Revista Brasileira de Farmacognosia 28 (2018) 626–630

Brazilian Journal of Pharmacognosy
REVISTA BRASILEIRA DE FARMACOGNOSIA
www.elsevier.com/locate/bjp

Original Article

Thermal and chemical characterization of *Dicksonia sellowiana* extract by means of thermal analysis

Lucca C. Malucelli[a], Tadeu Massulo[b], Washington L.E. Magalhães[c], Nayana C.F. Stofella[d], Eliane C. Vasconcelos[a,b], Marco Aurélio S. Carvalho Filho[a,b], Fábio S. Murakami[d,*]

[a] *Programa de Pós-graduação em Gestão Ambiental, Universidade Positivo, Curitiba, PR, Brazil*
[b] *Programa de Pós-graduação em Biotecnologia Industrial, Universidade Positivo, Curitiba, PR, Brazil*
[c] *Embrapa Florestas, Colombo, PR, Brazil*
[d] *Programa de Pós-graduação em Ciências Farmacêuticas, Departamento de Farmácia, Universidade Federal do Paraná, Curitiba, PR, Brazil*

ARTICLE INFO

Article history:
Received 17 April 2018
Accepted 10 July 2018
Available online 1 August 2018

Keywords:
Thermogravimetry
Thermal behavior pyrolysis
Thermal disposal

ABSTRACT

Dicksonia sellowiana Hook., Dicksoniaceae, is a tree-fern which is being recently used in medicine mainly for its phytotherapic activities. While several other studies have focused on *D. sellowiana* extract characterization in terms of its biological and antioxidant activity, the novelty of this work aims to understand the fate of this extract during thermal disposal through thermogravimetry/differential thermal analysis, thermogravimetry/mass spectrometry, Fourier transform infrared spectroscopy and elemental analysis, to further characterize this plant's extract. Thermal analysis revealed mass loss within three well-defined steps, with the respective mass signals represented generated during heating. Light-volatiles were released during the first step, with release of NO_2, CO_2, and ethanol in the following, as a result of extract pyrolytic decomposition. Furthermore, mass signals variation during heating indicated the release of harmless by products in contrast to other pharmaceutical and personal care products. Finally, chemical characterization confirmed the observed under thermal analysis suggesting a highly polar structure within extract's composition.

Introduction

Popularly known in Brazil as "xaxim" or "samambaiaçu" (Tidwell et al., 1970; Rogge et al., 1999), *Dicksonia sellowiana* Hook., Dicksoniaceae, is a plant widely distributed in Central and South America (Fernandes, 2000). This plant trunk has been used to prepare vases, stakes, plates, dust, and substratum for ornamental plants (Gomes et al., 2006). While indigenous population have been using *D. sellowiana* parts to treatment, mainly against scabies, pruritus, parasitic diseases and asthma use in medicine is quite recent. Its intense growth and harvest leaves the plant as one of the most endangered species in Brazil (Gomes et al., 2006; Ibama, 2008).

A growing interest has been given on studying this plant's by products, as they presented antioxidant and biological activity, showing potential as active compounds in medicine (Rattmann et al., 2009, 2011). From a previous study, it was possible to verify that the best extraction method, according to yield, polyphenolics, flavonoids, proanthocyanidins and steroids content, was the one through Soxhlet extraction, thus used in this study and described elsewhere (Oliveira et al., 2016).

Thermal analysis becomes an important tool for characterization dry extracts and plant products. Thermogravimetry (TG), differential thermal analysis (DTA) and mass spectrometry (MS) has been used to provide information regarding decomposition and volatiles evaporation of raw materials and pharmaceuticals as a function of time and temperature. Recent studies have shown the applications of different thermal analysis techniques in pharmaceutical technology and characterization of dry extracts from medicinal plants (Lemes et al., 2018; Santana et al., 2018). Cuinica and Macêdo (2018) reported the characterization of *Urtica dioica*, Urticaceae, drug samples and its extracts by thermal methods and Leite et al. (2018) have been applied TG/DTA in order to study dry extracts of *Myracrodruon urundeuva*.

