Resin Glycosides. XXI.[1] Tuguajalapins I—X, the Resin Glycosides Having Long-Chain Fatty Acid Groups from the Root of *Merremia hungaiensis*

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Received March 22, 1994; accepted May 30, 1994

Ten resin glycosides (jalapins) named tuguajalapins I—X were isolated from the root of *Merremia hungaiensis*. Their structures have been determined on the bases of chemical and spectral data. Unlike the jalapins so far reported, all of their acyl groups consist of two or three long-chain fatty acids, that is, palmitic, stearic and/or arachidic acids.

Keywords resin glycoside; jalapin; *Merremia hungaiensis*; Convolvulaceae; long-chain fatty acid

In extended chemical studies on the resin glycosides, characteristic constituents of Convolvulaceae plants, we examined the root of *Merremia hungaiensis* LINGELISH. *et* BORZA, a Chinese crude drug "Tu Gua" used for treatment of chronic hepatitis, children's tantrums and hernia,[2] and ten jalapins[3] were obtained in the pure state. In this paper, we describe the isolation and structure elucidation of these compounds.

The MeOH extract of the root of *M. hungaiensis* was shaken with $CHCl_3$–MeOH–H_2O (1 : 1 : 1, v/v) and the $CHCl_3$-soluble portion was subjected to a combination of silica gel ($CHCl_3$–MeOH–H_2O), Cosmosil 140C_{18} ($CHCl_3$–MeOH) and Sephadex LH-20 ($CHCl_3$–MeOH) column chromatographies with various solvent systems to yield the resin glycoside fractions (frs. 1—4).

Prior to finer separation, the component glycosidic and fatty acids of the fractions were examined. A part of frs. 1 and 2 was hydrolyzed with 5% KOH to give a mixture of organic acids and a glycosidic acid fraction. The former was treated with diazomethane and analyzed by gas liquid chromatography (GLC), which revealed the presence of myristic, palmitic, stearic and arachidic acids. The latter was purified over silica gel column to give a glycosidic acid (**11**). Compound **11** was identified as operculinic acid A obtained previously from Rhizoma Jalapae Braziliensis, the root of *Ipomoea operculata* (Gomes) MARTIN,[4] by comparison of their physical and spectral data.

Conventional preparative HPLC with MeOH of the intact resin glycoside fraction on various octadecyl silylated (ODS) columns was unsuccessful. All substances applied were retained because of strong interaction between the octadecyl group of the packing materials and long-chain fatty acid groups in the resin glycosides. Then, we employed a phenyl-type reversed-phase column for preparative HPLC, and obtained ten compounds named tuguajalapins I—X (**1**—**10**).

The ^{1}H-NMR spectrum of **1** showed signals arising from five hexosyl moieties in addition to signals ascribable to four fatty acid groups. Treatment of **1** with 5% KOH followed by methylation gave methyl palmitate and a glycosidic acid methyl ester, which was identical with operculinic acid A (**11**) methyl ester. In the negative ion FAB-MS, **1** exhibited the $[M-H]^-$ ion peak at *m/z* 1714, and the diagnostically important fragment ion peaks at *m/z* 271, 417 and 545, showing the presence of a macrocyclic ester linkage in the second sugar (Rha) of the glycosidic acid residue.[5] A comparison of the ^{1}H-NMR spectrum of **1** with that of **11** showed that the signals due to 3-H of Rha, 2-H of Rha′, 4-H of Rha″, 6-H_a and 6-H_b of Glc were shifted downfield by 1.03, 0.67, 1.55, 0.78 and 0.28 ppm, respectively. These observations revealed that **1** consists of 3 mol of palmitic acid and 1 mol of **11**, and these palmitic acids are linked with 2-OH of Rha′, 4-OH of Rha″ and 6-OH of Glc. Further, the jalapinolic acid residue is combined with 3-OH of Rha to form a macrocyclic ester structure. This conclusion was further supported by the fact that the octaacetate (**1a**) obtained by acetylation of **1** showed, in the electron impact-mass spectra (EI-MS), the characteristic fragment ion peaks represented in Fig. 2. Thus, the structure of **1** is defined as (*S*)-jalapinolic acid 11-*O*-[6-*O*-*n*-hexadecanoyl-β-D-glucopyranosyl-(1→3)]-*O*-[4-*O*-*n*-hexadecanoyl-α-L-rhamnopyranosyl-(1→4)]-*O*-(2-*O*-*n*-hexadecanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-fucopyranoside, intramolecular 1,3″-ester.

On alkaline hydrolysis followed by methylation, compounds **2** and **3** yielded methyl palmitate and the methyl ester of **11**. Their negative ion FAB-MS were almost the same as that of **1**, suggesting that they are isomeric to each other. The ^{1}H-NMR spectrum of **3** showed, compared with that of **1**, upfield (0.58 ppm) and downfield (1.30 ppm) shifts of 3-H and 2-H of Rha, respectively. The structure of **3** was therefore concluded to differ only in the position of the intramolecular ester linkage, that is, the carboxyl group of jalapinolic acid combines with 3-OH of Rha instead of 2-OH in **1** (Fig. 1). On the other hand, in comparison with **3**, compound **2** exhibited upfield (0.81 and 0.68 ppm) and downfield (1.39 ppm) shifts, respectively, of 6-H_a, 6-H_b and 4-H of Glc. Accordingly, **2** was concluded to be the positional isomer of **3** whose palmitoyl residue is located at 4-OH of Glc in place of that at 6-OH in **3** (Fig. 1).

