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Hydroxylated furanoditerpenoids from pupal cases produced by the bruchid beetle *Sulcobruchus sauteri* inside the seeds of *Caesalpinia decapetala*

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ABSTRACT

Seven undescribed hydroxylated cassane-type furanoditerpenoids were isolated from pupal cases formed from the secretion/excretion of the larvae of the wild bruchid seed beetle *Sulcobruchus sauteri* in infested *Caesalpinia decapetala* seeds, and their structures were elucidated by interpreting their spectra. The hydroxylated furanoditerpenoids found in the pupal cases were not present in the seeds of the host plant. Caesalacetal and caesaljapin obtained from the intact seeds exhibited larvicidal activity against the larvae of *Aedes albopictus*, while the hydroxylated furanoditerpenoids isolated from the pupal cases were inactive. The larvae of *S. sauteri* are proposed to detoxify larvicidal diterpenoids that occur in the seeds of the host plant by regiospecific hydroxylation.

1. Introduction

The seeds of *Caesalpinia decapetala* (Roth) Alston (Leguminosae: synonym *Caesalpinia decapetala* var. *japonica*, with the common Japanese name 'jaketsuibara') have been used as an insecticide, an antidiarrheal agent, and a febrifuge for malarial fever in oriental traditional medicine (Namikoshi et al., 1987). The seeds have been reported to contain cassane-type furanoditerpenoids, such as caesaljaponin A (**1**) (Kamikawa et al., 2015). The seed-eating larvae of the wild bruchid beetle *Sulcobruchus sauteri* specifically infest the seeds of *C. decapetala*, feed on their cotyledon, and produce pupal cases (Fig. 1) prior to pupation, using secretion/excretion products inside the seeds (Watanabe, 1985). In the course of our investigations into biologically active compounds involved in the relationship between the seed-eating larvae of the bruchid beetle and its host plant, we isolated seven undescribed hydroxylated furanoditerpenoids from the MeOH extracts of the pupal cases produced by *S. sauteri*. In this paper we report our investigations into the structures and larvicidal activities of the furanoditerpenoids isolated from the intact seeds of *C. decapetala* and the pupal cases produced by the bruchid beetle *S. sauteri*.

2. Results and discussion

The intact seeds of *C. decapetala* and the pupal cases produced by the larvae of the bruchid beetle *S. sauteri* inside the infested seeds (Fig. 1) were extracted with MeOH. Each of the concentrated MeOH extracts was suspended in water and successively partitioned with hexane and EtOAc. Each EtOAc-soluble portion was subjected to analysis by HPLC with photodiode-array detection (HPLC-PDA) (Fig. 2). The EtOAc-soluble fraction of the intact seeds showed the presence of relatively apolar components (Fig. 2A), which were identified as caesaljaponin A (**1**), caesaljaponin B (**2**) (Kamikawa et al., 2015), caesalacetal (**3**) (Kamikawa et al., 2016a), and caesaljapin (**4**) (Ogawa et al., 1992; Kamikawa et al., 2016a) based on comparisons of their spectroscopic data with those of authentic samples after isolation by silica gel column chromatography (CC), while HPLC analysis of the EtOAc-soluble portion derived from the pupal cases revealed the presence of several major polar components (Fig. 2B). This portion was subjected to octadecylsilyl (ODS) CC followed by purification by ODS or silica gel CC to afford compounds **5**–**11** (Fig. 3).

Compound **5** was isolated as a colorless oil with an optical rotation, $[\alpha]_D$, of -28° (c 0.04, MeOH). Positive-ion HRESIFTMS revealed an $[M+Na]^+$ ion peak at m/z 413.1570 (calcd for $C_{21}H_{26}O_7Na^+$, 413.1571), consistent with the molecular formula $C_{21}H_{26}O_7$ (nine degrees of unsaturation). IR-absorption bands at 3396, 1760, and 1724 cm^{-1} implied the presence of hydroxyl, γ-lactone, and ester functionalities. The ^1H NMR spectrum exhibited a pair of doublets at δ_H 6.46 (1H, d, J = 1.8 Hz, H-15) and 7.36 (1H, d, J = 1.8 Hz, H-16), indicating the

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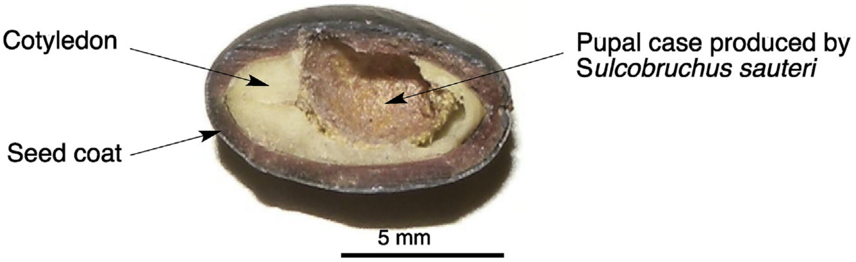

Fig. 1. Cross-section of an infested seed of *C. decapetala*.

