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Investigations on Turkish *Colchicum* and *Merendera* Species

Türkiye'nin *Colchicum* ve *Merendera* Türleri Üzerinde Araştırmalar

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Abstract

This study was performed to summarize the botanical and phytochemical properties of Turkish *Colchicum* and *Merendera* species .

Key words. Turkish *Colchicum, Merendera,* alkaloids, phenolics

Investigations on *Colchicum* species

The first floristic and taxonomical researches on *Colchicum* species growing in Turkey began with Boissier's Flora Orientalis in 1884 and then continued by Brickell in vol 8 and Persson in vol 11 of the Flora of Turkey (Brickell 1984, Persson 2000). Except floras, Stefanoff's monograph (Stefanoff 1926) and Baytop's book (Baytop and Mathew 1984) are remarkable references in the field of *Colchicum* taxonomy. In the following years, the most of the anatomical, cytological and micromorphological studies on *Colchicum* species have been carried out Küçüker *et al.*,(Engel and Küçüker 1994; Küçüker 1987, 1990, 1995; Küçüker and Çelebioğlu 1988).

There are also some thesis about Turkish *Colchicum* species from the botanical point of view (Ece (Asan) 2002; Malyer 1979; Özcan 1995; Özyurt 1978; Sungu 1993; Şık 1997).

The main phytochemical researches began by Baytop T. and Özcöbek G. in 1970 on the alkaloids of *Colchicum chalcedonicum, micranthum, szovitsii* and *turcicum* corms (Baytop and Özcöbek 1970).

In following researches, first the corms and the seeds of Turkish *Colchicum* species have been qualitatively and quantitatively investigated (Sütlüpınar 1983,1998). As a result of the investigations, alkaloid content of *C.baytopiorum, bivonae, bornmuelleri, cilicicum, kotschyi* and *speciosum* species were found as rich as or even richer than *C.autumnale*.

Later, especially the species containing rich alkaloids, were evaluated from the point of mainly tropolonic alkaloids by HPLC and phenolics by TLC or GC-MS in different parts of the plants (Ondra *et al.*, 1995c; Šimánek *et al.*, 1990).

The phenolic fractions also have been tested for their cytoprotective effect on tBH-induced injury on isolated rat hepatocytes. The results indicate that phenolic fractions containing luteolin, reduced the tBH-induced LPX and leakage of LDH (Ulrickovà *et al.*, 1995).

Colchicum bivonae Guss. (Orhon 1982). Only the corms were studied.

Alkaloids: Neutral : Colchicine, cornigerine, N-deacetyl-N-formylcolchicine, 2- and 3-demethylcolchicine, β-lumicolchicine, γ-lumicolchicine, N-deacetyl-N-formylcolchicilin (New). Basic : O-methylkreysigine.

Colchicine and 3-demethylcolchicine were the major alkaloids in corms of this plant.

Colchicum bornmuelleri Freyn. (Ondra *et al.*, 1995a): Corms, flowers, leaves, seeds and capsules were studied.

Alkaloids: Colchicine, 2- and 3- demethylcolchicine, N-formyl-N-deacetylcolchicine, cornigerine, demecolcine, 2- and 3- demethyldemecolcine.

Phenolics: 4-hydroxybenzoic, 2,4-, 2,5- and 3,4-dihydroxybenzoic, vanillic, p-coumaric, ferulic, caffeic, 3-(3,4-dimethoxyphenyl)-2-propenoic acids and luteolin.

Colchicum cilicicum (Boiss.) Dammer (Sütlüpınar *et al.*, 1988): Corms, flowers, leaves, seeds and stems were studied.

Alkaloids: β- and γ-lumicolchicine, colchicine, 2- and 3-demethylcolchicine, cornigerine, N-formyl-N-deacetylcolchicine, N-methyldemecolcine, demecolcine, 2- and 3-demethyldemecolcine, β- and γ-lumidemecolcine, N-ethoxycarbonyldemecolcine (New).

Phenolies: Apigenin (in flowers), luteolin (in corms), benzoic, 2-hydroxy-6-methoxybenzoic, vanillic acid.

Colchicum kotschyi Boiss. (Ondra *et al.*, 1994a): Corms, leaves and seeds were studied..

Alkaloids: Colchicine, 2- and 3-demethylcolchicine, colchifoline, demecolcine, 2- and 3-demethyldemecolcine.

