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UV protection and singlet-oxygen quenching activity of intramolecularly hydrogen-bonded hydroxyanthraquinone derivatives found in aloe

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This paper is dedicated to Professor Paul F. Barbara of University of Texas at Austin who passed away on October 31, 2010 at the age of 57 years from complications following a cardiac arrest.

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ABSTRACT

The UV protection and singlet-oxygen ($^1O_2$) quenching activity of intramolecularly hydrogen-bonded hydroxyanthraquinone derivatives found in aloe have been studied by means of laser spectroscopy. The UV protective activity provided by excited-state intramolecular proton-transfer (ESIPT) in these molecules correlates with their $^1O_2$ quenching activity, and the UV protective molecules have high $^1O_2$-quenching function. The reason for this correlation can be understood by considering ESIPT-induced distortion of ground-state potential surfaces in encounter complexes with $^1O_2$.

1. Introduction

Aloe is a flowering fleshy plant with succulent sharp leaves. The cosmetic and healing properties of aloe have been highly valued by a lot of people (Cleopatra, Aristotle, Alexander the Great and so on) for thousands of years [1–6]. For example, legend says that aloe was one of Cleopatra's beauty secrets. In the present age, aloe gel is an active ingredient in hundreds of cosmetics, skin lotions and sun blocks for UV protection. Accordingly, it can be expected that excited-state intramolecular proton-transfer (ESIPT [7–11]) in aloe species, as well as in various skin sun-blocks [12], provides the UV protection on skin, and aloe species also quench harmful singlet oxygen ($^1O_2$, $^1\Delta_g$ state [13]) generated on UV-irradiated skin [14].

In a previous paper [15], we reported the UV protection and $^1O_2$ quenching of aloesaponarin I (methyl 3,8-dihydroxy-1-methyl-9,10-dioxo-9,10-dihydroanthracene-2-carboxylate, abbreviated as AS1, Fig. 1) found in aloe [16]. In AS1, the ESIPT along one of the intramolecular hydrogen-bonds (C_8-O-H$\cdots$O=C_9) provides the UV protection, and the functional groups participating in the ESIPT play important roles also in the $^1O_2$ quenching. AS1 has a $^1O_2$-quenching rate-constant larger than vitamin E that is well-known as an efficient $^1O_2$ quencher [13,17], and AS1 has a long duration of action due to its resistance to UV degradation and chemical attacks by $^1O_2$ and free radicals.

Aloe contains various intramolecularly hydrogen-bonded hydroxyanthraquinone derivatives such as AS1 [16], and it is expected that those molecules can also be UV protective and have $^1O_2$ quenching activity. The reaction in which $^1O_2$ and anthraquinone participate is also a topic of interest [18]. Accordingly, in the work presented here, we have studied the ESIPT-based UV-protective and $^1O_2$-quenching functions of intramolecularly hydrogen-bonded hydroxyanthraquinone derivatives found in aloe [16] by means of laser spectroscopy.

2. Experimental

Fig. 1 shows the ground-state (S_0-state) structures of the molecules used in the present work. Each of these molecules