Furthermore, MS can reveal the nature of released volatiles under sample's heating, thus aiding in the interpretation of results obtained from thermal degradation (Zayed et al., 2017). For example, thermal analysis has been used to study the behavior of pharmaceuticals degradation products during drug disposal after its expiration since toxic by-products may be released during thermal degradation (Colman et al., 2016).

---

[*] Corresponding author.
E-mail: fsmurakami@ufpr.br (F.S. Murakami).

https://doi.org/10.1016/j.bjp.2018.07.001

While the aforementioned studies have been focused on *D. sellowiana* pharmacological and biological action for phytotherapic activities in medicine, neither of them have attempted to assess its behavior during thermal decomposition, and also its chemical structure and properties, which should influence on its effect on organism.

Therefore the novelty of this work is to understand its behavior under simulated thermal disposal by means of thermogravimetry/mass spectrometry (TG-MS) and thermogravimetry/differential thermal analysis (TG-DTA). These thermally coupled techniques were applied to address extract's thermal decomposition and released volatiles, in order to understand its behavior under simulated thermal disposal. Fourier transform infrared spectroscopy (FTIR) and elemental analysis were used for chemical composition analysis of *D. sellowiana* extract.

2. Material and methods

2.1 *Dicksonia sellowiana extract processing*

Dicksonia sellowiana Hook., Dicksoniaceae, samples were harvested in Colombo, Paraná, with authorization of Registro Nacional de Cultivar do Ministério da Agricultura Pecuária e Abastecimento (RNC/MAPA – 28394). The botanical identification was performed at Herbarium of Department of Botany of Federal University of Paraná and vouchers specimen is deposited under number 46579.

D. sellowiana extract was obtained from leaves through soxhlet/ethanol extraction (Rattmann et al., 2009, 2011). Briefly, *D. sellowiana* leaves were oven dried until constant weight and latter triturated in knife mill and sieved (35-mesh). Hydro-ethanolic extract was obtained by dissolving 10 g of powdered dry leaves in ethanol (70%, v/v) in a round flask connected to a soxhlet apparatus. Ethanol (200 ml) was added for 3 h. Afterwards, the obtained extract was concentrated to 100 ml and filtered in a 0.45 μm membrane filter, followed by oven drying. The oven-dried sample was used for characterization studies. All other reagents used in this study were of reagent grade.

2.2 Thermogravimetry–differential thermal analysis (TG–DTA)

The simultaneous TG–DTA curves were obtained with a heating rate of 10 °C min^{-1} in temperature range of 30–600 °C, by using alumina crucibles and samples' mass about 5 mg. The experiments were carried out under nitrogen atmosphere at flow rate of 50 ml min^{-1}, in a DTG-60 system (Shimadzu, Japan). The instrument was preliminarily calibrated with standard mass and with standard calcium oxalate monohydrate. All mass loss percentages were determined using TA-60 WS data analysis software.

2.3 Thermogravimetry–mass spectrometry (TG–MS)

Thermogravimetry coupled to mass spectrometry was used to study chemical composition of plant extract through volatiles analysis under sample heating. The experiments were carried out in a SDT Q600 MS (TA Instruments, USA). Samples about 2 mg were heated up to 600 °C, under nitrogen flow of 50 ml min^{-1} and heating rate of 5 °C min^{-1}. The equipment generates separate TG curve and MS spectra, where the last was measured up to 350 scans, analyzing *m/z* intensity in relation to temperature.

2.4 Elemental analysis

Carbon, hydrogen, nitrogen, sulphur and oxygen (by mass difference) contents were determined in a CHNS elemental analyzer from Vario Macro Cube using 2.5 mg of oven dried *D. sellowiana* extract sample.