Phenolics: 4-hydroxybenzoic, 2,5- and 3,4- dihydroxybenzoic, vanillic, 4-coumaric, caffeic, ferulic, 3-(4-hydroxyphenyl)-propanoic, 3-(4-hydroxy-3-methoxyphenyl)-propanoic acids, 3,4-dihydroxybenzaldehyde, vanillin, 3-(4-hydroxy-3-methoxyphenyl)-propenol and luteolin.

Colchicum macrophyllum B.L.Burtt (Ondra *et al.*, 1994b): Corms, flowers, leaves and seeds were studied.

Alkaloids: Colchicine, 2- and 3-demethylcolchicine, N-deacetyl-N-formylcolchicine, colchifoline, demecolcine, 2- and 3- demethyldemecolcine.

Phenolics: 4-hydroxybenzoic, 2,5- , 2,6- and 3,4-dihydroxybenzoic, 3-(4-methoxyphenyl) propanoic, caffeic, 4-coumaric, ferulic, vanillic acids and luteolin.

Colchicum speciosum Stev. (Ondra *et al.*, 1995b): Corms, flowers, leaves, seeds and capsules were studied.

Alkaloids: Colchicine, 2- and 3- demethylcolchicine, N-formyl- N-deacetylcolchicine, colchifoline, cornigerine, demecolcine, 2- and 3- demethyldemecolcine.

Phenolics: 4-hydroxybenzoic, 2,5- , 2,6- and 3,4-dihydroxybenzoic, cinnamic, vanillic, p-coumaric, caffeic acids, vanillin, isovanillin, 4-hydroxyphenylmethanol, 2-(3-hydroxy-4-methoxyphenyl)-ethanol, 2-(3,4-dihydroxyphenyl)-ethanol and luteolin.

Colchicum szovitsii Fish. et Mey. (Tojo *et al.*, 1990): The bulbs were studied from the point of only phenethylisoquinoline alkaloids.

Two new trioxygenated phenethylisoqinolines were found namely (+)-colchiethanamine and (+)-colchiethine except four known monomeric alkaloids namely (-)-autumnaline, (-)-isoautumnaline, (+)-dysoxyline and (+)-homolaudanosine.

Colchicum triphyllum G.Kunze (Ondra *et al.*, 1995c): Corms, flowers, leaves and seeds were studied.

Alkaloids: Colchicine, 2- and 3-demethylcolchicine, colchifoline, cornigerine, demecolcine, 2- and 3-demethyldemecolcine.

Phenolics: 2,5- , 2,6- and 3,4-dihydroxybenzoic, vanillic, coumaric, ferulic, caffeic acids, vanilin.

Colchicum turcicum Janka (Baytop *et al.*, 1980, Husek *et al.*, 1990): Corms, flowers, leaves and seeds were studied.

Alkaloids: Colchicine, 3-demethylcolchicine, β-lumicolchicine, colchifoline, cornigerine, N-deacetyl-N-formyl- colchicine, demecolcine, 2- and 3- demethyldemecolcine.

Phenolics: Vanillic acid, luteolin.

The major alkaloids from the corms were colchicine and demecolcine, while, in the flowers, the major alkaloid proved to be colchicine with 3-demethyldemecolcine and demecolcine as minor alkaloids. Colchicine in the flowers was thirty times more than in the corms.

The seeds of *C.turcicum* are the first source for colchifoline as a major alkaloid. Among the basic alkaloids, demecolcine and 2-demethyldemecolcine were found. It is noteworthy that 2-demethyldemecolcine usually present in traces, was found in larger amounts than demecolcine.

The results of alkaloids are also summarized in Table 1 for all studied species.

Investigations on *Merendera* species

Four *Merendera* species grow in Turkey and there is not any botanical research on these species except Flora of Turkey vol 8.

The phytochemical studies began with Ulubelen A. and Tanker M. in 1975. They worked initially on polypeptides and amino acids and then the alkaloids of *Merendera caucasica* (syn. *M.manissadjiani* or *M.trigyna*) (Ulubelen and Tanker 1975, 1978).

Our team with Chech collaborators worked on the alkaloids and phenolics of three *Merendera* species (Husek *et al.*, 1989a ; Šimánek *et al.*, 1990). The alkaloid content (colchicine, 2- and 3-demethylcolchicine, N-formyl-N-deacetylcolchicine, cornigerine, demecolcine) of corms, leaves and flowers of *Merendera kurdica* and corms of *M.manissadjiani* and *M.sobolifera* was determined by HPLC.

