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Mid-infrared spectroscopy and short wave infrared hyperspectral imaging—A novel approach in the qualitative assessment of *Harpagophytum procumbens* and *H. zeyheri* (Devil's Claw)

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ABSTRACT

Harpagophytum procumbens (Burch.) DC. ex Meisn. subsp. *procumbens* (Pedaliaceae) is an important African medicinal plant growing in the Kalahari region of southern Africa. This species, together with its close taxonomic ally *Harpagophytum zeyheri* are collectively referred to as Devil's Claw and are used interchangeably for the treatment of inflammation-related disorders. Although the two taxa are botanically and chemically similar, *H. zeyheri* contains lower levels of harpagoside and these two species have not been proven to exhibit equipotent pharmacological activity. Due to these taxonomic similarities, effective quality control methods are required to distinguish between the two species. Differentiation between the two species was achieved using single point mid-infrared spectroscopy in combination with chemometric data analysis. The orthogonal projections to latent structures discriminant analysis (OPLS-DA) model had good predictive ability, as illustrated by the model statistics: R^2X (cum predictive + orthogonal) = 0.86 and Q^2 (cum) = 0.63. Short wave infrared (SWIR) hyperspectral imaging could distinguish between the two species with acceptable model statistics: R^2X and R^2Y of 0.99 and 0.78, respectively. This study demonstrated that both MIR single point spectroscopy and SWIR hyperspectral imaging coupled with chemometric modelling is a reliable and rapid method to determine the authenticity of *Harpagophytum* spp.

1. Introduction

Harpagophytum procumbens (Burch.) DC. ex Meisn. subsp. *procumbens* (Pedaliaceae) is an important African medicinal plant found in the Kalahari region of southern Africa which includes Namibia, South Africa, Botswana, Angola, Zimbabwe, Zambia and Mozambique. According to ethnobotanical information, secondary root tubers are used to treat painful inflammation of the joints and muscles in rheumatism and arthritis, back pain, and as a tonic for gastro-enterological disturbances (Mncwangi et al., 2012; van Wyk and Gericke, 2000). A topical ointment prepared with animal fat or petroleum is traditionally applied to treat sores, ulcers and boils (van Wyk and Gericke, 2000). Other traditional uses of *H. procumbens* include the treatment of fever, diabetes, diarrhoea and blood disease (Stewart and Cole, 2005). Studies have confirmed that extracts of the secondary tubers of *H. procumbens* are effective in the treatment of degenerative rheumatoid arthritis, osteoarthritis, tendonitis, kidney inflammation, heart disease, dyspepsia and loss of appetite (Stewart and Cole, 2005; Viljoen et al., 2012).

H. procumbens and the closely related *Harpagophytum zeyheri* are collectively known as Devil's Claw and are used interchangeably (Kemper, 1999). The British and European Pharmacopoeias make reference to both *H. procumbens* and *H. zeyheri* but *H. procumbens* is the species of choice as it has been shown to contain higher amounts of the biologically active ingredient, harpagoside (Mncwangi et al., 2012). *H. zeyheri* has been included in formulations as an adulterant where *H. procumbens* is used as starting material (McGregor et al., 2005), largely due to the declining natural populations of *H. procumbens*. *H. procumbens* is extensively commercialised which creates a conducive environment for adulteration which may have negative consequences for both the trader and the consumer (Stewart and Cole, 2005).

Phytochemical studies have confirmed the presence of iridoid glycosides such as harpagoside, procumbide and harpagide, phenylethanoid glycosides such as acteoside and isoacteoside

Abbreviations: ATR, attenuated total reflectance; MIR, mid-infrared; OPLS-DA, orthogonal projections to latent structures discriminant analysis; PCA, principal component analysis; SWIR, short wave infrared; SNV, standard normal variate.

