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BENZOIC ACID DERIVATIVES FROM *STOCKSIA BRAHUICA*

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Key Word Index—*Stocksia brahuica*; Sapindaceae; ethyl 3,5-dihydroxy-4-methoxybenzoate; 2-hydroxy-3-methylbenzoic acid.

Abstract—Two new benzoic acid derivatives, ethyl 3,5-dihydroxy-4-methoxybenzoate and 2-hydroxy-3-methylbenzoic acid, have been isolated from the aerial parts of *Stocksia brahuica*. They have been identified by mass and NMR spectroscopy. 3,4,5-Trihydroxybenzoic acid, 3,4,5-trimethoxybenzoic acid, methyl 4-hydroxybenzoate and *n*-propyl 4-hydroxybenzoate have also been isolated for the first time from this source. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Stocksia brahuica belongs to the family *Sapindaceae*, grows well in the inner valleys of Pakistan[1]. Phytochemical work on the genus *Stocksia* has not yet been reported. However, the other genera of the same family show the presence of flavones [2], diterpenes [3], indoles [4], triterpenes and saponins [5]. We now report the isolation and identification of two new natural benzene derivatives, ethyl 3,5-dihydroxy-4-methoxybenzoate (**1**) and 2-hydroxy-3-methylbenzoic acid (**2**) from *S. brahuica*. Four other benzoic acid derivatives, 3,4,5-trihydroxybenzoic acid (**3**), 3,4,5-trimethoxybenzoic acid (**4**), methyl 4-hydroxybenzoate (**5**) and *n*-propyl 4-hydroxybenzoate are also reported for the first time from this species.

RESULTS AND DISCUSSION

Compound (**1**) was obtained as a light brown amorphous substance from the chloroform soluble portion of the methanolic extract. The UV spectrum showed intense absorption bands at 211 and 260 nm. The IR spectrum exhibited absorption bands at 3460, 3300, 1700, 1615, 1240, 1190 and 1040 cm^{-1} corresponding to O–H, C–H (aromatic), C=O, C=C (aromatic) and C–O, respectively. The HREI mass spectrum revealed the $[M]^+$ at *m/z* 212.0664 (calculated 212.0684) corresponding to the molecular formula $C_{10}H_{12}O_5$, with five degrees of unsaturation. The peaks at *m/z* 167 (100%, $[M\text{-}OEt]^+$) and 139 $[M\text{-}OEt\text{-}CO]^+$ showed the presence of an ethoxyl group, attached to the carbonyl carbon. Correlation between the methyl and ethylene protons was observed in the ^1H-^1H COSY spectrum. The positions of the aromatic protons, ester, methoxyl and, ultimately, hydroxyl groups were confirmed by HMBC correlations (Fig. 1).

Compound (**2**) was obtained as white amorphous powder from the ethyl acetate-soluble portion. The UV spectrum showed an intense absorption band at 203 nm. The IR spectrum exhibited absorption bands at 3325, 3075, 2600–3020, 1695, 1595 and 1220 cm^{-1} corresponding to O–H, C–H (aryl), O–H (carboxylic), C=O, C=C (aromatic) and C–O, respectively. The HREI mass spectrum revealed the $[M]^+$ at *m/z* 152.0485 (calcd 152.0473) corresponding to the molecular formula $C_8H_8O_3$, with five degrees of unsaturation. The fragment ions at *m/z* 134 and 106 in the EI mass spectrum showed the loss of H_2O and then CO. Correlations between H-4, H-5 and H-6, H-5 in the ^1H-^1H COSY spectrum confirmed that H-4 and H-6 were *ortho* to H-5. The positions of methyl, hydroxyl and carbonyl groups were confirmed with the help of HMBC correlations (Fig. 1).

Compounds **3**–**6** were also isolated and characterized from their spectral data. The structures of **3**–**6** were confirmed by comparing the observed and calculated ^{13}C chemical shift values in the ^{13}C-NMR spectrum and also with the help of reported spectroscopic data [6, 7, 8]. From the best of our knowledge compounds **1** and **2** are new natural products, whereas **3**–**6** are reported in this communication as new compounds from *S. brahuica*.

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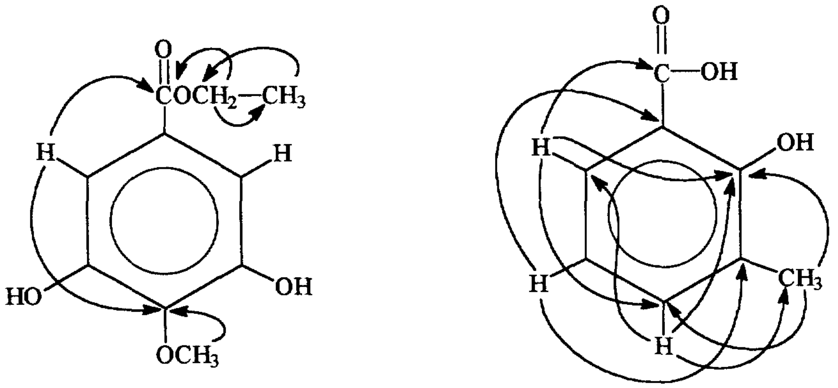


Fig. 1. HMBC spectral correlations of compounds **1** and **2**.

