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Phenolics and flavonoids from *Haematoxylon campechianum*

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Abstract

One new natural phenolic, the 5′-*O*-methyl-7′-ethyl ester of *p*-dehydrodigallic acid, was isolated and identified from the bark of *Haematoxylon campechianum*. In addition, two known flavonoids, quercetin 3-*O*-methyl ether and genistein and three known phenolics, gallic acid, methyl gallate and ethyl gallate, were also isolated. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Haematoxylon campechianum; Leguminosae; Bark; Dicarboxylic ester of *p*-dehydrodigallic acid

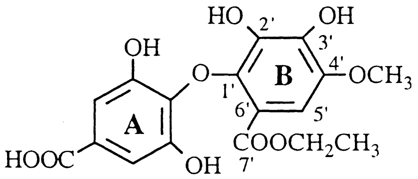
1. Introduction

Haematoxylon campechianum collected from the Orman Botanical Garden, Giza, Egypt, was found to contain neoflavonoids and terpenoids (Lolor & Martin, 1959). One of the reported neoflavonoids, haematoxylin, exhibited antiinflammatory activity (Handa, Chawla, & Sharma, 1992). Moreover, the wood extract has been used as a source of dyes (Paris & Rousselet, 1958). In a previous study, 18 phenolics and flavonoids were isolated and identified from twigs of *H. campechianum* (El-Sayed, Michael, Kandil, Ishak, & Mabry, 1994). In another previous investigation, two new gallotannins, 2,6-*bis*-*O*-galloylglucose and 2-*O*-trigalloyl-1,3,4,6-tetra *bis*-*O*-galloyl glucose, were also isolated and identified from the leaves, in addition to four known gallotannins and four known flavonoids (Kandil, El-Sayed, Michael, Ishak, & Mabry, 1996).

In the present study, a new *p*-dehydrodigallic acid, along with several flavonoids and phenolics were isolated and identified from the bark of the title species.

2. Results and discussion

Chemical investigation of the bark of *H. campechianum* led to the isolation of a new natural phenolic dicarboxylic ester of *p*-dehydrodigallic acid (**1**).



(1)

Column chromatography of the concentrate from the aqueous acetone extract of the bark on Sephadex LH-20 using ethanol, water and acetone mixture for gradient elution, afforded four crude samples containing gallic acid, methyl and ethyl gallates and the new phenolic compound.

The ^1H NMR spectrum of **1** showed a two-proton singlet at δ 6.99 typical for gallic acid and a one-proton singlet at δ 7.09 for an aromatic proton (ring B). The presence of a three-proton signal at δ 3.8 is in accord with the methyl group being at the 5′-position *para* to the C–O–C group attached to ring A, an assignment supported by a signal at δ 61.0 in the ^{13}C NMR spectrum. The presence of a quartet at δ 4.2 and a triplet at δ 1.3 for the ethyl group suggested an ethyl ester of the carboxylic group in ring B at position 7′, rather than at position 7 in ring A. This assignment is supported by the presence of signals at δ 52.0 (CH_2CH_3) and δ 14.0 ($-CH_2CH_3$) in the ^{13}C NMR spectrum. Also, the presence of two carboxyl signals at δ 168.9 and δ 169.9, due to the substitution of one of the two carboxylic groups, (Nawwar, Buddrus, & Bauer, 1982; Kandil & Nassar, 1998) was in accord with the ester group being attached to ring B.

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Therefore, the structure of the new compounds is the 5′-*O*-methyl-7′-ethyl of *p*-dehydrodigallic acid. Its structure was confirmed by positive CI-mass spectrometry, which showed peaks at *m*/*z* 381$[M+1]^+$, 365 $[M\text{-}15]^+$ and 351 $[M\text{-}29]^+$ for to the loss of methyl and ethyl groups, respectively and also a peak at *m*/*z* 337 due to the loss of carbon dioxide.

This is the first report of this ester as a natural product, although the diacid had been previously isolated as an intermediate during the acid hydrolysis of isochestannin (Huining, Gen-Ichiro, & Itsuo, 1988). Hydrolyzable tannins having a dehydrohexahydroxy-diphenoyl group were not previously reported from this species.

3. Experimental

3.1. Plant material

Bark of *H. campechianum* (Leguminosae) was collected from the Orman Botanical Garden, Giza, Egypt. A voucher specimen is deposited in the National Research Centre Herbarium (CAIRC).

3.1.1. Extraction, isolation and identification

Dried ground bark (500 g) was extracted with 50% aq. Me_2CO (2 × 2 l) at room temp. for 24 h. After removing solvent under red. pres., 500 mg of extract was obtained. The cond aq. extract was fractionated by cc using Sephadex LH-20 as adsorbent; yields: gallic acid (50 mg), methyl gallate (100 mg), ethyl gallate (60 mg) and the new compound (20 mg). Pc was carried out on Whatman No. 1 using BAW [(6:1:2), (*n*-BuOH–HOAc–H_2O)], 15% HOAc and H_2O. The NMR spectra were recorded on a Varian GEMINT spectrometer. ^1H and ^{13}C chemical shifts were measured relative to acetone-d6 at 200 and 50 MHz, respectively and are reported as δ-values to TMS as int. standard. Known compounds were identified by comparing their UV, ^1H NMR and R_f-values with those of authentic samples.

3.1.2. 5′-O-*Methyl-7′-ethyl ester of* p-*dehydrodigallic acid (**1**)*

$R_f \times 100$ Pc: BAW 40, 15% HOAc 12, H_2O 15. ^1H NMR: δ 7.09 (s, 2H, H-2,6), 6.99 (s, 1H, H-6′), 4.2 (q, CH_2CH_3), 3.8 (s, CH_3, COO), 1.2 (t, CH_2CH_3). ^{13}C NMR: δ 168.0 (COO), 169.9 (COO), 121.7 (C-1), 119 (C-2), 140.3 (C-3), 147.4 (C-4), 146.5 (C-5), 166.8 (C-6), 120.5(C-1′), 147.2 (C-2′), 138.8 (C-3′), 135.2 (C-4′), 143.7 (C-5′), 111.2 (C-6′), 61.0 (OCH_3), 52.0 (CH_2CH_3), 14.2 (O-CH_2CH_3). +ve CIMS *m*/*z*: 381 $[M+1]^+$, 365 $[M\text{-}15]^+$, 351 $[M\text{-}29]^+$, 337 $[M\text{-}CO_2]^+$.

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