Indian Journal of Chemistry
Vol. 49B, January 2010, pp. 112-114

Note

Pypyrones from *Goniothalamus wightii*, Hook. f. and Thoms., Annonaceae

G Jayakumar*[1], M D Ajthabai[2], B Harikumar[3], P K Viswanathan[4], B Remeshkumar[1] & G Rajkumar[5]

[1]Department of Chemistry, N. S. S. College, Pandalam 689501, India

[2]Department of Chemistry, M.G. College, Trivandrum 695004, India

[3]Department of Chemistry, T. K. M. College of Arts and Science, Kollam 691005, India

[4]S. N. College, Chempazhanthy, Trivandrum 695587, India

[5]TBGRI, Palode 695562, India

E-mail: jayakumarmgcollege@yahoo.com

Received 31 January 2008; accepted (revised) 8 September 2009

Two linear compounds and three lactones are isolated from the leaves and stem bark of *Goniothalamus wightii*. Two of these are new compounds. The structures of the compounds are elucidated with the help of spectral studies and comparison with literature data.

Keywords: Linear compounds, new lactones, *Goniothalamus wightii*, Annonaceae

Annonaceae is a family which is rich in compounds with unique structural features. *Goniothalamus* is an important genus of this family which is found to elaborate highly bioactive lactones and acetogenins[1-7]. Previous investigations on *Goniothalamus cardiopetalus* yielded a number highly bioactive lactones, acetogenins and aromatic oil[8-10]. As a part of the ongoing programme to locate new bioactive compounds herein is presented results of the investigations on another endemic species of *Goniothalamus*, *Goniothalamus wightii.*

Goniothalamus wightii, Hook. f. and Thoms. (Annonaceae) is a small sized tree growing in the wild forests of Bonacadu Hills, Trivandrum district, Kerala, India[11]. There is no phytochemical or pharmacological report on this species so far. Chromatography of the hexane extract of the leaves and bark of this plant yielded five compounds. The details of isolation and structure elucidation of the isolates is the primary subject of this communication.

Compound **1**, isolated as white crystals from the hexane fractions gave characteristic absorption of a hydroxyl group in IR at 3339 cm^{-1}. ^1H NMR spectrum had signals due to two carbinolic protons as a triplet at δ 3.65, a methylene multiplet extending from δ 1.58 to 1.25 integrating to 34 protons and a methyl triplet at δ 0.87 as the only features. The ^{13}C NMR presented absorptions due to 19 carbon atoms with the carbinolic carbon resonating at δ 63.1 and the end methyl at δ 14.08. The FAB mass spectrum gave a molecular ion at *m/z* 284. These pointed to a straight chain aliphatic alcohol with molecular formula $C_{19}H_{40}O$. Compound **2**, isolated from hexane-chloroform fractions had spectral features due to a lactone ring and an aliphatic chain. The IR spectrum gave the characteristic absorptions of a saturated δ-lactone at 1741 and 1720 cm^{-1} (Ref. 12). ^1H NMR multiplet centered at δ 1.25 (22H) and a number of fragments in the mass spectrum separated by 14 mass units indicated an aliphatic chain with at least 12 C atoms. An important feature of the NMR spectrum was the absorption due to a deshielded proton as a triplet at δ 4.04 which, in the absence of hydroxyl group, was assigned to the proton adjacent to the lactone oxygen. Since only one such proton could be detected, this could be the point of attachment of the aliphatic chain. The other characteristic protons of the lactone ring were observed at δ 2.26 (1H, m, H-3a), 2.04 (1H, m, H-3b) and 1.57 (2H, m, H-4) and by comparison with literature data the presence of the pyrone ring was confirmed[12]. The end methyl of the aliphatic chain resonated as a triplet at δ 0.88. The FAB mass spectrum gave a molecular ion at *m/z* 268 which with the help of NMR data lead to the assignment of the formula $C_{17}H_{32}O_2$ to the molecule. Thus, compound **2** is identified as 6-dodecyl pyran-2-one.

