by a Yazawa micromelting point apparatus (hot-stage type) and are uncorrected. Uv spectra were recorded on a Shimadzu UV-265 spectrophotometer and ir spectra were recorded on a Hitachi 260-30 spectrophotometer. ^{1}H and ^{13}C nmr spectra were recorded on a JEOL JNM GX-400 FTNMR spectrometer using tetramethylsilane as an internal standard. Chemical shifts (δ) are expressed as ppm and coupling constants (J) are in Herz. Ms spectra recorded on a JEOL JMS D-300 and DX-303 spectrometer. Optical rotation recorded on a JASCO DIP-4 Digital polarimeter. Wakogel C-200 and Wakogel B-5FM were used for column chromatography and thin layer chromatography (tlc), respectively.

Isolation of Artonin M (1), N (2), O (3), and P (4) from the Bark of A. rigida Bl.

The extraction on the bark of A. rigida (1 Kg) with n-hexane, benzene, acetone, and MeOH afforded each extracts as described in the previous paper.[7] The acetone extarct (29 g) was chromatographed on a silica gel (250 g) column using benzene-acetone as eluting solvents. The fraction (2 g) eluted with benzene : acetone = 6 : 1 was rechromatographed on a silica gel (200 g) column with n-hexane : ethyl acetate = 6 : 1 (frs. 1-6), 3 : 1 (frs. 7-11), 1 : 1 (frs. 12-18) and ethyl acetate (frs. 19 and 20), each fraction monitored by tlc. The combined fraction (frs. 11 and 12, 0.1 g) was subjected to flash chromatography (silica gel, solvent, n-hexane : ethyl acetate = 4 : 1) followed by high performance liquid chromatography (solvent, n-hexane : ethyl acetate = 3 : 2, column, Senshu Pak SSC Silica 4251-N , 1 cmø x 25 cm, detector, uv 280 nm) to give artonin M (**1**, 2 mg). The combined fraction (frs. 13 and 14, 0.1 g) was purified by preparative tlc (silica gel, solvent, chloroform : acetone = 15 : 1) to give artonin N (**2**, 3 mg). The combined fraction (frs. 15-18 , 0.4 g) was purified by preparative tlc (silica gel, solvent, n-hexane : acetone = 3 : 2, n-hexane : ethyl acetate = 3 : 1) to give artonin O (**3**, 14 mg). The fraction (18.8 g) eluted with benzene : acetone = 1 : 1 on the initial column chromatography was chromatographed on a silica gel (250 g) with benzene : acetone = 6 : 1 (frs. 1'-2'), 5 : 1 (frs. 3'-5'), 4 : 1 (frs. 6'-9'), 3 : 1 (frs. 10'-12'), 2 : 1 (frs. 13'-16'), 1 : 1 (frs. 17'-22') as eluting solvents of 300 ml each. The fractions 4' (2 g) was rechromatographed on a silica gel (100 g) column chromatography using benzene-acetone as eluting solvents. A part (0.8 g) of the fraction eluted with benzene : acetone = 2 : 1 was purified by preparative tlc (silica gel, solvent, chloroform : MeOH = 10 : 1, benzene : acetone : 2 : 3) to give artonin P (**4**, 30 mg).

Artonin M (**1**)

Compound **1** was recrystallized from n-hexane-acetone to give yellow plates, mp 240-249°C (decomp.), $[\alpha]_D^{22}$ 0° (c = 0.09, MeOH). $FeCl_3$ test: positive (brown). Mg-HCl test: positive (red). Uv λ_{max}^{MeOH} nm (log ε): 228 (4.21), 291 (4.21), 337 (infl 3.87), 380 (4.01). Ir ν_{max}^{KBr}

cm^{-1}: 3350 (br), 1650, 1630, 1600, 1460, 1380. EI-ms: m/z (rel. int.) 502 (M^+, 76), 487 (100), 433 (10), 417 (41), 393 (33), 377 (27), 203 (5). HR-ms: m/z 502.1994 (M^+, $C_{30}H_{30}O_7$ requires 502.1992).

