A NOVEL RESIN GLYCOSIDE, MERREMIN (TUGUAJALAPIN X DIMER), FROM *MERREMIA HUNGAIENSIS*[1)]

Naoki NODA,[a] Kyoko TSUJI,[a] Toshio KAWASAKI,[a] Kazumoto MIYAHARA,*,[a] Hiroshi HANAZONO[b] and Chon-Ren YANG[c]

Faculty of Pharmaceutical Sciences, Setsunan University,[a] 45-1, Nagaotoge-cho, Hirakata, Osaka 573-01, Japan, Faculty of Pharmaceutical Sciences, Fukuoka University,[b] 8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-01, Japan, and Kunming Institute of Botany,[c] Academia Sinica, Kunming, Hei-Long-Tan, 650204 Yunnan, China

A novel resin glycoside, merremin (**1**), has been isolated from the root of *Merremia hungaiensis* (Convolvulaceae). The structure has been determined to be an ester-type dimer of tuguajalapin X (**2**) on the basis of chemical and spectral data.

KEY WORDS resin glycoside; ester-type dimer; *Merremia hungaiensis*; merremin; Convolvulaceae

In our systematic studies on the characteristic constituents, resin glycosides, of the Convolvulaceae plants, we have isolated a novel resin glycoside named merremin (**1**) from the roots of *Merremia hungaiensis*.[1)] This paper concerns the structure of **1**.

Fraction 3 obtained in the preceding paper[2)] was subjected to HPLC with a Unisil Q PH (10 μm, 16.7 mm x 25 cm, GL Sciences Inc.) using MeOH to give **1** (75 mg).[3)]

The negative HR FAB-MS (*m/z* 2952.9336 $[M-H]^-$) revealed that the molecular formula of **1** is $C_{156}H_{280}O_{50}$, which corresponds to 2 units of tuguajalapin X (**2**, $C_{78}H_{140}O_{25}$)[2)] obtained previously (Fig.1).

Treatment of **1** with 5% KOH followed by methylation with diazomethane gave methyl esters of palmitic acid and operculinic acid A (**3**), a glycosidic acid obtained from *Ipomoea operculata*.[4)] In view of the molecular weight of **1** and its components, **1** was considered to have 2 mol of operculinic acid A and 4 mol of palmitic acid.

The ^{1}H-NMR spectrum of **1** showed the signals due to ten anomeric protons in addition to those assignable to the fatty acid groups; and, when compared with that of **3**, remarkable downfield shifts of the signals ascribable to ARha H-2 (1.26 ppm), ARha' H-2 (0.88 ppm), ARha" H-4 (1.55 ppm) AGlc H_2-6 (0.33 and 0.42 ppm), BRha' H-2 (1.22 ppm) and BRha" H-4 (1.56 ppm) were observed. Furthermore, the diagnostic fragment peaks[5)] in the negative FAB-MS (Fig. 2) suggested that **1** consists of 2 units of **2** and that the carboxyl group of the jalapinolic acid in one unit B is combined with OH of sugar moiety in another unit A.

Mild alkaline hydrolysis of **1** with 28% NH_4OH and 1,4-dioxane (1:1)[6)] for 13 h at 40°C gave two products, **2** (4.4 %) and **4** (8.0 %),[2)] together with unreacted **1**. The former was identified as

* To whom correspondence should be addressed.

tuguajalapin X (**2**, unit A) by FAB-MS, ^{1}H- and ^{13}C-NMR spectral comparison. On the other hand, the ^{1}H-NMR spectrum of **4** (*m/z*: 1493 $[M-H]^-$) showed equivalent H_2-2 signals (δ 2.45, triplet) similar to those of **3**, and acylation shifts were seen at Rha' H-2 (1.23 ppm) and Rha" H-4 (1.56 ppm). Therefore, **4** was concluded to be an acylated glycosidic acid as shown in Fig. 1 (unit B).

Taking the hydrolysis product **2** and the down-field shifts at H_2-6 of AGlc in **1** into account, the full structure of **1** is defined as presented in Fig. 1.

