Hydrodistillation of *Trachelospermum jasminoides* Lindl. flowers. An analysis of essential oil, hydrolate and polyphenols content of the process wastes.

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ABSTRACT

Trachelospermum jasminoides (Lindl.) is a woody evergreen plant of the Apocynaceae family mainly used as ornamental/hedge plant. Its stems and leaves are used in traditional Chinese medicine with the name of "*Luoshiteng*". Although some studies have been devoted to the phytochemistry of *luoshiteng*, little is known about the chemical composition of its flowers. In this study, the volatile composition of the flowers of *T. jasminoides* has been studied. The Gas chromatographic - Mass spectrometry analysis (GC/FID-MS) of the essential oil and hydrolate allowed identifying 43 compounds with linalool as main compound for both of them. Phytochemical investigation was completed by the High Performance Liquid Chromatography – Mass spectrometry (HPLC/DAD-ESI-MS) analysis of hydrodistillation wastes (liquid and solid) which revealed the presence of biologically active compounds such as chlorogenic acids and other polyphenols. This study contributes to the definition of the phytochemistry of *T. jasminoides* and provides the first data on the composition of the hydrodistillation wastes preparatory to their valorisation in the future.

KEYWORDS

Trachelospermum jasminoides, hydrodistillation, essential oil, hydrolate, polyphenols, wastes.

1. Introduction

Trachelospermum jasminoides (Lindl.) (*T. jasminoides*) is a lianas woody plant of the family Apocynaceae and mainly spread throughout in the Southern Chinese province of the Yangtze River (1). It is an evergreen plant, robust and with prolonged abundant flowering from spring to early summer. These features have made it very common as an ornamental/hedge plant all over the world. Its stems and leaves are a traditional Chinese medicine known as "Luoshiteng" due to their biological activities (2). Several studies have been conducted to elucidate the phytochemistry of this medicinal plant (3-5) and to consolidate its traditional pharmaceutical activities. Some compounds of ethanolic extract of *T. jasminoides* are able to suppress the lipopolysaccharide (LPS) stimulated inflammatory responses in macrophages (6). Likewise, its water extract is an effective anti-inflammatory agent in carr-induced inflammation exerting its anti-inflammatory effects by suppressing TNF-α and nitric oxide serum levels (7). Furthermore, antitumor and antiviral activities of the water/ethanolic extracts or their single compounds have been reported (8). Up to now, only one study was published on the composition of *T. jasminoides* volatile fraction (9) and none on the chemical composition of the non-volatile fraction of its flowers. *T. jasminoides* flowers contain metabolites with biological activity as per as the wastes (liquid and solid) of their hydrodistillation. The aim of this study is to contribute to the knowledge on volatile and non-volatile chemical composition of the flowers of *T. jasminoides* collected in the southern part of Italy (Eastern Sicily) by means the study of their essential oil (EO) and hydrolate (Hyd), together with the polyphenols content of the solid residue extracted with ethyl acetate (AcSR), ethanol (EtSR) and lyophilized water waste (lyoWW) obtained from the hydrodistillation process.

2. Experimental section

2.1 Chemicals

All solvents used were high-purity American Chemical Society (ACS) solvents from VWR (Milan, Italy); acetonitrile and water (VWR, Milan, Italy) were of HPLC grade. Pure reference standards: Caffeic acid, *p*-Coumaric acid, Quercetin-3-*O*-rutinoside and Luteolin were obtained from Fluka (Milan, Italy); volatile standards were purchased from Aldrich Chemical Co., Extrasynthese (Lyon, France) and Fluka (Milan, Italy).

2.2 Plant material

Samples of the flowers of *T. jasminoides* were collected in a private garden located in Catania (Sicily), GPS 37, 577450N 15,101926E. The sampling has been carried out in the early mornings during the month of May 2019. Samples after rapid transportation to the lab were immediately hydrodistilled. The sample was identified and botanically classified by the Department of Biological, Geological and Environmental Sciences of the University of Catania. A voucher specimen was photographed, dried and stored in the herbarium of the Institute of Biomolecular Chemistry of Catania, with the number 0001/2019.

