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Distinction of eight *Lycium* species by Fourier-transform infrared spectroscopy and two-dimensional correlation IR spectroscopy

Xia Yao [a], Yong Peng [a,*], Qun Zhou [b], Peigen Xiao [a], Suqin Sun [b,*]

[a] Institute of Medicinal Plant Development, Chinese Academy of Medical Sciences & Peking Union Medical College, Beijing 100193, PR China
[b] Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Analysis Center, Tsinghua University, Beijing 100084, PR China

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ABSTRACT

Eight species of *Lycium* fruits were differentiated by Fourier-transform infrared spectroscopy (FT-IR), second derivative IR spectra and two-dimensional correlation infrared spectroscopy (2D-IR). Their entire infrared spectra in the range of 4000–400 cm^{-1} were generally similar based on the peaks position and intensities. The findings indicated that the chemical constituents in these species of herbs were not distinctively different. However, variation in peak intensity were observed at about 2926, 2855, and 1745 cm^{-1} in the infrared spectra among these species for their easy differentiation. Much difference in their second derivative pattern among the eight species also provided information for easy differentiation. These species of *Lycium* fruits were further identified by their 2D-IR spectra. The findings provide a rapid and new operational procedure for the differentiation of different species of *Lycium* plants. The visual and colorful 2D-IR spectra can provide dynamic structural information of chemical components in analyte and demonstrated as a powerful and useful approach for the identification of herbs.

1. Introduction

Fructus Lycii (fruit of *Lycium barbarum* also known as Gouqizi in Chinese) is widely used as a traditional Chinese medicine in many countries. It can be used for nourishing the kidney and protecting essence, nourishing the liver and brightening eyes. There are about 80 species of genus *Lycium* (Solanaceae) all over the world, from which 7 species and 3 varieties of this genus plants are distributed in China, but only *L. barbarum* fruits were used as medicine according to the "China pharmacopoeia" [1,2]. To discriminate the different species rightly is important. Fourier-transform infrared spectroscopy (FT-IR) is considered as an alternative identification technique replacing traditional method, since it is a fast, easy to handle, and highly reproducible analytical technique. Currently, different species of *Lycium* are usually distinguished through micro-section, observation and analysis by professionals.

Two-dimensional correlation infrared (2D-IR) spectroscopy was proposed by Noda in 1986 [3], receiving much attention in recent years. The construction of 2D correlation IR spectra is based on the detection of dynamic changes of a system under an external perturbation. Such a perturbation induces selective changes in molecular constituents associated with individual normal modes of vibration in the system. The correlation analysis is applied to a set of spectra taken during the perturbation, so as to yield 2D-IR spectra [4,5]. This novel 2D method can treat spectral fluctuations as an arbitrary function of almost any kind of physical variables, such as time, temperature, pressure, concentration and composition. It can emphasize spectral features which cannot be observed in conventional one-dimensional spectra. The 2D-IR spectroscopy has advantages of high resolution and good repetition. And it now has successfully applied on the studies of molecular structure, biology, traditional Chinese medicines, etc. [6–14].

The technology of modern IR spectroscopy can analyze and identify complex intermixture system in a holistic manner. The technology takes the infrared spectra of high SNR (signal-to-noise ratio) as its basis, combines with second derivative IR spectra of higher resolution and 2D-IR spectra of much higher resolution, so that it can analyze and identify complex intermixture system [5–7].

In this paper, our samples are the fruits of *Lycium yunnanense* Kuang et A.M. Lu (A), *Lycium dasystemum* Pojark. var. *rubricaulium* A.M. Lu (B), *L. dasystemum* Pojark. (C), *Lycium chinense* Mill. (D), *Lycium truncatum* Y.C. Wang (E), *Lycium cylindricum* Kuang et A.M. Lu (F), *L. barbarum* L. (G) and *Lycium chinense* Mill. var. *potaninii* A.M. Lu (H), they are similar in appearance and difficult to tell. The eight samples were studied using FT-IR spectroscopy, second derivative IR spectroscopy and 2D correlation IR spectroscopy for the first time.

* Corresponding authors. Tel.: +86 10 62894462 (Y. Peng); tel.: +86 10 62781689; fax: +86 10 62782485 (S. Sun).
E-mail addresses: ypeng@implad.ac.cn (Y. Peng), sunsq@mail.tsinghua.edu.cn (S. Sun).

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2. Experiments

2.1. Apparatus

Spectrum GX Fourier-transform infrared spectrometer (Perkin–Elmer, USA), equipped with a deuterated triglycine sulfate (DTGS) detector, was used with a programmable temperature controller (Model CKW-II, Beijing Chaoyang Automatic Instrument Factory, China). All raw IR spectra were recorded from an accumulation of 32 scans in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}.

2.2. Samples

Eight samples: Fruits of *L. yunnanense* Kuang et A.M. Lu (A), *L. dasystemum* Pojark. var. *rubricaulium* A.M. Lu (B), *L. dasystemum* Pojark. (C), *L. chinense* Mill. (D), *L. truncatum* Y.C. Wang (E), *L. cylindricum* Kuang et A.M. Lu (F), *L. barbarum* L. (G) and *L. chinense* Mill. var. *potaninii* A.M. Lu (H), are identified and provided by Ningxia Academy of Agriculture and Forestry Sciences. All the samples are air-dried.

