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SHORT COMMUNICATION

Chemical characterization of polyphenols from *Daucus muricatus* growing in Algeria by RP-UHPLC-ESI-QTOF-MS/MS

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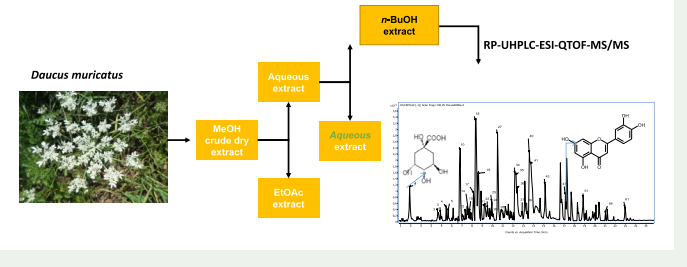
ABSTRACT

In the present work, reversed phase (RP) ultra-high-performance liquid chromatography (UHPLC) coupled to quadrupole-time-of-flight (QTOF) mass spectrometry in tandem has been used for the identification of the main phenolic compounds in the aerial parts of *Daucus muricatus*. The characterisation of the compounds was carried out taking into account retention time, mass accurate measurements, the generated molecular formulae and fragmentation pattern. These data were contrasted with literature and databases, as well as with those of authentic standards when possible. The proposed method provided tentative identification of 30 phenolic and other polar compounds, including hydroxycinnamic acid derivatives, flavonoids and hydroxybenzoic acid derivatives. As a note, hydroxycinnamic acid derivatives were found to be the most diverse phenolic class of *Daucus muricatus*.



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1. Introduction

Algeria is a country with a high floral biodiversity, where traditional medicine has its place, for a long time. As part of our ongoing chemical investigation of Algerian medicinal plants, in this study we focus on *Dacus muricatus*. *Daucus* is a genus belonging to the family Apiaceae.

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In the genus *Daucus,* the most known species is *D. carota* L. (carrots), which are consumed worldwide. However, there are a plenty of species. As an example, in Algeria, this genus is represented by more than 27 species living in arid and uncultivated widespread along the Algerian west coast (Bendiabdellah et al. 2012). *D. muricatus* is a small herbaceous plant that grows on maritime sands and cliffs (Bendiabdellah et al. 2012). It is also known by other names considered synonyms: *Caucalis murica, Platyspermum muricatum* and *Artedia muricata* (Sáenz Laín 1981). This species is one of the farthest species on the genetic tree of *Daucus* (Al-Safadi 2008) and it is expected variability in the phytochemical composition compared to *D. carota*. As first step to understand its potential pharmacological uses, the characterisation of its chemical constituents is a requirement since little is known about this species (Spooner et al. 2013). Nevertheless, recent studies have described that aerial part oils was mainly composed by terpenic hydrocarbon compounds (62.3–72.2/100 g) (Bendiabdellah et al. 2012), while the hydrosol from aerial parts consisted of volatile phenolic and phenylpropanoid compounds such as thymol (11.7%), myristicine (7.5%), isochavicol (7.4%) and isochavicol-2-methyl butyrate (5.8%) (Djabou et al. 2014). These studies were performed by gas chromatography coupled to flame ionisation detector and mass spectrometry (MS).

Therefore, the objective of the present study was to study the phytochemical profile of the aerial parts *D. muricatus* by reversed phase (RP)-ultra-high-performance liquid chromatography (UHPLC) coupled to a quadruple-time-of-flight (QTOF) mass analyser to perform MS in tandem. This technology has enabled the characterisation of hundreds of phytochemicals in plants that explains our interest in its use to perform this study.

2. Results and discussion

2.1. RP-UHPLC-ESI-QTOF-MS analysis of the butanol extract of D. muricatus

The base peak chromatogram of *D. muricatus* aerial parts resulting from RP-UHPLC-ESI-QTOF-MS analysis is shown in (Figure S1). The compounds characterised are listed in Table S1. This characterisation work was carried out by comparing retention times and mass spectra with those of authentic standards, when possible. If standards were unavailable, (in most of the cases), phenolic compounds were identified on the basis of accurate mass of the molecular $[M - H]^-$ ions and tandem mass spectrometry (MS/MS) data. The results of accurate mass measurements fit well with the elemental composition of the compounds.

In this way, 30 compounds were tentatively characterised and classified into 4 groups: 13 hydroxycinnamic acid derivatives, 5 benzoic acid derivatives, 8 flavonoids and other polar compounds (Table S1). We also showed the results of unknown peaks, since we could not match this information with the available literature. These results are quite interesting since probably these compounds have never been reported. Further studies using nuclear magnetic resonance after purification of these compounds are expected to clarify their structures.