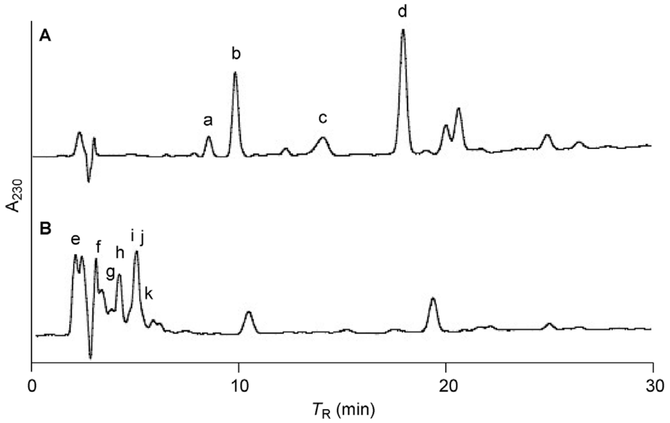

Fig. 2. Representative HPLC-PDA profiles of the EtOAc-soluble fractions of: (A) the intact seeds of *C. decapetala* and (B) the pupal cases produced by *S. sauteri*. Detection was performed at 230 nm. a, caesaljaponin B (**2**); b, caesaljaponin A (**1**); c, caesalacetal (**3**); d, caesaljapin (**4**); e, norcaesalsauterol (**11**); f, 2,7-dihydroxycaesaljapin (**7**); g, caesalsauteolide (**5**); h, caesalsauterol (**9**); i, 2-hydroxycaesalacetal (**8**); j, 6-acetylcaesalsauterol (**10**); k, 2-hydroxycaesaljapin (**6**).

presence of a 1,2-disubstituted furan ring, which was supported by a UV absorption maximum at 216 nm (log ε 4.02) as well as IR absorption bands at 1507 and 1456 cm^{-1} (Jiang et al., 2002; Ochieng et al., 2012; Kamikawa et al., 2015, 2016a, 2016b). The ^{13}C NMR and DEPT spectra, as well as HSQC spectrum, revealed the presence of 21 carbon signals that correspond to three methyl groups (including a methoxy carbon), five methylenes, three methines (including an oxygenated carbon), six quaternary carbons (including two oxygenated carbons), and two carbonyl carbons, in addition to the four *sp*^{2} carbon atoms at δ_C 148.6 (C-12, s), 122.4 (C-13, s), 109.1 (C-15, d), and 143.1 (C-16, d) of the 1,2-disubstituted furan ring. The $^1H{-}^1H$ COSY and HSQC spectra established the presence of four partial structures (C-1/C-2/C-3, C-5/C-6/C-7, C-9/C-11, and C-15/C-16), as shown in Fig. 4. The connectivity between C-3 and C-5 through C-4 was determined on the basis of HMBC correlations from H_3-19 to C-3, C-4 and C-5. The connectivities between the remaining partial structures were deduced by analysis of the HMBC spectroscopic data, which included key correlations from H-1 to C-5, C-10, and C-20, from H-7 to C-8, from H_2-11 to C-8, C-12, and C-13, from H-15 to C-12, from H-16 to C-13, and from H_3-17 to C-8, C-13, and C-14, which resulted in the cassane-type furanoditerpene skeleton in **5** (Fig. 4). The HMBC correlations from H_3-19 and the methoxy protons at δ_H 3.70 (H_3-21) to the carbonyl carbon at δ_C 178.5 (C-18) established that the methoxycarbonyl group is attached to C-4. Since the presence of the furan ring, the A–C rings, and two carbonyl groups account for eight of the nine degrees of unsaturation, compound **5** must have a lactone ring, which is supported by the IR absorption band at 1760 cm^{-1}. The chemical shifts of C-8 (δ_C 88.5) and C-20 (δ_C 180.5) indicated the presence of a γ–lactone moiety bridged between C-8 and C-10. The chemical shifts of H-2/C-2 (δ_H 4.22 and δ_C 63.8) and C-14 (δ_C 70.1) indicated that C-2 and C-14 bear hydroxyl groups. All other HMBC correlations supported the overall structure of **5**, as shown in Fig. 4. The relative configuration of **5** was established by coupling-constant analyses and NOESY data (Fig. 5). NOESY correlations between H-9 and both H-5 and H-7α indicated that these protons were all axial and *α*-oriented. On the other hand, the NOESY correlation between H-2 and Me-19 indicated that the hydroxyl group at C-2 and Me-19 were α- and β-oriented, respectively. The equatorial and α-orientation of 2-OH was supported by the large vicinal coupling constant of 11.9 Hz between H-2 and both H-1α and H-3α. The NOESY correlation between H-7β and Me-17 indicated that Me-17 was β-oriented, which was supported by the other NOESY correlation between H-15 and Me-17. The absolute configuration of **5** was determined by comparison of the experimentally acquired electronic circular dichroism (ECD) spectrum of **5** with that calculated using the time-dependent density functional theory (TDDFT) method. Compound **5** exhibited positive Cotton effects (CEs) at 190 nm (Δε +2.01) and 247 nm (Δε +0.42), and a negative CE at 216 nm (Δε −2.86), which were in good agreement with those calculated for the 2*S*-configured model (Fig. 6). Consequently, the structure of **5** was established as shown in Fig. 3. The compound was named caesalsauteolide.

