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FLAVONOIDS OF *ARTEMISIA SPICIGERA*

B.ÇUBUKÇU *, L.BİTİŞ (ÖZTÜRKMEN)*

SUMMARY

23 wild *Artemisia* species grow in Turkey (1,2) and some of them have not yet been investigated chemically. This report is one of the series on the chemical investigations of the Turkish *Artemisia species* (3-8).

Seven flavonoids (hispidulin, apigenin, luteolin, quercetin, apigenin 7-glucoside, patuletin 3-glucoside and rutin) have been isolated from the aerial parts of *A.spicigera.*

ÖZET

Türkiye'de yetişen 23 *Artemisia* türünün (1,2) bazıları daha henüz kimyasal açıdan incelenmemiştir. Bu çalışma, *Artemisia* türlerinin kimyasal yapısını araştıran bir seri incelemenin bir bölümünü oluşturmaktadır (3-8).

Yapılan çalışmalar sonucunda, *A.spicigera* türünün topraküstü kısımlarından hispidulin, apigenin, luteolin, quercetin, apigenin 7-glucoside, patuletin 3-glucoside and rutin izole edilmiştir.

Key Words: *Artemisia spicigera,* flavonoids.

INTRODUCTION

Many species of the large genus *Artemisia* (Compositae, tribe Anthemideae) have been used for many centuries in folk medicine. The volatile sub-

(*) Faculty of Pharmacy, Department of Pharmacognosy, University of Istanbul, 34452, İstanbul, Turkey.

stances of *A.spicigera* are used like *A.austriaca* in folk medicine in Eastern part of Turkey as an antiseptic (8), whereas the essential oil of it shows an antimicrobial effect (9). The vapor is prepared by boiling the plant and is used for vaginal purposes by women in Anatolia.

A.spicigera has previously been investigated from its volatile oil and sesquiterpene lactones stand points. α-pinen,camphene, p-cymen,camphor and 1,8-cineol have been found in volatile oil (10,11). As sesquiterpene lactones, 1 α Hydroxyeudesm-4(15)-en-5α,6β,11βH-12,6-olide(=11β,13-dihydro-1-epireynosin), 1α,4α-Dihydroxyeudesm-2-en-5α,6β,11β H-12,6-olide, 3-oxo-1,4(15)-dien-5α,6β,11βH-eudesm-12,6-olide, erivanin, alkhanin, α-santonin, β-santonin, and the phenolic compound brevifolin have been isolated (12,13).

RESULTS AND DISCUSSION

In this work the flavonoids of *A.spicigera* have been investigated for the first time. Hispidulin, apigenin, luteolin, quercetin, apigenin 7-glucoside, patuletin 3-glucoside and rutin have been obtained from the aerial parts of the plant. None of the isolated flavonoids were new for the genus since their presence in other *Artemisia* species were shown by several workers.

A.spicigera can be considered as "poor" in accordance with percentage and the number of the flavonoid compounds. The major flavonoid of this plant is hispidulin (6-methoxy apigenin). Hispidulin was previously isolated from 15 different *Artemisia* species *(A.campestris ssp.glutinosa, A.cina, A.deserti, A.frigida, A.glacialis, A.gorjaevii, A.herba-alba, A.judaica, A.lindleyana, A.ludoviciana var. ludoviciana, A.mogoltavica, A.monosperma, A.namanganica, A.saissanica, A.sublessingiana).*

The flavonoids obtained in this work have simple and hydrophyllic structure. The chromatographic data for flavonoids are given in Table 1.

Table 1: Chromatographic data for flavonoids from *Artemisia spicigera* C. Koch.

Flavonoid	Color in UV (366)*	Color in UV/NH_3 (366)*	Color in UV/NA (254)*	Interpretation
Hispidulin	p	y	ol-y	free C-5 OH and C-4' OH
Apigenin	p	g-y	g-y	free C-5 OH and C-4' OH
Luteolin	p	y	or-y	free C-5 OH,C-3' and C-4' OH
Quercetin	y	y	or-r	free C-5 OH and C-3 OH, C-3' and C-4' OH
Apigenin 7-glucoside	p	y	y	free C-5 OH and C-4' OH
Patuletin 3-glucoside	p	y	or	free C-5 OH,C-3' and C-4' OH
Rutin	p	y	or	free C-5 OH,C-3' and C-4' OH

* UV,long wavelength 366 nm, short wavelength 254 nm. p=purple, y=yellow, or=orange, g=green, ol=olive, r=red. NA (Naturstoffreagenz-A) in MeOH.