Tuguajalapin IV (**4**) exhibited, in the negative mode FAB-MS, the $[M-H]^-$ ion peak at *m/z* 1742, which was 28 mass units (C_2H_4) larger than that of **1**, besides the same fragment peaks at *m/z* 271, 417 and 545 as those of **1**. Alkaline hydrolysis of **4** in the same manner as for **1**

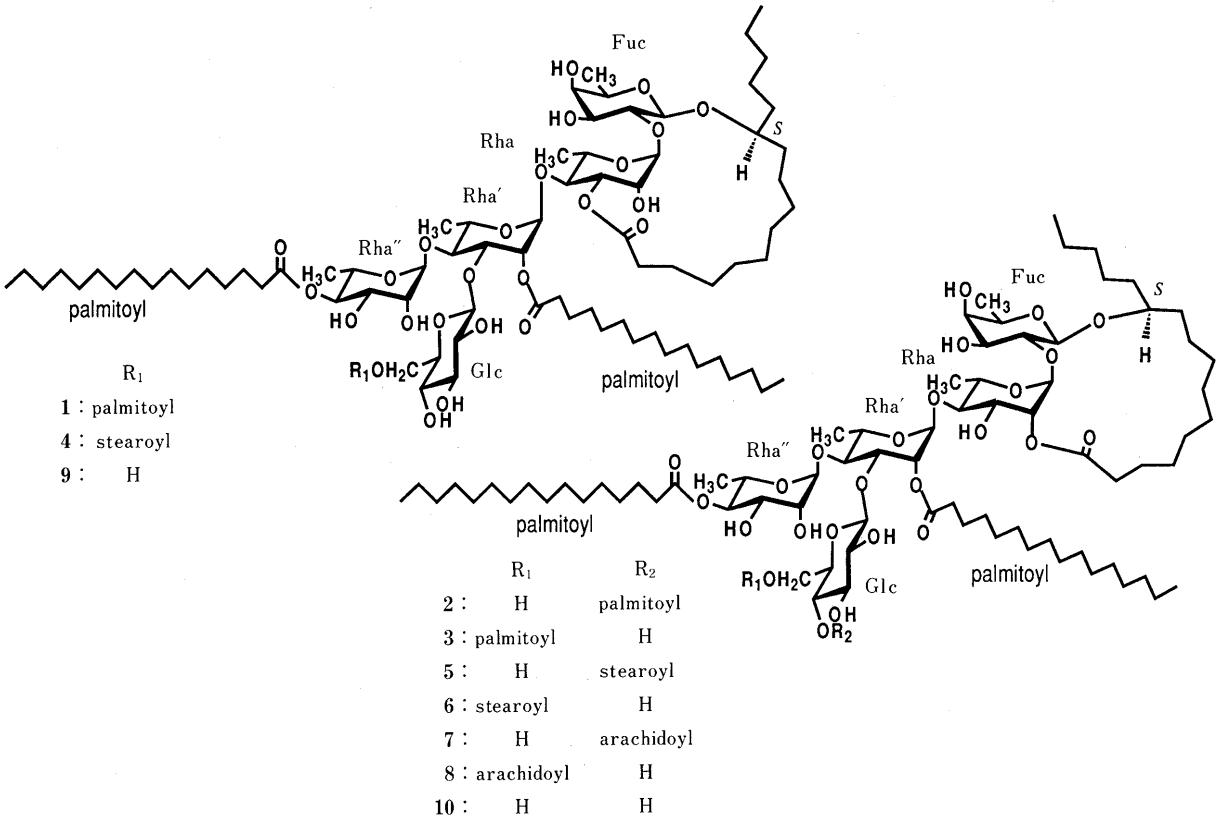

Fig. 1

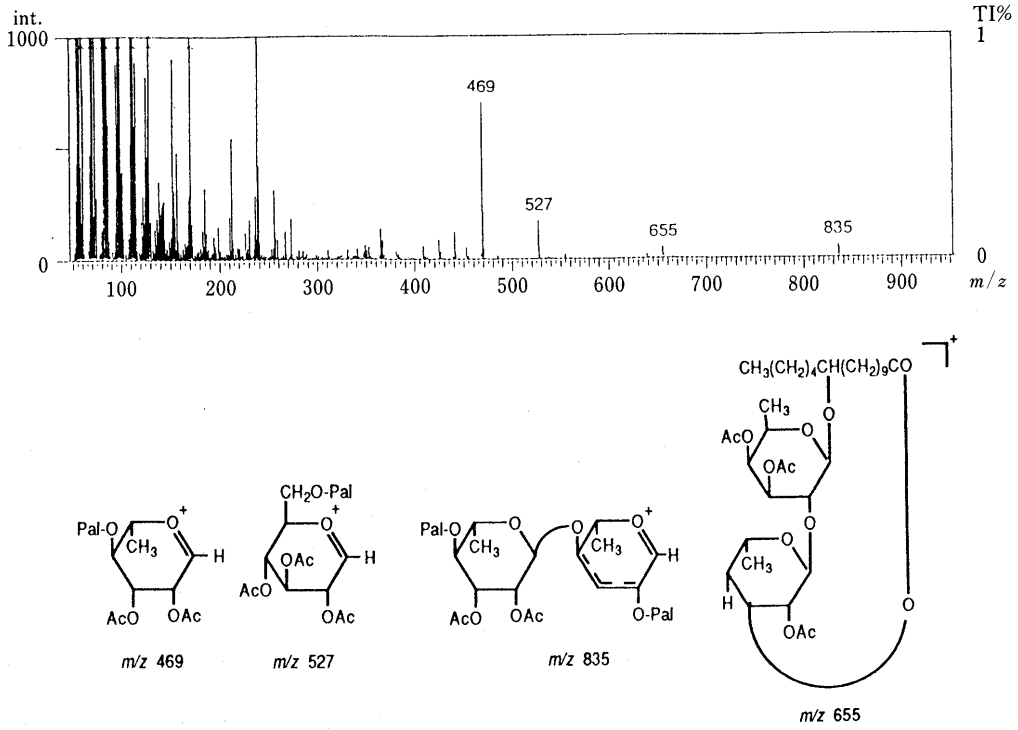

Fig. 2. EI-MS of **1a**

gave methyl stearate and methyl palmitate along with **11**. In the ^{1}H-NMR spectra of **4** and **1**, the proton signals at lower field were the same, suggesting that **4** is an analog of **1** and one of the three palmitic acid groups in **1** is replaced by a stearic acid group in **4**. Acetylation of **4** gave an octaacetate (**4a**), which showed characteristic peaks due to the fragment ions represented in Fig. 2, indicating the stearoyl group to be located at 6-OH of Glc. Accordingly,

