QUALITATIVE AND QUANTITATIVE ASPECTS IN ANALYSIS OF GINSENG PHARMACEUTICALS USING VIBRATIONAL SPECTROSCOPY

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Abstract. FT-IR, FT-Raman and second derivative vibrational spectroscopy has been used in order to reveal some qualitative and quantitative aspects regarding the starch and saponine content of commercial Ginseng pharmaceuticals. Both powder and liquid samples were analysed suggesting that the starch content of a Ginseng product is favourable to be monitored in saturated solution using vibrational spectroscopy.

Key words: Ginseng, FT-IR, FT-Raman spectroscopy.

INTRODUCTION

Ginseng, the root of *Panax Ginseng*, has been considered as an important component of traditional prescription in Korea and China. It exhibits central nervous system-depressant and antipsychotic activity, protection of stress ulcer, increase of gastrointestinal motility and weak anti-inflammatory action [1, 5–7, 9, 12]. The oriental ginseng is native to Manchuria and Korea, but another common form of ginseng is known as American ginseng (*Panax quinquefolius*).

The efficacy and quality of ginseng differ widely according to the growing conditions, especially the cultivation area (Korea, China, America, Canada), although it comes from the same species. Its activity also depends on the part of the plant root that is processed, so it is an increasing demand for a reliable and fast analytical method in evaluating and controlling the quality of Ginseng products.

A new type of authentication process involved uses the recent technique of proteomics as well as FT-IR and FT-Raman spectroscopy [3, 8, 10, 11]. It has recently been reported that pattern recognition techniques combined with rapid and non-destructive analytical instrumentation have already attracted considerable attention for the purpose of classification or discrimination. Because ginseng is a very complex mixture, as are other herbal medicines products, the individual FT-IR

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or Raman spectra are often very similar to each other. However, the spectral features of ginseng in specific regions were slightly different from each other and these spectral differences resulted in the successful classification of ginseng based on its origin [2, 5, 12]. Such analysis may be applied to test the authenticity of particular products and ensure their proper use, providing a useful tool in preventing the fraudulent substitution of one type of ginseng for another.

Ginsengosides are the main active constituents of ginseng. The root, root-stock, stems, leaves, flowers and flower-buds of the ginseng plant contain more than 30 ginsengosides [2–4, 6, 9]. The accepted nomenclature of the individual saponins named Rx (*x* = o, a, b1, b2, c, d, e, f, g1, g2…) is based on the sequence of spots detected after silica gel thin layer chromatography. Ginsengosides are tri-terpenoid glycosides of the dammaran series. They can be divided into three types according to the characteristics of their chemical structure, oleanolic acid, panaxadiol and panaxtriol types. The chemical structures of these ginsengosides have been detected by IR, MS, NMR and chemical reactions [2]. Ginsengosides are highly glycosylated and their activity often differs depending on the number of glycosyl units attached [4, 5]. Chemical structures of two different ginsengoside are presented in Fig. 1.

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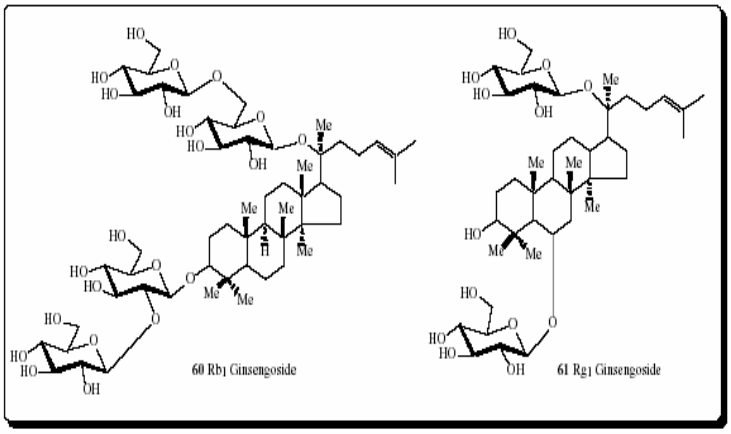

Fig. 1. The molecular structure of two different ginsengoside [5].

In the present paper, FT-IR, FT-Raman and second derivative vibrational techniques are used in order to demonstrate the ability of the vibrational techniques to qualitative and quantitative characterize the starch and saponine content of commercial Ginseng pharmaceuticals. Both powder and liquid samples were analysed and the recorded spectra were discussed and compared with previously reported data on different ginseng species.