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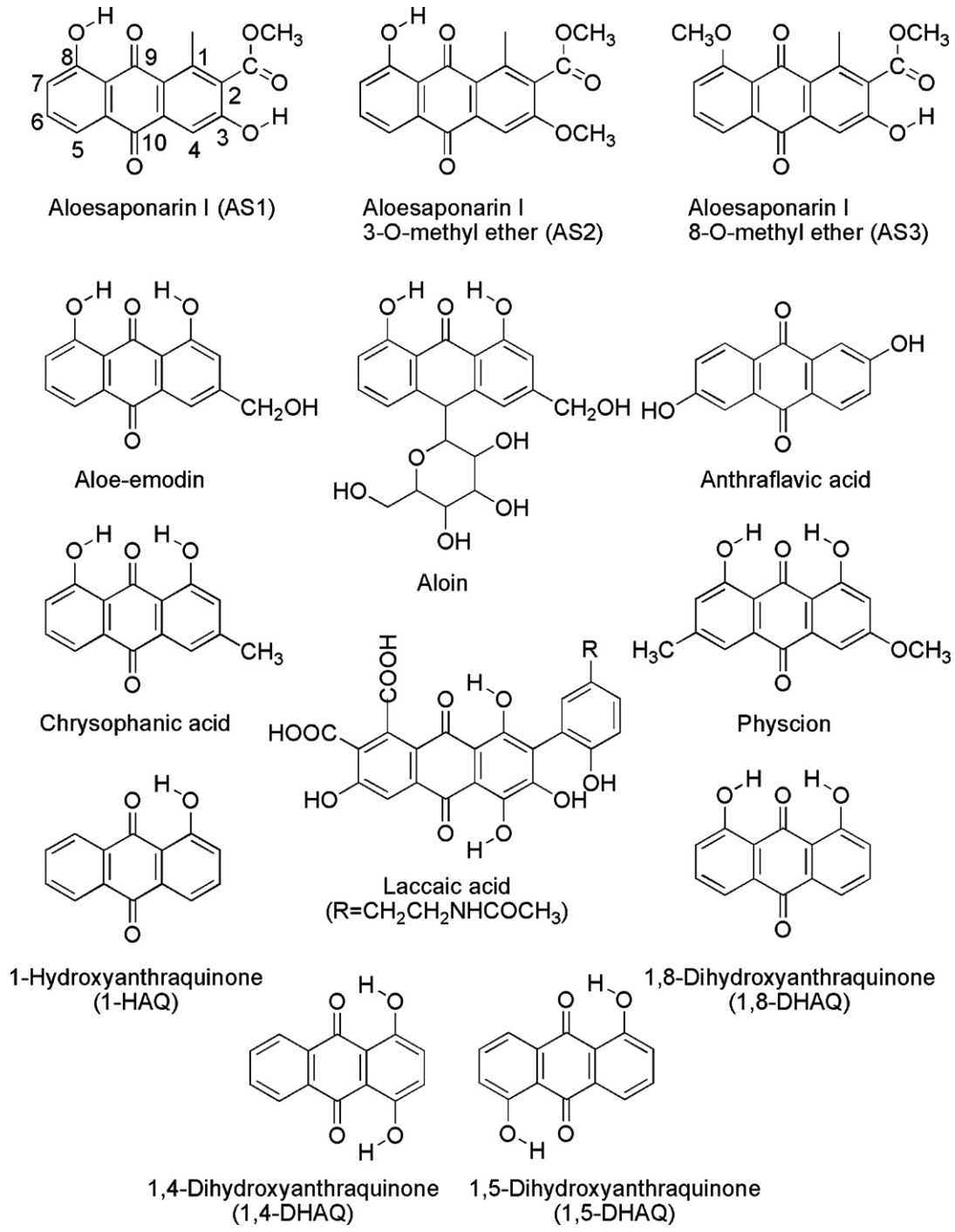

Fig. 1. Structure of molecules used in the present work.

except aloin is a hydroxyanthraquinone (HAQ). The UV protection and $^1O_2$ quenching activity of AS1, aloesaponarin I 3-O-methyl ether (methyl 8-hydroxy-3-methoxy-1-methyl-9,10-dioxo-9,10-dihydroanthracene-2-carboxylate, AS2) and aloesaponarin I 8-O-methyl ether (methyl 3-hydroxy-8-methoxy-1-methyl-9,10-dioxo-9,10-dihydroanthracene-2-carboxylate, AS3) were studied in a previous work [15]. AS1, aloe-emodin, aloin and chrysophanic acid are chemical constituents characteristics of aloe [16]. Some molecules similar in molecular structure to laccaic acid or physcion are also found in aloe [16]. Originally thought to be one compound, laccaic acid has been separated into four compounds [19], but in the present study, the structure of the major compound shown in Fig. 1 [19] is used in estimation of the molar concentration. Reported contents of the above-mentioned components present in aloe are given in Table 1 [20–23]. Although anthraflavic acid is not a chemical constituent characteristics of aloe [16], it is found in rhubarb, which is one of ancient and well-known Chinese herbal medicines and also contains various HAQs [24]. Since the above-mentioned molecules except aloin have a common skeletal moiety and are different in the side group(s) attached to it, we have also studied the skeletal molecule (1-hydroxyanthraquinone, 1-HAQ) and its derivatives; 1,4-dihydroxyanthraquinone (quinizarin, 1,4-DHAQ), 1,5-dihydroxyanthraquinone (anthrarufin, 1,5-DHAQ) and 1,8-dihydroxyanthraquinone (chrysazin, 1,8-DHAQ). The compounds