Among the 4 Turkish *Merendera* species (*attica, kurdica, sobolifera* and *trigyna*), *M.sobolifera* was found to have the richest alkaloid content. In the corms of all three species, the major alkaloid is colchicine and demecolcine the only basic tropolone.

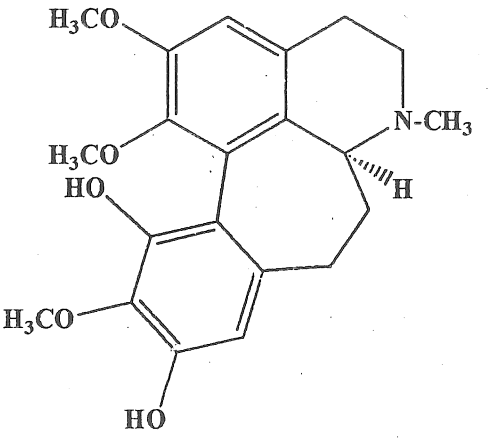
In addition, five homoaporphine alkaloids (baytopine, bechuanine, CC-24, kreysigine and O-methylkreysigine) were isolated from the leaves and flowers of *M.kurdica*. The major homoaporphine alkaloid of this plant is a new one (Husek *et al.*, 1989b). This alkaloid was named as BAYTOPINE to show our gratitudes to Prof.Dr. Turhan Baytop who had collected *Merendera kurdica* plant material from Van-Bahçesaray and also made great contribution to the field of research on Turkish *Colchicum* and *Merendera* species.

Table 1. The alkaloids of Turkish *Colchicum* species

Substances	*bivonae*	*bornmuelleri*	*cilicicum*	*kotschyi*	*macrophyllum*	*speciosum*	*triphyllum*	*turcicum*
	c	c,fl,l,s,caps	c,fl,l,s,st	c,l,s	c,fl,l,s	c,fl,l,s,caps	c,fl,l,s	c,fl,l,s
1. Colchicine	+*	+	+(c,fl*,l,s*,st)	+(c*,l,s*)	+(c*,fl*,l,s)	+	+	+(c*, fl*,l,s)
2. 2-demethylcolchicine	+	+	+(fl*,st)	+(c,l,s)	+(fl,l,s)	+	+	
3. 3-demethylcolchicine	+*	+	+(fl*,l,s,st)	+(c,l,s)	+(c*,fl,l,s)	+	+	+(c,l,s)
4. β-lumicolchicine	+		+ (c,fl,l,s,st)					+(c)
5. γ-lumicolchicine	+		+(c,fl,s,st)					
6. Cornigerine	+	+	+(c,fl,s,st)			+	+	+(c,s)
7. Colchifoline		+		+(c,l,s)	+(fl,s)	+	+	+(c,l,s*)
8. N-formyl-N-deacetyl-colchicine		+	+(c,st)		+(c,fl,l)	+		+(s)
9. Demecolcine		+	+(c,fl*,l,s,st)	+(c,l*,s*)	+(c,fl,l,s*)	+	+	+(c*, fl,l,s*)
10. 2-demethyldemecolcine		+	+(fl-trace-)	+(c,l*,s)	+(fl,l,s)	+	+	+(c,l*,s)
11. 3-demethyldemecolcine		+	+(fl*,l,st)	+(c,s)	+(c,fl,s)	+	+	+(c, fl*,l,s)
12. N-methyldemecolcine			+(c)					
13. β-lumidemecolcine			+(c,fl,l,st)					
14. γ-lumidemecolcine			+(c,fl,st)					
15. O-methylkreysigine	+							
16. N-deacetyl-N-formyl-colchicilin (NEW)	+							
17. N-ethoxycarbonyl demecolcine (NEW)			+(c)					

caps= capsules, c=corms, fl=flowers, l=leaves, s=seeds, st=stems.
* major alkaloid

Baytopine was isolated by preparative TLC (C_6H_6-AcOEt-Et_2NH_2, 7:2:1) from basic $CHCl_3$ extract of flowers and leaves of *M.kurdica*.



Baytopine

Ether extracts of the three species were examined by TLC for phenolics. Benzoic, 2-hydroxy-6-methoxybenzoic and vanillic acids were identified as aromatic acids. Luteolin was present in all studied *Colchicum* and *Merendera* species as the flavon.

Özet

Bu çalışmada, Türkiye'de yetişen *Colchicum* and *Merendera* türleri üzerinde yapılan botanik ve fitokimyasal araştırmalar özetlenip sonuçları değerlendirilmiştir.

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