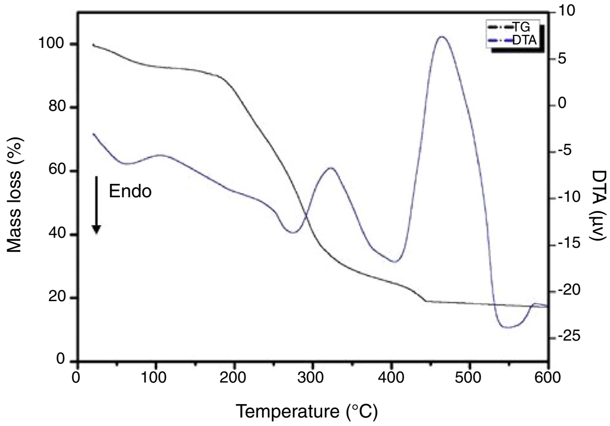

Fig. 1. TG-DTA curves of *Dicksonia sellowiana* extract under N_2 atmosphere.

2.5 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectrum was obtained on a Shimadzu FTIR-8400 spectrometer (Kyoto, Japan) through diffuse reflectance method (Fuller and Griffiths, 1978) and resolution of 8 cm^{-1} using the average of 40 scans in the wavenumber range of 3500–500 cm^{-1}.

3. Results and discussion

3.1 Thermogravimetry–differential thermal analysis (TG–DTA)

The TG-DTA curves obtained for *D. sellowiana* extract under N_2 atmosphere (pyrolysis) are presented in Fig. 1 and Table 1.

The extract's thermal behavior was divided into three consecutive steps, with the first one related to loss of loosely bound water due to sample dehydration (Böer et al., 2013). Until 200 °C, *D. sellowiana* extract presented thermal stability, showing minor variation in mass. Approximately at 200 °C, a great mass loss was observed (~64, wt%), resulting in consecutive endothermic and exothermic curves in DTA profile, and probably related to non-oxidative degradation of extract. Exothermic peaks are characteristic during the thermal degradation of plant extracts. Slavov et al. (2016) observed a similar behavior during thermal assessment of extracts from different plant sources (rose, marigold and chamomile), as their thermal degradation took place after 220 °C. Finally, from 350 to 600 °C, the sample was thoroughly degraded, leaving 20% residual mass, as a result of a non-oxidative atmosphere used for thermal analysis. A similar behavior was described by Xu et al. (2014) showing the effect of atmosphere on pyrolysis of China Shenhua coal liquefaction plant.

Table 1
Thermogravimetry/differential thermal analysis steps under nitrogen atmosphere. Distinct experimental condition levels.

TG results		DTA	
Step	Δm (%)	ΔT (°C)	T_p (°C)
1st	7.19	20.30–100.78	54.74 (endo)
2nd	64.73	170.65–358.76	271.99 (endo) 322.33 (exo)
3rd	27.81	358.76–600	462.75 (exo)

Δm, mass variation; ΔT, temperature variation; T_p, peak temperature.

