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Cistus incanus a promising herbal tea rich in bioactive compounds: LC–MS/MS determination of catechins, flavonols, phenolic acids and alkaloids—A comparison with *Camellia sinensis*, Rooibos and Hoan Ngoc herbal tea

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ABSTRACT

Cistus incanus is called a medicine herbal plant due to its antimicrobial, anti-inflammatory, cytotoxic and anti-ulcerogenic properties. Considering these unique properties, quantification of the bioactive compounds of its infusion by liquid chromatography-tandem mass spectrometry is very important because of the rising consumption of this beverage. In this study the content of 28 phenolic compounds and theirs derivatives, alkaloids and vitamin B of water extract of *Cistus incanus* tea was examined and the results were compared with the results from other types of popular in the market teas. The *Cistus incanus* infusions were tested for content of flavanols, flavonols, organic acids, vitamin B and alkaloids and were compared with *Camellia sinensis,* Hoan Ngoc herbal tea and Rooibos infusions. *Camellia sinensis* infusions generally contained more catechins (1.56–82.65 mg/g) than *Cistus incanus* (1.02–2.73 mg/g) but there was no catechin-3-gallate in any *Camellia sinensis* infusions. Caffeine, theobromine and theophylline were found practically only in *Camellia sinensis* (6.22–14.19 mg/g) and Vietnamese herbal tea (2.97 mg/g) while trigonelline was found at higher concentrations in both *Cistus incanus* (6.29–14.34 μg/g) and Rooibos infusions (10.54–14.29 μg/g) than in *Camellia sinensis* infusions (0.30–2.88 μg/g). Principal component analysis revealed both similarities and differences among the infusions.

1. Introduction

Cistus is a perennial shrub, known also by its common name rock-rose. It is a part of relatively small family of *Cistaceae*: 180 species are divided into 8 genera. These 8 genera which make the family are: *Cistus* L., *Crocanthemum* Spach, *Fumana* (Dunal) Spach, *Halimium* (Dunal) Spach, *Helianthemum* Mill., *Hudsonia* L., *Lechea* L., and *Tuberaria* (Dunal) Spach. Despite the fact that *Cistaceae* family is associated mainly with the Mediterranean areas (Spain, Portugal, Greece, Morocco, France, and Turkey), three genera are found naturally across the ocean, in Mexico (*Crocanthemum* Spach and *Lechea* L.) and in the USA (*Hudsonia* L.) (Guzmán, and Vargas, 2009).

The extract from *Cistus* species has been used in folk medicine due to its antimicrobial, anti-inflammatory, cytotoxic and antiulcerogenic properties which were lately proved (Barrajon-Catalan et al., 2010; Küpeli and Yesilada, 2007; Yesilada et al., 1997). It has also been used in wound healing and as vasodilator remedy (Belmokhtar et al., 2009). It is worth noticing that not every *Cistus* species possess the whole range of properties listed above because composition of extract can be much different even in the same genera (Barrajón-Catalán et al., 2011).

The phenolic compounds of lyophilized extract of *Cistus incanus* and *monspeliensis* are: (+)-catechin, (–)-gallocatechin, and gallic acid (Santagati et al., 2008). *Cistus ladanifer, Cistus salviifolius, Cistus populifolius* and *Cistus libanotis* are specially rich in ellagitannins, *Cistus clusii, Cistus laurifolius* and *Cistus monspeliensis* contain significant amounts of flavonoids and much less ellagitannins. In contrast, *Cistus crispus, Cistus incanus* and *Cistus albidus* contain a phenolic profile mostly based on flavonoid compounds. Barrajón-Catalán et al. (2011) showed that *Cistus* subgenus and its chemotype evolutionarily separated from the two other subgenus (*Leucocistus* and *Halimioides*) and possess higher level of flavonoids.

Latest studies have shown that *Cistus incanus* herb contains gallocatechin-(4α→6)-gallocatechin-(4α→8)-gallocatechin and epigallocatechin-3-O-gallate-(4ß→8)-epigallocatechin-3-O-gallate-(4ß→8)-gallocatechin with potent anti-inflammatory properties (Mansoor et al., 2016). There is only little information available on the bioactive compounds such as catechins and alkaloids of this wild plant infusion determined by LC–MS/MS. Usually, the characterization of flavonoid

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Table 1
Names of the analytes, retention times (RT), polarity, the *m/z* values of their precursor and product ions and collision energies used for fragmentation.

