

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*¹ 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* species². The flavonoids were identified mainly by UV spectral analyses using UV shift reagents as well as ¹H NMR spectral data. For the structure determination of the new flavanone, ¹H and ¹³C 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 λ_{max} (MeOH) nm (log ϵ): 325 (2.0), 285 (3.4). IR ν_{max} ($CHCl_3$) cm^{-1} : 3460, 3020, 2920, 2840, 1640, 1580, 1510, 1460, 1340, 1275, 1160, 1090, 1060, 1030, 870, 805, 760. 1H NMR δ : 5.30 (1H, dd, J=3.5 and 12 Hz, H-2 β), 3.04 (1H, dd, J=12 and 17 Hz, H-3 α), 2.75 (1H, dd, J=3.5 and 17 Hz, H-3 β), 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 δ : 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]⁺ ($C_{16}H_{14}O_6$)(100), 286 [$M - Me + 1$]⁺ (15), 152 [A_1]⁺ (20), 150 [B_3]⁺ (78), 136 [$B_3 - Me + 10$]⁺ (86), 124 [$A_1 - CO$]⁺ (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 β -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 λ_{max} (log ϵ): 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 δ 5.30 (1H, dd, J=3.5 and 12 Hz, H-2 β) and 3.04 (1H, dd, J=12 and 17 Hz, H-3 α), 2.75 (1H, dd, J=3.5 and 17 Hz, H-3 β), which are typical for the C ring. The signals in the aromatic region indicated A and B ring protons, at δ 7.02 (1H, d, J=2 Hz, H₆) 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 ¹H and ¹³C 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*₁ and *B*₃ at *m/z* 152 and 150 respectively, in addition to the latter signal, the one at *m/z* 136 (*B*₃ - *Me* + 1) revealed³ the presence of the methoxyl group at ring B. The spectral data indicated 3'-*OCH*₃, 5'-*OH*-flavanone or 3'-*OH*, 5'-*OCH*₃ 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.

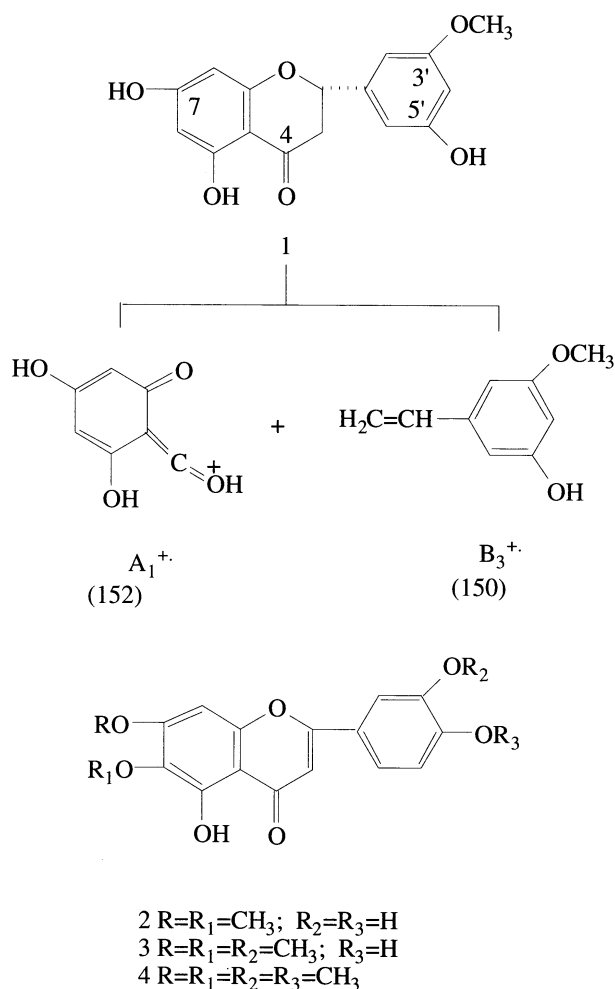


Figure 1.

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