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Note

Isolation and characterization of dehydrogoniothalamin from *Goniothalamus umbrosus*

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Three major compounds dehydrogoniothalamin, goniothalamin and 5-acetoxy goniothalamin have been isolated and characterized from the roots of *Goniothalamus umbrosus* Sinclair. Goniothalamin and 5-acetoxygoniothalamin have been previously reported from several *Goniothalamus* sp. However, dehydrogoniothalamin has not been reported so far.

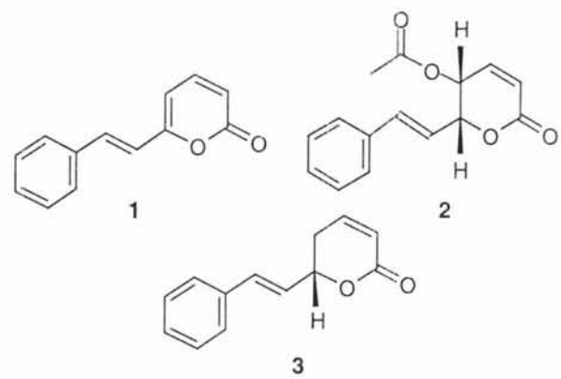
The genus *Goniothalamus* (Annonaceae) comprises some 115 species of trees and shrubs which are distributed throughout South and Southeast Asia[1]. About 17 species of *Goniothalamus* are estimated to be found in Sabah[2,3] although the actual number is not known. *Goniothalamus* sp. are widely used in traditional medicine. For example, *G. amuyon* is used for asthma and rheumatism[4], *G. macrophyllus* is used for the treatment of fever, malaria, cholera and as an abortifacient. *G. malayanus* and *G. scortechinii* are widely used as abortifacients, while *G. velutinus* is used to cure stomach ache and headache. Generally in Malaysia *Goniothalamus* sp. are widely used as abortifacients.

Phytochemical studies on *Goniothalamus* sp. have resulted in the isolation and characterization of bioactive compounds such as goniothalamin from *G. macrophyllus*, *G. scortechinii* and *G. malayanus*[5,6] and goniothalamin oxide from *G. macrophyllus*[7], both with teratogenic and embryotoxic activity. Goniothalenol from *G. giganteus*[8] and goniodiol 8-monoacetate from *G. amuyon*[9] both have antitumour activity.

The present note reports the isolation and characterization of dehydrogoniothalamin from *Goniothalamus umbrosus* Sinclair collected from Sabah, Malaysia. *G. umbrosus* is used by local communities in Sabah to cure headache, stomach ache, lumbago and also as an abortifacient.

Results and Discussion

Extraction of the ground roots of *G. umbrosus* with methanol followed by partition with hexane, dichloromethane, chloroform and extensive column chromatography and TLC afforded three major compounds which have been identified as dehydrogoniothalamin **1** (90 mg, 0.0082% of dry wt), 5-acetoxygoniothalamin **2** (40 mg, 0.0036% of dry wt) and goniothalamin **3** (30 mg, 0.0027% of dry wt). Goniothalamin and 5-acetoxygoniothalamin has been isolated from various *Goniothalamus* sp.[5-7,10]. The spectral data and other physical properties of goniothalamin and 5-acetoxygoniothalamin isolated from *G. umbrosus* were consistent with those previously reported[5-7,10].



Dehydrogoniothalamin **1** was isolated as yellow needles, mp 97-99 °C and gave a molecular ion (M^+) at 198.0 which is consistent with molecular formula $C_{13}H_{10}O_2$. A strong IR absorption at 1720 cm^{-1} suggested an α,β– unsaturated lactone moiety. Strong absorptions in the UV spectrum at λ_{max} nm (log ∈) 221 (4.64), 238 (4.73), 249 (4.73) and 363 (5.32) were indicative of a styryl residue. ^1H NMR showed the existence of 10 protons. Chemical shifts at 7.30-7.39 ppm (m, 5H) showed the existence of a phenyl ring. In ^1H NMR spectrum the signals at 6.8 ppm (d, J = 15.8 Hz, 1H) and 7.27 ppm (d, J = 15.9 Hz, 1H) attributed to H-7 and H-8, respectively suggest that these olefinic protons have the *trans* configuration, similar to goniothalamin and acetoxygoniothalamin with $J_{7,8}$ = 15 Hz. The NMR spectrum also showed 3 other olefinic protons at 6.16 ppm (d, J = 5.31 Hz,

1H), 7.48 (dd, J = 11.3 and 5.31 Hz, 1H) and 6.00 (d, J = 11.3 Hz, 1H) were assigned to H-3, H-4 and H-5, respectively.

Structural assignments were made by ^{1}H-^{1}H COSY, ^{1}H-^{13}C HETCOR, NOESY and NOE difference spectra.

Experimental Section

General. Melting points are uncorrected. ^{1}H and ^{13}C NMR were recorded on a Bruker spectrophotometer at 300 MHz for ^{1}H and at 75 MHz for ^{13}C, using $CDCl_3$ as solvent and TMS as internal standard. UV spectra were recorded on a Varian DMS 100 spectrophotometer while the GC-MS were obtained using a Shimadzu 2000A spectrophotometer.

