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Batatins III–VI, glycolipid ester-type dimers from *Ipomoea batatas*

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ABSTRACT

Batatins III–VI (**1**–**4**), glycolipid ester-type dimers, were isolated from the tuberous roots of sweet potato (*Ipomoea batatas*) using recycle high performance liquid chromatography. Their structures were characterized by means of several high-resolution NMR and mass spectrometry techniques. These compounds are the first examples of ester-type dimers which consist of two units of the heterotetrasaccharide operculinic acid C. Each unit was esterified by a different amount and type of acid residues: (2*S*)-methylbutanoic, cinnamic, decanoic (capric) and dodecanoic (lauric) acids. Batatins III–VI (**1**–**4**) are an example of the presence of a large number of resin glycoside congeners in each morning glory species caused by partial acylation of their constitutive saccharide cores.

1. Introduction

The functional diversity of monosaccharides presents the possibility of generating countless constitutional and stereochemical variations (diastereoisomers) on their covalent combination to form complex carbohydrates, as found in the chemical diversity of morning glory resin glycosides (Pereda-Miranda et al., 2010). Most of these oligosaccharides are glycosyl derivatives of (11*S*)-hydroxyhexadecanoic acid. Their sugar cores are composed by a heteropolysaccharide of only a few residues of D-glucose and/or epimers of pentoses (L-rhamnose, D-fucose, D-quinovose, and D-xylose). The structural complexity of these glycolipids primarily arises from the variable linkage positions among the saccharide units, the size of the macrolactone ring formed by the aglycone spanning two or more units of their oligosaccharide cores, and the multiple variations caused by acylation of the sugar cores (Pereda-Miranda et al., 2010). This chemical diversity makes it extremely difficult to access homogeneous quantities of oligosaccharides for structural identification. Consequently, the methodological approaches to achieve total homogeneity of oligosaccharides based on recycle HPLC offers the unique opportunity to have a series of pure oligosaccharides for spectroscopic and spectrometric characterization (Bah and Pereda-Miranda, 1997; Pereda-Miranda and Hernández-Carlos, 2002).

Polar members of the resin glycosides possess high molecular weights as a result of being ester-type polymers of glycolipids. Prior to this investigation, only eight ester-type dimers from only four different members of the morning-glory family (Convolvulaceae) had been isolated. Merremin was obtained from the roots of *Merremia hungaiensis* and is the first example of an ester-type heterodimer which consists of two units of the pentasaccharide operculinic acid A, each one esterified by two residues of hexadecanoic (palmitic) acid (Noda et al., 1995). Tricolorins H–J, three ester-type heterohexasaccharides, were purified from *Ipomoea tricolor* and consisting of two trisaccharide units of tricoloric acid C with a difference in the position for the ester-type linkage. Only tricolorin H was acylated in the macrocyclic unit by (2*S*)-methylbutanoic acid (Bah and Pereda-Miranda, 1997). Tyrianthins A and B, two acylated ester-type dimmers, were isolated from *Ipomoea orizabensis*. Scammonic acid A was determined to be the heterotetraglycosidic acid in both monomeric units and the esterifying residues were identified as nilic, 2-methylbutanoic, and butanoic acids (León-Rivera et al., 2009).

Native to tropical America, sweet potato (*Ipomoea batatas*) is a perennial vine that has been cultivated in Mexico, Central and lowland South America, and the Caribbean for over 5000 years because of its edible tubers. Today, it is cultivated around the world, especially in developing countries as a staple food, but also for its uses in folk remedies (Escalante-Sánchez et al., 2008). Batatins I–II were acylated ester-type dimers isolated from hexane-soluble extracts of the tuberous roots of this crop. Simonic acid B was confirmed as the glycosidic acid forming each of the two branched heteropentasaccharide units. Three acylating residues responsible for

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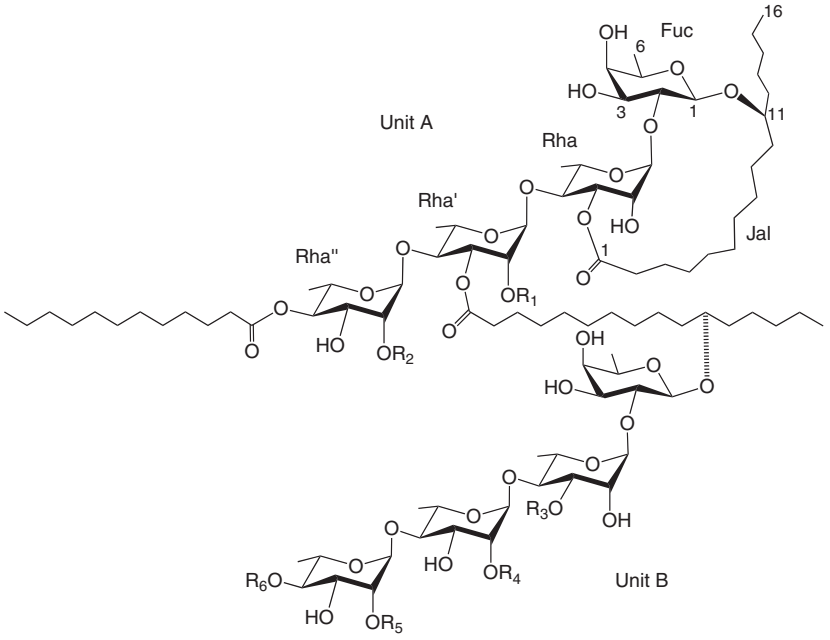
the lipophilicity of these high molecular weight oligomers were identified as (2*S*)-methylbutanoic, cinnamic, and dodecanoic (lauric) acids (Escalante-Sánchez and Pereda-Miranda, 2007). The present investigation describes the isolation and characterization of four novel ester-type dimers of the tetrasaccharide operculinic acid C and named batatins III–VI (**1–4**).



