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Identification of trichothecene-type mycotoxins in toxic mushroom *Podostroma cornu-damae* and biological specimens from a fatal case by LC–QTOF/MS

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ABSTRACT

In some autopsy cases, there are unknown natural toxins that are suspected to cause serious damage to the person. However, without reference materials, it is almost impossible to identify the suspicious natural toxins by GC–MS or LC–MS. In this case, a man drank mushroom –liquor with a meal at his home. Seven hours later, he was transported to the emergency room, and 12 hours later, he died. In the ingested mushroom-infused-liquor, there were pieces of mushroom that were estimated to be *Podostroma cornu-damae* (Hypocreaceae) based on their morphological characteristics. To identify the species, chemical component analysis was conducted using LC–QTOF–MS/MS. Monoisotopic mass, fragment ions, and isotope distributions were obtained from the LC–QTOF–MS/MS analysis. In addition, fragment ions and structure matching were tested for target compound confirmation. In this analysis, several toxic trichothecene-type mycotoxins were identified including roridin D, roridin E, roridin Q, satratoxin G, satratoxin H, satratoxin H 12′-acetate, satratoxin H 13′-acetate, satratoxin H 12′,13′-diacetate, and verrucarol. At autopsy, heart blood, peripheral blood, and the stomach contents were collected, and only satratoxin H was detected in these samples. This is the first finding of a trichothecene-type mycotoxin in a human biological sample from an expected case of *P. cornu-damae* intoxication. We demonstrated that LC–QTOF–MS/MS analysis was an effective method for mushroom intoxication cases in the absence of reference materials. Additionally, the experience, knowledge, and analytical methods we obtained in this study will be great assets for solving other cases of possible natural toxin intoxication.

1. Introduction

Among the thousands of species of mushrooms worldwide, approximately 100 species are known to be poisonous to humans, and about 30 species are considered toxicologically important, as they contain fatal toxins [1,2]. Toxic mushrooms can be classified into six groups according to their effects: those that (1) destroy cells and injure the liver and kidneys, (2) act on the autonomic nervous system, (3) inhibit acetaldehyde metabolism, (4) act on the central nervous system, (5) irritate the gastrointestinal tract, and (6) cause swelling or necrosis or disturb peripheral nerves [1]. Mushroom toxins can also be classified into nine groups according to their site of action: neurotoxins, neurovascular toxins, cardiotoxins, gastrointestinal toxins, hepatotoxins, nephrotoxins, myotoxins, immunologic/hematologic toxins, and mitochondrial toxins [2]. Various mushroom toxins are known including amatoxin, gyromitrin, coprine, muscarine, ibotenic acid-muscimol [3], and the toxicities, symptoms, and lethalities vary according to mushroom and toxin. Most cases of accidental toxic mushroom ingestion are caused by eating unidentified or misidentified wild mushrooms.

Podostroma cornu-damae (Hypocreaceae) was discovered in Sichuan, China and named *Hypocrea cornu-damae* Pat., and then renamed *P. cornu-damae* (Pat.) [4,5]. This fungus is known to grow in Korea, Japan, China, and Java, and the fruiting body resembles a red pencil or deer's horn [6] produces tricothecene-type mycotoxins. Saikawa et al. isolated four satratoxin H derivatives as well as roridin E and verrucarin J from this mushroom [7], and other satratoxins have been reported [8–10]. With the exception of verrucarin J, mice injected with 0.5 mg of these toxins into the abdomen died 1 day after the injection. The chemical structures of previously reported trichothecenes are shown in Fig. 1.

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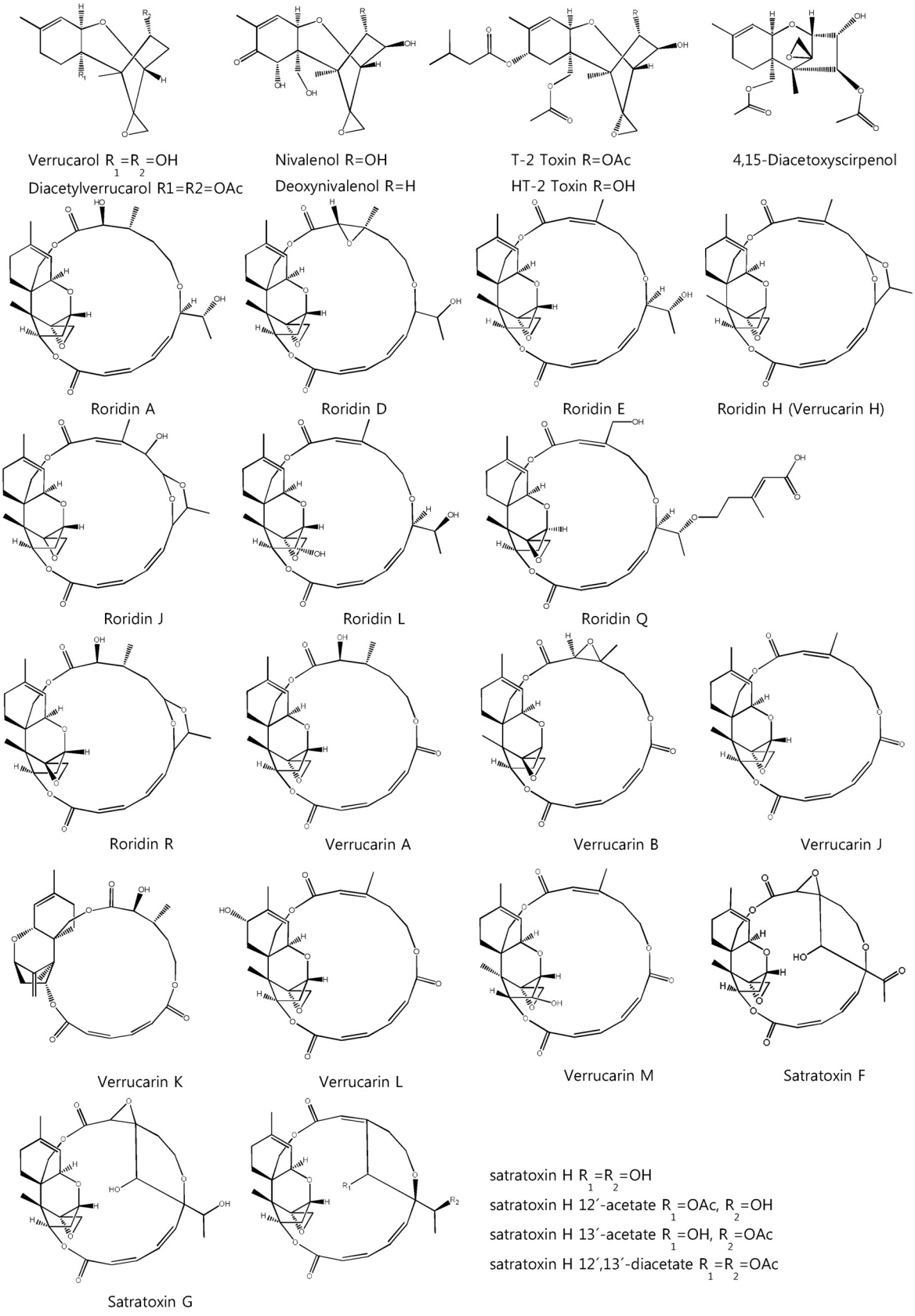

Fig. 1. Chemical structures of trichothecenes.