2.3 Hydrodistillation and GC-FID, GC-MS analysis of essential oil and hydrolate

Fresh flowers (248 g) were subjected to hydrodistillation in a Clavenger-type apparatus with 2 L for 3 hours. The oil (0.3 ml) was recovered with 1 ml of hexane and stored under N_2 in a sealed vial until required. The hydrolate was recovered from the apparatus and immediately the volatile part was extracted shakering 5 ml of water solution with 1 ml of hexane. After separation, the organic phase was immediately injected to the gas chromatographer. Gas chromatographic (GC) analyses were run on a Shimadzu gas chromatograph, Model 17-A equipped with a flame ionization detector (FID). The analytical conditions and oven temperature were the same as those reported previously (10). Percentages of compounds were determined from their peak areas in the GC-FID profiles. Gas-chromatography-mass spectrometry (GC/MS) was carried out in the fast mode on a Shimadzu GC/MS mod. GCMS-QP5050A, with the same column and the same operative conditions used for analytical GC-FID. The identity of components was confirmed on the basis of their GC retention index (relative to C_9-C_{20} *n*-alkanes on SPB-5 column), computer matching of spectral MS data as already reported (11-12) and whenever possible, co-injections with authentic samples.

2.4 Filtration of hydrodistillation water waste

The hydrodistillation water wastes (2L) were cooled at room temperature and then filtered on filter paper (Whatman, cat. n° 1004-930, grade 4). After filtration was frozen up to -18°C and then freeze-dried. 16.53 g of lyophilized powder (lyoWW) was obtained.

2.5 Extraction of hydrodistilled solid residue

The solid residue obtained from hydrodistillation was air dried at room temperature up to no difference of weight was observed. 27.54 g of solid residue was obtained. 1.58 g of this residue were finely ground and then defatted with 30 ml of hexane (24 hours under stirring). After filtration, the defatted residue was extracted with 30 ml of Ethyl acetate (24 hours, under stirring) and then filtered

on filter paper. 1 ml of this solution was filtered on on PTFE 0.45 mm filters (PALL Corporation), and put into 2 mL amber vials for HPLC analysis (AcSR). The solid residue was further extracted with 30 ml of ethanol (24 hours, under stirring) and then filtered on filter paper. 1 ml of this solution was filtered on on PTFE 0.45 mm filters (PALL Corporation), and put into 2 mL amber vials for HPLC analysis (EtSR).

2.6 HPLC-DAD and HPLC-ESI-MS analysis of water waste and extracts

Lyophilized water wastes and the solid residue extracts were analysed for their polyphenol content on an Ultimate3000 equipped with a binary high-pressure pump and a photodiode array detector Thermo Scientific, Italy). The data were processed through the Chromeleon Chromatography Information Management System v. 6.80. All chromatographic runs were performed using a reverse-phase column (Gemini C_{18}, 250 x 4.6 mm, 5 μm particle size, Phenomenex, Italy). Samples were eluted with a gradient of 5%-90% buffer B (2.5% formic acid in acetonitrile) over 50 min after which the system was maintained for 7 min at 100% Buffer B (13). The solvent flow rate was 1 mL/min. Quantifications were carried out as follows: at 330 nm for cinnamic acids using Caffeic acid and *p*-Coumaric acid as standards (R^2 = 0.9997 and R^2 = 0.9996 respectively) and 350 nm for Quercetin derivatives using Quercetin-3-*O*-rutinoside (R^2 = 0.9962) and Luteolin (R^2 = 0.9998) as standards. LC-MS analysis were performed using the same HPLC apparatus described above, whilst the ESI mass spectra were acquired using a Exactive Plus Orbitrap MS (Thermo Fisher Scientific, Inc., Milan, Italy), and a heated electrospray ionization interface. Mass spectra were recorded while operating in the negative ion mode, in the m/z range 120-1500 at a resolving power of 25000 (full-width-at-half-maximum at m/z 200). This was performed under the conditions already reported in a previous study (24). Data acquisition and analyses were performed using the Excalibur software.