MATERIALS AND METHODS

Commercial Ginseng powder used as soluble tea has been sampled for FT-IR and FT Raman spectroscopy. FT-IR spectrum was recorded in the region 4000–650 cm^{-1} using a Bruker EQUINOX 55 spectrometer with an Attenuated Total Reflectance (ATR) accessory. The internal reflection element was a ZnSe ATR plate (50 x 20 x 2 mm) with an aperture angle of 45°. A micro-Raman setup (Ramanscope II) connected with optical fiber to the FRA 106 S Raman module was employed in order to record the FT Raman spectrum. The 1064 nm line of a Nd:YAG laser was applied for excitation. An InGaAs detector was used. The laser power was 50 mW, the exposure time 1000 s and 40 overlaps were collected. The spectral resolution was 2.0 cm^{-1}.

RESULTS AND DISCUSSIONS

The characteristic vibrational modes of ginsengoside are due to oleanolic acid saponin, panaxadiol and panaxatriol saponins. The FT-IR spectrum (Fig. 2a) exhibits the characteristic fingerprint band features. For example the band at 3309 cm^{-1} is representative for C-H stretch, the band at 2923 cm^{-1} is due to the stretching vibration of $–CH_2–$ groups, the 1633 cm^{-1} line is due to the stretching vibration of carbonyl group in the volatile oils and other compounds containing C=O group [7]. Many C-O-C groups exhibit characteristic bands in the 1150 – 911 cm^{-1} spectral range and generally the strong band at 1026 cm^{-1} is assigned to the vibration of C-O in alcohol hydroxyl group. Compared with other recent studies in this field [3, 7, 10, 12], the bands at 1056–1026 cm^{-1} can be assigned as characteristic modes for distinguishing different types of ginseng (from America, Korea or China). The strong peak at 1026 cm^{-1} in our FT-IR spectrum is also an indicative of the starch content in the sample: the stronger the relative intensity of the band, the higher the starch content. This fact may be also proved by the second derivative spectrum. The peaks at 911, 856 and 766 cm^{-1} are assigned as characteristic absorption of the carbohydrate according to reference [10], respectively to carbohydrate I, II and III. The FT-IR spectrum of the previously reported ginseng species [7] contains also some characteristic bands of calcium oxalate from 1317 and 782 cm^{-1}. The relative intensity of these bands (as well as the carbohydrate's peaks) is weak in our FT-IR spectrum, revealing the low content of oxalates. The Raman spectrum of ginseng powder (Fig. 2b) exhibits the more accurate and well resolved bands than the IR one. However, the strong overlapping contributions make difficult to differentiate between sensitive related species.

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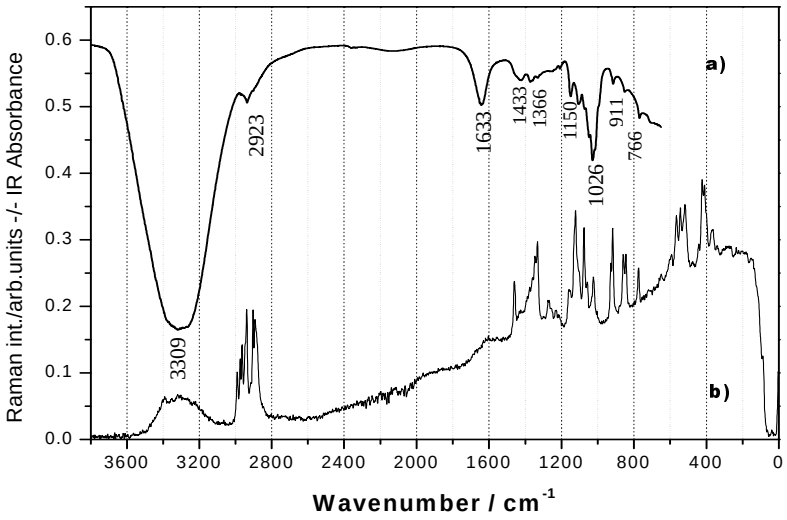

Fig. 2. a) FT-IR and b) FT Raman spectra of powder Ginseng from China.

Strong and well resolved bands in the FT-Raman spectrum (Fig. 2b) indicate the presence of the starch and carbohydrates and less the corresponding oxalate stretching. Another interesting feature is the weak band at 995 cm^{-1} present in the Raman spectrum and at 990 cm^{-1} in the secondary derivative FT-IR, closely related to the content of saponin [3, 7, 12]. It is well known that the content of saponin in wild American ginseng may reach 11% [7]. Therefore, different types of ginseng can be distinguished from each others taking into account the relative intensity of this band in the FT Raman spectrum [7, 8, 11].