This is the first report of this compound from a natural source. Compound **3**, isolated as white crystals, was the major isolate from this plant with a yield of 0.5% of the dry weight of the plant material. IR spectrum revealed signals due to an α,β-unsaturated ketone (1719 cm^{-1}), a monosubstituted aromatic ring (3027 cm^{-1}) and a double bond (1243 and 817 cm^{-1}). ^1H NMR spectrum had absorptions due to 12 hydrogens out of which 5 were aromatic and 4 olefinic. The chemical shifts and coupling pattern were identical with those reported for goniothalamin, a highly bioactive pyrone reported from many species

of *Goniothalamus*[13]. The identity of the compound was further confirmed by comparison with an authentic sample and also by examining the ^{13}C NMR and mass spectral data. Compound **4**, isolated as white crystals from chloroform fractions gave IR absorptions at 3391, 3036 and 1736 cm^{-1} indicating the presence of hydroxyl, phenyl and carbonyl groups. ^{1}H NMR spectrum presented absorptions due to 5 aromatic protons extending from δ 7.25 to 7.42 as a multiplet. A carbinolic proton absorption at δ 3.49 as a triplet corresponding to one proton indicated the presence of a secondary hydroxyl group in the molecule. ^{13}C NMR spectrum had signals due to 13 C atoms and the chemical shifts were typical of a pypyrone structure with a single hydroxyl group. The compound was identified as 9-deoxygoniopypyrone, previously reported from *Goniothalamus giganteus*[12] and *Goniothalamus leiocarpus*[14]. The identity was further confirmed by X-ray studies on the crystal[15].

Compound **5**, isolated as white crystals from chloroform fraction indicated the presence of a hydroxyl (3415 cm^{-1}), carbonyl (1714 cm^{-1}) and phenyl groups (3018 cm^{-1}) in the IR spectrum. ^{1}H NMR spectrum had characteristic absorptions of a monosubstituted phenyl group at δ 7.07 to 7.26 and a carbinolic proton at δ 3.99 as a triplet (J=8.4, 6 Hz). The other features of the ^{1}H NMR spectrum were same as those of compound **4** except for the shifts of H-7 and H-1 protons to higher fields and H-5 proton to slightly lower field. This indicated a change in the position of hydroxylation. This was clearer when the ^{13}C spectrum was analysed. The ^{13}C NMR spectrum indicated the presence of 13 carbon atoms with 6 phenyl carbons, one carbonyl carbon and a carbinolic carbon. The ^{13}C NMR DEPT spectrum showed a situation similar to that of **4** with two CH_2, nine CH and two quaternary C atoms. The carbonyl carbon expressed a shift to lower field. The carbonyl carbon of **4** absorbed at δ 169.1, which was shifted to δ 172.16 in **5**. Similarly, C-5 was shifted from δ 65.69 to 67.21 in **5**. All these point to the sole possibility of hydroxylation at C-4. This is further supported by the observation of matching coupling constant values for the C-4 and C-5 hydrogens. The H-4 proton is resonating as a triplet with coupling constants 8.4 and 6 Hz while the H-5 hydrogen, also a triplet is having the coupling constant of 8.4 Hz. This also points to the hydroxylation at C-4 and so in comparison with **4** compound **5** is identified as 9,8-deoxy-4-hydroxy pypyrone. This is the first report of this natural product.

Experimental Section

Melting points were determined on an electrically heated melting point apparatus and are uncorrected. IR spectra were measured in a Perkin-Elmer FTIR spectrometer. ^{1}H NMR were recorded at 300 MHz using $CDCl_3$ as solvent and TMS as internal standard. ^{13}C NMR spectra were measured at 75 MHz. Mass spectral measurements were carried out in a Jeol-SX-120 mass spectrometer. TLC's were run on glass plates coated with silica gel G and visualized using iodine vapour. Column chromatography over silica gel (100-200 mesh) was employed for the separation of components.

Plant material

The leaves of *Goniothalamus wightii* were collected during December 2004 from Bonacadu forests, Trivandrum District, Kerala, India and authenticated by Dr Mohan, Scientist, TBGRI, Palode where a voucher specimen has been deposited.

Extraction and isolation

The shade dried leaf powder (500 g) was repeatedly extracted with hexane in the cold (1×10 L) and the combined extract was evaporated to dryness resulting in 35 g of gummy residue. 30 g of the extract was chromatographed on a glass column packed with 500 g silica gel (100-200 mesh) and was eluted with hexane-chloroform mixtures of gradually increasing polarity. 50 mL fractions were collected; each was checked by TLC and pooled according to the TLC behaviour. Compound **1** resulted from the hexane eluents and compound **2** from 10% chloroform in hexane. Compounds **3** and **4** were separated from the 50% hexane-chloroform fractions and compound **5** from the chloroform fractions (**Figure 1**).

