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CHEMICAL INVESTIGATIONS ON THE ROOTS OF YELLOW FLOWERING *ASPHODELINE* SPECIES IN TURKEY

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SUMMARY

Four *Asphodeline* species with yellow flowers growing in Turkey (*A. baytopae* E.Tuzlacı, *A. brevicaulis* (Bertol.) J.Gay ex Baker subsp. *brevicaulis* var. *brevicaulis*, *A. liburnica* (Scop.) Reichb. and *A. lutea* (L.) Reichb.) have chemically been investigated .

The existence of two flavonoids (apigenin and luteolin), six anthracene derivatives (aloe-emodin, asphodelin, chrysophanol, isochrysophanol, physcion and rhein) and a phenolic acid (chlorogenic acid) have been shown in the roots of the species. The amount of anthracene derivatives in these four species has also been compared. *A.baytopae* was found the richest species in anthracene derivatives whereas *A. brevicaulis* subsp. *brevicaulis* var. *brevicaulis* was the poorest .

ÖZET

Türkiye'de yetişen sarı çiçekli dört *Asphodeline* türü (*A. baytopae* E.Tuzlacı, *A. brevicaulis* (Bertol.) J.Gay ex Baker subsp. *brevicaulis* var. *brevicaulis, A. liburnica* (Scop.) Reichb.ve *A. lutea* (L.) Reichb.) kimyasal olarak incelenmiştir.

Farklı yörelerden toplanan dört *Asphodeline* türünün köklerinde altı antrasen türevi (aloe-emodin, asfodelin, krizofanol, izokrizofanol, fiskiyon ve rein);

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iki flavonoit (apigenin ve luteolin) ile bir fenolik asit varlığı gösterilmiştir. Ayrıca türlerin taşıdığı antrasen türevlerinin miktarları tayin edilmiş ve antrasen türevleri bakımından en zengin türün *A.baytopae* türü olduğu, *A. brevicaulis* subsp. *brevicaulis* var. *brevicaulis* türünün ise en zayıf tür olduğu anlaşılmıştır.

Key words: *Asphodeline*, anthraquinones, flavonoids, phenolic acid.

INTRODUCTION

The genus *Asphodeline* (Liliaceae) is known as "Çiriş otu, Kiriş otu, Deli Kiriş" like the genus *Asphodelus* and *Eremurus* in Turkey (1,2). The genus *Asphodeline* has fourteen species and according to the recent papers, this genus has been divided into two sections (3): 1. Sect. *Asphodeline* and 2. Sect. *Appendicigera*. Sect. *Asphodeline* includes the yellow flowering *Asphodeline* species.

The anthraquinone derivatives of the roots of *Asphodeline* species are used in some skin diseases (4).

Previous investigations on the aerial parts of *Asphodeline* species with white flowers reported the presence of anthraquinone derivatives, flavonoids, sesquiterpenlactones and lipids (5-7). In this work, the roots of Turkish *Asphodeline* species with yellow flowers (*A. baytopae*, *A. brevicaulis* subsp. *brevicaulis* var. *brevicaulis*, *A. liburnica* and *A. lutea*) have been chemically investigated for the first time.

RESULTS AND DISCUSSION

The anthracene derivatives, the flavonoids and the phenolic acid content of the roots of four *Asphodeline* species with yellow flowers have been examined and six anthracene derivatives, two flavonoids and one phenolic acid have been isolated and their structures have been elucidated. Three anthracene derivatives ; isochrysophanol, physcion and rhein are the new compounds for *Asphodeline* species.

The substances isolated from the roots of four *Asphodeline* species are given in Table 1.

The anthracene derivatives of the roots of four *Asphodeline* species have also been investigated quantitatively (8) and consequently *A.baytopae* was

Table 1: The substances of the roots from yellow flowering *Asphodeline*

SPECIES	ANTHRACENE DERIVATIVES	PHENOLIC ACID
A.baytopae	Aloe-emodin Asphodelin Chrysophanol Isochrysophanol	Chlorogenic acid*
A.brevicaulis subsp.*brevicaulis* var.*brevicaulis*	Aloe-emodin* Chrysophanol*	Chlorogenic acid*
A..liburnica	Aloe-emodin Asphodelin Chrysophanol Rhein	Chlorogenic acid*
A..lutea	Aloe-emodin Chrysophanol Physcion	Chlorogenic acid
	FLAVONOID DERIVATIVES	
	Apigenin* Luteolin	

* Identified only chromatographically

found as the richest species for anthracene derivatives whereas *A.brevicaulis* subsp. *brevicaulis* var. *brevicaulis* was the poorest. The results are given in Table 2.