2.2. Structural identification

2.2.1. Hydroxycinnamic acid derivatives

This study showed that hydroxycinnamic acid derivatives are useful markers of *D. muricatus,* most of them present caffeic acid and its derivatives, coumaric acid and ferulic acid. Five isomers of caffeoylquinic acid were found. Compound **10** yielded $[M - H]^-$ ion at *m/z* 353,

and its MS/MS showed major fragment at *m/z* 191 with the quinic acid moiety and *m/z* 179 representing the caffeoyl moiety (Figure S2). This compound was characterised as caffeoyl quinic acid stereoisomer 1. Compound **18** was identified as another isomer with a *m/z* value of 707 [2 M – H]$^-$ This one was generated due to the formation of dimer during the ESI ionisation and the major fragment was found at *m/z* 191 (quinic acid) as before (Simirgiotis et al. 2013). The comparison with the standard chlorogenic acid enabled to confirm this assignment. In addition, compounds **19**, **22** and **24** were proposed as another isomers of caffeoyl quinic acid with molecular ions [M – H]$^-$ at *m/z* 353, giving a similar fragmentation pattern. Compound **17** was characterised as caffeic acid hexoside with *m/z* 341. It had a representative fragment at *m/z* 179 corresponding to the deprotonated caffeic acid by the loss of the hexose moiety (162 u) (Hossain et al. 2010). The difference between both molecules is possible thanks to accurate mass measurements.

Coumaroyl quinic acid isomer is was proposed for compound **25**, in the MS/MS spectra of this compound the loss of quinic acid moiety gave the most prominent fragment ion at *m/z* 191. This was also observed for compound **27** (*m/z* 367), which is characteristic of 5-*O*-feruloyl quinic acid (Clifford et al. 2003). In a similar way, product fragments at 339 and 191 indicated that compound **28** could be derived from caffeic and quinic acids [M – H]$^-$ *m/z* 531.1148) (Ammar et al. 2015). Compounds **37** and **39** have been tentatively assigned as dicaffeoylquinic acid isomers with [M – H]$^-$ at *m/z* 515, whose fragmentation pattern was also characterised by the loss of caffeoyl groups and the presence of a fragment at *m/z* 191 (Long et al. 2012). Compound **61** was characterised as a caffeoyl derivative, since it gave a product ion at MS/MS 311 corresponding to [M – H-caffeoyl]$^-$.

2.2.2. Flavonoids

In the present study, flavonoids were mainly represented by nine flavones or derivatives (Table S1, Figure S3). Compound **26** was characterised as luteolin *C*-pentoside *C*-hexoside with an [M – H]$^-$ at *m/z* 579 (Ammar et al. 2015). It was characterised by the loss of 120 u, characteristic of the fragmentation of *C*-glycosides compounds. The rest of luteolin derivatives were characterised by the presence of major fragment ions at *m/z* 285 with *O*-substituents. For example, compound **34** corresponding to luteolin 7-*O*-glucoside, yielded [M – H]$^-$at *m/z* 447. Its MS/MS fragmentation showed the major fragment at 285 corresponding the loss a glucosyl moiety (162 u). Therefore, compound **41** ([M – H]$^-$ *m/z* 489) was proposed as luteolin 7 -*O*-(6″-*O*-malonyl))-β-D-glucoside. Similarly, compound **35** was characterised as *O*-glucuronide derivative of luteolin at [M – H]$^-$ *m/z* 461 since produced a major fragment *at m/z* 285 after the loss of glucuronide moiety (176 u) (Justesen 2000). The aglycone was compound **47** which had [M – H]$^-$ ion at *m/z* 285. This compound gave a major fragment at *m/z* 133 [$C_8H_5O_2$]$^-$ and it can be confirmed with a commercial standard. The compound apigenin 7-*O*-glucoside **40**, which has [M – H]$^-$ ion at *m/z* 431, was identified by its intense ion in MS/MS at *m/z* 269 due to the loss of the glucosyl molecule.

2.2.3. Hydroxybenzoic acids and derivatives

The analysis of the butanol extract of *D. muricatus* revealed the presence of five hydroxybenzoic acid derivatives. Two hydroxybenzoic acid isomers at *m/z* 137 (compounds **2** and **8)**. Compound **5** was proposed as vanillic acid hexoside with a [M – H] $^-$ at *m/z* 329. The collision-induced dissociation of this compound produced the major fragment *at m/z* 167 corresponding to vanillic acid molecule. Compound **14** gave a precursor ion [M – H] $^-$ at *m/z*

299 corresponding to hydroxybenzoic acid hexoside, the loss of hexose moiety was characterised by deprotonated hydroxyl benzoic acid at *m/z* 137.

2.2.4. Other compounds

Compound **1** had a $[M - H]^-$ at *m/z* 191, and it was identified as quinic acid and other compounds were found as pentestimide at *m/z* 443, methyl glucopyranoside oxo pentanoic acid at *m/z* 293 and methyl glycopyranosyloxy pentanoicacid at *m/z* 293.

3. Experimental

The experimental section is available online in supplementary material.

4. Conclusions

RP-UHPLC-ESI-QTOF-MS/MS is a powerful analytical method for the characterisation of phenolic and other compounds. This technique allowed to obtain the MS and MS/MS data of 30 compounds in the butanolic extract of the aerial parts of *D. muricatus* in the negative ionisation mode. Among them, 26 phenolic compounds have been characterised. The importance of the characterisation of chemical constituents help to provide the basis for further investigations into the bioactivity of *D. muricatus* to understand its traditional medicinal uses.

Supplementary material

Supplementary material relating to this paper is available online, Experimental, Figures S1–S3, and Table S1.

Disclosure statement

No potential conflict of interest was reported by the authors.

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