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Note

# Iridoids from *Teucrium yemense*

**Essam Abdel-Sattar**

*College of Pharmacy, Cairo University, El-Kasr El-Aini Street, Cairo 11562, Egypt*

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The aerial parts of *Teucrium yemense* yielded two iridoid glycosides. Their structures were elucidated by spectral means as teucardosid and 8-*O*-acetylharpagid.

**Key words :** *Teucrium yemense* , *Labiatae*, Iridoids, 8-O-acetylharpagid, Teucardosid, NMR

## INTRODUCTION

In previous reports (Abdel-Satter *et al.*, 1995; Abdel-Sattar, 1995), four new *neo*-clerodane diterpenes, T-cadinol and poliumoside were isolated from the aerial parts of *Teucrium yemense*. It has been reported that genus *Teucrium* contains iridoids of the aucubin and harpagid-types (Ruhdrofer and Rimpler, 1981a). It was of interesting to investigate the plant under study for the presence of iridoids due to its importance from the chemotaxonmical point of view.

## MATERIALS AND METHODS

### General

IR spectra were recorded on Pye Unicum Sp3-300. $^1$H NMR and $^{13}$C NMR were recorded in $CD_3OD$, TMS as int. standard. Standard Varian software was used for 2D NMR COSY and HETCOUR, employing a Varian XL-300 and Joel EX-400 instruments.

### Plant material

The aerial parts of *Teucrium yemense* were collected in Abha, Saudi Arabia in 1995. A voucher specimen was deposited in the herbarium of the college of pharmacy, King Saud University, Riyadh, Saudi Arabia.

### Extraction and isolation

The dried gound aerial parts of *T. yemense* (490 g) were percolated with acetone. The acetone extract (20 g) was dissolved in 100 ml MeOH and diluted with equal amounts of water and left in refrigerator for 48 hr. The aqueous methanolic solution was filtered and the undissolved marc was washed with cold MeOH-$H_2O$ (1 : 1). The filtrate and combined washings were concentrated and shaked with $CHCl_3$ followed by EtOAc. The aqueous mother liquor left after extraction was evaporated under reduced pressure (3 g) and chromatographed on Si gel column (15×3.5 cm) using $CH_2Cl_2$-MeOH (4 : 1) as elutings system. Fractions of 100 ml were collected. Fractions eluted between 800-1200 ml were pooled together and evaporated under reduced pressure to give dark yellowish brown residue (0.49 g). The previous residue was adsorbed on small amounts by $CH_2Cl_2$-MeOH (9 : 1) as eluting systems. Compound **1** was obtained from of Si gel and chromatographed on another Si gel column (15×2 cm), using $CH_2Cl_2$ followed fractions eluted be- tween 500-600 ml (fr. A), while compound **2** eluted in fractions eluted between 700-850 ml (fr. B). Fractions A and B were further purified using small sephadex columns (MeOH) to give 40 and 100 mg of compounds **1** and **2**, respectively.

### 8-*O*-acetylharpagid [1]

Pale yellowish gum, IR $\nu$ (film) cm$^{-1}$: 3450 (OH), 1710 (C=O), 1650 (C=C), $^1$H NMR (400 MHz) δ: 6.38 (1H, d, $J$=6.3 Hz, H-3), 6.06 (1H, d, $J$=0.9 Hz, H-1), 4.91 (1H, dd, $J$=1.4, 6.3 Hz, H-4), 4.59 (1H, d, $J$=7.8 Hz, H-1'), 3.89 (1H, dd, $J$=12.2, 2 Hz, H-6), 3.8-3.1 (4H, sugar protons), 2.84 (1H, br.s, H-9), 2.17 (1H, d, $J$=15.1 Hz, H-7A), 2.00 (3H, S, $CH_3CO$-8), 1.92 (1H, dd, $J$=15.1, 4.4 Hz, H-7B) and 1.44 (3H, s, H-10).

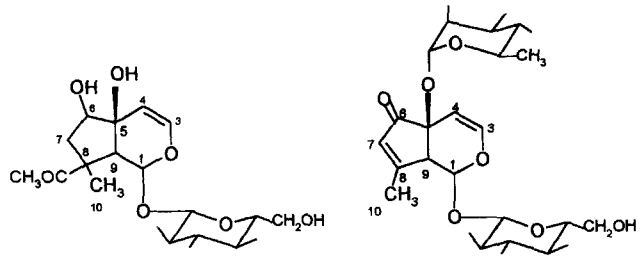
### Teucardosid [2]

Pale yellowish amorphous powder, mp. less than 80°C (uncorr.); IR $\nu$ (KBr) cm$^{-1}$: 3450, 1715 (C=O), 1660 (C=C). $^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) δ: see Table I.

