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Phytochemicals of Liverworts: Biological Activity and Their Application to Cosmetics, Foods and Medicines

Plenary Talk

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Abstract

There are 6000 species of liverworts in the world. Almost all liverworts possess beautiful cellular oil bodies. Many species of liverworts possess characteristic fragrant odors and an intense pungent, sweet, or bitter taste. Generally, liverworts are not damaged by bacteria, fungi, insect larvae and adults, snails, slugs, and other small mammals. Although liverworts possess such bioactive products, their isolation and structural elucidation were neglected for almost a century. Since 1972, we collected more than 800 species of liverworts around the world and chemically analyzed them with respect to their chemistry, pharmacology, and application as sources of cosmetics and human diets, and as medicinal or agricultural agents. The biological activities of liverworts are due to the terpenoids and aromatic compounds which are present in the oil bodies in each species. Several hundred new compounds have been isolated from the essential oils and solvent extracts of liverworts, and more than 60 new carbon skeletal terpenoids and aromatic compounds such as bis–bibenzyls, marchantin A (1) and riccardin A (2), which are very rare natural products, were found. Most of the liverworts studied elaborate characteristic scent, pungent, and bitter tasting compounds, many of which show antimicrobial, antifungal, antiviral, allergenic contact dermatitis, cytotoxic, insecticidal, anti–HIV, superoxide anion radical release, plant growth regulatory, neurotrophic, NO production inhibitory, muscle relaxing, antiobesity, piscicidal, nematocidal activity, and many others. The most characteristic chemical phenomenon of the liverworts is that most of the sesqui– and diterpenoids are enantiomers to those found in higher plants. It is very noteworthy that different liverwort species of the same genus like *Frullania tamarisci* and *F. dilatata* (Frullaniaceae) each produces sesquiterpene lactone enantiomers, (+)–frullanolide (3) and (–)-frullanolide (4). When the large thalloid liverwort, *Conocephalum conicum*, was completely sealed into a plastic sac which was covered by a glass plate for 1, 6, and 9 months, its morphology and each chemical profile were dramatically changed. The major monoterpene, (+)–bornyl acetate (5) included in the original thallus, disappeared and menthyl cinnamate (6) was newly created. The chemical profiles of the cultured *C. conicum* are very similar to that of the Japanese most expensive mushroom *Tricholoma matsutake*, which is used as consommé soup in Japan. Thus, the production of the volatiles of *T. matsutake* can be produced limitless from the liverwort on laboratory and industry scales.

When the thalloid liverwort *Marchantia paleacea* subsp. *diptera* was cultured under the same conditions as mentioned above, (S)–(–)-perillaldehyde (7), which is the most important aroma

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for *Perilla frutescens* (Lamiaceae) and is used in Japanese cuisine and herbal medicines, and is not included in the original liverwort, was elaborated in 50% yield, along with 1–perillyl alcohol (8) and shisool (9). Thus, (S)–(–)-perillaldehyde (7) can be created limitless for a year in this simple manner.

Almost all of the *Radula* liverwort species mainly produce bibenzyls and prenyl bibenzyls. It is noteworthy that *R. perrottetii* and *R. marginata* biosynthesize perrottetinene (PET) (10) and perrottetinenic acid (11), the structures of which are very similar to that of the well–known psychoactive compound tetrahydrocannabinoid (THC) (11) obtained from *Cannabis sativa*. PET (10) showed the same psychoactivity as that of THC and more potent antiinflammatory activity than THC (11).

In this paper, the bio– and chemical diversity of liverworts and their bio– and pharmacological activities, including characteristic odor and taste, as well as the possibility of liverworts as cosmetics, foods, and medicals, are surveyed.

Keywords: Liverworts, marchantins, riccardins, perrottetinene, *Radula*, *Conocephalum conicum*

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