

Note

Two 2-naphthoic acids from *Diospyros paniculata*

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Phytochemical investigation of the heartwood, root and stem of *Diospyros paniculata* results in the isolation of 2-naphthoic acids **1** and **2**, 2-naphthaldehydes, naphthoquinones, steroids and terpenoids.

Keywords: 2-Naphthoic acids, *Diospyros paniculata*, 2-naphthaldehydes, naphthoquinones, steroids, terpenoids

IPC: Int.Cl.⁸ C07C

Diospyros is a large genus (Fam: Ebenaceae) and nearly 36 species of this genus are available in India¹. Species of this genus are reported to contain antibiotic², termicidal³ and antitumoral⁴ activities. The *Diospyros* species are rich sources of naphthalenes and naphthoquinones. Present work deals with the phytochemical investigation of *Diospyros paniculata*, an uninvestigated species.

In this communication, we report the isolation of two 2-naphthoic acids, characterized as 4,5,6-trimethoxy-2-naphthoic acid **1** and 5-hydroxy-4,6-dimethoxy-2-naphthoic acid **2** along with three 2-naphthaldehydes and betulinic acid from the chloroform extract of the heartwood of *D. paniculata*.

The 2-naphthaldehydes were identified as 5-hydroxy-4-methoxy-2-naphthaldehyde, 4,5,6-trimethoxy-2-naphthaldehyde and 6-hydroxy-4,5-dimethoxy-2-naphthaldehyde⁵. Chemical investigation of the chloroform extract of the root resulted in the isolation

of well-known compounds, 7-methyljuglone, 8'-hydroxyisodospyrin, isodospyrin, stigmasterol, ursolic acid and betulinic acid. The chloroform extract of the stem resulted in the isolation of lupeol, isodospyrin⁶, plumbagin and elliptinone⁷.

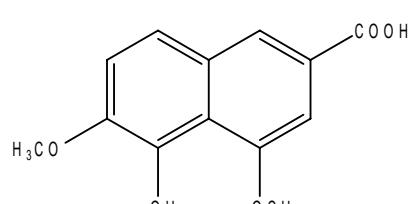
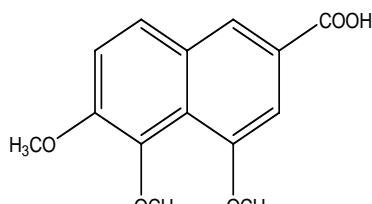
Results and Discussion

Compound **1** was crystallised from methanol as pale yellow plates, m.p. 210-11°C. It produced brisk effervescence with sodium bicarbonate solution indicating the presence of a carboxyl function. The UV-Vis (240, 313, 330, 342 nm) and IR spectral data also revealed the nature of the compound **1** as a naphthoic acid derivative⁸.

The ¹H NMR spectra exhibited three singlets, two *meta* coupled doublets and two *ortho* coupled doublets. The three singlets at δ 3.74, 3.91 and 3.94 each integrating to three protons were due to three methoxyl groups in the compound. Since in 2-naphthaldehydes and naphthoic acids isolated from *Diospyros* species, oxygenation at 4, 5 and 6 positions is very common, the methoxyl groups were placed at 4, 5 and 6 positions.

The two *meta* coupled doublets at δ 8.08 (*J* = 1.2 Hz) and 7.27 (*J* = 1.2 Hz) each integrating to one proton were assigned to C-1 and C-3 protons. The two *ortho* coupled doublets at δ 7.48 (*J* = 8.9 Hz) and 7.80 (*J* = 9.2 Hz) were assigned to C-7 and C-8 protons.

The APT CMR spectra showed seven positive signals and seven negative signals. The downfield negative signals at δ 167.38 represented the carboxyl carbon atom. The upfield positive signals at δ 56.05, 56.58 and 61.08 corresponded to the three methoxy carbon atoms. The remaining six negative signals were assigned to six quaternary carbon atoms and four positive signals assigned to four methine carbons.



The EIMS spectrum of the compound **1** revealed an intense molecular ion peak at m/z 262, corresponding to the molecular formula $C_{14}H_{14}O_5$. Based on the above spectral data, compound **1** was characterized as 4,5,6-trimethoxy-2-naphthoic acid.

Compound **2** was crystallised from methanol as brown crystals, m.p. 255°C. It was identified as a naphthoic acid derivative from its preliminary reactions and UV-Vis absorption values. The IR spectrum showed the presence of carboxyl group (1689, 2533-3133 cm^{-1}) and also phenolic hydroxyl (3382 cm^{-1}) group. Compound **2** was inferred as hydroxynaphthoic acid derivative.

The 1H NMR spectra of compound **2** revealed the presence of a phenolic hydroxyl group, two methoxyl substituents and four aromatic protons. Further, it revealed that it should also be a 4,5,6-trioxygenated-2-naphthoic acid. Therefore, the two methoxyl substituents and hydroxyl groups should be in the 4,5,6-positions.