TABLE I. ^{1}H-NMR Spectral Data for **1**—**11**

		1	2	3	4	5
Fuc-	1	4.82 (d, 8.1)	4.70 (d, 7.3)	4.72 (d, 7.5)	4.82 (d, 7.9)	4.70 (d, 7.3)
	2	4.51 (dd, 8.1, 9.6)	4.13[a)]	4.15 (dd, 7.5, 9.5)	4.50 (dd, 7.9, 9.5)	4.13[a)]
	3	4.20 (dd, 9.6, 3.5)	4.03[a)]	4.04[a)]	4.19 (dd, 9.5, 3.0)	4.03[a)]
	4	3.92 (br d, 3.5)	3.95 (d, 3.1)	3.99[a)]	3.92 (br d, 3.0)	3.95 (d, 3.1)
	5	3.81 (br q, 6.3)	3.73 (q, 6.5)	3.76 (br d, 6.3)	3.80 (br q, 6.5)	3.73 (q, 6.5)
	6	1.51 (d, 6.3)	1.49 (d, 6.4)	1.51 (d, 6.3)	1.51 (d, 6.5)	1.49 (d, 6.4)
Rha-	1	6.31 (d, 1.8)	5.49 (d, 1.8)	5.49 (d, 1.7)	6.30 (d, 1.3)	5.49 (d, 1.8)
	2	5.25 (br s)	5.90 (dd, 1.8, 3.0)	5.93 (dd, 1.7, 3.2)	5.25 (br s)	5.90 (dd, 1.8, 3.0)
	3	5.64 (dd, 3.2, 9.7)	4.99 (dd, 3.0, 9.8)	5.06[a)]	5.63 (dd, 1.5, 9.7)	4.99 (dd, 3.0, 9.8)
	4	4.65 (dd, 9.7, 9.7)	4.15[a)]	4.23 (dd, 9.5, 9.5)	4.65 (dd, 9.7, 9.7)	4.15[a)]
	5	4.99 (m)	4.46 (dq, 10.0, 6.1)	4.51 (m)	4.98 (dq, 9.7, 6.2)	4.46 (dq, 10.0, 6.1)
	6	1.60 (d, 6.3)	1.63 (d, 6.1)	1.68 (d, 6.1)	1.60 (d, 6.2)	1.63 (d, 6.1)
Rha′-	1	5.64 (d, 1.8)	5.87 (d, 1.5)	6.09 (d, 1.8)	5.63 (d, 1.5)	5.87 (d, 1.5)
	2	5.84 (dd, 1.8, 3.4)	6.26 (dd, 1.5, 3.2)	6.05 (dd, 1.8, 3.2)	5.83 (br s)	6.26 (dd, 1.5, 3.2)
	3	4.66 (dd, 3.4, 9.5)	4.80 (dd, 3.2, 9.2)	4.74 (dd, 3.2, 9.2)	4.66[a)]	4.80 (dd, 3.2, 9.2)
	4	4.35 (dd, 9.5, 9.5)	4.34[a)]	4.36 (dd, 9.2, 9.2)	4.36[a)]	4.34[a)]
	5	4.36[a)]	4.37[a)]	4.39 (m)	4.35[a)]	4.37[a)]
	6	1.63 (d, 5.6)	1.67 (d, 5.5)	1.67 (d, 5.8)	1.62 (d, 5.7)	1.67 (d, 5.5)
Rha″-	1	6.19 (br s)	6.22 (d, 1.5)	6.22 (d, 1.6)	6.18 (br s)	6.22 (d, 1.5)
	2	4.92 (dd, 1.8, 3.4)	4.96 (dd, 1.5, 3.2)	4.92 (dd, 1.6, 3.4)	4.91 (br s)	4.96 (dd, 1.5, 3.2)
	3	4.48 (dd, 3.4, 9.1)	4.56 (dd, 3.2, 9.2)	4.53 (dd, 3.4, 9.5)	4.47 (dd, 3.1, 9.3)	4.56 (dd, 3.2, 9.2)
	4	5.76 (dd, 9.1, 9.1)	5.80 (dd, 9.2, 9.2)	5.77 (dd, 9.5, 9.5)	5.75 (dd, 9.3, 9.3)	5.80 (dd, 9.2, 9.2)
	5	4.36[a)]	4.39[a)]	4.36 (m)	4.35[a)]	4.39[a)]
	6	1.43 (d, 6.2)	1.44 (d, 6.4)	1.43 (d, 6.2)	1.43 (d, 6.2)	1.44 (d, 6.4)
Glc-	1	5.06 (d, 7.9)	5.10 (d, 7.6)	5.06 (d, 7.5)	5.06 (d, 7.7)	5.10 (d, 7.6)
	2	4.02 (dd, 7.9, 9.2)	4.01[a)]	3.99[a)]	4.02 (dd, 7.7, 9.0)	4.01[a)]
	3	4.12[a)]	4.14[a)]	4.04[a)]	4.12[a)]	4.14[a)]
	4	4.11[a)]	5.41 (dd, 9.8, 9.8)	4.02[a)]	4.12[a)]	5.41 (dd, 9.8, 9.8)
	5	3.99 (m)	3.84[a)]	3.76[a)]	3.99 (m)	3.84[a)]
	6_a	5.05 (dd, 3.6, 11.8)	4.05[a)]	4.96 (dd, 1.8, 11.6)	5.05 (dd, 3.7, 11.6)	4.05[a)]
	6_b	4.81 (dd, 1.8, 11.8)	3.92[a)]	4.60 (dd, 4.6, 11.6)	4.80 (dd, 1.7, 11.6)	3.92[a)]
Jla-	2	2.35 (ddd, 3.0, 7.4, 14.9)	2.27 (m)	2.27 (ddd, 3.9, 8.2, 14.7)	2.35 (ddd, 3.0, 7.2, 14.8)	2.27 (m)
	2	2.82 (m)	2.45[a)]	2.43 (ddd, 4.2, 8.5, 14.7)	2.82 (m)	2.45[a)]
	11	3.87 (m)	3.83[a)]	3.86 (m)	3.87 (m)	3.83[a)]
	16	0.95 (t, 7.1)	0.88 (t, 7.0)	0.88 (t, 7.0)	0.95 (t, 7.0)	0.88 (t, 7.0)
Org-	2	2.45 (m)	2.35[a)]	2.35 (t, 7.0)	2.45 (m)	2.35[a)]
	2	2.45 (m)	2.35[a)]	*ca.* 2.5	2.45 (m)	2.35[a)]
	2	2.53 (m)	2.48[a)]	*ca.* 2.5	2.53 (m)	2.48[a)]
CH_3		0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)
		0.88 (t, 7.1)	0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)
		0.88 (t, 6.9)	0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)