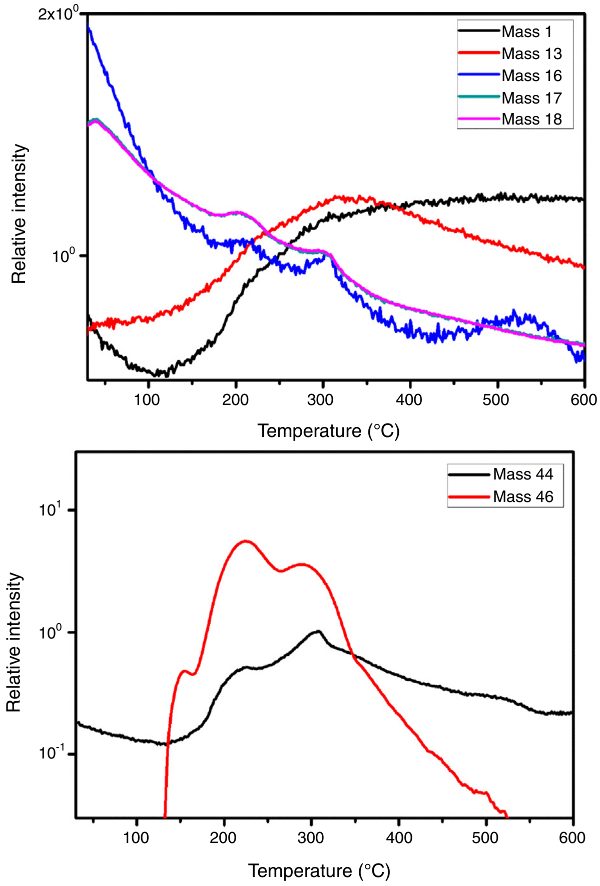

Fig. 2. Evolution of selected released volatiles from *Dicksonia sellowiana* extract under thermal degradation (N_2 atmosphere).

3.2 Thermogravimetry–mass spectrometry (TG–MS)

For further thermal characterization of extract, volatiles release was analyzed through thermogravimetry coupled to mass spectrometry (TG-MS). As expected, and in accordance to TG-DTA curve (Fig. 1), thermal degradation was divided into three consecutive steps with their respective volatiles release.

Obtained mass spectra was divided in most relevant volatiles released under controlled heating up to 600 °C. During analysis of gaseous products released under heating, the probable molecules related to mass spectra were as follow: 1 (H), 13 (CH), 16 (CH_4), 17 (NH_3), 18 (H_2O), 44 (CO_2) and 46 (NO_2). Main volatile compounds release from *D. sellowiana* extract through controlled heating is represented in Fig. 2.

As observed in TG-DTA results of extract (Fig. 1 and Table 1), thermal events corresponding to mass losses were in the range of 30–100 °C (Phase I), 100–360 °C (Phase II) and 360–600 °C (Phase III).

It may be inferred from the results expressed in Table 2 that, in Phase I, the main release of volatiles is related to dehydration process (H_2O), followed by light volatiles emission, such as NH_3, CO_2 and CH_4 (Sanchez-Silva et al., 2012; Qiao et al., 2015).

Furthermore, *m/z* 44 shows higher intensity from 150 to 220 °C, and next, from 250 to 300 °C, confirming the hypothesis of CO_2 release during extract pyrolytic combustion (second mass loss) and degradation of decomposition products (third mass loss). It is noted that water vapor release is gradual and more intense until 200 °C as expected, where loosely bound water was first easily removed, with a lower elimination in the following. On phase II, decreased liberation of NH_3, H_2O and CH_4 was still observed, however, a brief increase was noticed near 200 and 300 °C, which is in the range of thermal peaks observed on DTA curves. In addition, CH and H release increased after 300 °C, corresponding to the range of highly exothermic peaks as indicated on DTA.

Release of the mentioned molecules is probably a result of sample non-oxidative degradation, levels which remains constant up to 600 °C. From phase III on, volatiles release proved to be constant as most of organic matter had already been consumed through pyrolysis. Release of molecules with mass 14 and 28 observed on mass spectrum is related to the carrier gas (nitrogen) used for sample's thermal degradation (pyrolysis) (Nowicki and Ledakowicz, 2014).

Finally, *m/z* 46 release presented two major peaks between 200 and 300 °C, which are probably related to NO_2 emission under heating, being that a decomposition product of pyrolyzed extract. As a common ingredient in modern medicine formulations, thermal disposal of this extract appears to be harmless in matter of released volatiles in this process, in contrast to other pharmaceutical and personal care products (PPCP) (Colman et al., 2016).

3.3 Elemental analysis

Elemental analysis of plant extracts is important for quality assurance, as required by drug safety regulations (Pohl et al., 2016). The elemental composition of *D. sellowiana* extract was determined through elemental analysis, to evaluate the presence of CHNS (and oxygen by mass difference), and the results are demonstrated in Table 3.