Compound **6** was obtained as a colorless oil with an optical rotation, $[\alpha]_D$, of +8° (*c* 0.1, MeOH). Negative-ion HRESIFTMS analysis revealed an $[M–H]^-$ ion peak at *m/z* 375.1817 (calcd for $C_{21}H_{27}O_6^-$, 375.1813), consistent with the molecular formula $C_{21}H_{28}O_6$. The NMR spectra of **6** were almost identical to those of caesaljapin (**4**) (Ogawa et al., 1992; Kamikawa et al., 2016a) except for the presence of additional oxygenated methine signals at δ_H 4.19 (m) and δ_C 65.2 (CH), which indicated the presence of a new hydroxyl group. Analyses of the $^1H{-}^1H$ COSY and HSQC spectra revealed the additional hydroxyl group to be located at C-2 (Fig. 4). The α-orientation of the 2-OH was evidenced by the large $^3J_{H1\alpha\text{-}H2}$ (11.7 Hz) and $^3J_{H2\text{-}H3\alpha}$ (12.2 Hz) coupling constants. All other HMBC and NOESY correlations supported the overall structure and relative configuration of **6**, as shown in Figs. 4 and 5. The ECD spectrum of compound **6** exhibited a positive CE at 216 nm (Δε +2.67), which was similar to that of caesaljapin (**4**) ($\Delta\varepsilon_{218}$ +8.89) (Kamikawa et al., 2016a). As it had been reported that the CE attributed to the π–π* transition of a furan chromophore in such a furanoditerpenoid is mainly affected by the chirality of C-14 (Wu et al., 2014), the absolute configuration at C-14 in **6** was assigned to be *R*. Consequently, the structure of **6** was established as shown in Fig. 3. The compound was named 2-hydroxycaesaljapin.

Compound **7** was obtained as a colorless oil with an optical rotation, $[\alpha]_D$, of +3° (*c* 0.2, MeOH). Negative-ion HRESIFTMS revealed an $[M–H]^-$ ion peak at *m/z* 391.1765 (calcd for $C_{21}H_{27}O_7^-$, 391.1762), consistent with the molecular formula $C_{21}H_{28}O_7$, which differs from that of 2-hydroxycaesaljapin (**6**) by one oxygen atom. This difference suggested that compound **7** contains an additional hydroxyl group. The NMR spectra of **7** were almost identical to those of **6** except for the absence of the C-7 methylene signals and the presence of additional oxymethine signals at δ_H 3.51 (td, J = 10.7 and 4.9 Hz) and δ_C 72.3 (CH). The $^1H{-}^1H$ COSY and HMBC spectra indicated that compound **7** is a 7-hydroxylated derivative of **6** (Fig. 4). The large ^1H coupling constant of 10.7 Hz between H-7 and both H-6β and H-8 is evidence of

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