3. Results and discussion

3.1 Essential oil and hydrolate chemical composition

The yield in EO is very low (0.12 % v/w) compared with the only data reported in literature (9), but nevertheless the GC-MS analysis allows to identify 43 components covering 73.11% of the total composition of the essential oil (see Table 1, and Figure 1). Also the chemical composition seems to be very different. The essential oil composition of the sample collected in Italy shows a predominance of oxygenated monoterpenes (almost 42%), followed by sesquiterpenes (almost 17%). Both monoterpene hydrocarbons and other compounds are below 10%. In the Italian sample the main compound is linalool (26.2%) followed by geranyl propanate (8.7%) and *Z*-jasmone (7.3%). *cis*-Farnesol (5.1%), *trans*-nerolidol (3.3%), limonene (3.0%) and α-terpineol (2.6%) complete the main

compounds list. It is not easy to draw conclusions about the compositional differences of essential oils when the available comparative data are so lacking. What is certain is that the chemical composition of an oil is strongly conditioned by the pedoclimatic conditions in which the plant grows. The chemical composition of the essential oil sampled in the south of Italy lets one incline towards the presence of a different chemotype in this case, linalool-chemotype. Moreover, even in Pansanit and Pripdeevech (9) work significant compositional differences emerge in two samples from different regions of Thailand. Unfortunately, the lack of further phytochemical data does not allow to confirm this hypothesis as well as to enlarge the comparative considerations.

Under a biological point of view, the high percentage of linalool present in the EO of *T. jasminoides* flowers makes it interesting for the potential application in the medical field. Linalool is a monoterpene alcohol with anti-inflammatory and anti-oxidant properties. A recent study indicates the linalool may be therapeutically useful in treating neurodegenerative conditions due to its beneficial impact on mitochondrial integrity as well as ability to limit oxidative stress (15). Linalool effectively exerts a protective role in ovalbumin-induced airway inflammation and its protective effects are closely related to the downregulation of inflammatory mediators and MAPKs/NF-κB signalling (16). Interesting is the recent study on effective protection of intranasal linalool in ischemic rats (17).

Hydrolates consist of the water saturated with the more hydro soluble fraction of the EO and contain biologically active volatile compounds. In the case of plants with a low content of essential oils, as in our case, could be difficult isolate the essential oil and hydrolates could be considered an interesting secondary product or by-products. Hydrolates have a much softer scent and lower biological activity than the corresponding essential oils but certain of them also show antimicrobial properties (18). Chemical composition of hydrolate obtained from Italian sample is dominated by oxygenated monoterpens. This class cover more than 78% of the total hydrolate composition. Monoterpene hydrocarbons and sesquiterpenes are absent and the other compounds are below 6%. For the same reasons of the EO, the high presence of linalool (45.7%, see Table 1 and Figure1) in the hydrolate of Italian *T. jasminoides* makes this secondary product potentially of great interest in the pharmacological and microbiological field.

3.2 Polyphenol composition of water and solid wastes of the hidrodistillation process

The hydrodistillation process produce two kind of wastes. The water in contact with the plant material and the plant solid residue. Hydrodistillation, as well as steam distillation, is a long and high-energy consumption process. For this reason, in recent years the interest in the possibility to exploit the waste of these industrial processes has intensified. The large volume of by-products generating during distillation is nowadays a concern that some industries try to overcome by producing energy or