It has been reported⁹ that in hydroxynaphthaldehydes, when the hydroxyl group is at the *peri*-position (C-5), it appears around δ 10.00 while when it is in the *ortho* position (C-6), it appears around δ 6.00. The signal due to phenolic hydroxyl at downfield (δ 9.62, exchanged with D_2O) indicated that it should be in *peri*-position (C-5). Therefore, the phenolic hydroxyl must be at C-5 position and the two methoxyl groups (two upfield singlets at δ 3.73 and 3.96) should be at C-4 and C-6 positions.

The signal due to C-1 and C-3 protons appeared at δ 8.06 and 7.28, respectively while C-7 and C-8 protons appeared as two *ortho* coupled doublets centered at δ 7.25 and 7.70, respectively.

In the SEFT CMR spectrum of the compound, seven positive signals and six negative signals were observed. The downfield positive signal at δ 167.47 represented the carboxylic carbon atom whereas the two upfield negative signals at δ 61.21 and 56.01 were due to the two methoxyl carbon atoms. The six quaternary carbon atoms appeared as six positive signals at δ 154.83, 149.91, 140.78, 129.42, 125.13 and 123.03, corresponding to C-4, C-5, C-6, C-2, C-9 and C-10 carbon atoms, respectively. The chemical shift values for C-1, C-3, C-7 and C-8 carbon atoms were observed as negative signals at δ 123.87, 104.54, 119.71 and 126.34, respectively.

In the EIMS spectrum, the appearance of a molecular ion peak at m/z 248 was in agreement with the molecular formula $C_{13}H_{12}O_5$. From these spectral

data, compound **2** was characterized as 5-hydroxy-4,6-dimethoxy-2-naphthoic acid.

Experimental Section

General. Melting points were determined in sulphuric acid-bath and are uncorrected. UV-Vis spectra were recorded using Shimadzu 160 UV-Vis spectrophotometer; IR spectra on a Jasco FT-IR spectrophotometer; 1H NMR spectra in $CDCl_3$ and CMR in $CDCl_3$ on a Jeol FT 300 MHz spectrometer (compound **1**) and Bruker AMX 400 MHz spectrometer (compound **2**) with TMS as an internal standard; and EIMS on a Finnigan MAT 1020 C instrument.

Collection of plant material

The plant materials of *D. paniculata* used in this work were collected from Theni in Tamilnadu. The species was identified by Fr.Dr K M Matthew S.J., Herbarium Director, The Rapinat Herbarium, Trichy.

Extraction and Isolation

The fresh heartwood of *D. paniculata* were cut into small pieces and air-dried. This air-dried chips (5 kg) were then extracted under reflux with hot chloroform.

The chloroform extract was concentrated *in vacuo* and was chromatographed over a column of silica gel (Qualigens 60-120 mesh) and eluted with pet. ether (60-80°C)-chloroform, pure chloroform and chloroform-ethyl acetate mixture. The compounds **1** and **2** were obtained from chloroform-ethyl acetate (90:10) mixture.

4,5,6-Trimethoxy-2-naphthoic acid: Pale yellow plates, m.p. 210-11°C; EIMS: m/z 262 (M^+); UV-Vis ($EtOH$): 240, 313, 330, 342 nm; IR (KBr): 1680 cm^{-1} ; 1H NMR ($CDCl_3$): δ 3.94, 3.91 and 3.74 (9H, 3s, 3 \times OCH_3), 8.08 (d, 1H, H-1, J = 1.2 Hz), 7.27 (d, 1H, H-3, J = 1.2 Hz), 7.48 (d, 1H, H-7, J = 8.9 Hz), 7.80 (d, 1H, H-8, J = 9.2 Hz); APT CMR ($DMSO-d_6$): δ 167.38 (-COOH), 155.64 (C-4), 152.07 (C-5), 143.63 (C-6), 130.31 (C-2), 126.29 (C-8), 126.13 (C-9), 123.83 (C-1), 123.09 (C-10), 116.02 (C-7), 104.62 (C-3), 61.08, 56.58 and 56.05 (3 \times OCH_3).

5-Hydroxy-4,6-dimethoxy-2-naphthoic acid: Brown crystals, m.p. 255°C; EIMS: m/z 248 (M^+); UV-Vis ($EtOH$): 216, 244, 315, 330 and 345 nm; IR (KBr): 3382 (-OH), 1689 (C=O) cm^{-1} ; 1H NMR ($CDCl_3$): δ 3.73 and 3.96 (6H, 2s, 2 \times OCH_3), 7.28 (s, 1H, H-3), 8.06 (s, 1H, H-1), 7.25 (d, 1H, H-7), 7.70 (d, 1H, H-8) and 9.62 (s, 1H, C₅-OH); SEFT CMR

(DMSO-*d*₆): δ 167.47 (-COOH), 154.83 (C-4), 149.91 (C-5), 140.78 (C-6), 129.42 (C-2), 126.34 (C-8), 125.13 (C-9), 123.87 (C-1), 123.03 (C-10), 119.71 (C-7), 104.54 (C-3), 61.21 and 56.01 (2×OCH₃).

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