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## A New Flavanone from *Teucrium Alyssifolium*

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From the aerial parts of *Teucrium alyssifolium* in addition to previously obtained *neo*-clerodane diterpenoids, a new flavanone alyssifolinone and three flavones cirsilinol, cirsilineol and luteolin-6,7,3', 4'-tetramethyl ether, were isolated. The structure of the compounds was established by spectral data, and by TLC comparison for the known compounds.

**Keywords:** *Teucrium alyssifolium*, Lamiaceae, flavanone, alyssifolinone, flavones.

### Introduction

In a previous study of the aerial parts of *Teucrium alyssifolium*<sup>1</sup> four new rearranged *neo*-clerodane diterpenoids were isolated and their structures were established by using 1D and 2D NMR techniques including APT, SINEPT, HETCOR and HMBC experiments as well as X-ray crystallographic analysis.

In the present study, from more polar fractions of the same plant extract, a flavanone, alyssifolinone (**1**) and three flavones, cirsilinol (**2**), cirsilineol (**3**) and luteolin-6,7,3',4'-tetramethyl ether (**4**) were obtained. Although the flavanones are rare in *Teucrium* species, these three methoxylated flavones are common and considered as chemotaxonomic markers for *Teucrium* species<sup>2</sup>. The flavonoids were identified mainly by UV spectral analyses using UV shift reagents as well as <sup>1</sup>H NMR spectral data. For the structure determination of the new flavanone, <sup>1</sup>H and <sup>13</sup>C NMR spectral analyses as well as HREI mass spectrum were also included in addition to UV shift experiments.

## Experimental

### General

The spectra were recorded with the following instruments: UV, Varian Techtron 635 in MeOH. IR, Perkin Elmer 983 in  $CHCl_3$ .  $^1H$  and  $^{13}C$  NMR, Bruker AC 200L in  $CDCl_3$ . HREIMS, VG ZabSpec.

### Plant Material

The aerial parts of *Teucrium alyssifolium* Stapf. (endemic to Turkey) were collected from Muğla (Köyceğiz-Sandras mountain) south western Turkey, at an altitude of 1600 m in June 1993. The plant was identified by Dr. Kerim Alpınar (Istanbul), a voucher specimen was deposited in the Herbarium of the Faculty of Pharmacy, University of Istanbul, ISTE 65136.

### Extraction and Isolation of the Compounds

Air dried and powdered plant material (1.4 kg) was extracted with distilled acetone at room temperature. 72 g of residue was obtained by evaporating to dryness in a vacuum. The residue was fractionated in a Si gel column (5x70 cm) eluting with hexane; a gradient of EtOAc was added up to 100 %, followed by EtOH. The polar fractions of the column yielded alyssifolinone 10 mg, luteolin-6,7,3',4'-tetramethyl ether 20 mg, cirsilineol 25mg and circiliol 17 mg.

### Alyssifolinone

Amorphous compound. UV  $\lambda_{max}$  (MeOH) nm (log  $\epsilon$ ): 325 (2.0), 285 (3.4). IR  $\nu_{max}$  ( $CHCl_3$ )  $cm^{-1}$ : 3460, 3020, 2920, 2840, 1640, 1580, 1510, 1460, 1340, 1275, 1160, 1090, 1060, 1030, 870, 805, 760.  $^1H$  NMR  $\delta$ : 5.30 (1H, dd, J=3.5 and 12 Hz, H-2 $\beta$ ), 3.04 (1H, dd, J=12 and 17 Hz, H-3 $\alpha$ ), 2.75 (1H, dd, J=3.5 and 17 Hz, H-3 $\beta$ ), 3.89 (3H, s, OMe), 7.02 (1H, d, J=2, H-6), 6.89 (1H, d, J=2 Hz, H-8), 6.88 (1H, br s), 5.98 (2H, br s) (three aromatic protons of B-ring), 11.98 (1H, br s) (hydrogen bond between C-5 OH and C-4 carbonyl).  $^{13}C$  NMR  $\delta$ : C-2 80.3, C-3 44.1, C-4 197.1, C-5 163.0, C-6 97.1, C-7 168.1, C-8 96.2, C-9 163.4, C-10 102.2, C-1' 130.3, C-2' 114.5, C-3' 156.9, C-4' 118.9, C-5' 157.4, C-6' 112.5, OMe 56.4. HREIMS  $m/z$  (rel. int.): 302.0984 [ $M$ ]<sup>+</sup> ( $C_{16}H_{14}O_6$ )(100), 286 [ $M - Me + 1$ ]<sup>+</sup> (15), 152 [ $A_1$ ]<sup>+</sup> (20), 150 [ $B_3$ ]<sup>+</sup> (78), 136 [ $B_3 - Me + 10$ ]<sup>+</sup> (86), 124 [ $A_1 - CO$ ]<sup>+</sup> (18).