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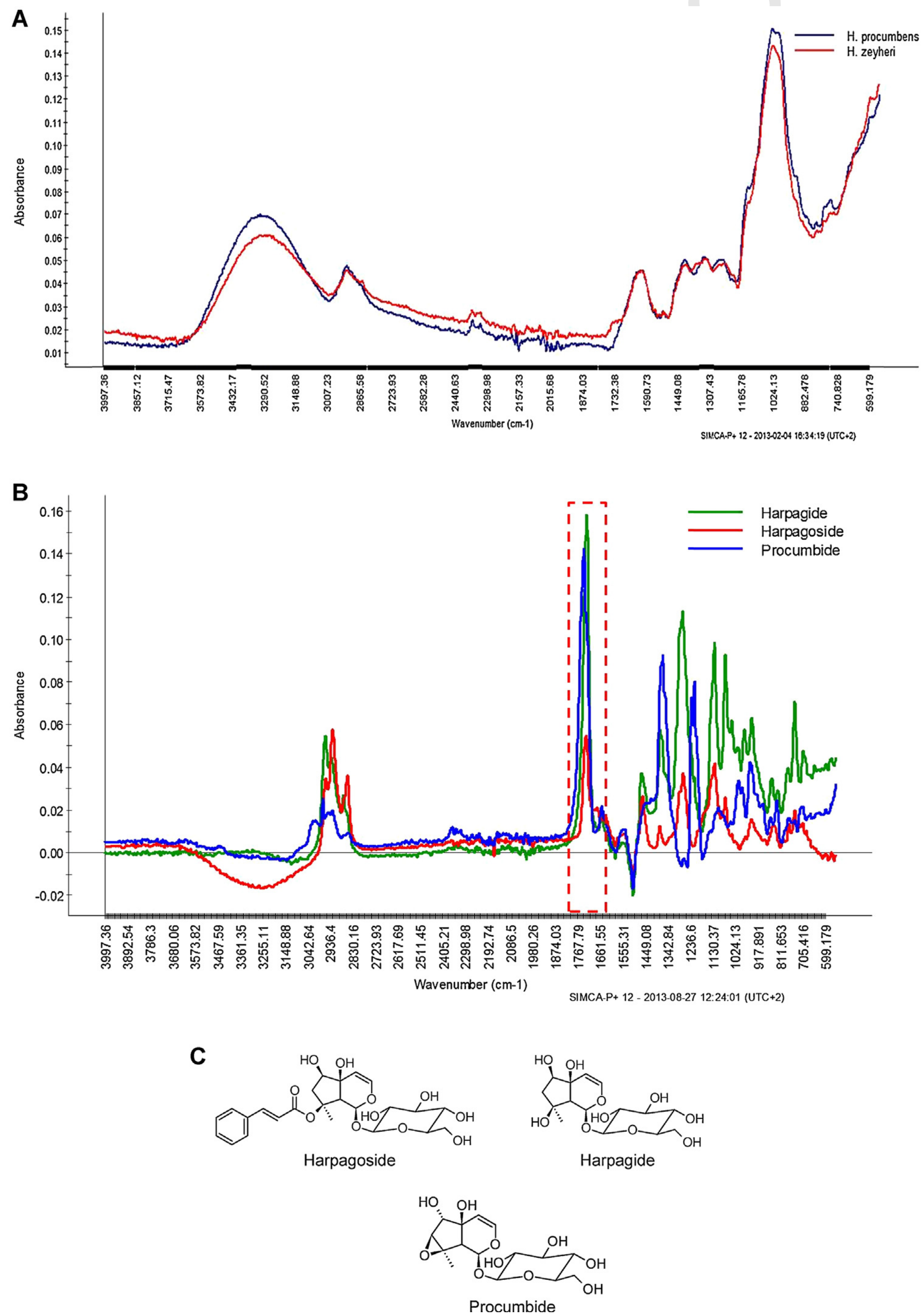
and other substances including harpagoquinones, amino acids, flavonoids, phytosterols and carbohydrates in Devil's Claw (Gruenwald, 2002; Kikuchi et al., 1983; Kurkin, 2003). However, only harpagoside is used as a biomarker to determine the quality of raw material and products. Various chromatographic and spectroscopic methods have been developed for the quality assurance of *H. procumbens* raw material and products. Using NIR-FT-Raman spectroscopy, Baranska et al. (2005) identified characteristic key bands in *H. procumbens* raw materials, ethanol extracts and tablets. Diagnostic key bands were observed in the frequency range of 1600–1700 cm^{-1}, which is similar to the wavenumber region for harpagoside, and is assigned to –C═O, –C═C and benzene ring stretching vibrations. Schulz and Baranska also developed a calibration model for harpagoside using HPLC as a reference method. Raman mapping was used to visualise the spatial distribution of harpagoside in different samples (Schulz and Baranska, 2007).

Quality control (QC) is a major concern in the herbal and phytomedicine industry; vibrational spectroscopy is one of the modern methods used in raw material identification and in-process monitoring (Reich, 2005). Vibrational spectroscopy offers various advantages over current analytical techniques; these include its robustness, efficiency, non-destructiveness and cost-effectiveness. In addition, minimal or no sample preparation is



Q3 **Fig. 1.** (A) MIR spectra of powdered *H. procumbens* (blue) and *H. zeyheri* (red) secondary root tubers. (B) MIR spectra of three iridoid glycosides (harpagoside, harpagide and procumbide) isolated from *H. procumbens*. (C) Chemical structures of harpagoside, harpagide and procumbide. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

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