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A caffeic acid ester from *Halocnemum strobilaceum*

Simon Gibbons[a,*], K.T. Mathew[b], Alexander I. Gray[c]

[a]*Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Kuwait University, P.O. Box 24923, Safat 13110, Kuwait*
[b]*The Herbarium, Department of Biological Science, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait*
[c]*Department of Pharmaceutical Sciences, University of Strathclyde, 27 Taylor street, Glasgow G4 0NR, Scotland, UK*

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Abstract

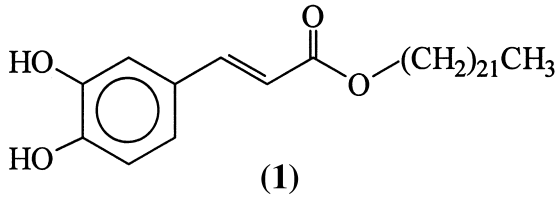
A new *n*-alkyl ester of 3,4-dihydroxycinnamic acid (caffeic acid) has been isolated from the halophytic plant, *Halocnemum strobilaceum*. Its structure was elucidated by NMR and mass spectroscopy. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Halocnemum strobilaceum; Chenopodiaceae; Caffeic acid ester; Docosyl-3,4-dihydroxycinnamate; Docosyl caffeate

1. Introduction

The flora of Kuwait consists of ca. 400 species of native and naturalized vascular plants (Daoud & Al-Rawi, 1985; Al-Rawi, 1987). The largest plant families in the descending order of species representation are Gramineae, Asteraceae, Cruciferae, Leguminosae, Chenopodiaceae and Caryophyllaceae, accounting for (Boulos & Drosari, 1994) ca. 60% of the flora. Annuals that sprout after the November rains and complete their life cycle before summer (June onwards) account for the bulk of the taxa (ca. 70%). The rest of the flora is represented by perennials that tolerate a variety of stress conditions, such as salinity and extreme heat during the summer months.

The Chenopodiaceae has a cosmopolitan distribution with its centres of diversity in xeric and halophytic regions, such as the coastal areas of the Arabian Gulf. In Kuwait, the family is represented by 18 perennial taxa that are exceptionally hardy and tolerate very high temperatures, which at ground level may reach 84°C (ROPME, 1998). Some members of this family are known for their ability to produce alkaloids (Hegnauer, 1989), in particular pyridines from *Anabasis* (Sadykov, Mukhamedzhanov, & Aslanov, 1967) and quinolines from *Haloxylon* (Michel, Sandberg, Haglid, & Norin, 1967). In a start to a study of the natural products chemistry of the desert flora of Kuwait, we have investigated the halophyte, *Halocnemum strobilaceum* (Pall.) M. Bieb., from which we have isolated the new caffeic acid ester (**1**).



(1)

2. Results and discussion

By Biotage™ flash chromatography, compound (**1**) was isolated as a white waxy solid. The EI mass spectrum indicated the presence of an $[M]^+$ at m/z 488, with fragments that indicated the presence of a long-chain alkyl group with multiple losses of 14 mu (CH_2). The ^1H NMR spectrum (Table 1) exhibited signals for three aromatic protons in a 2,5,6 substitution pattern, two broad hydroxyl singlets (δ 5.65 and δ 6.05), which together with two protons of a *trans*-double bond ($J = 15.9$ Hz), indicated the presence of a 3,4-dihy-

* Corresponding author.

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droxy-*trans*-cinnamate (caffeate) moiety. Further signals for a deshielded methylene (δ 4.19), a methylene envelope and a methyl triplet, indicated the presence of a long alkyl chain. The carbon spectrum (Table 1) confirmed the presence of a dihydroxy cinnamate derivative with resonances attributable to a carbonyl group (δ 168.0), two deshielded oxygen bearing quaternary carbons, five methine carbons and a shielded aromatic quaternary carbon. Subtraction of the elements of 3,4-dihydroxy-cinnamate ($C_9H_7O_4$) from the M_r (488), left an alkyl chain of M_r 309, which was equivalent to the C_{22} *n*-alkyl docosyl chain from the parent alkane, docosane.

Compound (**1**) is therefore assigned as the new ester docosyl-3,4-dihydroxy-*trans*-cinnamate (docosyl caffeate). Such long-chain esters of caffeic acid are uncommon in nature, although hexacosanyl and triacontanyl caffeates have been isolated from *Pongamia glabra* (Saha, Mallik, & Mallik, 1991). Similar compounds with long-chain alcohols but with *p*-coumarate as the esterifying acid, have been encountered in Asteraceae growing in arid conditions, for example, in *Artemisia assoana* Willk. (Anthemidae) (Martinez, Barbera, Sanchez-Parareda, & Marco, 1987) and *A. campestris* (Vajs, Jeremic, Stefanovic, & Miloslavljevic, 1975).

It is possible that natural product (**1**) and related compounds may have a role in the stress management of halophytic plants. For example, they may be associated with water retention within the plant cells with the hydrophobic long alkyl chain being 'anchored' within the cell membrane and the hydrophilic hydroxycinnamate portion remaining within the cell, thus retaining a hydration shell.

3. Experimental

NMR were recorded in $CDCl_3$ using a Bruker AMX-400 spectrometer.

3.1. Plant material

This was collected from the Shuaikh campus of Kuwait University in March 1998. A voucher specimen (SG 983 102) has been deposited at the Kuwait University Herbarium (KTUH), Khaldiyah, Kuwait.

3.2. Extraction and isolation of compound (*1*)

Whole herb (800 g) was extracted at room temp. with $CHCl_3$ (3×2.5 l) and MeOH (2×2.5 l). The $CHCl_3$ extract was evapd under vacuum to give a residue of 19.1 g. This was then subjected to Biotage flash chromatography (Flash 75 S silica gel cartridge) eluting with hexane with increasing 10% amounts of EtOAc and finally 10% MeOH in EtOAc. The residue from the fr. eluted with 30% EtOAc in hexane was washed ($\times 5$) with hexane (10 ml) to yield compound (**1**) (30 mg).

Table 1
^1H and ^{13}C NMR data for compound (**1**). .Coupling constants Hz in parenthesis. Resonances denoted * may be interchangeable

Carbon	δ_H	δ_C
1	-	127.8
2	7.09 d (1.7)	114.6
3	-	144.0
4	-	146.5
5	6.87 d (8.2)	115.7
6	7.01 dd (1.7, 8.2)	122.6
7	7.57 d (15.9)	144.9
8	6.27 d (15.9)	116.0
9	-	168.0
OH-3*	6.05 br s	-
OH-4*	5.65 br s	-
CH_2-1′	4.19 t (6.7)	65.1
CH_2-2′	1.68 m	32.1
CH_2-3′- CH_2-21′	1.10-1.40 m	22-32
CH_3-22′	0.88 t (6.4)	14.3

3.3. Docosyl-3,4-dihydroxy-trans-cinnamate (*1*)

White waxy solid. Found: 488 $[M]^+$, $C_{31}H_{52}O_4$ requires 488. IR υ_{max} (film): 3446, 3286 (br, OH), 2954, 2915, 2848, 1686, 1600, 1527, 1471, 1271, 1178, 979, 719 cm^{-1}. EIMS *m/z*: 488 $[M]^+$, 460, 180, 163, 111, 97, 82, 69, 56.

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