From elemental analysis, the values of nitrogen and sulphur were 0.24% and 0.56%, respectively. The content of carbon (39.30%), hydrogen (6.96%) and oxygen (52.94%) presented higher content on evaluated extract sample, which is expected because of ethanol-based extraction method. The lower percentage of nitrogen is evidenced by the high C/N molar ratio (190.96) and the data

Table 2
Released molecules of *Dicksonia sellowiana* extract detected on TG-MS analysis.

Relative intensity							
	m/z = 1	m/z = 13	m/z = 16	m/z = 17	m/z = 18	m/z = 44	m/z = 46
T_r (°C)							
0–100	3.00 ± 0.30	4.34 ± 0.06	3.11 ± 0.44	36.52 ± 1.88	163.19 ± 8.15	583.27 ± 78.40	−2.52 ± 2.53
100–200	2.93 ± 0.18	4.71 ± 0.23	2.13 ± 0.14	30.52 ± 1.11	137.21 ± 4.84	585.69 ± 465.23	80.68 ± 107.03
200–300	3.86 ± 0.25	5.74 ± 0.25	1.92 ± 0.06	27.55 ± 1.13	124.13 ± 4.94	2651.45 ± 703.54	221.85 ± 57.95
300–400	4.37 ± 0.06	6.14 ± 0.09	1.69 ± 0.12	23.86 ± 1.17	107.47 ± 5.35	2202.48 ± 470.96	34.51 ± 26.48
400–500	4.50 ± 0.04	5.68 ± 0.15	1.55 ± 0.03	21.80 ± 0.34	98.01 ± 1.64	1278.36 ± 122.09	4.27 ± 2.38
500–600	4.53 ± 0.03	5.27 ± 0.10	1.55 ± 0.06	20.71 ± 0.28	92.72 ± 1.27	905.29 ± 85.99	−0.34 ± 1.95
T_r (°C)	172–426	142–464	169–329	169–329	169–329	174–405	167–356
T_{p1} (°C)	308	319	204	204	204	221	222
T_{p2} (°C)	–	–	304	304	304	309	293

T_r, temperature range; T_{p1}, first peak; T_{p2}, second peak; *m/z*, mass-to-charge ratio.

Table 3
Elemental analysis of *Dicksonia sellowiana* extract dried sample.

Sample	Elemental analysis content (%)					Molar ratio				
	Carbon (C)	Hydrogen (H)	Nitrogen (N)	Sulfur (S)	Oxygen (O)	C/H	C/O	C/N	H/C	O/C
D. sellowiana extract	39.30	6.96	0.24	0.56	52.94	5.64	0.74	190.96	2.11	1.01

obtained in TG-MS corroborates with the low relative intensity release on NH_3 and NO_2 experimental assay.

Also, the presence of high O/C molar ratio suggests a hydrophilic aspect of *D. sellowiana* extract (Szymczycha-Madeja et al., 2013; Rajapaksha et al., 2015), probably for using ethanol as a solvent during extract processing.

3.4 Fourier transformed infrared spectroscopy (FTIR)

FTIR was performed to further characterize extract composition and its functional groups. The spectra of *D. sellowiana* extract is shown in Fig. 3.

The broad peak between 3500 cm^{-1} and 3200 cm^{-1} corresponds to an O–H stretch vibration, which indicates the presence of hydroxyl groups in *D. sellowiana* extract. Those groups are attributed both to hydroxylated molecules of the extract (such as polyphenols) and to the moisture content of the extract (Santana et al., 2018). The presence of a minor intensity peak in the region of 2975–2950 cm^{-1} represents an O–H stretching, which might indicate the presence of alcohol and amide groups as well corresponding to C–H vibrations of the CH_3 group (Ighodaro et al., 2016). A probable N=O stretching vibration is observed in the region 1650–1600 cm^{-1} (Ismail et al., 2013). Furthermore, weak peaks on this same region should also indicate presence of C=C groups, while absorption within this range might indicate a structure containing carbonyl groups, strong peaks are not evident this drug extract (Silverstein et al., 2014).