compost from the biomass (19). In reality, these by-products are rich of fine chemicals and pharmaceutical building blocks, which can be valued in another way if identified and quantified. They can contain both biologically active thermostable substances and fragments of molecules generated mainly by thermal degradation that still maintain a high biological activity. In this study, the polyphenolic profile of *T. jasminoides* flowers hydrodistillation wastes has been analysed and results are summarized in Table 2. The lyophilized water waste (lyoWW) profile (Figure 2) is dominated by three compounds (1, 3 and 4, table 2); UV and mass spectra allow to identify these components as caffeoylquinic acids derivatives. They represent the 6% w/w of the lyophilized powder obtained from hydrodistillation. Traces of other biologically active compounds in lyoWW such as quercetin-3-*O*-rutinoside (8) has been also recorded. Identification of caffeic acid (5) and quercetin-3-*O*-rutinoside (8) was based on the comparison of their UV, mass spectra and retention times with those of reference substances. Luteolin-7-*O*-glucoside (13), quercetin (15) and luteolin (16) have been identified in AcSR and EtSR (Table 2) at quantitative level lower than 1 mg in 1 g of dried solid residue. For the quantity and quality of polyphenols content, the lyoWW seems to be the more interesting waste fraction due the presence mainly of chlorogenic acids which have wide biological activities, including anti-oxidant, anti-inflammatory and neuroprotective (20-21). These compounds have been detected in other flowers extracts and infusions also used in traditional medicine as a folk remedy (22-24).

4. Conclusions

This work is the first complete study on the volatile and non-volatile chemical profiles of *T. jasminoides* flowers growing in the South of Italy. The volatile composition of the flowers has been studied by means of the gas chromatographic analysis of the essential oil and the hydrolate (an interesting secondary product of the distillation of this plant) both rich in linalool. In addition, the problem of the exploitation of the distillation wastes was addressed in this study. Through the analysis of the polyphenols content of the lyophilized water wastes and of the solid plant residue, this study shows that part of the biologically active chemical profile, mainly chlorogenic acids, remains after the thermal treatment of hydrodistillation maintaining its interest for an exploitation and potential use in the pharmaceutical and cosmetic fields.

Acknowledgements

Thanks are due to Mr. Antonio Greco (ICB-CNR, Catania) for his skilful technical assistance.

REFERENCES

1. H. Wang, X. Cheng, W. Chen, L. Li and L. Chen, *Complete plastome sequence of Trachelospermum jasminoides (Lindley) Lemaire (Apocynaceae)*, Mitochondrial DNA B, **4**(1), 2086-2087 (2019**)**.

2. J. Zhang, Z. Yin and J. Liang, *A new isoflavonoid glycoside from the aerial parts of Trachelospermum jasminoides,* Chin. J. Nat. Med., **11**(3), 274-276 (2013).

3. A. Sakushima and S. Nishibe, *Taxifolin 3-Arabinoside from Trachelospermum jasminoides var. pubescens,* Phytochemistry, **27**(3), 948-950 (1988).

4. L. Jing, N. J. Yu, Y. S. Li, L. Fu and Y. M. Zhao, *Novel lignans from the stems and leaves of Trachelospermum jasminoides*, Chin. Chem. Lett.**, 22**, 1075-1077 (2011).

5. J. Zhang, Z. Q. Yin and J. Y. Liang, *Flavonoids from Trachelospermum jasminoides,* Chem. Nat. Comp. **49**(3), 507-508 (2013).

6. J. N. Choi, Y. Choi, J. Lee, I. C. Noh, J. W. Park, W. S. Choi and J. H. Choi, *Anti-inflammatory effects of β-sitosterol-β-D-glucoside from Trachelospermum jasminoides (Apocynaceae) in lipopolysaccharide stimulated RAW 264.7 murine macrophages*, Nat. Prod. Res.**, 26**(24), 2340-2343 (2012).

7. M. Sheu, P. Chou, H. Cheng, C. Wu, G. Huang, B. Wang, J. Chen, Y. Chien and M. Huang, *Analgesic and anti-inflammatory activities of a water extract of Trachelospermum jasminoides (Apocynaceae)*, J. Ethnopharmacol.**, 126**, 332-338 (2009).

