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Buchariate: An Aromatic Ester from *Salvia bucharica*

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Salvia bucharica belonging to the family Lamiaceae (Labiatae), afforded a new aromatic ester named buchariate [1- (*p*-hydroxybenzoyloxy)-3-oxo-octane (**1**)] along with twelve known constituents for the first time from our investigated source. The structures of all the isolated constituents were determined through spectroscopic techniques and comparison with literature values. The structure of new constituent (**1**) was elucidated through extensive 2-D NMR experiments.

(*Keywords*: *Salvia bucharica*, Lamiaceae, Buchariate, Aromatic ester, Characterization, 2D-NMR)

Introduction

Salvia is the largest genus of the family Lamiaceae, previously called Labiatae.[1] Various members of the genus *Salvia* have immense medicinal importance. Some interesting biological activities have been reported for extractives of various species of the this genus. The diterpenoids of *S. officinalis* show antiviral activity.[2] Many *Salvia* species have also shown cytostatic and antibacterial activities.[3-4] *S. bucharica* locally called "sursuadah" is an aromatic plant found in Pakistan, Afghanistan and Centra.[5] The plant is used traditionally for the treatment of liver disorders.

Salvadiones-A, B and salvadiol have recently been reported by us.[6-7] In this last communication on *S.bucharica*, we wish to describe the isolation and characterization of a new constituent, buchariate [1-(*p*-hydroxybenzoyloxy)-3-oxo-octane (**1**)] along with twelve known constituents which have never been isolated so far from our investigated source. They include: anagadiol,[8] lupeol,[9] oleanolic acid,[10] stigmasterol,[11] stigmasterol glucoside,[11] β-sitosterol,[11] β-sitosterol glucoside,[11] apigenin,[12] 7-O-β-D-glucopyranosylapigeni,[13] 5-hydroxy-4′, 7-dimethoxy flavone,[14-15] salvagenin[16] and crisilinol.[16]

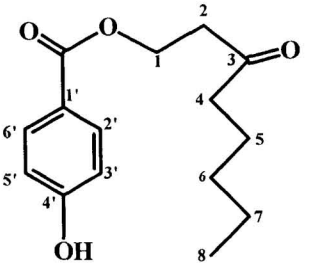
Results and Discussion

Compound **1** was obtained as a yellowish oil from the ethyl acetate soluble part of the methanolic extract of *S.bucharica* . The UV spectrum of **1** showed intense absorption bands at λ_{max} 274 and 258 nm. The IR spectrum exhibited strong absorption bands at 3410, 1735 and 1720 cm^{-1} due to hydroxyl, ester and ketonic functions, respectively. The EI MS showed the molecular ion peak at *m/z* 264. The base peak of stable acylium ion (Fig. 1a) appeared at *m/z* 121. The molecular formula was determined through HR MS as $C_{15}H_{20}O_4$ (calcd. *m/z* 264.1361, observed *m/z* 264.1365) showing six degrees of unsaturation.

The ^{1}H-NMR spectrum of **1** showed a pair of doublets each with two protons integration at δ 7.07 and 6.75 with a coupling constant of 8.6 Hz. It showed the presence of AA'BB' system and confirmed through COSY-45° experiment (Fig. 1b). The ^{1}H-NMR spectrum also showed three triplets each of two protons integration at δ 4.23 (J = 7.1 Hz), δ 2.85 (J = 7.1 Hz) and at δ 2.27 (J = 7.3 Hz). The same coupling constants (7.1 Hz) of two triplets at δ 4.23 and 2.85 indicated their adjacent positions and confirmed through COSY-45° experiment. The remaining triplet at δ 2.27 was due to the H-4. Another most upfield triplet of three protons integration appeared at δ 0.87 (J = 7.2 Hz) due to the only methyl present in the molecule. The triplets at δ 2.27 and 0.87 were found to couple with a broad singlet of six protons integration at δ 1.24 in COSY-45° spectrum (Fig-1b), this broad singlet was due to the three carbon chain (H-5 - H-7).

The thirteen carbon signals in the BB spectrum were resolved through DEPT experiment into one methyl, six methylene, two methine and four quaternary carbon atoms. The downfield quaternary carbons at δ 211.4, 167.1 and 156.7 were assigned to C-3, *OCO* and C-4`, respectively. All the chemical shifts (^{1}H and ^{13}C) were confirmed through HMQC, HMBC and COSY-45° techniques (Fig. 1b) and partial comparison with the reported data of related compounds.[17]

Thus, **1** is assigned as 1- (*p*-hydroxybenzoyloxy)-3-oxooctane and named buchariate. To the best of our knowledge this compound is not known yet from any natural source and therefore, would be a new addition in the constituents of *S.bucharica* as well as natural products.