fragment ions (m/z) for peracetates (**2a**—**10a**) of **2**—**10**

	A	B	C(R_1)	D(R_2)	E	F
2a	-	469	-	527(palmitoyl)	655	835
3a	-	469	527(palmitoyl)	-	655	835
4a	-	469	555(stearoyl)	-	655	835
5a	-	469	-	555(stearoyl)	655	835
6a	-	469	555(stearoyl)	-	655	835
7a	-	469	-	583(arachidoyl)	655	835
8a	-	469	583(arachidoyl)	-	655	835
9a	331	469	-	-	655	835
10a	331	469	-	-	655	835

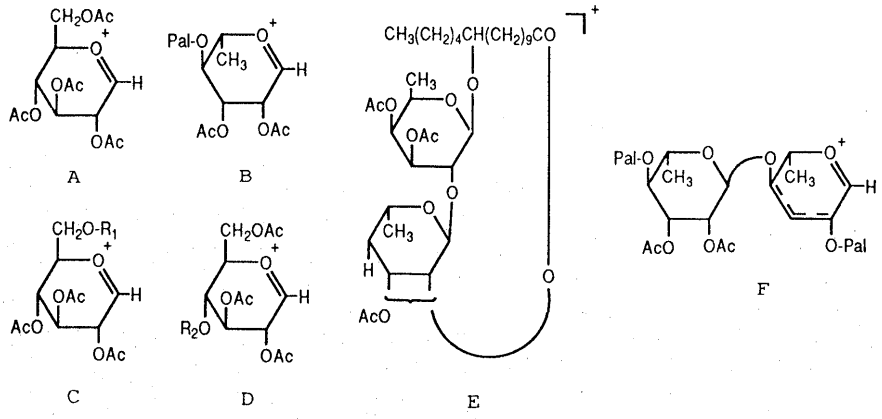

Fig. 3. Fragments for **2a**—**10a**

TABLE I. (continued)