8. Z. Zhao, X. He, Y. Zhao, Y. Sun, X. Chen, Y. Cun, L. Huang, Y. Bai and X. Zheng, Phytochemistry, pharmacology and traditional uses of plants from the genus *Trachelospermum* L., Molecules**, 22,** 1406 (2017).

9. A. Pansanit and P. Pripdeevech, *Constituents, antibacterial and antioxidant activities of essential oils from Trachelospermum jasminoides flowers*, Nat. Prod. Comm.**, 9**(12), 1791-1794 (2014).

10. T. Tuttolomondo, G. Dugo, G. Ruberto, C. Leto, E. M. Napoli, A. G. Potorti, M. R. Fede, G. Virga, R. Leone, E. D'Anna, M. Licata and S. La Bella, *Agronomical evaluation of Sicilian biotypes of Lavandula stoechas L. spp. stoechas and analysis of the essential oils*, J. Ess. Oil Res. **27**(2), 115-124 (2015).

11. S. La Bella, T. Tuttolomondo, G. Dugo, G. Ruberto, C. Leto, E. M. Napoli, A. G. Potorti, M. R. Fede, G. Virga, R. Leone, E. D'Anna and M. Licata, *Composition and variability of the essential oil of the flowers of Lavandula stoechas from various geographical sources*, Nat. Prod. Comm., **10**(11), 2001-2004 (2015).

12. R. P. Adams, 'Identification of Essential Oil Components by Gas Chromatography/Mass Spectrometry', Allured Publ. Corp. **2007**, Carol Stream, IL, USA.

13. A. Saija, A. Speciale, D. Trombetta, C. Leto, T. Tuttolomondo, S. La Bella, M. Licata, G. Virga, G. Buonsangue, M. C. Gennaro, E. Napoli, L. Siracusa and G. Ruberto,

Phytochemical, ecological and antioxidant evaluation of wild Sicilian Thyme: Thymbra capitata (L.) Cav, Chem. Biodivers., **13**, 1641e1655 (2016).

14. E. Napoli, L. Siracusa, G. Ruberto, A. Carrubba, S. Lazzara, A. Speciale, F. Cimino, A. Saija and M. Cristani, *Phytochemical profiles, phototoxic and antioxidant properties of eleven Hypericum species: a comparative study*, Phytochemistry, **152**, 162-173 (2018).

15. A. M. Sabogal-Guáqueta, F. Hobbie, A. Keerthi, A. Oun, A. Kortholt, E. Boddeke and A. Dolga, *Linalool attenuates oxidative stress and mitochondrial dysfunction mediated by glutamate and NMDA toxicity*, Biomed. Pharmacother., **118**, 109295 (2019).

16. M. G. Kim, S. M. Kim, J. H. Min, O. K. Kwon, M. H. Park, J. W. Park, H. I. Ahn, J. Y. Hwang, S. R. Oh, J. W. Lee and K. S. Ahn, *Anti-inflammatory effects of linalool on ovalbumin-induced pulmonary inflammation*, Int. Immunopharmacol., **74**, 105706 (2019).

17. A. M. Barrera-Sandoval, E. Osorio and G. P. Cardona-Gomez, *Microglial-targeting induced by intranasal linalool during neurological protection postischemia*, Eur. J. Pharmacol., **857**, 172420 (2019).

18. R. Prusinowska, K. Smigielski, A. Stobiecka and A. Kunicka-Styczynska, *Hydrolates from lavender (Lavandula angustifolia) – their chemical composition as well as aromatic, antimicrobial and antioxidant properties*, Nat. Prod. Res., **30**(4), 386-393 (2016).

19. I. Mendez-Tovar, B. Herrero, S. Perez-Magarino, J. A. Pereira, S. Asensio and M. C. Manzanera, *By-product of Lavandula latifolia essential oil distillation as source of antioxidants*, J. Food Drug. Anal., **23**, 225-233 (2015).

20. Y. Mei, D. Pan, Y. Jiang, W. Zhang, X. Yao, I. Dai, Y. Yu and X. Yao, *Target discovery of chlorogenic acid derivatives from the flower buds of Lonicera macranthoides and their MAO B inhibitory mechanism*, Fitoterapia, **134**, 297-304 (2019).