Merremin (**1**) isolated in the present study is, unlike many resin glycosides so far reported, the first example of an ester-type dimer, which consists of 2 units of the same glycosidic acids partially acylated by fatty acids. This finding may suggest that "rhamnoconvolvulin" from the roots of *I.*

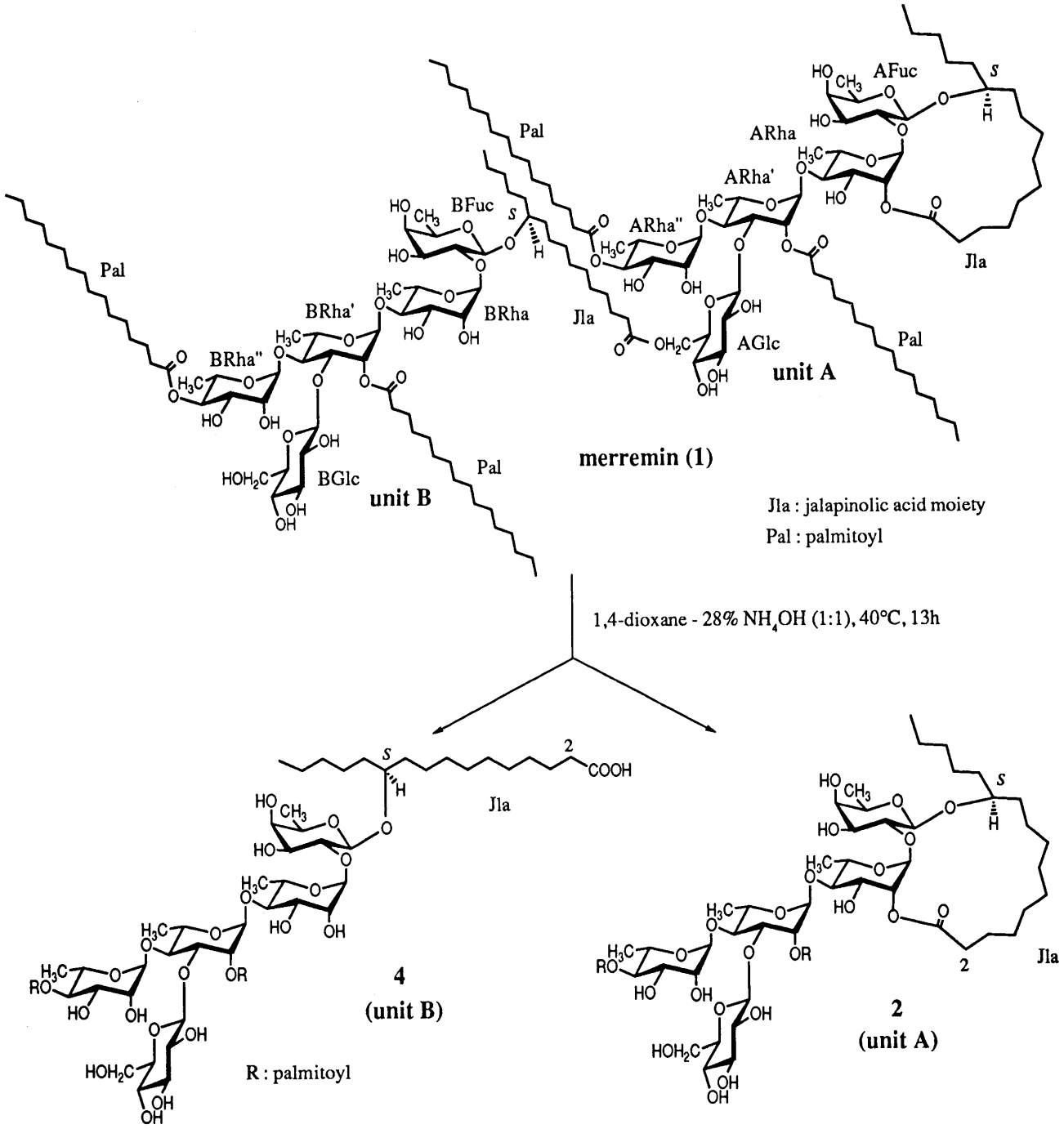

Fig. 1 Structures of **1**, **2** and **4**

operculata reported by Mannich and Schumann[7] could be a mixture of oligomers[8] of resin glycosides acylated by lower organic acids.

