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Caffeic anhydride from *Solanum sodomeum* (Solanaceae)

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ABSTRACT

S. sodomeum is distributed in north of Africa, Spain, Portugal, Balearic islands, Corsica, Sardinia, Italy, Sicily, Dalmatia. In Libya it is distributed in Tripoli and Tokra. Phytochemical investigation on the plant has resulted in the isolation of number compounds; the extracts have been used in the indigenous system of medicine for a number of purposes. The phenolic compound I caffeic anhydride has been isolated from the toluene-soluble fraction by column chromatography after hydrolysis at 30 °C in a two-phase system containing an aqueous hydrochloric acid and toluene extract of the fresh berries of the plant, collected from the Libyan coast. Its structure was determined by means of IR, ^{1}H -NMR, ^{13}C-NMR, APT and mass spectra techniques, this is the first report of caffeic anhydride [(2E)-3-(3,4-Dihyroxyphenyl)prop-2-enoic Anhydride;1]from the Solanaceae family.

Keywords: Solanaceae, *S.sodomeum*, Caffeic anhydride, Chromatography.

INTRODUCTION

The *solanaceae* is certainly one of the most economically important plant families in the world, with about 2950 species in 94 genera, many of which are edible, while others are poisonous [1]. The Solanum includes about one-half of the species of *solanaceae*, with more than 1700 species; they are widespread in the tropical and temperate zones. In Libya, it is represented by 2 cultivated and 3 wild species (*S. tuberosum, S. nigrum, S. sublobatum, S. melongena and S. sodomeum*) [2-3]. *S. sodomeum* L. is commonly known as apple of sodom and Dead Sea apple, grows wild as erect bushy dark green perennial shrub to 1.5 meter high. Green purplish-brown stems. Leaves are hairy and deeply lobed with prickles along the stalks. Flowers are purple to white. Fruits are round mottled green coloured when immature, ripening yellow, drying brown [3]. The chemical constituents of *S. sodomeum* L. have been reported to be alkaloids, steroids and Saponins.

MATERIALS AND METHODS

General instrumentation

Infrared spectra were recorded in KBr discs using Unicam Mattson FT-IR 1000 series spectrometer. Nuclear magnetic resonance was determined in deuterodimethylsulfoxide (DMSO-d_6) on Varian Mercury VX-300 (300 MHz) chemical shift are expressed in ppm (δ). The electron impact mass spectra were measured at 70 eV on MS Finnigan mat SSQ7000 spectrometer.

Liquid C.C. was carried out using silica gel (70-230 mesh). Analytical and preparative TLC was carried out on pre-coated silica gel GF_{254} plates and coated silica gel GF_{254} plates (20 × 20 cm) respectively. The plates were visualized under ultra violet light (366 nm).

Plant material

Fresh *S.sodomeum* L. yellow berries used were collected in May 2006 from wild plants in the Tokra district. The plant was identified by Botany department of Benghazi University.

Extraction and isolation

Fresh yellow berries (0.5 kg) were minced, and the formed paste (thick slurry) which was transferred to the reaction vessel with a minimal volume of water (100 ml), and seeded out. The paste with 160 ml of HCl (36%) and 1000 ml toluene was warmed under stirring for 5h at 30 °C. Following phase separation, the upper, pale-yellow toluene layer was siphoned out, and combined from five times evaporated to yield 6.45 g of the dark brown gummy crude, subjected to wet column chromatography using silica gel (300g) using petroleum ether (40-60°) chloroform gradient mixtures to give 11 fractions, each fraction monitored by TLC.

Compound **I** (3 mg) was separated from the oil fraction 9, eluted with pet. ether (40-60°)-chloroform (8:2), was purified by preparative TLC on silica coated by using n Hexane: Ethyl acetate (1:1), showed on visualization by UV (336 nm) and NH_3 vapour.

Compound **I** [Caffeic anhydride]: Yellowish amorphous powder, IR (KBr): 3450-2500, 1700, 1651, 1616, 1527 cm^{1}. ^{1}H NMR (300 MHz, DMSO-d_6): 6.19 (1H, d, *J* =15.6 H-2), 6.77 (1H, d, *J* = 8.1 Hz, H-8), 6.92 (1H, dd, *J* = 8.1, 1.9 Hz, H-9), 7.05 (1H, d, *J* = 1.9 Hz, H-5), 7.45 (1H, d, *J* = 15.6 H-3). ^{13}C NMR (75 MHz, DMSO-d_6): 115.3 (CH), 115.9 (CH), 116.5 (CH), 126.6 (C), 145.2 (CH), 146.14 (C), 148.6 (C), 168.5 (C=O), 121.8 (CH).MS (EI, 70 eV): m/z (%) = 180 (100), 163 (32.32), 145.04 (6.73), 136 (41.23), 134 (39.15), 117 (8.69), 89 (23.51), 77 (12.69), 51 (10.62).

RESULTS AND DISCUSSION

Isolation and structure elucidation

Column chromatography of the toluene-soluble fraction of *S. sodomeum* led to the isolation of compound I, its structure was established by IR, NMR and mass spectroscopy.