2.3. Procedure

The dried fruits of eight species of *Lycium* were pulverized into fine powder of over 100 mesh, and then 2–4 mg of sample blended with KBr powder, ground again and pressed into a tablet. After that, the IR spectra of all samples were collected. To obtain the 2D-IR correlation spectra, the prepared tablet was put into the sample pool with temperature controller, and the IR spectra were recorded at room temperature and the dynamic spectra at different temperatures from 50 to 120 °C at an interval of 10 °C.

2.4. Data processing

The raw FT-IR data was processed with PE spectrum software of Perkin–Elmer FT-IR spectrometer (Version 5.0.1). The second derivative IR spectra were obtained after 13-point smoothing of the original IR spectra. 2D-IR correlation spectra were obtained by treatment of the series of temperature-dependent dynamic spectra, which were obtained after baseline correction and 13-point smoothing of the original spectra, with 2D-IR correlation analysis software programmed by Department of Chemistry of Tsinghua University, Beijing, China.

3. Results and discussion

3.1. IR spectra of eight Lycium species

The chemical compounds of the fruit of *Lycium* plants are polysaccharides, organic acids, steroids, peptides, flavonoids, etc. [15]. Fig. 1 shows the FT-IR spectra of the eight samples at the room temperature. As a kind of macro-fingerprinting feathers of natural product complex, several characters can be extracted, such as, the strongest peak at 3368 cm^{-1} belonging to the stretching vibration of O—H groups, the peak at 2926 and 2855 cm^{-1} assigning to the stretching vibration of —CH_2 groups, the peak at 1745 cm^{-1} due to the stretching vibration of C=O groups in the volatile oils and other compounds embodying carbonyl group[16], and the stronger peaks in the range of 1200–1000 cm^{-1} mainly attributed to the

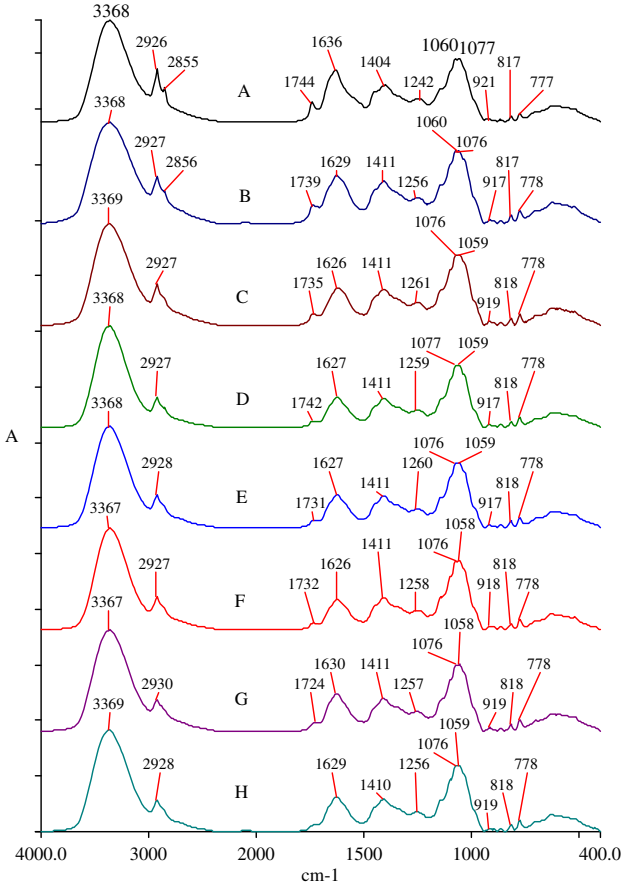

Fig. 1. FT-IR spectra of eight *Lycium* species samples (A–H).

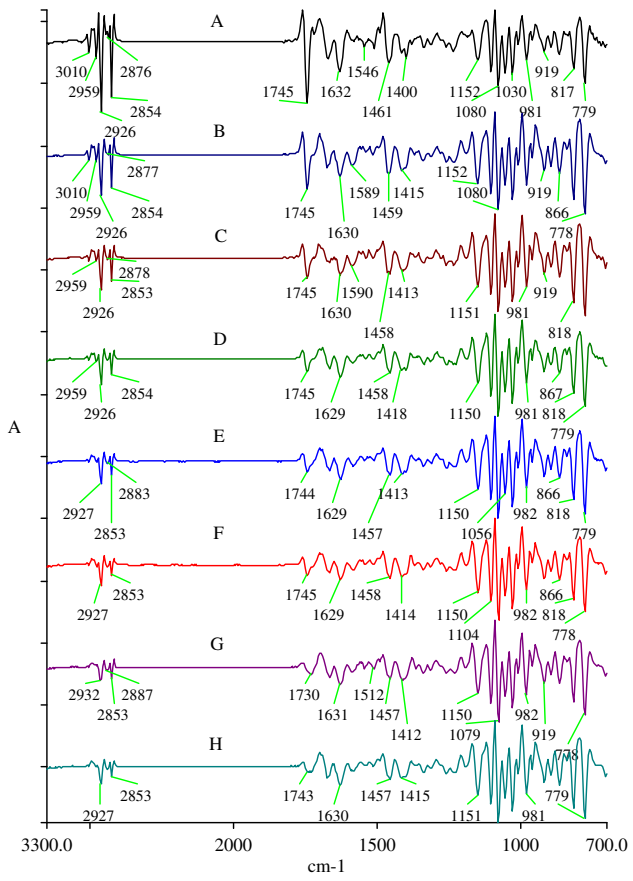

Fig. 2. The second derivative IR spectra of eight *Lycium* species samples (A–H).