## Results and Discussion

The HREIMS of alyssifolinone (**1**) indicated a molecular formula  $C_{16}H_{14}O_6$  ( $m/z$  302.0984, calc. 302.0990). The compound appeared purple under UV light, when exposed to  $NH_3$  vapour and sprayed with NA reagent (Naturstoffreagenz A: diphenyl boric acid  $\beta$ -amino ester) indicating either a substituted hydroxyl group at C-4' or a hydrogen in that position. The UV spectra, recorded in MeOH and using shift reagents, indicated a flavanone structure, especially band I having lower intensity compared to band II. In MeOH  $\lambda_{max}$  (log  $\epsilon$ ): 325 (2.2), 285 (3.4); NaOMe: 321 (2.4), 248 (2.0);  $AlCl_3$  and  $AlCl_3/HCl$ : 378 (2.1), 315 (3.6); NaOAc: 325 (3.2), 290 (2.2);  $NaOAc/H_3BO_3$ : 325 (2.0), 290 (3.1). The  $^1H$  NMR spectrum showed a flavanone structure with the signals at  $\delta$  5.30 (1H, dd, J=3.5 and 12 Hz, H-2 $\beta$ ) and 3.04 (1H, dd, J=12 and 17 Hz, H-3 $\alpha$ ), 2.75 (1H, dd, J=3.5 and 17 Hz, H-3 $\beta$ ), which are typical for the C ring. The signals in the aromatic region indicated A and B ring protons, at  $\delta$  7.02 (1H, d, J=2 Hz, H<sub>6</sub>) and 6.89 (1H, d, J=2 Hz, H-8), 6.88

(1H, br s) and 5.98 (2H, br s) the latter two protons having no splitting but being broad signals corresponded three meta protons in the B ring at C-2', C-4' and C-6'. At C-3' and C-5' there could be one hydroxyl and one methoxyl or both places could carry the two hydroxyl groups. The assignment of the methoxyl group either to ring A or B was not possible from the <sup>1</sup>H and <sup>13</sup>C NMR spectra. The mass degradation of **1** indicated that the methoxyl group should be at ring B rather than A (Figure 1). There were two significant peaks for *A*<sub>1</sub> and *B*<sub>3</sub> at *m/z* 152 and 150 respectively, in addition to the latter signal, the one at *m/z* 136 (*B*<sub>3</sub> - *Me* + 1) revealed<sup>3</sup> the presence of the methoxyl group at ring B. The spectral data indicated 3'-*OCH*<sub>3</sub>, 5'-*OH*-flavanone or 3'-*OH*, 5'-*OCH*<sub>3</sub> flavanone structure for alyssifolinone (**1**). It is obvious that the placement of the substituents does not make any difference either at C-3' or C-5' due to the free rotation of ring B.

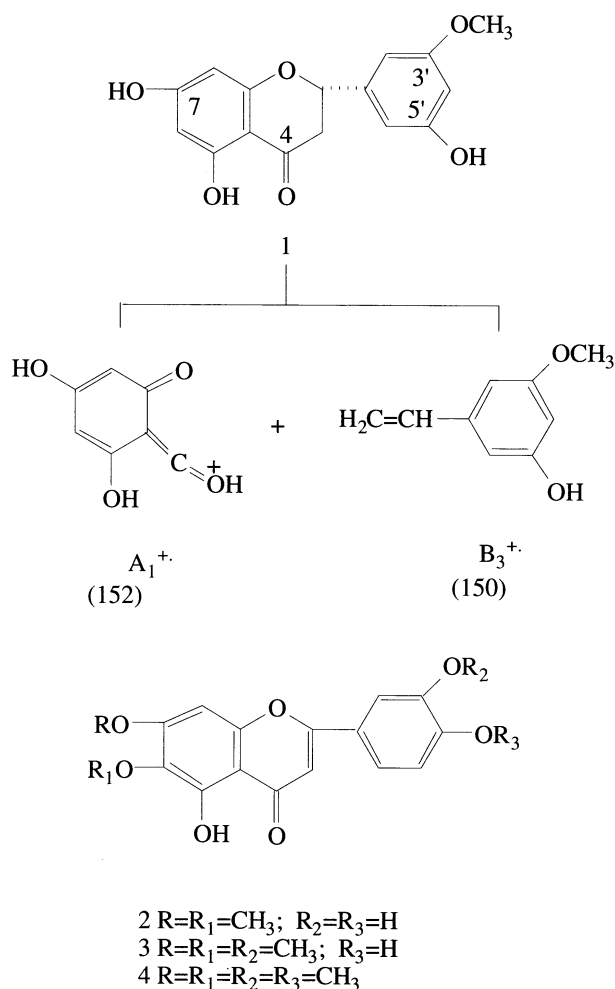


Figure 1.

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