	R_1	R_2	R_3	R_4	R_5	R_6
1	H	H	deca	dodeca	H	deca
2	H	H	deca	deca	H	dodeca
3	mba	CA	H	mba	CA	dodeca

2. Results and discussion

Batatins III (**1**) and IV (**2**) were isolated by recycle-preparative HPLC from a hexane-soluble resin glycoside mixture of the white-skinned cultivar, while the members V (**3**) and VI (**4**) of this series were obtained from a chloroform-soluble extract of the purple-skinned variety. Compounds **1–4** were submitted to saponification and yielded a water-soluble glycosidic acid and an organic solvent-soluble acidic fraction. In all cases, the glycosidic acid was characterized as operculinic acid C, hexadecanoic acid (11*S*)-[*O*-6-deoxy-α-L-mannopyranosyl-(1→4)-*O*-6-deoxy-α-L-mannopyranosyl-(1→4)-*O*-6-deoxy-α-L-mannopyranosyl-(1→2)-6-deoxy-β-D-galactopyranosyl]oxy. The sequence of glycosidation for this isolated glycosidic acid and the absolute configuration for its sugar core and aglycone have been extensively reported. This glycosidic acid was originally isolated from the resin glycosides of *Ipomoea operculata* (Ono et al., 1989) and named mammoside I after its isolation from *Merremia mammosa* (Kitagawa et al., 1997). It has also been isolated from the resin glycosides of *I. batatas* (Escalante-Sánchez et al., 2008; Noda et al., 1992; Noda and Horiuchi, 2008; Yoshikawa et al., 2010), *Ipomoea murucoides* (Chérigo et al., 2009), *I. operculata* (Ono et al., 1992), *Ipomoea pes-caprae* (Escobedo-Martínez and Pereda-Miranda, 2007), and *Ipomoea stolonifera* (Noda et al., 1998). The organic-solvent soluble fractions were analyzed by GC–MS and the liberated acids were identified by comparison with authentic samples as previously described (Chérigo et al., 2008; Escobedo-Martínez et al., 2010; Pereda-Miranda et al., 2006). From compounds **1** and **2,** two peaks were detected: *n*-decanoic (deca) and *n*-dodecanoic (dodeca) acids; compounds **3** and **4** afforded three peaks: 2-methylbutanoic (mba), cinnamic (CA), and *n*-dodecanoic acids.

In the negative ESIMS, batatins III (**1**) and IV (**2**) showed the same iodine adduct at *m/z* 2477 $[M+I]^-$. HRESIMS registered the exact mass at *m/z* 2348.5427 for the quasimolecular ion $[M-H]^-$ of **1** (calcd for $C_{124}H_{219}O_{40}$ −13.8 ppm) and at *m/z* 2348.5467 for the ion of **2** (calcd for $C_{124}H_{219}O_{40}$ −15.5 ppm), which corroborated that these natural compounds represent a pair of diastereoisomers. They shared the same high-mass fragment ions at *m/z* 1019 [macrocyclic unit A]$^-$ and 1173 [unit B–H–$C_{10}H_{18}O$]$^-$, resulting from the cleavage of an ester-type dimer linkage. These peaks confirmed an asymmetric substitution pattern for each tetrasaccharide core (Bah and Pereda-Miranda, 1997; Escalante-Sánchez and Pereda-Miranda, 2007). Negative-ion FABMS was successful in detecting the fragment ion for intact monomeric unit B at *m/z* 1329, allowing for the exact mass estimation of a triacylated operculinic acid C by observing the ester elimination at 991 [1173−$C_{12}H_{22}O$]$^-$ and 837 [991−$C_{10}H_{18}O$]$^-$. Other shared fragments were produced by the common glycosidic cleavage of the sugar moieties observed in all resin glycosides (Escalante-Sánchez et al., 2008; Kitagawa et al., 1997; Pereda-Miranda et al., 2005). For example, peaks resulting from cleavage of the anomeric linkage at the four methylpentose moiety (Rha″) in each pentasaccharide (units A and B) were observed in secondary ion mass spectroscopy at *m/z* 329 $[C_6H_{10}O_4+C_{12}H_{23}O]^-$ and 301 $[C_6H_{10}O_4+C_{10}H_{19}O]^-$ for compound **1** and suggested that this monosaccharide was substituted either by a decanoyl or dodecanoyl residue. In contrast, dimer **2** only