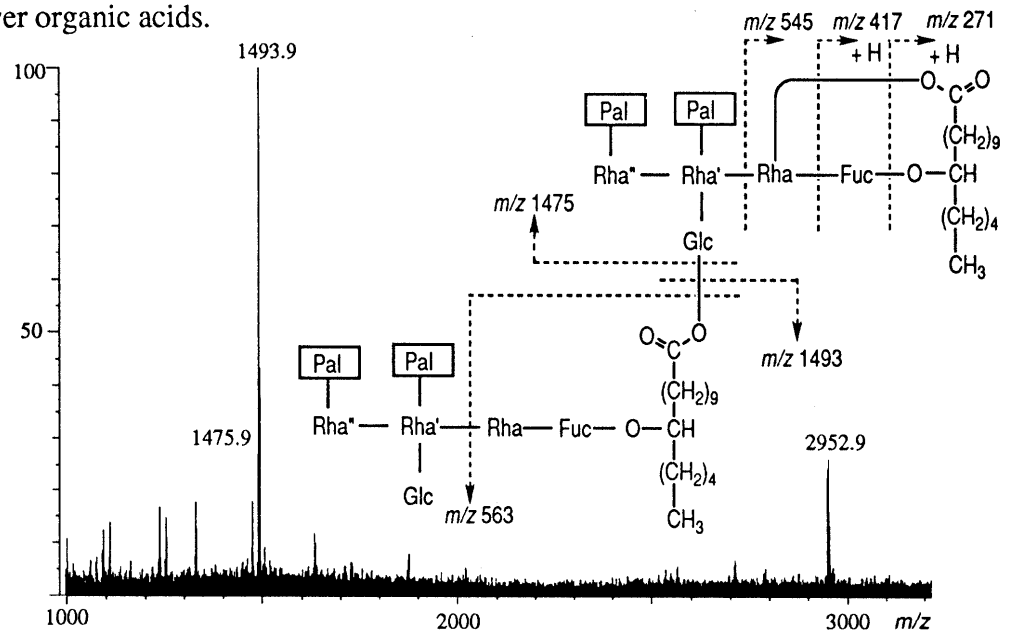

Fig. 2 A Part of Negative FAB-MS of **1**

REFERENCES AND NOTES

1) Part XXII in the series "Resin Glycosides". For Part XXI see ref. 2).
2) Noda N., Tsuji K., Miyahara K., Yang C-L., *Chem. Pharm. Bull.*, **42**, 2011 - 2016 (1994).
3) The signals marked with # are overlapping. δ in ppm from TMS (coupling constants, *J* (Hz) are in parentheses). **1**: mp 104-109°C, $[\alpha]_D^{23}$ -27.7° (*c*=1.4, $CHCl_3$). Negative FAB-MS *m/z*: 2951 $[M-H]^-$, 1493, 1475, 563, 545, 417, 271. Negative HR FAB-MS *m/z*: 2952.9336 $[M-H]^-$, Calcd. for $C_{156}H_{279}O_{50}$ 2952.9289. ^{1}H-NMR (pyridine-d_5, 600 MHz) δ: 2.26-2.45 (m, 2 x H_2-2 of Jla), 2.36-2.47 (m, 4 x H_2-2 of Pal), 0.89 (t, 7.0, 5 x CH_3), 0.96 (t, 7.0, CH_3), sugar part, unit A: Fuc, 4.71 (d, 7.5, H-1), 4.14 (dd, 7.5, 9.5, H-2), 4.01# (H-3), 3.97# (H-4), 3.75 (br q, 6.3, H-5), 1.51 (d, 6.3, H_3-6); Rha, 5.48 (d, 1.6, H-1), 5.91 (dd, 1.6, 3.2, H-2), 5.05# (H-3), 4.22 (dd, 9.4, 9.4, H-4), 4.87# (H-5), 1.57 (d, 6.2, H_3-6); Rha', 6.06 (d, 1.6, H-1), 6.02 (dd, 1.6, 3.1, H-2), 4.74 (dd, 3.1, 8.7, H-3), 4.35# (H-4), 4.38# (H-5), 1.67 (d, 6.3, H_3-6); Rha", 6.21 (d, 1.2, H-1), 4.88# (H-2), 4.47# (H-3), 5.75 (dd, 9.7, 9.7, H-4), 4.35# (H-5), 1.42 (d, 6.3, H_3-6); Glc, 5.04 (d, 7.5, H-1), 3.97# (H-2), 4.00# (H-3), 4.03# (H-4), 3.70 (m, H-5), 4.68 (dd, 3.6, 11.7, H_a-6), 4.84# (H_b-6), unit B: Fuc, 4.80 (d, 7.9, H-1), 4.49# (H-2), 4.15 (dd, 9.5, 3.4, H-3), 3.95 (br d, 3.4, H-4), 3.81 (br q, 6.5, H-5), 1.53 (d, 6.3, H_3-6); Rha, 6.23 (br s, H-1), 4.64 (dd, 1.4, 3.2, H-2), 4.61 (dd, 3.2, 9.4, H-3), 4.22 (dd, 9.4, 9.4, H-4), 4.50# (H-5), 1.66 (d, 6.3, H_3-6); Rha', 5.76 (br s, H-1), 6.36 (dd, 2.0, 3.2, H-2), 4.77 (dd, 3.2, 9.3, H-3), 4.32 (dd, 9.3, 9.3, H-4), 