On fingerprint region, a doublet band is present between 1450 cm^{-1} to 1375 cm^{-1}, indicating C–H bending vibration of molecule methyl groups (–CH_3). Also, abroad peak is present between 1100 cm^{-1} and 1000 cm^{-1}, probably related to an alkoxy C–O stretching vibration, suggesting the presence of alcohol groups within compound structure (Silverstein et al., 2014). In addition, the *D. sellowiana* extract spectra indicates a substituted aromatic C–H bonds between 780 and 650 cm^{-1}. At last, it may also be extracted from the results that chemical structure of sample is highly polar, as indicated by the abundance of broad peaks within spectrum.

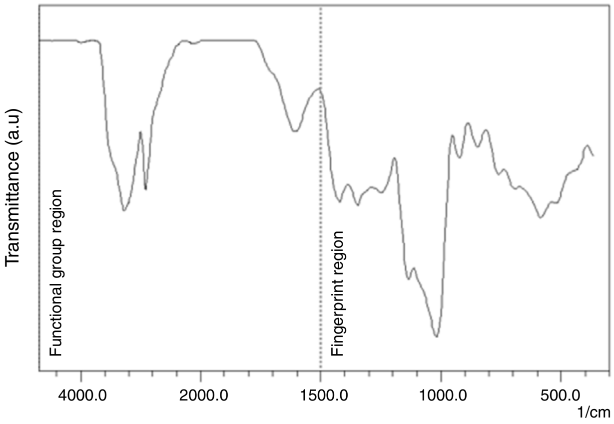

Fig. 3. FT-IR spectra of *Dicksonia sellowiana* extract.

4. Conclusion

TG-DTA curved showed degradation within three consecutive steps, divided into loss of loosely bound water (approximately until 100 °C), and followed by mass stability until 200 °C. Then, extract depolymerization (200–350 °C) and extract thermal degradation (350–600 °C) were responsible for major mass loss in sample. Low ash residue indicated minor presence of inorganic compounds in hydroalcoholic extract.

TG-MS results confirmed the thermal behavior observed in TG-DTA curves and, in addition, revealed the most prominent released volatiles of the sample during thermal degradation. During TG first step (30–100 °C), main release of volatiles was related to dehydration (H_2O) and light volatiles emission (NH_3, CO_2 and CH_4). Next, major release of $CO_2$was observed during sample depolymerization and degradation. Intense release of CH and H, related to these processes, led to the intense exothermic events observed on DTA curves. Volatiles release results suggests thermal disposal of this extract is harmless in comparison to other PPCPs, when present in a formulation.

Elemental analysis results revealed an extract rich in carbon, oxygen and hydrogen atoms, as expected for processing method used for obtaining the aforementioned extract. FTIR spectrum analysis confirmed the observed for elemental analysis, suggesting a highly polar structure for *D. sellowiana* extract, which was further confirmed for the low O/C molar ratio (CNHS).

This work shows that thermal disposal of *D. sellowiana* extract results in the release of harmless by products, in contrast to other PPCPs. This should increase the application of this efficient antioxidant and antimicrobial in pharmaceutical applications, particularly when regarding regulatory issues, where this safe disposal may be used as a commercial claim.

Conflicts of interest

The authors would like to thank CNPq and Embrapa Florestas for financially supporting this work and Interphytos Ltda and JEN Biotechnologies for providing the *Dicksonia sellowiana* for analysis.

The coordination of experimental design and guiding analyses were performed by FSM, MASCF and ECV. LCM and TM contributed in collecting plant sample and the extract processing. LCM, WLEM and NCFS carried out the characterization tests. NCFS, LCM and FSM contributed to data analysis, writing and critical reading of the manuscript. All the authors have read the final manuscript and approved the submission.

The authors declare no conflicts of interest.

References

Böer, T.M., Procópio, J.V.V., Nascimento, T.G., Macêdo, R.O., 2013. Correlation of thermal analysis and pyrolysis coupled to GC–MS in the characterization of tacrolimus. J. Pharm. Biomed. Anal. 73, 18–23.

