

CONSTITUENTS OF THE LEAVES OF *CYNARA CARDUNCULUS* L. NATURALIZED
AROUND SINOP

SİNOP YÖRESİNDE YABANİLEŞMİŞ OLARAK YETİŞEN *CYNARA CARDUNCULUS* L.
YAPRAKLARININ BİLEŞENLERİ

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Cynara scolymus is the species cultivated in Turkey as artichoke. The other species *C. cardunculus* is cultivated in Europe but not in Turkey and it is only found around Sinop naturalized. There isn't any reported investigation on this naturalized form of artichoke. In this study naturalized *C. cardunculus* leaves are investigated for its sesquiterpene lactones, flavonoids and phenolic acid compounds. As a result cynaropicrin as a sesquiterpene lactone compound, apigenin, apigenin-7-glycoside, luteolin-7-glycoside and naringenin-7-rutinoside as flavonoid compounds and chlorogenic acid as phenolic acid compound have been isolated and identified. Trace of cynarin which is the most important phenolic acid compound of *Cynara* species could be found.

Türkiye'de enginar olarak *Cynara scolymus* türünün kültürü yapılmaktadır. Diğer bir tür olan *C. cardunculus* ise Avrupa'da kültürü yapılan bir bitki olmasına karşılık yurdumuzda yetiştirilmemekte, sadece Sinop yöresinde yabanileşmiş halde bulunmaktadır. Yabanileşmiş bu tür üzerinde yapılmış kimyasal bir çalışma bulunmamaktadır. Bu çalışmada, yabanileşmiş olarak yetişen *C. cardunculus* yaprakları üzerinde sesquiterpen lakton flavon ve fenolik asit bileşikleri yönünden araştırma yapılmış ve sesquiterpen lakton olarak sinaropikrin, flavon bileşikleri olarak apigenin, apigenin-7-glikozit, luteolin-7-glikozit ve naringenin-7- rutinozot, fenolik asit bileşiği olarak ise klorojenik asit izole edilmiş ve tanımlanmıştır. *Cynara* türlerinin önemli fenolik asit bileşiği sinarin ise ancak eser miktarda bulunabilmiştir.

Keywords: *Cynara cardunculus* L.; Sesquiterpene lactone compounds; Flavonoids; Phenolic acid compounds; Cynaropicrin

Anahtar kelimeler: *Cynara cardunculus* L.; Sesquiterpen lakton bileşikler; Flavon bileşikler; Fenolik asit bileşikler; Sinaropikrin

Introduction

The immature flowering parts of *Cynara* species, especially two *Cynara* species known as *Cynara cardunculus* and *C. scolymus*, are used as vegetable since 15th century(1,2). *C. scolymus* is a Compositae plant which is cultivated widely in both Europe and Turkey and the other is *C. cardunculus* which is cultivated in Europe but not in Turkey. In Turkey it is only found around Sinop naturalized. The extracts of the leaves of these two species are used in phytomedicines for their hepatoprotective actions. These extracts stimulate bile flow, improve liver function, alleviate distension, reduce serum cholesterol, protect against arteriosclerosis, capture free radicals and protect the liver (3-10). The valuable compounds in the leaves of these two *Cynara* species are sesquiterpene lactone compounds especially cynaropicrin, phenolic acid compounds, particularly cynarin and flavonoid compounds of luteolin derivative(11-13).

The most important of these compounds is cynarin, a phenolic acid compound. It is mainly

responsible for the hepatoprotective action of the plant extract. Flavonoid compounds also take role in reducing serum cholesterol action and protecting against arteriosclerosis. Sesquiterpene lactone compounds have sitostatic actions (1,14,15).

The aim of this study was to isolate these important compounds if they were existing in the leaves of *Cynara cardunculus* which is naturalized around Sinop and has not been studied before.

Materials and Methods

Material: *Cynara cardunculus* L. is a plant to 1m. Leafless part of stem below capitulum short (1-4 cm). Leaves tomentose-arachnoid; cauline decurrent with long clustered spines, ovate lanceolate, deeply spiny dentate, each subtended by cluster of spines; lower leaves up to 50x30 cm. Capitula ovoid, 4-5 x 5 cm. Phyllaries greyish-green to purple with adpressed ovate basal part topering abruptly to involute 15-20 mm spine; outer spines reflexed middle pentat, inner phyllaries with narrowly ovate, spinose mucronate, erect appendages. Achenes 6x2 mm. Pappus 2-2.5 cm. Na-

turalized collected plant is from Sinop, Akliman. The material which was collected on 13th of August 1993 was identified by Prof.Dr. Ertan Tuzlacı (Herbarium Nr: MARE 4143)(16).

