SHORT PAPER

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A new isoprenylated chalcone, artoindonesianin J, from the root and tree bark of *Artocarpus bracteata*

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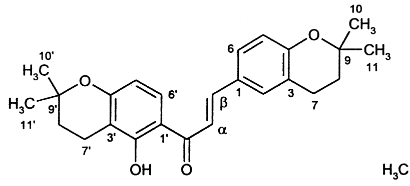
A new prenylated chalcone artoindonesianin J, the structure of which was determined on the basis of spectroscopic evidence, was isolated from the root and tree bark of *Artocarpus bracteata* Hook, together with three known flavonoids, kanzonol, 6-(3-methylbut-2-enyl)-apigenin and carpachromene.

Keywords: isoprenylated chalcone, artoindonesianin J, *Artocarpus bracteata*

Artocarpus is one of the most important genera in the family Moraceae growing in the tropical and subtropical regions.[1] This genus has been found to be a rich source of a variety of flavonoids characterised by the presence of an isoprenyl substituent at C-3, and 2′,4′-dioxygenation or 2′,4′,5′-trioxygenation patterns in the B ring.[2-4] Most of the species investigated have been shown to produce flavone derivatives and only a few contain chalcone or flavanone derivatives. As part of a systematic exploration of Indonesian moraceous plants, we have isolated a number of isoprenylated flavones from several Indonesian *Artocarpus* species.[5-8] Some of these compounds have shown cytotoxic properties and inhibitory effects on of K$^+$-dependent amino acid uptake into *Bombyx mori* midgut.[5-8] In this paper, we report the chemical investigation of another species, *A. bracteata* Hook, for which no previous investigations have been reported.

The dried powdered root and tree bark of *A. bracteata* were extracted successively with hexane, benzene, acetone and MeOH. The hexane extract was fractionated using silica gel chromatography and the fraction rich in artoindonesianin J (**1**) was repeatedly subjected to chromatography to give a pure sample of compound **1** after crystallisation. Using the same methods, three known isoprenylated flavonoids, kanzonol (**2**),[9,10] 6-(3-methylbut-2-enyl)apigenin (**3**)[11] and carpachromene (**4**),[12] were isolated from the benzene and acetone extracts. Artoindonesianin J (**1**) was obtained as yellow needles, m.p. 135–136°C. Its molecular formula, $C_{25}H_{28}O_4$, was determined from the high-resolution FABMS spectrum in which the $[M+1]^+$ ion was observed at *m*/*z* 393.2076 (calcd. 393.2066). The UV spectrum of **1** showed absorption maxima typical of a chalcone and was similar to those of **2**. It was unchanged on the addition of NaOH, $AlCl_3$ and NaOAc. The IR spectrum of **1** exhibited absorptions assignable to an



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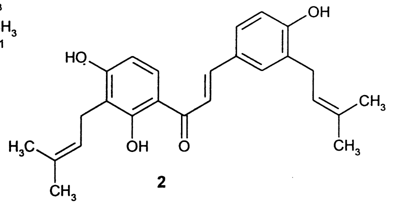

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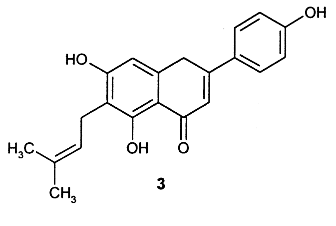

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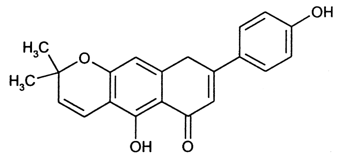

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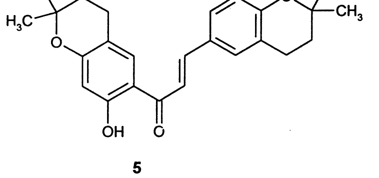

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

Table 1 ^{13}C NMR data of compounds **1, 2** and **5** [δ_C values (ppm)]

Carbon	**1**[a]	**2**[a]	**5**[b]	Carbon	**1**[a]	**2**[a]	**5**[b]
C=O	192.3	192.3	191.8	C-1′	112.9	114.1	114.3
C-α	117.7	117.7	118.1	C-2′	164.0	163.5	161.3
C-β	144.5	144.5	144.5	C-3′	109.3	114.1	104.9
C-1	126.7	127.5	126.7	C-4′	160.6	161.5	164.1
C-2	130.5	130.9	130.9	C-5′	109.5	107.7	112.6
C-3	121.4	127.6	121.4	C-6′	128.4	129.2	130.1
C-4	156.8	156.9	156.8	C-7′	16.4	29.7	22.4
C-5	117.4	116.3	117.4	C-8′	31.9	121.1	32.6
C-6	127.9	128.3	127.8	C-9′	75.7	135.8	75.5
C-7	22.4	21.7	21.9	C-10′	26.7	17.9	27.0
C-8	32.6	121.0	32.6	C-11′	26.7	25.8	27.0
C-9	75.2	135.6	75.5				
C-10	26.9	17.9	27.0				
C-11	26.9	25.8	27.0				

[a] Measured at 75 MHz in [^{2}H]chloroform.