Compound **I** was obtained as Yellowish amorphous powder. The IR spectrum displayed intense absorption bands at 3450-2500 cm-1 (OH phenolic), 1700 and 1651 (Asymmetric and symmetric C=O), 1616 and 1527 cm-1 (C=C-aromatic).

The ^{13}C-NMR spectrum displayed nine carbons resonances, APT experiments confirmed the presence of four quaternary and five methine. The carbonyl resonance at δ_C 168.5 was due to anhydride group (C-1). The two vinylic carbons appeared at δ_C 116.5 and 145.2 for C-2 and C-3 respectively. The downfield signals at δ_C 146.1 and 148.6 were assigned to two oxygenated quaternary aromatic at C-6 and C-7 respectively and at δ_C 115.3, 115.9, 121.8 for three aromatic methine carbons at C-5, C-8 and C-9 respectively.

The ^{1}H-NMR spectrum indicated the presence of trisubstituted benzene ring with *AMX* system at δ_H 6.77 (d, $J_{8,9}$ =8.1 Hz), δ_H 7.05 (d, $J_{5,9}$ = 1.9 Hz) and δ_H 6.92 (dd, $J_{8,9}$ = 8. 1, $J_{5,9}$ = 1. 9 Hz) were due to H-8, H-5 and H-9 respectively, and *trans*-configured olifinic protons at δ_H 6.12 (H-2) and δ_H 7.40 (H-3) with large coupling constant 15.9 Hz. The broad peak at δ_H 9.3 was assigned to two hydroxyl phenolic proton 6-OH and 7-OH.

Table 1: ^{13}C-^{1}H NMR (75/300 MHz in DMSO-d_6) spectral data, δ (*J* Hz) for compound I in comparison with spectral data for Caffeic anhydride (1) and Caffeic acid (2)

C	I		Caffeic anhydride (1)		Caffeic acid (2)	
	δ_C	δ_H	δ_Ca	δ_Ha	δ_Cb	δ_Hc
1	168.5		168.6		168.1	
2	116.5	6.19,*d* (15.6)	117.8	6.23,*d* (15.7)	115.7	6.17
3	145.2	7.45,*d* (15.6)	144.0	7.46,*d*(15.7)	144.4	7.41
4	126.6		128.5		125.6	
5	115.3	7.05,*d* (1.9)	114.9	7.01,*d* (1.9)	114.6	7.02
6	146.1		146.0		145.4	
7	148.6		148.2		148.2	
8	115.9	6.77,*d* (8.1)	116.5	6.75,*d* (8.0)	115.2	6.76
9	121.8	6.92,*dd* (8.1,1.9)	122.7	6.92,*dd* (8.0,1.9)	121.1	6.96
6-OH		9.3				9.12
7-OH		9.3				9.52
COOH						12.1

[a]*Data (^{13}C,100 MHz and ^{1}H, 400 MHz in CD_3OD) from Iqbal, K et al.[4].*
[b]*Data (^{13}C,100 MHz in DMSO-d6) from Dürüst, N et al.[5].*
[c]*Data (^{1}H, 360 MHz in DMSO-d6) from Iwahashi, H.et al.[6].*

Table (1) shows The comparison of NMR spectral data of isolated I with the previously published data of caffeic anhydride (1) and caffeic acid (2) which was a very close agreement except for absent of hydroxyl acid group gave strong evidence that the compound I was Caffeic anhydride.

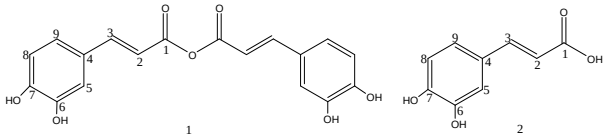
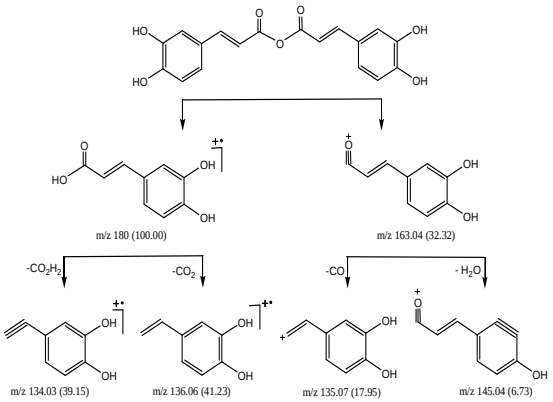


Figure 1: Caffeic anhydride (1) and Caffeic acid (2)

The EI mass spectrum did not show the molecular ion but exhibited the structure fragmentation. Some fragmentation of compound I are presented in scheme (1)



Scheme [1] The fragmentation of compound I

From the spectral data gave preferably that compound I was symmetric, with two identical benzene rings. Thus, the structure I was indicated as caffeic anhydride, this is the first report of Caffeic anhydride from the Solanacea family.

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