## RESULTS AND DISCUSSION

From fractionated acetone extract (see experimental), compound **1** and **2** were isolated using series of col-

*Correspondence to*: Essam Abdel-Sattar, College of Pharmacy, Cairo University, El-Kasr El-Aini Street, Cairo 11562, Egypt



1 2

**Table I.** $^{1}$H- and $^{13}$C-NMR data of compound **1**

| No. | $^{1}$H NMR | $^{13}$C NMR |
|---|---|---|
| 1 | 5.83 (1H, d, *J*=2.4 Hz) | 93.08, d |
| 3 | 6.44 (1H, d, *J*=6.3 Hz) | 144.73, d |
| 4 | 4.99 (1H, dd, *J*=6.3, 1.1 Hz) | 103.24, d |
| 5 | - | 77.52, s |
| 6 | - | 204.73, s |
| 7 | 5.96 (1H, br.m) | 129.23, d |
| 8 | - | 175.64, s |
| 9 | 3.54 (1H, br.s) | 55.37, d |
| 10 | 2.26 (3H, br.s) | 18.23, q |
| | **Glucose** (at C-1) | |
| 1' | 4.60 (1H, d, *J*=7.5) | 99.53, d |
| 2' | 3.26 (1H, m) | 74.71, d |
| 3' | 3.37 (1H, m) | 77.89, d |
| 4' | 3.28 (1H, m) | 71.61, d |
| 5' | 3.29 (1H, m) | 78.37, d |
| 6' A | 3.30 (1H, dd, *J*=12, 2 Hz) | 62.78, d |
| B | 3.66 (1H, dd, *J*=12, 5.6 Hz) | |
| | **Rhamnose** (at C-5) | |
| 1'' | 5.43 (1H, d, *J*=1.8 Hz) | 97.70, d |
| 2'' | 3.83 (1H, m) | 72.88, d |
| 3'' | 3.70 (1H, m) | 72.14, d |
| 4'' | 3.32 (1H, m) | 74.03, d |
| 5'' | 3.77 (1H, m) | 70.43, d |
| 6'' | 1.19 (1H, d, *J*=6.3) | 17.97, d |

umns chromatography on Si gel and end purification step on sephadex LH20 column. Compound **1** was identified as 8-*O*-acetylharpagid by comparison of its $^{1}$H NMR data with that reported in literature (Hostettmann *et al.*, 1979) and by TLC comparison with authentic samples using different solvent systems. Compound **2** gave positive Molisch's test for sugars and/or glycosides and showed IR spectrum similar to that of **1**. The $^{1}$H NMR spectrum of compound **2** showed an olefinic proton at δ 5.96 (H-7) instead of the two aliphatic protons (two dd, δ 2.17 and 1.94, H-7A, B) signal in **1**, indicating double bond formation between carbons 6 and 7. $^{1}$H and $^{13}$C NMR spectra of compound **2** showed also the absence of acetyl group at C-8. The $^{13}$C NMR showed the presence of a carbonyl group at δ 204.73 (C-^) instead of the hydroxyl group in **1**. $^{1}$H and $^{13}$C NMR spectra of compound **2** showed in addition to the glucose moiety at C-1, another sugar moiety identified as rham- nose by acid hydrolysis (Ruhdrofer and Rimpler, 1981a), which was confirmed by observation of its anomeric proton δ 5.43 (H-1''). The coupling constant, *J*=1.8 Hz indicated α-configuration at H-1''. The $^{1}$H NMR spectrum showed also a doublet (3H) at δ 1.19, *J*=6.3, assigned for methyl protons of rhamnose moiety. Rhamnose moiety was shown to be attached to the hydroxyl group at C-5 and was confirmed by its upfield shift to 77.52 ($^{13}$C-NMR) relative to free one (Chaudhuri and Sticher, 1980; Belofsky and Stermitz, 1988). From the foregoing spectral data and by comparison with reported data in literature (Ruhdorfer and Rimpler, 1981a; Ruhdorfer and Rimpler, 1981b), compound **2** was identified as teucarosid.

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