Colman, M.D., Lazzarotto, S.R.S., Lazzarotto, M., Hansel, F.A., Colman, T.A.D., Schnitzler, E., 2016. Evolved gas analysis (TG-DSC-FTIR) and (Pyr-GC–MS) in the disposal of medicines (aceclofenac). J. Anal. Appl. Pyrolysis 119, 157–161.

Cuinica, L.G., Macêdo, R.O., 2018. Thermoanalytical characterization of plant drug and extract of *Urtica dioica* L. and kinetic parameters analysis. J. Therm. Anal. Calorim. 133, 591–602.

Fernandes, I., 2000. Taxonomia dos representantes de Dicksoniaceae no Brasil. Pesquisas Bot. 50, 5–26.

Fuller, M.P., Griffiths, P.R., 1978. Diffuse reflectance measurements by infrared Fourier transform spectrometry. Anal. Chem. 50, 1906–1910.

Gomes, G.S., Randi, A.M., Puchalski, A., Santos, D.S., Reis, M.S., 2006. Variability in the germination of spores among and within natural populations of the endangered tree fern *Dicksonia sellowiana* Hook. (Xaxim). Braz. Arch. Biol. Technol. 49, 1–10.

Ibama, 2008. Lista Oficial das Espécies da Flora Brasileira Ameaçadas de Extinção. Instrução normativa n° 6 de, 23 de setembro de 2008, Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis. Ministério do Meio Ambiente, Brasília DF.

Ighodaro, O.M., Akinloye, O.A., Ugbaja, R.N., Omotainse, S.O., Faokunla, O., 2016. FTIR analysis of *Sapium ellipticum* (Hochst) pax ethanol leaf extract and its inhibitory effects on pancreatic α-amylase and intestinal α-glucosidase activities in vitro. Egypt. J. Basic Appl. Sci. 3, 343–349.

Ismail, M.M., Morsy, G.M., Mohamed, H.M., El-Mansy, M.A.M., Abd-Alrazk, M.M.A., 2013. FT-IR spectroscopic analyses of 4-hydroxy-1-methyl-3-[2-nitro-2-oxoacetyl-2 (1H) quinolinone (HMNOQ). Spectrochim. Acta A 113, 191–195.

Lemes, B.M., Novatski, A., Ferrari, P.C., Minozzo, B.R., Justo, A.S., Petry, V.E.K., Vellosa, J.C.R., Sabino, S.R.F., Gunha, J.V., Esmerino, L.A., Beltrame, F.L., 2018. Physicochemical, biological and release studies of chitosan membranes incorporated with *Euphorbia umbellata* fraction. Rev. Bras. Farmacogn., http://dx.doi.org/10.1016/j.bjp.2018.05.001.

Leite, R.S., Souza, V.G., Salvador, I.S., Oliveira, A.H., Lima-Neto, A., Basílio, I.J.L.D., Aragão, C.F.S., Macedo, R.O., Souza, F.S., 2018. Evaluation of compatibility between dried extracts of *Myracrodruon urundeuva* Allemão and pharmaceutical excipients by TG and DTA. J. Therm. Anal. Calorim. 133, 633–639.

Nowicki, L., Ledakowicz, S., 2014. Comprehensive characterization of thermal decomposition of sewage sludge by TG–MS. J. Anal. Appl. Pyrolysis 110, 220–228.

Oliveira, V., Zuchetto, M., Oliveira, C., Paula, C.S., Duarte, A., Miguel, M., Miguel, O., 2016. Efeito de diferentes técnicas extrativas no rendimento, atividade antioxidante, doseamentos totais e no perfil por CLAE-DAD de *Dicksonia sellowiana* (Presl.) Hook, Dicksoniaceae. Rev. Bras. Pl. Med. 18, 230–239.

Pohl, P., Dzimitrowicz, A., Jedryczko, D., Szymczycha-Madeja, A., Welna, M., Jamroz, P., 2016. The determination of elements in herbal teas and medicinal plant formulations and their tisanes. J. Pharm. Biomed. Anal. 130, 326–335.