1

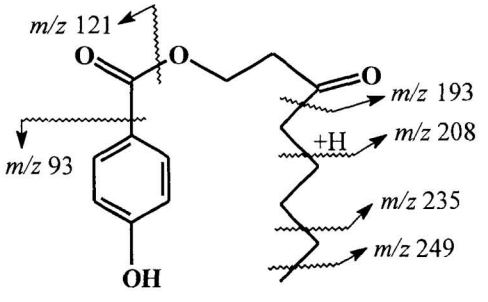


Fig. **2a** Possible mass fragmentation of **2**

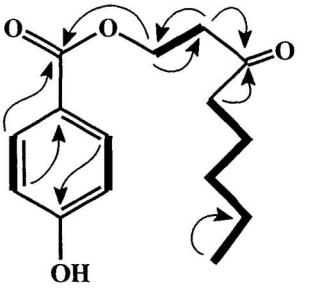


Fig. **2b** H-H COSY ▬
HMBC ⟶

Experimental

Optical rotation was measured on a *JASCO DIP-360* polarimeter. The IR and UV spectra were recorded on *JASCO 320-A and Hitachi UV 3200* spectrophotometers, respectively. The EI and HREI MS were recorded on *JMS HX 110* with a data system and on *JMS-DA 500* mass spectrometers. The ^{1}H & ^{13}C-NMR, COSY, HMQC and HMBC spectra were taken in $CDCl_3$ with TMS as an internal standard on *Bruker AM-400* NMR spectrometer.

a) Collection and identification

The plant material was collected from Baluchistan (Pakistan) in June, 1997, and identified by Dr. R. B. Tareen, Department of Botany, Baluchistan University, Quetta (Pakistan) where a voucher specimen (No. 354) of the plant material is deposited in the herbarium of the department.

b) Extraction and isolation

The air-dried (6 Kg) and ground plant material was extracted with hexane (15L x 3) and then with methanol (15L x 2). After removing the methanol under reduced pressure, the methanolic gummy residue (428.4g) was obtained. This was partitioned between EtOAc and H_2O. The EtOAc soluble part, after concentration (129.4g), was subjected to column chromatography over silica gel (70-230 mesh) using mixtures of hexane-$CHCl_3$ and $CHCl_3$-MeOH in order of increasing polarity as mobile phase.

The fractions eluted with 90% $CHCl_3$ in hexane were subjected to repeated flash chromatography (Si. gel 230-400 mesh) using various combinations of hexane-acetone. Repeated preparative TLC (Si gel F_{254}) of fraction obtained with 10% acetone in hexane from flash chromatography, developed with 0.5% MeOH in $CHCl_3$, afforded **1** as an oil (16.1 mg, 0.00026%).

1- (*p*-hydroxybenzoyloxy)-3-oxooctane (1). $C_{15}H_{20}O_4$. $[\alpha]_D^{29}$ 0° (*c* 0.411, $CHCl_3$); **IR** ν_{max} ($CHCl_3$) cm^{-1}: 3410 (OH), 1720 (C=O), 1735 (OCO); **UV** (MeOH), λ_{max} nm (logϵ): 274 (0.75), 258 (1.22); **HREI MS**: *m/z* 264.1365; **EI MS** *m/z* (rel. int.): 464 $[M]^+$ (8) ,121 (100) and see Fig. **1a**; **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ 7.07(2H, d, *J* = 8.6 Hz, H-2` and H-6`), 6.75(2H, d, *J* = 8.6 Hz, H-3` and H-5`), 4.23 (t, *J*= 7.1 Hz, H-1), 2.85 (t, *J*= 7.1 Hz, H-2), 2.27 (t, *J*= 7.3 Hz, H-4), 1.24 (6H, br.s, H-5 - H-7), 0.87 (t, *J* = 7.2 Hz, H-8); **^{13}C-NMR** (($CDCl_3$, 125 MHz): δ 127.4 (C-1`), 130.1(C-2` and C-6`), 115.4 (C-3` and C-5`), 156.7 (C-4`), 167.1 (OCO), 64.9 (C-1), 34.4 (C-2), 211.4 (C-3), 31.9 (C-4), 29.3 (C-5), 29.2 (C-6), 25.0 (C-7) and 22.7 (C-8).

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