Hispidulin-UVλ_{max}^{MeOH} nm: 275,336; (+NaOMe): 275,328,394; (+$AlCl_3$): 267 sh, 280 sh, 302, 358; (+$AlCl_3$+HCl): 263 sh, 275 sh, 303, 355; (NaOAc): 275, 305, 352, 372; (+NaOAc+H_3BO_3): 277, 338.

Apigenin-UVλ_{max}^{MeOH} nm: 269,304 sh, 337; (NaOMe): 273,325,392; (+$AlCl_3$): 268, 302, 345, 381; (+$AlCl_3$+HCl): 270, 297, 339, 377; (+NaOAc): 276, 305, 385; (+NaOAc+H_3BO_3): 268, 299 sh, 339.

Luteolin-UVλ_{max}^{MeOH} nm: 242 sh, 253,267,288,348; (+NaOMe): 264,328 sh, 400; (+$AlCl_3$): 272, 302 sh, 329 sh, 420; (+$AlCl_3$+HCl): 258, 273, 296 sh, 357, 387; (+NaOAc): 268, 322, 396; (+NaOAc+ H_3BO_3): 260, 368, 435 sh.

Quercetin-UVλ_{max}^{MeOH} nm: 254 sh, 300 sh, 369; (+NaOMe): 247 sh, 320 (dec.); (+$AlCl_3$): 271, 302 sh, 331, 460; (+$AlCl_3$+HCl): 264, 300 sh, 356, 427; (+NaOAc): 272, 330 (dec.), 388; (+NaOAc+H_3BO_3): 261, 300 sh, 387.

Apigenin 7-glucoside-UVλ_{max}^{MeOH} nm: 268, 332; (NaOMe): 267, 304 sh, 382; (+$AlCl_3$): 275, 298, 345, 382; (+$AlCl_3$+HCl): 276, 297, 340, 381; (+NaOAc): 268, 295 sh, 384; (+NaOAc+ H_3BO_3): 268, 334.

Patuletin 3-**glucoside**-UVλ_{max}^{MeOH} nm: 257, 265 sh, 296 sh, 355; (+NaOMe): 269, 333, 407; (+$AlCl_3$): 275, 305 sh, 330 sh, 430; (+$AlCl_3$+HCl): 268, 300 sh, 383, 389; (+NaOAc): 273, 324, 391; (+NaOAc+H_3BO_3): 263, 300 sh, 378; ^{1}H NMR (200 Mhz, MeOH-d4): δ 3.80 (3H, s, OCH_3), 6.42 (1H, s, H-8), 7.34 (1H, d, J= 8 Hz, H-5'), 7.56 (1H, dd, J=8 and 2 Hz, H-6'), 7.65 (1H, d, J=2 Hz, H-2').

Rutin-UVλ_{max}^{MeOH} nm: 257, 268 sh, 297 sh, 357; (+NaOMe): 270, 328, 410; (+$AlCl_3$): 274, 307 sh, 327 sh, 433; (+$AlCl_3$+HCl): 267, 301 sh, 361, 400; (+NaOAc): 273, 323, 395; (+NaOAc+H_3BO_3): 261, 294, 380.

EXPERIMENTAL

Plant Material - Aerial parts of *A.spicigera* were collected at the flowering time in September from Kayseri. A voucher specimen identified by Prof.Dr.N.Özhatay has been deposited in the Herbarium of the Faculty of Pharmacy, University of Istanbul (ISTE 58240).

Extraction and Isolation - The dried plant material (1 kg) was first extracted with petroleum ether (yield 4.12%) to remove the lipophilic compounds and then with EtOH (95°) in a Soxhlet apparatus. The concentrated EtOH extract was diluted with H_2O and extracted with C_6H_6 (yield 1.36%), $CHCl_3$ (yield 0,64%) and EtOAc (yield 2,52%) respectively for fractionation.

Chromatographic analysis has shown the presence of flavonoid aglycons in the chloroform extract and flavonoid glycosides in the ethylacetate extract. As a result of this work hispidulin (32 mg), apigenin (15 mg), luteolin (7.9 mg), quercetin (3.2 mg), apigenin 7-glucoside (4.7 mg), patuletin 3-glucoside (24 mg) and rutin (9 mg) have been isolated.

For the isolation and purification of the flavonoids, column, preparative thin layer, and paper chromatography have been used. The structure of flavonoids have been identified by Rf values, colour reactions, and spectroscopic methods (UV, IR, ^{1}H-NMR) on comparison with authentic samples or with their data.

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