		6	7	8	9	10	11
Fuc-	1	4.72 (d, 7.5)	4.70 (d, 7.3)	4.72 (d, 7.5)	4.82 (d, 7.8)	4.70 (d, 7.5)	4.79 (d, 7.9)
	2	4.15 (dd, 7.5, 9.5)	4.13[a]	4.15 (dd, 7.5, 9.5)	4.51 (dd, 7.8, 7.8)	4.14[a]	4.47 (dd, 7.9, 9.5)
	3	4.04[a]	4.03[a]	4.04[a]	4.20 (dd, 7.8, 3.2)	4.04[a]	4.13 (dd, 9.5, 3.5)
	4	3.99[a]	3.95 (d, 3.1)	3.99[a]	3.92 (br d, 3.2)	4.03[a]	3.93 (br d, 3.5)
	5	3.76 (br q, 6.3)	3.73 (q, 6.5)	3.76 (br q, 6.3)	3.82 (br q, 6.2)	3.73 (br q, 6.3)	3.79 (br q, 6.4)
	6	1.51 (d, 6.3)	1.49 (d, 6.4)	1.51 (d, 6.3)	1.52 (d, 6.2)	1.49 (d, 6.3)	1.52 (d, 6.2)
Rha-	1	5.49 (d, 1.7)	5.49 (d, 1.8)	5.49 (d, 1.7)	6.33 (d, 1.2)	5.49 (d, 1.2)	6.22 (d, 1.3)
	2	5.93 (dd, 1.7, 3.2)	5.90 (dd, 1.8, 3.0)	5.93 (dd, 1.7, 3.2)	5.24 (br s)	5.91 (dd, 1.2, 3.0)	4.67 (dd, 1.3, 3.4)
	3	5.06[a]	4.99 (dd, 3.0, 9.8)	5.06[a]	5.66 (dd, 2.8, 10.0)	5.00 (dd, 3.0, 9.3)	4.60 (dd, 3.4, 9.2)
	4	4.23 (dd, 9.5, 9.5)	4.15[a]	4.23 (dd, 9.5, 9.5)	4.67 (dd, 10.0, 10.0)	4.15 (dd, 9.3, 9.3)	4.21 (dd, 9.2, 9.2)
	5	4.51 (m)	4.46 (dq, 10.0, 6.1)	4.51 (m)	4.99 (dq, 10.0, 6.2)	4.47 (dq, 9.3, 6.2)	4.86 (dq, 9.2, 6.1)
	6	1.68 (d, 6.1)	1.63 (d, 6.1)	1.68 (d, 6.1)	1.60 (d, 6.2)	1.64 (d, 6.2)	1.60 (d, 6.1)
Rha'-	1	6.09 (d, 1.8)	5.87 (d, 1.5)	6.09 (d, 1.8)	5.62 (d, 1.5)	5.88 (br s)	5.88 (d, 1.7)
	2	6.05 (dd, 1.8, 3.2)	6.26 (dd, 1.5, 3.2)	6.05 (dd, 1.8, 3.2)	6.00 (dd, 1.5, 3.2)	6.30 (dd, 1.8, 3.0)	5.17 (dd, 1.7, 3.3)
	3	4.74 (dd, 3.2, 9.2)	4.80 (dd, 3.2, 9.2)	4.74 (dd, 3.2, 9.2)	4.64 (dd, 6.5, 8.2)	4.77 (dd, 3.0, 8.5)	4.72 (dd, 3.3, 9.0)
	4	4.36 (dd, 9.2, 9.2)	4.34[a]	4.36 (dd, 9.2, 9.2)	4.32 (dd, 8.2, 8.2)	4.34[a]	4.48 (dd, 9.0, 9.0)
	5	4.39 (m)	4.37[a]	4.39 (m)	4.37[a]	4.37[a]	4.39 (dq, 9.0, 6.1)
	6	1.67 (d, 5.8)	1.67 (d, 5.5)	1.67 (d, 5.8)	1.63 (d, 5.8)	1.66 (d, 6.5)	1.59 (d, 6.1)
Rha''-	1	6.22 (d, 1.6)	6.22 (d, 1.5)	6.22 (d, 1.6)	6.22 (d, 1.6)	6.24 (br s)	6.20 (d, 1.5)
	2	4.92 (dd, 1.6, 3.4)	4.96 (dd, 1.5, 3.2)	4.92 (dd, 1.6, 3.4)	4.91 (dd, 1.6, 3.0)	4.95 (dd, 2.0, 3.0)	4.87 (dd, 1.5, 3.6)
	3	4.53 (dd, 3.4, 9.5)	4.56 (dd, 3.2, 9.2)	4.53 (dd, 3.4, 9.5)	4.48[a]	4.56 (dd, 3.0, 9.2)	4.42 (dd, 3.6, 9.4)
	4	5.77 (dd, 9.5, 9.5)	5.80 (dd, 9.2, 9.2)	5.77 (dd, 9.5, 9.5)	5.77 (dd, 9.2, 9.2)	5.80 (dd, 9.2, 9.2)	4.21 (dd, 9.4, 9.4)
	5	4.36 (m)	4.39[a]	4.36 (m)	4.35[a]	4.38[a]	4.29 (dq, 9.4, 6.2)
	6	1.43 (d, 6.2)	1.44 (d, 6.4)	1.43 (d, 6.2)	1.44 (d, 6.2)	1.45 (d, 6.3)	1.57 (d, 6.2)
Glc-	1	5.06 (d, 7.5)	5.10 (d, 7.6)	5.06 (d, 7.5)	5.10 (d, 8.0)	5.06 (d, 7.5)	5.23 (d, 7.5)
	2	3.99[a]	4.01[a]	3.99[a]	3.96 (dd, 8.0, 8.0)	3.97[a]	3.95 (dd, 7.5, 8.8)
	3	4.04[a]	4.14[a]	4.04[a]	4.12 (dd, 8.0, 8.0)	4.07[a]	4.19 (dd, 8.8, 8.8)
	4	4.02[a]	5.41 (dd, 9.8, 9.8)	4.02[a]	4.17[a]	3.95[a]	4.10 (dd, 8.8, 8.8)
	5	3.76[a]	3.84[a]	3.76[a]	3,89 (ddd, 8.0, 8.0, 2.8)	3.76[a]	3.94[a]
	6_a	4.96 (dd, 1.8, 11.6)	4.05[a]	4.96 (dd, 1.8, 11.6)	4.48[a]	4.41[a]	4.51 (dd, 6.1, 11.9)
	6_b	4.60 (dd, 4.6, 11.6)	3.92[a]	4.60 (dd, 4.6, 11.6)	4.36[a]	4.10[a]	4.26 (dd, 2.4, 11.9)
Jla-	2	2.27 (ddd, 3.9, 8.2, 14.7)	2.27 (m)	2.27 (ddd, 3.9, 8.2, 14.7)	2.29 (m)	2.27 (m)	2.52 (t, 7.4)
	2	2.43 (ddd, 4.2, 8.5, 14.7)	2.45[a]	2.43 (ddd, 4.2, 8.5, 14.7)	2.70 (m)	2.44[a]	
	11	3.86 (m)	3.83[a]	3.86 (m)	3.89[a]	3.83 (m)	3.97[a]
	16	0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)	0.94 (t, 7.0)	0.88 (t, 7.0)	0.92 (t, 7.0)
Org-	2	2.35 (t, 7.0)	2.35[a]	2.35 (t, 7.0)	2.43[a]	2.34 (ddd, 2.5, 7.5, 7.5)	
	2	*ca.* 2.5	2.35[a]	*ca.* 2.5	2.47[a]	2.49 (ddd, 3.0, 7.5, 7.5)	
	2	*ca.* 2.5	2.48[a]	*ca.* 2.5			
CH_3		0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)	
		0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)	
		0.88 (t, 7.0)	0.88 (t, 7.0)	0.88 (t, 7.0)			

δ in ppm from TMS (coupling patterns and coupling constants (J) in Hz are given in parentheses). Fuc, fucopyranosyl; Rha, rhamnopyranosyl; Glc, glucopyranosyl; Jla, jalapinolic acid moiety; Org, organic acid. All assignments are based on the ^{1}H–^{1}H COSY and NOESY spectral data. *a*) Signals are overlapping.

the structure of **4** was concluded to be (*S*)-jalapinolic acid 11-*O*-[6-*O*-*n*-octadecanoyl-β-D-glucopyranosyl-(1→3)]-*O*-[4-*O*-*n*-hexadecanoyl-α-L-rhamnopyranosyl-(1→4)]-*O*-(2-*O*-*n*-hexadecanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-fucopyranoside, intramolecular 1,3″-ester.

Compounds **5** and **6** gave, on alkaline hydrolysis, the same components as those of **4**. The ^{1}H-NMR spectra of **5** and **6** were quite similar to those of **2** and **3**, respectively, including the proton signals shifted downfield by acylation (Table I). As expected, the EI-MS of their acetates **5a** and **6a** gave diagnostic fragment peaks at *m/z* 655, 555 and 469 (Fig. 3), hence their structures were considered to be as shown in Fig. 1.