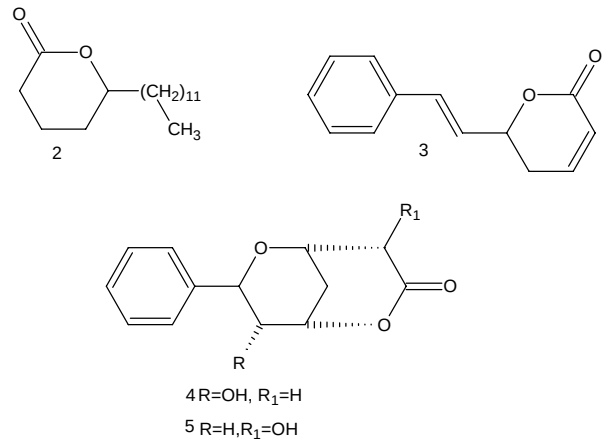

Figure 1

Table I — ^{1}H NMR chemical shifts of compounds **4** and **5** at 300 MHz, ($CDCl_3$, TMS)

Carbon atom	Compd **4**	Compd **5**
1	4.88 (1H, m)	4.3 (1H, dd, *J*=6.4,12.84 Hz)
4	2.95 (1H, dd, *J*=19.3,1.03 Hz)	3.99 (1H, t, *J*=8.4, 6 Hz)
	2.84 (1H, dd, *J*=19.3, 4.97 Hz)	3.58(1H, brs, OH)
5	4.42 (1H, m)	4.48 (1H, d, *J*=8.4 Hz)
7	4.44 (1H, d, *J*=9.6 Hz)	4.2 (1H, t, *J*=6.4 Hz)
8	3.49 (1H, t, *J*=7.7 Hz)	2.71(1H, dd, *J*=7.6, 15.6 Hz)
	2.99 (1H, d, *J*=6.5 Hz, 8OH)	2.49 (1H, dd, *J*=6.4,15.6 Hz)
9	2.18 (s)	2.11(1H, t, *J*=8.4, 6.4 Hz) 1.79 (1H, m)
Ph	7.42-7.25 (5H, m)	7.26-7.07 (5H, m)

Table II — ^{13}C NMR chemical shifts of compounds **4** and **5** (75 MHz, $CDCl_3$)

Carbon atom	Compd **4**	Compd **5**
1	76.18	72.29
3	169.05	172.16
4	36.49	76.18
5	65.68	67.21
7	74.10	71.4
8	72.53	39.02
9	29.82	30.93
1′	138.12	127.9
2′	127.44	126.02
3′	127.44	126.98
4′	128.49	127.9
5′	128.42	126.28
6′	128.49	126.02

Compound 1: White crystals, m.p. 72°C, IR (KBr): 3339, 2917, 2649, 1473, 1061, 729, 719 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.65 (2H, t, H-1), 0.87 (3H, t, H-19), 1.25-1.58 (m); ^{13}C NMR ($CDCl_3$): δ 63.1 (CH_2OH), 14.08 (CH_3), 32.81 (C-2).

Compound 2: White crystals, m.p. 83°C, IR (KBr): 2916, 2848, 1741, 1720, 1464, 1367, 1244, 1170, 1041, 723 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.04 (1H, m, H-6), 2.26 (1H, m, H-3a), 2.04 (1H, m, H-3b), 1.25-1.57 (m), 0.85 (3H, t, H-18).

Compound 3: White crystals, m.p. 82°C, IR (KBr): 3027, 2917, 1719, 1381, 1243, 1147, 1053, 1020, 968, 817, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.3 (5H, m), 6.84 (1H, q, H-4), 6.79 (1H, d, H-8), 6.2 (1H, dd, H-7), 6.1 (1H, d, H-3), 5.05 (1H, dd, H-6), 2.47 (2H, m, H-5); ^{13}C NMR ($CDCl_3$): δ 165.1 (C-2), 144 (C-3), 135 (C-4), 29.9 (C-5), 77.9 (C-6), 128.6 (C-7), 133.1 (C-8), 128.3×2, 126.7×2, 125.5, 121.7.

Compound 4: White crystals, m.p. 143°C, IR (KBr): 3391, 3284, 3068, 3036, 2961, 1736, 1699, 1335, 1211, 1100, 1079, 735 cm^{-1}; ^{1}H NMR (**Table I**); ^{13}C NMR (**Table II**).

Compound 5: White crystals, m.p.147°C, IR (KBr): 3415, 3018, 3012, 2399, 1714, 1622, 1602, 1521, 1423, 1220, 1031, 742 cm^{-1}; ^{1}H NMR (**Table I**); ^{13}C NMR (**Table II**)

Acknowledgement

The authors thank KSCSTE, Govt. of Kerala for financial assistance and Principal, Mahatma Gandhi College, Thiruvananthapuram for necessary facilities.

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