Table 2: The quantitative results of anthracene derivatives in *Asphodeline* species

Species	**Total Anthraquinone and Anthranol Derivatives (%)**	**Anthraquinone Derivatives (%)**	**Antranol Derivatives (%)**
Asphodeline baytopae E. Tuzlacı	0.60	0.44	0.16
A. brevicaulis (Bertol.) J. Gay ex Baker subsp. *brevicaulis* var. *brevicaulis*	0.41	0.32	0.09
A. liburnica (Scop.) Reichb.	0.59	0.41	0.18
A. lutea (L.) Reichb.	0.53	0.38	0.15

EXPERIMENTAL

Plant Material - The roots of the four *Asphodeline* species were collected from different regions .The voucher specimens have been deposited in the Herbarium of Faculty of Pharmacy,University of Istanbul (ISTE) and identified by Prof.Dr. E.Tuzlacı (Marmara University).

The materials, the collecting regions and dates and ISTE numbers are given in Table 3.

Table 3: The collecting regions, dates and ISTE numbers of the *Asphodeline* roots

Material	Region	Date	ISTE Number
Asphodeline baytopae E. Tuzlacı	İçel	29.5.1994	66270
Asphodeline brevicaulis (Bertol.) J. Gay ex Baker subsp. *brevicaulis* var. *brevicaulis*	Muğla	24.5.1994	66269
Asphodeline liburnica (Scop.) Reichb.	Edirne	20.6.1994	66280
Asphodeline lutea (L.) Reichb.	İçel	30.5.1994	66279

Extraction and Isolation (9) - For the extraction of the anthracene derivatives, the material was extracted with EtOH in Soxhlet apparatus.The concentrated EtOH extract was diluted with water and extracted with ether.The concentrated ether extract was extracted with 10 % $NaHCO_3$ solution (w/v,water) and 10 % KOH solution(w/v, water) successively.The obtained $NaHCO_3$ and the KOH extracts were acidified with 2 N HCl separately and then extracted with ether. The anthracene derivatives were obtained from the ether extract. Flavonoids have also been isolated from this extract.

For the isolation and purification of the anthracene derivatives, the flavonoids and the phenolic acid compound, column and preparative thin layer chromatography have been used. The structures of the purified substances have been identified by colour reactions, by comparing their Rf values on TLC with authentic samples and by using spectroscopic methods (UV, IR, ^{1}H-NMR and MS).

Aloe-emodin-UVλ_{max}^{MeOH} nm: 226, 261 sh, 289, 430; (+NaOH): 276 sh, 428, 516.

Asphodelin - U Vλ_{max}^{MeOH} nm: 223, 261, 284 sh, 435; (+NaOH): 217, 274 sh, 513.

Chrysophanol - U Vλ_{max}^{MeOH} nm: 224, 248 sh, 286 sh, 428; (+NaOH): 217, 274 sh, 513.

Isochrysophanol - U Vλ_{max}^{MeOH} nm: 223, 254 sh, 286 sh, 429; (+NaOH): 224, 282, 510;

IR ν_{max}^{KBr} cm^{-1} : 3431, 1735, 1623, 1543, 1459, 1095, 801;

^{1}H-NMR (200 MHz, $CDCl_3$): δ ppm 2.47 (3H, s, 2-CH_3), 7.32 (1H, m, H-6), 7.67 (1H, dd, J=2 ve 9 Hz, H-7), 7.72 (1H, d, J= 9 Hz, H-3), 7.75 (1H, dd, J=2 ve 9 Hz, H-5), 7.82 (1H, d, J=9 Hz, H-4), 12.04 (1H, s, OH), 12.15 (1H, s, OH);

MS m/e : 254 $[M]^+$, (base), 239 $[M-15]^+$, 237 $[M-17]^+$, 226 $[M-28]^+$, 197 $[M-57]^+$, 167 $[M-87]^+$, 149, 97.

Physcion -UVλ_{max}^{MeOH} nm: 207, 222, 254 sh, 286 sh, 433; (+NaOH): 224 sh, 271 sh, 314 sh, 510;

Rhein - U Vλ_{max}^{MeOH} nm: 217, 253, 291 sh, 433; (+NaOH): 214, 253, 308, 495;

Luteolin - U Vλ_{max}^{MeOH} nm: 242 sh, 253, 263, 288, 346; (+NaOMe): 265, 328 sh, 395;

(+$AlCl_3$): 265, 302 sh, 329 sh, 421; ($AlCl_3$ + HCl): 258, 265, 296 sh, 357, 387;(+NaOAc): 265, 322, 396; (+ NaOAc + H_3BO_3): 265, 368,435 sh.

Chlorogenic Acid-UVλ_{max}^{MeOH} nm: 208.

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