21. P. Wan, M. Xie, G. Chen, Z. Dai, B. Hu, X. Zeng and Y. Sun, *Anti-inflammatory effects of dicaffeoylquinic acids from Ilex kudingcha on lipopolysaccharide-treated RAW264.7 macrophages and potential mechanisms*, Food Chem. Toxicol., **126**, 332-342 (2019).

22. I. Jabeur, E. Pereira, C. Caleja, R. C. Calhelha, M. Sokovic, L. Catarino, L. Barros and I. C. F. R. Ferreira, *Exploring the chemical and bioactive properties of Hibiscus sabdariffa L. calyces from Guinea-Bissau (West Africa)*, Food Funct., **10**, 2234 (2019).

23. A. Kicel, A. Owczarek, P. Gralak, P. Ciszewski and M. A. Olszewska, *Polyphenolic profile, antioxidant activity, and pro-inflammatory enzymes inhibition of leaves, flowers, bark and fruits of Cotoneaster integerrimus: A comparative study*, Phytochem. Lett., **30**, 349-355 (2019).

24. A. Piovesana, E. Rodrigues and C. P. Zapata Norena, *Composition analysis of carotenoids and phenolic compounds and antioxidant activity from hibiscus calyces (Hibiscus sabdariffa L.) by HPLC-DAD-MS/MS*, Phytochem. Anal., **30**, 208-217 (2018).

305 Table 1. Chemical composition of Sicilian *T. jasminoides* essential oil and hydrolate

#[a]	RI[b]	RI[c]	Components	% Essential oil	% Hydrolate
1	830	859	3*Z*-Hexenal	-	1.78 (±0.01)
2	842	862	2*E*-Hexenol	-	1.33 (±0.01)
3	971	979	octen-3-ol	0.34 (±0.02)	1.48 (±0.01)
4	979	985	6-methyl-hepten-2-one	0.23 (±0.01)	0.78 (±0.01)
5	982	990	myrcene	1.20 (±0.00)	-
6	1011	1024	*p*-cymene	0.26 (±0.00)	-
7	1019	1026	*o*-cymene	0.11 (±0.01)	-
8	1024	1029	limonene	2.95 (±0.01)	-
9	1033	1037	*cis*-ocimene	0.15 (±0.00)	-
10	1055	1050	*trans*-ocimene	0.28 (±0.00)	-
11	1072	1072	*cis*-linalool oxide	-	1.60 (±0.03)
12	1084	1088	terpinolene	0.59 (±0.01)	-
13	1087	1090	dehydro-linalool	-	4.37 (±0.03)
14	1097	1096	linalool	26.24 (±0.04)	45.67 (±0.11)
15	1111	1111	6-camphenol	0.20 (±0.00)	-
16	1118	1122	*trans*-*p*-mentha-2,8-dien-1-ol	-	5.82 (±0.10)
17	1133	1137	*cis*-*p*-mentha-2,8-dien-1-ol	0.58 (±0.09)	3.87 (±0.12)
18	1151	1159	citronellal	0.08 (±0.00)	-
19	1165	1170	*p*-mentha-1,5-dien-8-ol	-	0.51 (±0.00)
20	1173	1177	terpinen-4-ol	0.65 (±0.01)	1.42 (±0.01)
21	1186	1188	α-terpineol	2.57 (±0.01)	11.42 (±0.05)
22	1194	1196	*cis*-piperitol	0.27 (±0.01)	-
23	1204	1205	verbenone	0.18 (±0.01)	2.51 (±0.07)
24	1212	1223	linalool formate	0.18 (±0.00)	-
25	1222	1229	nerol	0.77 (±0.01)	-
26	1247	1252	geraniol	1.00 (±0.13)	-
27	1248	1243	carvone	-	0.84 (±0.11)
28	1265	1265	geranial	0.36 (±0.01)	-
29	1298	1299	geranyl formate	0.21 (±0.01)	-
30	1301	1299	carvacrol	-	0.84 (±0.03)
31	1302	1324	*E*-jasmonol	0.12 (±0.01)	-
32	1325	1335	δ-elemene	0.32 (±0.00)	-
33	1330	1341	5-indanol	0.63 (±0.00)	-
34	1358	1364	eugenol	0.09 (±0.01)	-
35	1376	1390	α-copaene	0.40 (±0.00)	-
36	1382	1391	*E*-jasmone	0.30 (±0.00)	-
37	1403	1419	*Z*-jasmone	7.30 (±0.21)	-
38	1430	1439	α-guajene	0.60 (±0.01)	-
39	1436	1444	6,9-guaiadiene	0.67 (±0.01)	-
40	1439	1457	alloaromadendrene	0.94 (±0.01)	-
41	1462	1495	γ-amorphene	1.19 (±0.00)	-
42	1483	1505	geranyl propanoate	8,66 (±0.03)	-
43	1498	1506	valencene	0.18 (±0.01)	-
44	1508	1519	δ-cadinene	0.38 (±0.01)	-
45	1535	1532	*trans*-nerolidol	3.28 (±0.21)	-
46	1557	1583	caryophyllene oxide	0.18 (±0.00)	-
47	1566	1595	β-calacorene	2.18 (±0.06)	-
48	1684	1698	*cis*-farnesol	5.11 (±0.27)	-
49	1790	1822	farnesyl acetate	1.38 (±0.25)	-
			Monoterpenes hydrocarbons	**5.28**	**-**
			Oxygenated monoterpenes	**41.95**	**78.87**
			Sesquiterpenenes	**16.81**	**-**
			Others	**9.07**	**5.37**
			Total	**73.11**	**84.24**