Compounds **7** and **8** each showed the $[M-H]^-$ ion peak at *m/z* 1770 in the negative ion FAB-MS, and furnished, on alkaline hydrolysis, methyl palmitate and arachidate in addition to **11** methyl ester. The ^{1}H-NMR spectra of **7** and **8** were almost indistinguishable from those of **2** and **3**, respectively. EI-MS examination of their acetates (**7a** and **8a**) revealed that **7** is an analog of **2**, in which the palmitic acid group at 4-OH of Glc in **2** is replaced by an arachidic acid group in **7**, while **8** is an isomer of **7** in which the 6-OH position of Glc is acylated by arachidic acid instead of palmitic acid in **3**.

Tuguajalapins IX (**9**) and X (**10**) gave, in their negative mode FAB-MS, the same $[M-H]^-$ ion peak at *m/z* 1475, and were proved to be palmitic acid and **11**, respectively. Analyses of their ^{1}H- and ^{13}C-NMR spectra and of the EI-MS of their acetates (**9a** and **10a**) revealed that they are deacylates in which the fatty acid group at 6-OH of Glc was released from **1** or **4**, and **3**, **6** or **8**, respectively. Figure 1 shows their structures.

All the compounds obtained in this work are so-called resin glycosides belonging to the "jalapin" category[3] and they resemble operculins I, II, V, VII, VIII, XIII, XIV and XV isolated from Rhizoma Jalapae Braziliensis,[6] which are composed of the common glycosidic acid, operculinic acid A, with two types of macrocyclic ester structure, and organic acids, that is, decanoic and/or lauric acids. Tuguajalapins are the first examples of jalapins acylated with long-chain fatty acids, palmitic, stearic and/or arachidic acids.

Recently, we found that the behavior of fr. 3 on TLC with various solvents was quite different from that of frs. 1 and 2, whereas their alkaline hydrolysis products were almost the same. Investigation of fr. 3 is in progress.

Experimental

Melting points (mp) were determined on Yanaco MP-S3 apparatus and

are uncorrected. The NMR spectra were recorded on a GE NMR OMEGA 600 instrument at 600 MHz (^{1}H) and 150 MHz (^{13}C) at a probe temperature of 35 °C, using tetramethylsilane (TMS) as an internal reference. The EI- and negative ion FAB (using triethanolamine as the matrix)-MS were taken on a JEOL JMS DX-300 spectrometer. High-resolution MS were measured on a JEOL JMS HX-110 using *m*-nitrobenzyl alcohol as the matrix. Optical rotations were measured with a JASCO DIP-140 polarimeter. TLC was carried out on silica-gel pre-coated Al sheets (Merck Art. 9385). Column chromatography was carried out on Merck Silica-gel 60 (230—400 mesh, Art. 9385), Cosmosil 140C_{18}-OPN (Nacalai Tesque, Inc.), MCI gel CHP-20P (100—200 mesh, Mitsubishi Chemical Industries) and Sephadex LH-20 (25—100 mm, Pharmacia Fine Chemicals). Preparative HPLC was conducted over Unisil Q PH (10 μm, 16.7 × 250 mm, GL Sciences Inc.) with a JASCO 880-PU pump equipped with JASCO 830-RI.

Preparation of the Resin Glycoside Fraction The roots of *M. hungaiensis* were collected in Fengui, Dali county, Yunnan province and a voucher specimen was deposited in the Herbarium of Kumming Institute of Botany, Chinese Academy of Sciences. The dried roots (3.0 kg) were powdered and extracted with MeOH (6 l) under reflux to give a dark brown syrup (370 g) after removal of the solvent. The syrup (227 g) was shaken with $CHCl_3$–MeOH–H_2O (1 : 1 : 1, 2 l) and the lower phase was concentrated. The residue (59.9 g) was subjected to column chromatography on silica-gel ($CHCl_3$–MeOH, 10 : 1→9 : 1→7 : 3→MeOH) to afford the resin glycoside fractions; fr. 1 (20.0 g), fr. 2 (23.7 g) fr. 3 (13.1 g) and fr. 4 (3.1 g).

Analysis of the Component Organic and Glycosidic Acids of Resin Glycoside Fraction A mixture of fr. 1 (0.5 g) and fr. 2 (0.5 g) was added to 5% KOH (10 ml) and heated at 90 °C for 3 h. The reaction mixture was acidified to pH 4.0 and shaken with ether (20 ml). The ether layer was dried over Na_2SO_4 and then concentrated to give an oil (250 mg). After methylation of the oil with diazomethane, it was examined by GLC (column, 2 m × 3 mm glass column packed with silicone OV-17; carrier N_2, 1.5 kg/cm^2; column temperature 170—230 °C elevated by 3 °C/min), t_R (min): 2.45 (methyl myristate), 4.60 (methyl palmitate), 7.95 (methyl stearate), 12.20 (methyl arachidate).

The water-soluble portion was passed through MCI gel CHP20P (H_2O→acetone) and the acetone eluate was concentrated to dryness to give a powder (500 mg). This was chromatographed on silica-gel ($CHCl_3$–MeOH–H_2O, 7 : 3 : 0.1, v/v) to give **11** (490 mg). The ^{1}H- and ^{13}C-NMR spectra of **11** were superimposable on those of operculinic acid A.[4)]