[b] Measured at 75 MHz in [$^2H_6$]acetone.

hydroxyl and a chelated carbonyl group, suggesting that **1** contained an hydroxyl group at C-2′. The ^{1}H NMR spectrum of **1** disclosed the presence of *trans*-vinylic protons at δ_H 7.45 and 7.85 (each 1H, d, J=15.4 Hz) supporting a chalcone structure for **1**. The ^{1}H NMR spectrum of **1** also showed signals for five aromatic protons, three of which formed an ABX system at δ_H 7.44 (1H, d, J=2.1 Hz), 7.40 (1H, dd, J=8.5 and 2.1 Hz) and 6.82 (1H, d, J=8.5 Hz), attributable to the protons of the B ring substituted at C-3 and C-4. The other two formed an AX system at δ_H 7.70 and 6.36 (each 1H, d, J=9.1 Hz) and were assignable to the protons of a 2,3′,4′-trisubstituted A ring. Other features of the ^{1}H NMR spectrum of **1** included two singlets at δ_H 1.35 and 1.37 (each 6H, s) and four triplets at δ_H 1.82, 1.86, 2.37, 2.82 (each 2H, J=6.7 Hz), indicative of fused 2,2-dimethyldihydropyran moieties. These ^{1}H NMR findings were consistent with the structure **1** for artoindonesianin J. Supporting evidence for the structure **1** came from the ^{13}C NMR spectrum (Table 1), assigned with the aid of DEPT methods, which was in good agreement with that of **2** and the related chalcone 3,4-,4′,5′-*bis*-(2,2-dimethylchromano)-2′-hydroxychalcone (**5**).[11]

Experimental

Melting points were determined on Fischer John Melting Apparatus and were uncorrected. UV spectra were measured with a Varian Conc. 100 instrument. IR spectra were determined with Perkin Elmer FTIR Spectrum One spectrometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM 300 operating at 300 (^{1}H) and 75 (^{13}C) MHz using residual and deuterated solvent peaks as reference standards. Low and high resolution mass spectra were obtained with VG Autospec mass spectrometer (EI and FAB mode). Vacuum liquid (VLC) and column chromatography were carried out using Merck silica gel 60 GF$_{254}$ and silica gel G60 35-70 mesh. For TLC analysis, precoated silica gel plates (Merck Kieselgel 60 GF$_{254}$, 0.25 mm) were used.

Isolation of **1–4:** The dried powdered root barks (4.9 kg), collected from the Protected Forest of Rimbo Panti, Pasaman District, West Sumatra Province, Indonesia, in September 1996, were macerated successively with *n*-hexane, benzene, acetone and MeOH. One-quarter of the hexane extract (25 g) was fractionated by VLC (silica gel, *n*-hexane-EtOAc:9.5-0.5) into three fractions. The second fraction was repeatedly subjected to column chromatography over silica gel using *n*-hexane-EtOAc (95:5) as an eluting solvent to afford a dark yellow solid (34 mg), which was crystallized from diethyl ether-*n*-hexane to give **1** as yellow needles (3 mg). From the benzene (83 g) and acetone (44 g) extracts, **2**[9,10], **3**[11] and **4**[12] were obtained by the same method. The same compounds were also identified from the tree barks of the plant.

Artoindonesianin J (**1**) was obtained as yellow needles, m.p. 135–136°C; ν_{max}/cm^{-1} (KBr) 3500, 2975, 2929, 2853, 1634, 1614, 1589, 1562, 1492; λ_{max}/nm (log ε) (MeOH) 212 (3.36), 232 (3.04), 244 (sh), 314 (sh) and 376 (3.45); (MeOH+NaOH) unchanged; (MeOH+AlCl$_3$) unchanged; (MeOH+NaOAc) unchanged; δ_H (300 MHz, [^{2}H]chloroform) see text; δ_C (75 MHz, [^{2}H]chloroform) see Table 1; *m/z* 392 (M$^+$, 100%), 337 (10), 205 (17), 154 (32) (Found: [M+1]$^+$ 393.2078. $C_{25}H_{29}O_4$ requires M_r 393.2066).

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