306 [a] The numbering refers to elution order, and values (relative peak area percent) represent averages of 3 determinations [b] Retention index relative to standard
307 mixture of *n*-alkanes on SPB-5 column; [c] Retention index from literature.
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311 Table 2. Main polyphenols identified in *T. jasminoides* hydrodistillation wastes

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# peak	RT min.	Compound	HPLC-DAD λ-max (nm)	ESI(-)-MS	Mass Accuracy Values (ppm)	ESI(-)-MS fragments	mg/g of lyoWW	mg/g of AcSR	mg/g of EtSR
1	7.13	Caffeoylquinic acid derivative	243, *sh*295, 324	353.083	11.3	191.053, 179.034	20.3	-	-
2	9.21	*p*-Coumaroylquinic acid	310	337.089	8.3	-	0.62	-	-
3	10.24	Caffeoylquinic acid derivative	243, *sh*300, 325	353.083	11.3	173.044	18.13	-	-
4	10.89	Caffeoylquinic acid derivative	243, *sh*300, 325	353.083	11.3	191.053	20.15	-	-
5	11.82	Caffeic acid	244, *sh*300, 322	179.032	10.6	135.044	0.72	-	-
6	12.80	*p*-Coumaroylquinic acid	311	337.089	8.3	191.054	0.43	-	-
7	14.07	*p*-Coumaroylquinic acid	313	337.089	8.3	191.054	0.,89	-	-
8	19.80	Quercetin-3-*O*-rutinoside	255, 353	609.138	11.5	301.918	0.58	-	-
9	20.68	Quercetin-3-*O*-glucoside	255, 353	463.082	11.0	301.918	0.88	-	-
10	21.21	Quercetin-3-*O*-galactoside	255, 351	463.082	11.0	301.918	1.71	-	-
11	21.71	di-caffeoylquinic acid	242, *sh*300, 332	515.113	10.5	190.927, 178.975	2.32	-	-
12	22.87	di-caffeoylquinic acid	242, *sh*300, 326	515.113	10.5	190.927, 178.975	1.06	-	-
13	24.06	Luteolin-7-*O*-glucoside	255, 348	447.088	9.4	285.907	-	0.08	0.08
14	24.84	Quercetin rhamnoside	255, 350	447.088	9.4	301.915	1.15	-	-
15	33.29	Quercetin	254, 370	301.032	7.6	-	-	0.98	0.21
16	34.99	Luteolin	253, 265, 346	285.037	8.4	-	-	0.37	0.17