Isolation of Tuguajalapins I—X Fraction 1 (14.0 g) was chromatographed on silica-gel ($CHCl_3$–MeOH, 12 : 1→8 : 2) to give three fractions, fr. 5 (1.5 g), fr. 6 (6.1 g) and fr. 7 (7.0 g). Fraction 6 (5.0 g) was separated on a Cosmosil 140C_{18}-OPN column ($CHCl_3$–MeOH, 4 : 6) into fr. 8 (450 mg), fr. 9 (4.3 g) and fr. 10 (650 mg). Chromatography of fr. 9 on a Sephadex LH-20 column ($CHCl_3$–MeOH, 3 : 7) furnished fr. 11 (4.0 g) and fr. 12 (0.3 g), and the former was chromatographed on silica-gel ($CHCl_3$–MeOH, 20 : 1→15 : 1→10 : 1→8 : 2→MeOH) to give fr. 13 (551 mg), fr. 14 (23 mg), fr. 15 (230 mg), fr. 16 (330 mg) and fr. 17 (3 g). Fractions 14—16 were each subjected to HPLC (Unisil Q PH, GL Sciences; 10 μm, 16.7 × 250 mm; solvent, 98% MeOH) to give **2** (3 mg), **5** (6 mg) and **7** (7 mg) from fr. 14; **1** (32 mg) and **4** (45 mg) from fr. 15; **3** (55 mg), **6** (64 mg) and **8** (58 mg) from fr. 16. Fraction 2 was subjected to a combination of LH-20 and silica-gel chromatographies as described for fr. 9 to afford fr. 18, which was separated by HPLC on Unisil Q PH (MeOH) to give **9** (14 mg) and **10** (113 mg). **1**: Powder, mp 84—89 °C, $[\alpha]_D^{27}$ −36.3° (c=1.7, $CHCl_3$). Negative ion FAB-MS m/z (%): 1714 $[M-H]^-$ (58), 1475 (21), 1329 (10), 1237 (10), 999 (6), 837 (8), 691 (7), 545 (100), 417 (98), 271 (100). High resolution FAB-MS (positive) m/z: Found: 1738.1863 $[M+Na]^+$, Calcd for $C_{94}H_{170}NaO_{26}$: 1738.1878.

2: Powder, mp 84—89 °C, $[\alpha]_D^{27}$ −17.5° (c=1.0, $CHCl_3$). Negative ion FAB-MS m/z (%): 1714 $[M-H]^-$ (100), 1475 (36), 1237 (9), 545 (100), 417 (100), 271 (100). High-resolution FAB-MS (positive) m/z: Found: 1738.1857 $[M+Na]^+$, Calcd for $C_{94}H_{170}NaO_{26}$: 1738.1878. **3**: Powder, mp 82—88 °C, $[\alpha]_D^{25}$ −20.2° (c=2.2, $CHCl_3$). Negative ion FAB-MS m/z (%): 1714 $[M-H]^-$ (90), 1475 (31), 1329 (12), 1237 (13), 837 (10), 545 (100), 417 (100), 271 (100). High-resolution FAB-MS (positive) m/z: Found: 1738.1881 $[M+Na]^+$, Calcd for $C_{94}H_{170}NaO_{26}$: 1738.1878.

4: Powder, mp 78—85 °C, $[\alpha]_D^{21}$ −44.7° (c=3.5, $CHCl_3$). Negative ion FAB-MS m/z (%): 1742 $[M-H]^-$ (39), 1503 (16), 1475 (6), 1357 (10), 1237 (8), 1119 (5), 837 (8), 691 (6), 545 (100), 417 (100), 271 (100). High-resolution FAB-MS (positive) m/z: Found: 1766.2205 $[M+Na]^+$, Calcd for $C_{96}H_{174}NaO_{26}$: 1766.2191. **5**: Powder, mp 78—84 °C, $[\alpha]_D^{23}$ −20.4° (c=1.2, $CHCl_3$). Negative ion FAB-MS m/z (%): 1742 $[M-H]^-$ (100), 1503 (22), 1475 (39), 1357 (16), 1237 (20), 837 (18), 691 (20), 545 (82), 417 (100), 271 (100). High-resolution FAB-MS (positive) m/z: Found: 1766.2150 $[M+Na]^+$, Calcd for $C_{96}H_{174}NaO_{26}$: 1766.2191. **6**: Powder, mp 79—84 °C, $[\alpha]_D^{23}$ −23.6° (c=1.5, $CHCl_3$). Negative ion FAB-MS m/z (%): 1742 $[M-H]^-$ (33), 1503 (6), 1475 (4), 1357 (4), 1237 (2), 837 (3), 691 (3), 545 (23), 417 (100), 271 (26). High-resolution FAB-MS (positive) m/z: Found: 1766.2208 $[M+Na]^+$, Calcd for $C_{96}H_{174}NaO_{26}$: 1766.2191. **7**: Powder, mp 75—76 °C, $[\alpha]_D^{23}$ −25.0° (c=1.2, $CHCl_3$). Negative ion FAB-MS m/z (%): 1770 $[M-H]^-$ (100), 1532 (19), 1475 (38), 1385 (16), 1237 (17), 545 (100), 417 (100), 271 (100). High-resolution FAB-MS (positive) m/z: Found: 1794.2495 $[M+Na]^+$, Calcd for $C_{98}H_{178}NaO_{26}$: 1794.2504. **8**: Powder, mp 79—81 °C, $[\alpha]_D^{23}$ −44.7° (c=3.5, $CHCl_3$). Negative ion FAB-MS m/z (%): 1770 $[M-H]^-$ (12), 1532 (4), 1475 (2), 1385 (2), 1237 (3), 999 (1), 853 (2), 691 (2), 545 (21), 417 (100), 271 (26). High-resolution FAB-MS (positive) m/z: Found 1794.2488 $[M+Na]^+$, Calcd for $C_{98}H_{178}NaO_{26}$: 1794.2504. **9**: Powder, mp 77—80 °C, $[\alpha]_D^{21}$ −27.4° (c=1.2, $CHCl_3$). Negative ion FAB-MS m/z (%): 1475 $[M-H]^-$ (57), 1237 (37), 999 (13), 545 (63), 417 (100), 271 (100). High-resolution FAB-MS (positive) m/z: Found: 1499.9584 $[M+Na]^+$, Calcd for $C_{78}H_{140}NaO_{25}$: 1499.9582. **10**: Powder, mp 92—98 °C, $[\alpha]_D^{27}$ −15.6° (c=1.0, $CHCl_3$). Negative ion FAB-MS m/z (%): 1475 $[M-H]^-$ (88), 1237 (38), 999 (18), 545 (55), 417 (100), 271 (68). High-resolution FAB-MS (positive) m/z: Found: 1499.9581 $[M+Na]^+$, Calcd for $C_{78}H_{140}NaO_{25}$: 1499.9582. ^{1}H-NMR spectra of **1**—**10** (pyridine-d_5) δ: see Table I.