Qiao, Y., Chen, S., Liu, Y., Sun, H., Jia, S., Shi, J., Pedersen, C.M., Wang, Y., Hou, X., 2015. Pyrolysis of chitin biomass: TG–MS analysis and solid char residue characterization. Carb. Polym. 133, 163–170.

Rajapaksha, A.U., Vithanage, M., Ahmad, M., Seo, D.C., Cho, J.S., Lee, S.E., Lee, S.S., Ok, Y.S., 2015. Enhanced sulfamethazine removal by steam-activated invasive plant-derived biochar. J. Hazard. Mater. 290, 43–50.

Rattmann, Y.D., Crestani, S., Lapa, F.R., Miguel, O.G., Marques, M.C., Silva-Santos, J.E., Santos, A.R., 2009. Activation of muscarinic receptors by a hydroalcoholic extract of *Dicksonia sellowiana* Presl Hook (Dicksoniaceae) induces vascular relaxation and hypotension in rats. Vasc. Pharmacol. 50, 27–33.

Rattmann, Y.D., Mendéz-Sánchez, S.C., Furian, A.F., Paludo, K.S., de Souza, L.M., Dartora, N., Oliveira, M.S., Costa, E.M.S., Miguel, O.G., Sassaki, G.L., Iacomini, M., Mello, C.F., Franco, C.R.C., Silva-Santos, J.E., Cadena, M.S.C., Marques, M.C.A., Santos, A.R., 2011. Standardized extract of *Dicksonia sellowiana* Presl Hook (Dicksoniaceae) decreases oxidative damage in cultured endothelial cells and in rats. J. Ethnopharmacol. 133, 999–1007.

Rogge, G.D., Viana, A.M., Randi, A.M., 1999. Cryopreservation of spores of *Dicksonia sellowiana*: an endangered tree fern indigenous to South and Central America. Cryoletters 21, 223–230.

Sanchez-Silva, L., López-González, D., Villaseñor, J., Sánchez, P., Valverde, J.L., 2012. Thermogravimetric–mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis. Bioresour. Technol. 109, 163–172.

Santana, C.P., Fernandes, F.H.A., Brandão, D.O., Silva, P.C.D., Correia, L.P., Nóbrega, F.P., Medeiros, F.D., Diniz, P.H.G.D., Véras, G., Medeiro, A.C.D., 2018. Compatibility study of dry extract of *Ximenia americana* L. and pharmaceutical excipients used in solid state. J. Therm. Anal. Calorim. 133, 603–617.

Silverstein, R.M., Webster, F.X., Kiemle, D.J., Bryce, D.L., 2014. Spectrometric Identification of Organic Compounds, 7th ed. John Wiley & sons, New York.

Slavov, A., Panchev, I., Kovacheva, D., Vasileva, I., 2016. Physico-chemical characterization of water-soluble pectic extracts from *Rosa damascena*, *Calendula officinalis* and *Matricaria chamomilla* wastes. Food Hydrocoll. 61, 469–476.

Szymczycha-Madeja, A., Welna, M., Zyrnicki, W., 2013. Multi-element analysis, bioavailability and fractionation of herbal tea products. J. Braz. Chem. Soc. 24, 777–787.

Tidwell, W.D., Rushforth, S.R., Simper, A.D., 1970. Pre-cretaceous flowering plants: further evidence from Utah. Science 170, 547–548.

Xu, L., Tang, M., Liu, B., Ma, X., Zhang, Y., Argyle, M.D., Fan, M., 2014. Pyrolysis characteristics and kinetics of residue from China Shenhua industrial direct coal liquefaction plant. Thermochim. Acta 589, 1–10.

Zayed, M.A., Hawash, M.F., El-Desawy, M., El-Gizouli, A.M., 2017. Investigation of naproxen drug using mass spectrometry, thermal analyses and semi-empirical molecular orbital calculation. Arab. J. Chem. 10, 351–359.