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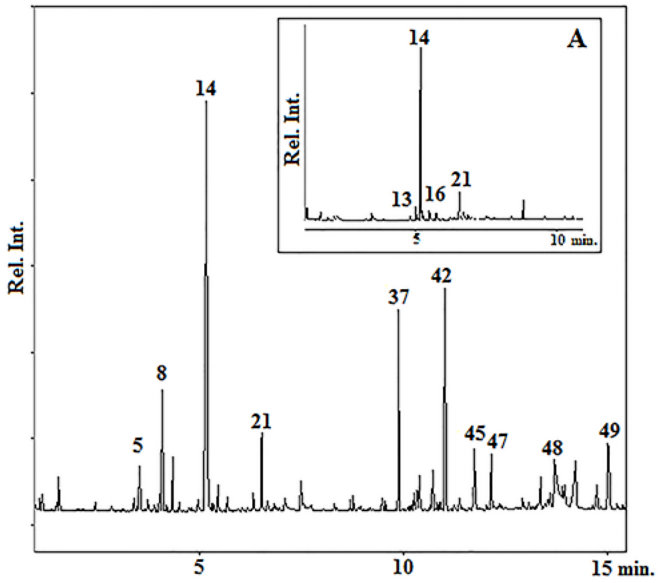

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315 **Figure 1.** GC-MS chromatograms of *T. jasminoides* essential oil and hydrolate in the box A.

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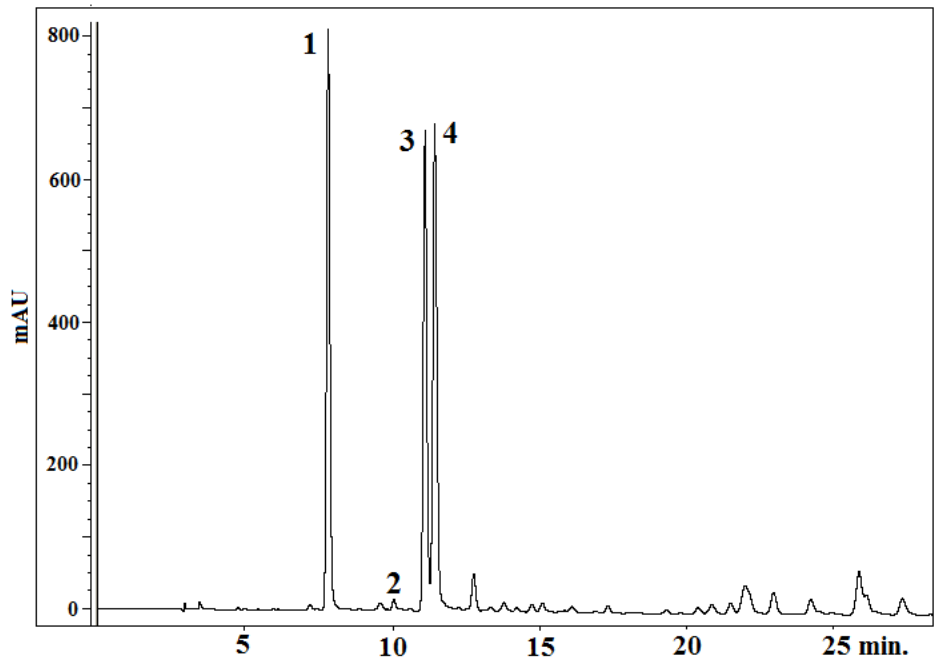

317

318 **Figure 2.** HPLC-DAD chromatogram of the lyophilized hydrodistillation waste of *T. jasminoides.*

319