Alkaline Hydrolysis of 1—10 Compounds **1**—**10** (3—10 mg) were each dissolved in 5% KOH (5 ml) and heated at 90 °C for 2 h. The reaction mixture was adjusted to pH 4.0 and extracted with ether (5 ml × 2). After removal of the solvent, concentrated aliquots were treated with diazomethane in ether and the reaction mixture was analyzed by GLC under the same conditions as for the resin glycoside fraction, t_R (min): 4.60 (methyl palmitate) from **1**—**10**, 7.95 (methyl stearate) from **4**, **5** and **6**, 12.20 (methyl arachidate) from **7** and **8**.

Each aqueous layer was desalted by column chromatography on MCI gel CHP-20P (H_2O→acetone) and then the solvent was removed. The residue (2—6 mg) in MeOH (0.5 ml) was treated with diazomethane in ether to furnish a product. Its ^{1}H-NMR spectrum was superimposable on that of operculinic acid A methyl ester.

Acetylation of 1—10 Usual acetylation of **1**—**10** (each 3 mg) yielded **1a**—**10a** (each 3 mg), respectively. **1a**: Syrup, $[\alpha]_D^{21}$ −44.4° (c=0.8, $CHCl_3$). EI-MS m/z (%): 835 (8), 655 (8), 527 (25), 469 (100). ^{1}H-NMR (pyridine-d_5) δ: 1.97, 2.01, 2.01, 2.05, 2.09, 2.12, 2.24, 2.26 (each 3H, s, OCOC$\underline{H}_3$). **2a**: Syrup, $[\alpha]_D^{23}$ −21.2° (c=0.8, $CHCl_3$). EI-MS m/z (%): 835 (8), 655 (9), 527 (31), 469 (100). ^{1}H-NMR (pyridine-d_5) δ: 1.98, 2.02, 2.13, 2.21, 2.24, 2.30, 2.39, 2.40 (each 3H, s, OCOC$\underline{H}_3$). **3a**: Syrup, $[\alpha]_D^{25}$ −24.4° (c=0.6, $CHCl_3$). EI-MS m/z (%): 835 (8), 655 (9), 527 (34), 469 (100). ^{1}H-NMR (pyridine-d_5) δ: 1.96, 1.98, 1.99, 2.12, 2.22, 2.28, 2.40, 2.44 (each 3H, s, OCOC$\underline{H}_3$). **4a**: Syrup, $[\alpha]_D^{27}$ −50.1° (c=0.5, $CHCl_3$). EI-MS m/z (%): 835 (7), 655 (8), 555 (18), 469 (100). ^{1}H-NMR (pyridine-d_5) δ: 1.97, 2.01, 2.01, 2.04, 2.09, 2.12, 2.24, 2.26 (each 3H, s, OCOC$\underline{H}_3$). **5a**: Syrup, $[\alpha]_D^{23}$ −25.6° (c=0.6, $CHCl_3$). EI-MS m/z (%): 655 (13), 555 (13), 469 (100). ^{1}H-NMR (pyridine-d_5) δ: 1.98, 2.02, 2.13, 2.21, 2.24, 2.30, 2.39, 2.40 (each 3H, s, OCOC$\underline{H}_3$). **6a**: Syrup, $[\alpha]_D^{25}$ −28.8° (c=0.5, $CHCl_3$). EI-MS m/z (%): 655 (13), 555 (13), 469 (100). ^{1}H-NMR (pyridine-d_5) δ: 1.96, 1.98, 1.99, 2.12, 2.22, 2.28, 2.40, 2.44 (each 3H, s, OCOC$\underline{H}_3$). **7a**: Syrup, $[\alpha]_D^{23}$ −29.9° (c=0.4, $CHCl_3$). EI-MS m/z (%): 655 (14), 583 (9), 469 (100). ^{1}H-NMR (pyridine-d_5) δ: 1.98, 2.02, 2.13, 2.21, 2.24, 2.30, 2.39, 2.40 (each 3H, s, OCOC$\underline{H}_3$). **8a**: Syrup, $[\alpha]_D^{25}$ −30.5° (c=0.5, $CHCl_3$). EI-MS m/z (%): 655 (6), 583 (14), 469 (100). ^{1}H-NMR (pyridine-d_5) δ: 1.96, 1.98, 1.99, 2.11, 2.22, 2.28, 2.40, 2.44 (each 3H, s, OCOC$\underline{H}_3$). **9a**: Syrup, $[\alpha]_D^{25}$ −61.2° (c=0.5, $CHCl_3$). EI-MS m/z (%): 835 (13), 655 (9), 469 (100), 331 (90). ^{1}H-NMR (pyridine-d_5) δ: 1.97, 1.97, 2.00, 2.04, 2.09, 2.12, 2.20, 2.24, 2.26 (each 3H, s, OCOC$\underline{H}_3$). **10a**: Syrup, $[\alpha]_D^{25}$ −31.6° (c=0.6, $CHCl_3$). EI-MS m/z (%): 835 (5), 655 (7), 469 (91), 331 (100). ^{1}H-NMR (pyridine-d_5) δ: 1.95, 1.96, 1.98, 2.13, 2.18, 2.23, 2.29, 2.38, 2.39 (each 3H, s, OCOC$\underline{H}_3$).

Acknowledgment We thank Professor Toshio Kawasaki of this University for valuable advice and Dr. Masatoshi Nishi and Mr. Shoji Inoue of this University for measurements of the NMR spectra and MS. Thanks are also due to Professors Kumihide Mihashi, Hikaru Okabe

and Mr. Hiroshi Hanazono of Fukuoka University for measurements of high-resolution MS and valuable discussions.

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