Using the advantage of the secondary derivative spectrum by the apparent enhancing of the spectral resolution, we enhanced the tiny differences in the 1600-800 cm^{-1} spectral range for both the FT-IR and FT-Raman spectra. The secondary derivative IR and Raman spectra of ginseng powder are presented in Figs. 3 and 4 respectively. Taking a closer examination of the observed bands, based on comparison with the Korean, Beijing and American ginseng species [7], we concluded a Chinese species as dominant in our spectra. The dominant fingerprints in fig.3 are rather similar to that of starch (data not shown) especially in the range of 920–1023 cm^{-1}. The intensity of the peak at 862 cm^{-1}in starch is stronger than that of the ginseng. Although the peaks at 1026 and 1050 cm^{-1}appears both in the starch and in Chinese ginseng, the intensity ratio of these two peaks are apparently different. So it is considered to estimate the starch content in ginseng: the stronger the relative intensity of the peak at 1026 cm^{-1} in secondary derivative spectrum, the lower the starch content.

As our sample has a commercial purpose as tea, we have investigated its behavior in diluted and saturated aqueous solution. Fig. 5 presents the detailed Raman spectrum of the solid sample compared to the spectra of the dissolved

These Figures are identical with Figures 7, 8 and 9 from ***Cavalu2005***

sample (diluted and saturated) in the 700–1800 cm^{-1} spectral range, where the characteristic fingerprints are displayed.

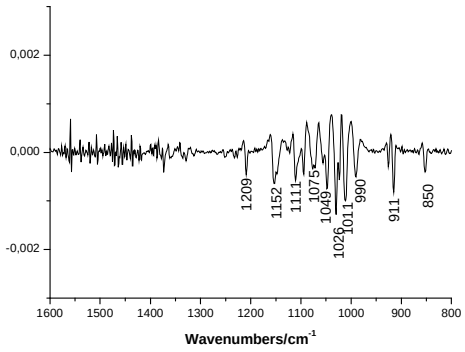

Fig. 3. Secondary derivative IR spectrum of ginseng powder.

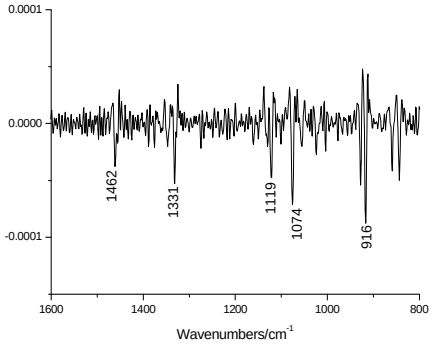

Fig. 4. Secondary derivative FT-Raman spectrum of ginseng powder.

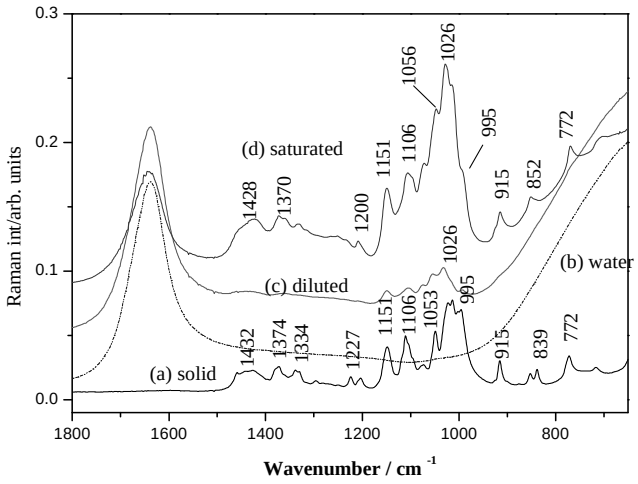

Fig. 5. FT-Raman spectra of a) powder ginseng, b) water, c) dilluted solution and d) saturated solution of ginseng. Excitation: 1064 nm, 50 mW.

One can observe that the spectral features are very well preserved in the saturated solution and the relative intensity of the bands in the range 950–1320 cm^{-1} similar to those from Raman spectrum of the powder. The starch content monitored through the relative intensity of the band at 1026 cm^{-1} is suitable to be monitored in saturated solution.

CONCLUSIONS

High quality FT-IR and FT-Raman spectra of the commercial Ginseng product were obtained and discussed. The second derivative vibrational analysis evidenced the special features closely related to the content of saponin and starch. Based on the comparison with other reported studies, we concluded a Chinese species as a dominant compound present in the analyzed samples. The vibrational analysis demonstrates that the starch content of a Ginseng product is favourable to be measured in aqueous saturated solution.

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