Artonin N (2)

Compound **2** was recrystallized from n-hexane-ether to give yellow needles, mp 223-230°C (decomp.), $[\alpha]_D^{22}$ 0° (c = 0.1, MeOH). $FeCl_3$ test: positive (brown). Mg-HCl test: positive (red). Uv λ_{max}^{MeOH} nm (log ε): 212 (4.36), 275 (4.29), 378 (4.10). Uv $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$: no shift. Ir ν_{max}^{KBr} cm^{-1}: 3450 (br), 1650, 1615, 1570, 1480, 1450, 1400, 1380. EI-ms: m/z (rel. int.) 502 (M^+, 97), 487 (36), 459 (100), 447 (99), 417 (18), 405 (10), 165 (3). HR-ms: m/z 502.2012 (M^+, $C_{30}H_{30}O_7$ requires 502.1992).

Artonin O (3)

Compound **3** was recrystallized from n-hexane-ether to give reddish prisms, mp 200°C (decomp.), $[\alpha]_D^{22}$ 0° (c = 0.07, MeOH). $FeCl_3$ test: positive (brown). Uv λ_{max}^{MeOH} nm (log ε): 213 (4.92), 261 (4.79), 313 (4.50), 380 (4.08). Ir ν_{max}^{KBr} cm^{-1}: 3450 (br), 1640, 1610, 1570, 1490, 1465, 1440, 1420. EI-ms: m/z (rel. int.) 502 (M^+, 65), 500 (55), 485 (100), 459 (43), 447 (46), 235 (36), 165 (4). HR-ms: m/z 502.1979 (M^+, $C_{30}H_{30}O_7$ requires 502.1992). ^1H Nmr (acetone-d_6): δ 1.64, 1.66, 1.76, 1.77 (each 3H, br s, C-16-CH_3, C-21-CH_3 and C-11-CH_3), 2.71 (1H, dd, J = 8 and 17, C-9-H), 3.20 (2H, br d, J = 7, C-19-H x 2), 3.35 (2H, br d, J = 7, C-14-H x 2), 3.37 (1H, dd, J = 1 and 17, C-9-H), 3.81 (1H, br d, J = 8, C-10-H), 4.62, 4.75 (each br s, C-12-H), 5.18, 5.26 (each 1H, m, C-15-H and C-20-H), 6.56 (1H, s, C-8-H), 13.03 (1H, s, C-5-OH).

Reaction of Artonin O (3) with Diazomethane (Formation of **3a**)

To a solution of **3** (3 mg) in ether (5 ml), cooled to 0°C, was added the ethereal solution of diazomethane prepared from nitrosomethylurea (14 mg) and the reaction mixture was stirred for 15 min at room temperature. After usual work up, the reaction product was purified by hplc (silica gel, Senshu Pak SSC Silica 4251-N, detector, uv 280 nm, solvent, n-hexane : ethyl acetate = 2 : 1) to give **3a** (3 mg).

Compound **3a**, pale yellow powder. EI-ms: m/z (rel. int.) 572 (M^+, 100), 529 (16), 517 (43), 489 (15), 349 (29), 337 (43). ^1H Nmr (acetone-d_6): δ 1.14, 1.50, 1.63, 1.76, 1.90 (each 3H, br s, C-16-CH_3, C-21-CH_3 and C-11-CH_3), 2.51 (1H, dd, J = 11 and 17, C-9-H), 2.95 (1H, dd, J = 4 and 17, C-9-H), 3.02 (1H, dd, J = 4 and 11, C-10-H), 3.08, 3.32 (each 2H, br d, J = 8, C-14-H x 2 and C-19-H x 2), 3.99, 4.04 (each 3H, s, OCH_3), 4.76 (1H, m, C-20-H), 4.93, 5.10 (each 1H, br s, C-12-H), 5.15 (1H, m, C-15-H), 6.57 (1H, s, C-8-H), 7.01 (1H, s, CH of pyrazol ring), 7.85 (1H, br s, NH of pyrazol ring, exchangeable with D_2O), 12.70 (1H, s, C-5-OH, exchangeable with D_2O).

Arttonin P (4)

Compound **4** was obtained as a reddish amorphous powder. $FeCl_3$ test: positive (brown). Uv λ_{max}^{MeOH} nm (log ε): 206 (4.53), 235 (sh 4.65), 267 (4.76), 365 (4.17). Ir ν_{max}^{KBr} cm^{-1}: 3450 (br), 1700, 1660, 1565, 1485, 1450. FAB-ms: m/z 449 $(M+H)^+$.

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15. In the structure of **3a**, the orientation of the diazomethane addition to the C-1' and 6' positions is not clear.

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