Plant material. *Goniothalamus umbrosus* Sinclair, was collected from Keningau, Sabah, Malaysia and a voucher specimen is deposited at the UKMS Herbarium. Roots samples were air dried at room temperature and ground to a fine powder.

Extraction and isolation. Roots powder (1.1 kg) was extracted with methanol (3 times). The extracts were combined and evaporated to dryness under reduced pressure below 50° C to give 80.0 g (7.3% of dry wt) of crude extract. The crude extract was dissolved in methanol:water and partitioned with hexane, dichloromethane and chloroform.

Each of the partitions was evaporated to dryness to give 18.0 g (1.6% of dry wt), 50.0 g (4.5% of dry wt) and 7.0 g (0.63% of dry wt) of hexane, CH_2Cl_2 and $CHCl_3$ partition, respectively. Purification of each partition was performed with column chromatography using silica gel (70-230 mesh, Merck). The hexane fraction consisted of two major fractions which were eluted with hexane and then hexane:CH_2Cl_2 (7:3). The fraction eluted with hexane:CH_2Cl_2 was further purified using prep. TLC (silica gel 60 F_{254}, Merck) and hexane:acetone (7:3) to give compound **1** with R_f 0.66 in hexane:EtOAc (1:1). Compound **1** was redissolved in hexane:acetone (7:3), filtered and the solvent evaporated to dryness at room temperature to give yellow needles.

The dichloromethane fraction was chromatographed on a silica column (70-230 mesh, Merck) and eluted sequentially with CH_2Cl_2, CH_2Cl_2:MeOH (8:2) and CH_2Cl_2:MeOH (1:1). The fraction obtained with CH_2Cl_2:MeOH (8:2) was further purified on prep. TLC (silica gel 60 F_{254}, Merck) using CH_2Cl_2:acetone (6:4) to give compound **2** as white needles with R_f 0.51 (in hexane:EtOAc; 1:1) and compound **3** as white needles with R_f 0.53 (in hexane:EtOAc, 1:1). Compounds **2** and **3** were identified as 5-acetoxy-goniothalamin and goniothalamin, respectively, by comparison of spectral data with authentic samples.

Characterization of dehydrogoniothalamin 1. Yellow needles; m.p. 97-99 °C; IR (cm^{-1}): 1720, 1575, 1500, 1320, 1100, 970, 925, 870; LRMS m/z (rel. int.): 198 [M^+, $C_{13}H_{10}O_2$] (100%), 170 [M^+ - CO] (35%), 141 $[C_{11}H_9]^+$ (44%) and 115 $[C_9H_7]^+$ (90%); ^{1}H NMR ($CDCl_3$): δ 7.30-7.39 (m, 5H, Ar-H), 7.48 (dd, J = 11.3 and 5.31 Hz, H-4), 7.27 (d, J =15.9, H-8), 6.80 (d, J = 15.8 Hz, H-7), 6.16 (d, J = 5.31 Hz, H-3), 6.00 (d, J = 11.3 Hz, H-5); ^{13}C NMR ($CDCl_3$): δ 169.7 (C-2), 149.1 (C-6), 143.1 (C-4), 138.5 (C-8), 136.4 (C-9), 129.1 (C-12), 128.9 (C-11 and C-13), 127.3 (C-10 and C-14), 121.6 (C-3), 118.7 (C-7) and 115.2 (C-5).

References

1 Airy-Shaw H K, *A Dictionary of the Flowering Plants and Fern*, (University Press, Cambridge), **1966**, p 489.

2 Masamune G, *Enumeratio Phanerogamarun Bornearum*, (Taihoku Imperial University, Japan), **1942**, p 286.

3 Ban N T, *Bot Zurn*, 59, **1974**, 660.

4 Perry L M, *Medicinal Plants of East and South East Asia*, (Massachusetts Institute of Technology Press, Cambridge), **1980**, p 18.

5 Jewers K, Davis J B, Dougan J, Manchanda A H, Blunden G, Kyi A & Wetchapinan S, *Phytochemistry*, 11, **1972**, 2025.

6 Zakaria M, Saito I & Matsunura, T, *Int J Crude Drug Res*, 27, **1989**, 92.

7 Sam T W, Chew S Y, Matsjeh S, Gan E K, Razak D & Mohamed A L, *Tetrahedron Lett*, 28, **1987**, 2541.

8 El-Zayat A E, Ferrigni N R, McCloud T G, McKenzie A T, Byrn S R, Cassaday J M, Chang C J & McLaughlin J L, *Tetrahedron Lett*, 26, **1985**, 955.

9 Wu Y C, Chang F R, Duh C Y, Wang S K & Wu T S, *Phytochemistry*, 31, **1992**, 2851.

10 Ahmad F B, Wan Ahmad T, Siraj O & Atan, M S, *Phytochemistry*, 30, **1991**, 2430.