Methods: Necessary isolation methods for each chemical group were subjected to the leaves of *Cynara cardunculus*. These methods are given below:

Isolation of sesquiterpene lactone compounds and flavonoid aglycones: Air dried leaves (800 g) were extracted with petroleum ether:ether:methanol (1:1:1) at room temperature according to percolation rules. Combined extracts were concentrated to dryness in vacuo. The residue was dissolved in methanol and left in refrigerator for 48 hours. The precipitate was removed by filtration, the filtrate was evaporated and then it was dissolved in methanol, chromatographed over a silica gel column and eluted with increasing petroleum ether-ether mixture up to 100% ether and then with ether-methanol mixture up to 100% methanol. The fractions were controlled by TLC (toluene:acetone 6:4). Fractions were combined to give 143 mg cynaropicrin and 4.9 mg common flavonoid compound apigenin by preparative TLC. The structure of cynaropicrin was identified by comparison with authentic samples and with interpretation of its UV, IR, ¹H-NMR spectra. The structure of apigenin was identified by comparison with authentic samples and with interpretation of its UV and IR spectra. The spectral analysis results of a special sesquiterpene lactone compound cynaropicrin are given below.

Cynaropicrin : UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 225; IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} :

3400, 1750, 1730, 1645, 1600, 1580, 1275; ¹H-NMR (200 MHz, CHCl₃) δ : 2.99 [dd, J=7.8,3 Hz, H-1], 2.25 [dd J=13,7 Hz,H-2a], 1.73 [ddd J=13,11,7 Hz, H-2b], 4.57 [t, J=7 Hz, H-3], 2.85 [brt, J=10.5 Hz, H-5], 4.28 [dd, J=9,10 Hz, H-6], 3.20 [tt, J=3,6.9 Hz, H-7], 5.15 [dt, J=5.9 Hz, H-8], 2.72 [dd, J=5.15 Hz, H-9a], 2.40 [dd, J=5,15 Hz, H-9b], 6.22 [d, J=3 Hz, H-13], 5.63 [d, J=3Hz, H-13'], 4.95 (brs, H-14), 5,15 (brs, H-14'), 5.49 [t, J=1 Hz, H-15], 5.38 [t, J=1 Hz, H-15'], 6.34 (brs, H-17), 5.97 (brs, H-17'), 4.39 (brs, H-19).

Isolation of flavonoid glycosides: The residue material left after the extraction of sesquiterpene lactone compounds was dried and then extracted with ethanol in Soxhlet. Ethanol extracts were evaporated to dryness in vacuo. The residue was dissolved in water, transferred to a separating funnel and extracted with firstly chloroform then with ethyl acetate. Ethyl acetate extract was chromatographed over a silica gel column and eluted with toluene-ethanol mixture beginning from toluene-ethanol (7:1) up to (1:1). Three flavonoid glycosides were isolated. These were apigenin-7-glycoside (10 mg), luteolin-7-glycoside (12 mg) and naringenin-7-rutinoside (19 mg). The structures of these substances were identified by comparison with authentic samples and with interpretation of their UV and IR spectra.

The glycosides of flavonoids were subjected to acid

hydrolysis. Aglycones and sugars were controlled by

necessary chromatographic methods with authentic samples.

Isolation of phenolic acid compounds: Air dried leaves (100 g) were extracted with boiling alcohol under a reflux condenser for half an hour. Ethanol extract was evaporated and the residue was dissolved in petroleum ether-ethanol (1:2) mixture, transferred to a separating funnel and extracted with water. Water phase was evaporated without vacuo. The residue was dissolved in methanol, filtered and left for 24 hours. This methanol extract was precipitated with ether(12). Cynarin could only be identified chromatographically because trace of it was found in the extract. Chlorogenic acid was isolated from this extract. The structure of phenolic acid compound was identified by comparison with authentic samples and with interpretation of its UV and IR spectra.

Results and Discussion

In this study 4 flavonoid compounds were isolated from the leaves of *Cynara cardunculus* naturalized around Sinop. These were apigenin, apigenin-7-glycoside, luteolin-7-glycoside and naringenin-7-rutinoside. Trace of effective phenolic acid compound cynarin existed in the extracts. Chlorogenic acid was isolated and identified as major phenolic acid compound. Ample amount of sesquiterpene lactone compound cynaropicrin was isolated and identified.

As a result it was found that the leaves of *Cynara cardunculus* include ample amount of cynaropicrin and flavonoid compounds, but the plant is a poor cynarin source. At the same time as we investigated the leaves of *Cynara scolymus* we found out chromatographically that it includes more cynarin. On this situation it was understood that the leaves of *Cynara cardunculus* naturalized in Turkey can be utilized for its sesquiterpene lactone compounds and flavonoids.

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