4.44 (dq, 9.3, 6.3, H-5), 1.65 (d, 6.3, H_3-6); Rha", 6.20 (br s, H-1), 4.93 (dd, 1.4, 3.2, H-2), 4.53 (dd, 3.2, 9.7, H-3), 5.76# (H-4), 4.37# (H-5), 1.43 (d, 6.2, H_3-6); Glc, 5.12 (d, 7.7, H-1), 3.99# (H-2), 4.10 (dd, 9.0, 9.0, H-3), 3.99# (H-4), 3.90 (m, H-5), 4.21# (H_a-6), 4.51# (H_b-6). **4**: mp 93-97°C, $C_{78}H_{142}O_{26}$, $[\alpha]_D^{24}$ - 24.4° (*c*=0.1, $CHCl_3$). Negative FAB-MS *m/z*: 1493 $[M-H]^-$, 1255, 1017, 855, 709, 563. ^{1}H-NMR (pyridine-d_5, 600 MHz) δ: 2.45 (t, 7.0, H_2-2 of Jla), 2.37-2.48 (2 x H_2-2 of Pal), 0.96 (t, 7.0, CH_3), 0.88 (t, 7.0, 2 x CH_3), sugar part, Fuc, 4.80 (d, 7.8, H-1), 4.50 (dd, 7.8, 9.5, H-2), 4.15# (H-3), 3.61 (br d, 4.4, H-4), 3.82 (br q, 6.5, H-5), 1.50 (d, 6.5, H_3-6); Rha, 6.24 (br s, H-1), 4.67 (br s, H-2), 4.61 (dd, 3.5, 9.5, H-3), 4.21 (dd, 9.5, 9.5, H-4), 4.90 (dq, 9.5, 6.2, H-5), 1.60 (d, 6.2, H_3-6); Rha', 5.71 (d, 1.7, H-1), 6.40 (dd, 1.7, 3.4, H-2), 4.82 (dd, 3.4, 9.4, H-3), 4.34 (dd, 9.4, 9.4, H-4), 4.47 (dq, 9.4, 6.1, H-5), 1.67 (d, 6.1, H_3-6); Rha", 6.24 (br s, H-1), 4.93 (br s, H-2), 4.50# (H-3), 5.77 (dd, 9.5, 9.5, H-4), 4.38 (dq, 9.5, 6.2, H-5), 1.40 (d, 6.2, H_3-6); Glc, 5.17 (d, 7.5, H-1), 4.02# (H-2), 4.01# (H-3), 4.15# (H-4), 3.98# (H-5), 4.56 (dd, 5.8, 11.0, H_a-6), 4.23# (H_b-6).
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7) Mannich C., Schumann P., *Arch., Pharm.*, **276**, 211 - 227 (1938). They proposed the molecular weight as 31018.
8) The "rhamnoconvolvulin" fraction obtained by us showed four peaks at *m/z* 1687, 3333, 4973, 6623 by MALDI TOF-MS (Kubo H., Ono M., Kawasaki T., Miyahara K., Abstracts of Papers (2), The 113th Annual Meeting of Pharmaceutical Society of Japan, Osaka, Mar. 1993, p. 171).

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