No.	Analyte	RT [min]	Polarity	Precursor ion [m/z]	Product ion [m/z]	Collision energy [eV]
1	Quinic acid	1.11	–	191	85	−30
2	Succinic acid	1.54	–	117	73	−17
3	Gallic acid	1.97	–	169	125	−20
4	(-)-Gallocatechin	3.40	–	305	125	−31
5	Protocatechuic acid	3.50	–	153	109	−22
6	(+)-Catechin	5.95	–	289	245	−23
7	Chlorogenic acid	6.13	–	353	191	−30
8	Caffeic acid	6.47	–	179	135	−20
9	Syringic acid	6.79	–	197	182	−18
10	(-)-Epicatechin	6.95	–	289	245	−23
11	(-)-Epigallocatechin 3-gallate	7.26	–	457	169	−24
12	(-)-Gallocatechin 3-gallate	7.80	–	457	169	−24
13	p-Coumaric acid	8.07	–	163	119	−22
14	Ferulic acid	8.96	–	193	134	−25
15	Sinapic acid	9.15	–	223	208	−19
16	(-)-Epicatechin-3-gallate	9.44	–	441	169	−28
17	Rutin	9.51	–	609	301	−51
18	(-)-Catechin 3-gallate	9.90	–	441	169	−28
19	Salicylic acid	11.00	–	137	93	−25
20	Myricetin	12.13	–	317	151	−35
21	Quercetin	12.48	–	301	151	−33
22	Kaempferol	12.68	–	285	93	−50
1	Trigonelline	1.04	+	138	92	28
2	Nicotinamide	1.08	+	123	80	25
3	Nicotinic acid	1.12	+	124	80	28
4	Theobromine	1.60	+	181	110	31
5	Theophylline	2.09	+	181	96	34
6	Caffeine	3.36	+	195	138	30

compounds in methanol extract has been reported but without their quantification (Riehle et al., 2013).

It has been shown that aqueous extract from *Cistus incanus* prevent DNA cleavage *in vitro*, which may give rise to health beneficial properties in humans (Attaguile et al., 2000). Some studies presented anti-influenza properties of *Cistus incanus* extract as shown on mice and humans with the best results exhibited when it was used to prevent the disease (Droebner et al., 2007; Ehrhardt et al., 2007). *Cistus incanus* extract was effective in reducing the average duration and severity of symptoms in patients with infection of the upper respiratory tract and these results show the possibility to treat patients with severe respiratory infections (Kalus et al., 2009). The mechanism of action could be that the large molecules such as catechins and other compounds specific for *Cistus incanus* appear to bind pathogens and thus inhibit them from penetrating into human cells (Ehrhardt et al., 2007). Aqueous leaves extract of *Cistus ladaniferus* was effective in decreasing blood glucose levels in STZ-induced diabetic rats and showed hypolipidemic effect by a significant reduction in plasma lipid parameters (El Kabbaoui et al., 2016). This herbal tea has antibacterial properties because it decreases significantly the amount of bacteria in organisms (Hannig et al., 2009), reduces bacterial adhesion (Hannig et al., 2008) and shows the Gram-positive bacteria inhibition (Viapiana et al., 2017). In addition, the identification of antibacterial components of fraction from *Cistus incanus*, as apigenin, kaempferide, cis- and trans-tiliroside, and the isomers of the *p*-coumaric acid-conjugated tiliroside was lately presented (Móricz et al., 2018). The *in vivo* antioxidant effect of the flavonoid aglycones isolated from *Cistus laurifolius*, quercetin-3,7-dimethyl-ether and kaempferol-3,7-dimethyl-ether was shown in mice model (Küpeli et al., 2006). What is more, the cytotoxic activity against human cancer cells was also reported (Andrade et al., 2009; Barrajon-Catalan et al., 2010).

The aim of the study was to examine content of 28 phenolic compounds and their derivatives, vitamin B and alkaloids in *Cistus incanus* herb available on the Polish market and compare the results with other types of teas (*Camellia sinensis*) and Rooibos herbal tea (*Aspalathus linearis)* available on the Polish market, as well as with the Hoan Ngoc herbal tea (*Pseuderanthemum palatiferum*) product available in Vietnam. The ultra-high performance liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS) was used for the analysis of these products because this technique can provide information about the exact concentrations of phenolic compounds and alkaloids. As a result it can be concluded which of them has a wider range of compounds that can benefit human immune system.

2. Materials and methods

2.1. Chemicals

(-)-Gallocatechin, (+)-catechin, (-)-epicatechin, (-)-epigallocatechin 3-gallate, (-)-gallocatechin 3-gallate, (-)-epicatechin-3-gallate, (-)-catechin 3-gallate, myricetin, quercetin, kaempferol, rutin, quinic acid, succinic acid, gallic acid, potocatechuic acid, chlorogenic acid, caffeic acid, syringic acid, p-coumaric acid, ferulic acid, sinapic acid, salicylic acid, trigonelline, nicotinamide, nicotinic acid, theobromine, theophylline and caffeine standards were purchased from Sigma-Aldrich (Steinheim, Germany) with the highest possible purity. MS-grade acetonitrile and methanol were supplied by POCH (Gliwice, Poland) and MS-grade formic acid was obtained from Sigma-Aldrich.

Highly purified water (the resistivity 18 MΩ cm) used throughout the study was obtained by deionization in the DEMIWA 5 ROSA system (Watek, Czech Republic) and double distillation in the Bi18 quartz apparatus (Heraeus, Hanau, Germany).

2.2. Liquid chromatography–mass spectrometry

The UltiMate 3000 RSLC chromatographic (Dionex, Sunnyvale, CA, USA) was used. 5 μL samples were injected into a Kinetex Evo C18 column (150 mm × 2.1 mm I.D.; 2.6 μm) (Phenomenex, Torrance, CA, USA) maintained at 35 °C. The mobile phase employed in the analysis consisted of 0.1% formic acid in water (A) and acetonitrile (B) at a flow rate of 0.3 mL/min in a gradient given in Supplementary Table 1. The LC column effluent was directed to the electrospray ionisation source