EXPERIMENTAL

General

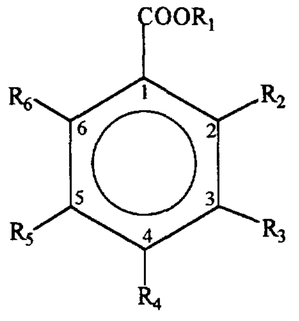
^{1}H-NMR were recorded on Bruker AM-400 and Bruker AM-300, ^{13}C NMR on Bruker AM-300. Precoated silica gel plates (Merck, silica gel 60, F_{254}, 0.25 mm) were used for prep. TLC.

Plant material

Fresh *S. brahuica* (13 kg) was collected from Baluchistan. The plant was shade-dried and, finally, chopped (7 kg).

Extraction and isolation

Dried material was extracted repeatedly with MeOH at room temp. The combined MeOH extracts were evapd under red. pres. and then partitioned between hexane and H_2O. The hexane sol. portion was separated and the aq. phase extracted with $CHCl_3$. The aq. layer, after the separation of the $CHCl_3$ sol. portion, was further extracted with EtOAc. The $CHCl_3$ and EtOAc sol. portions were evapd and the gummy residues obtained were chromatographed separately on silica gel columns, using hexane, hexane-$CHCl_3$, $CHCl_3$, $CHCl_3$-MeOH and MeOH. The fr. eluted with MeOH-$CHCl_3$ (3 : 97) from the $CHCl_3$ sol. portion contained **1**, along with small amounts of other impurities. Compound **1** (9.2 mg) was purified by prep. TLC (MeOH-$CHCl_3$, 1 : 9). The fr. eluted with MeOH-$CHCl_3$ (3 : 17) from the EtoAc sol. portion contained **2** in impure form. Compound **2** (23.7 mg) was purified by prep. TLC (MeOH-$CHCl_3$-H_2O, 20 : 80 : 1).



1 $R_1 = Et, \quad R_2 = R_6 = H, R_3 = R_5 = OH, R_4 = OMe$

2 $R_1 = R_4 = R_5 = R_6 = H, R_2 = OH, R_3 = Me$

3 $R_1 = R_2 = R_6 = H, R_3 = R_4 = R_5 = OH$

4 $R_1 = R_2 = R_6 = H, R_3 = R_4 = R_5 = OMe$

5 $R_1 = Me, \quad R_2 = R_3 = R_5 = R_6 = H, R_4 = OH$

6 $R_1 = n\text{-}Pr, \quad R_2 = R_3 = R_5 = R_6 = H, R_4 = OH$

Compound (**1**)

Light brown amorphous powder (9.2 mg), mp 111–113°. UV λ_{max} (MeOH) nm: 211.4, 259.6. IR ν_{max} ($CDCl_3$) cm^{-1}: 3460, 3300, 1700, 1615, 1240, 1190, 1040. HREIMS: $[M]^+$ *m/z* 212.0664 (calcd for $C_{10}H_{12}O_5$, 212.0684); EIMS: *m/z* 212 $[M]^+$, 167 $[M-OEt]^+$, 139 $[M-OEt-CO]^+$. ^{1}H NMR: Table 1. ^{13}C NMR: Table 2.

Table 1. ^{1}H NMR spectral data of compounds **1** and **2**.

Carbon	1	2
2	7.09 (*s*)	—
3	—	—
4	—	7.36 (*dd*, J=7.3, 1.7 Hz)
5	—	6.79 (*dd*, J=7.3, 7.9 Hz)
6	7.09 (*s*)	7.71 (*dd*, J=7.9, 1.7 Hz)
CH_3	1.30 (*t*, J=7.1 Hz)	2.2 (*s*)
OCH_2	4.24 (*q*, J=7.1 Hz)	—
OCH_3	3.86 (*s*)	—

Spectra recorded in C_3D_6O; δ in ppm, ref. TMS.

Table 2. ^{13}C NMR spectral data of compounds **1** and **2**.

Carbon	**1**	**2**
1	126.7 (C)	112.4 (C)
2	109.8 (CH)	161.3 (C)
3	151.1 (C)	126.9 (C)
4	140.3 (C)	137.2 (CH)
5	151.1 (C)	119.2 (CH)
6	109.8 (CH)	128.7 (CH)
C=O	166.4	173.1
CH_3	14.5	15.4
OCH_2	61.1	—
OCH_3	60.5	—

Spectra recorded in C_3D_6O; δ ref. TMS.

Compound (**2**)

White amorphous powder (23.7 mg), mp 159–161°. UV λ_{max} (MeOH) nm: 203. IR ν_{max} (KBr) cm^{-1}: 3325, 3070, 2600–3020, 1695, 1595, 1220. HREIMS: $[M]^+$ *m/z* 152.0485 (calcd for $C_8H_8O_3$, 152.0473). EIMS: *m/z* $[152]^+$, 134 $[M\text{-}H_2O]^+$, 106 $[M\text{-}H_2O\text{-}CO]^+$. ^1H NMR: Table 1. ^{13}C NMR: Table 2.

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