A NOVEL RESIN GLYCOSIDE, MERREMIN
(TUGUAJALAPIN X DIMER), FROM MERREMINIA HUNGAIENSIS1)

Naoki NODA,a Kyoko TSUJI,a Toshio KAWASAKI,a Kazumoto MIYAHARA,*a Hiroshi HANAZONOb and Chon-Ren YANGc

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 (Convulvulaceae). 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; Convulvulaceae

In our systematic studies on the characteristic constituents, resin glycosides, of the Convulvulaceae 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 paper2) 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 1H-NMR spectrum of 1 showed the signals due to ten anomic 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 peaks5) 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% NH4OH 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.

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tugujalapin 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 "rhamnoconvulvin" from the roots of 1.
**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 I](image-url)

**REFERENCES AND NOTES**

1) Part XXII in the series "Resin Glycosides". For Part XXI see ref. 2).


3) The signals marked with * are overlapping. \(\delta\) in ppm from TMS (coupling constants, \(J\) (Hz) are in parentheses).

1: mp 104-105°C, \([\alpha]_D^{23} -27.7^\circ\) (c=1.4, CHCl3). Negative FAB-MS \(m/z\): 2951 [M-H]*, 1493, 1475, 563, 454, 417, 271. Negative HR FAB-MS \(m/z\): 2952.9336 [M-H]*, Calcld. for C\(_{156}\)H\(_{279}\)O\(_{50}\) 2952.9289. \(^1\)H-NMR (pyridine-d\(_5\), 600 MHz) \(\delta\): 2.26-2.45 (m, 2 x H-2 of Jla), 2.36-2.47 (m, 4 x H-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); 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); 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); 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); 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\(_\alpha\)-6), 4.84* (H\(_\beta\)-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); 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); Rha", 5.75 (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 (ddq, 9.3, 6.3, H-5), 1.65 (d, 6.3, H-3); 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); 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\(_\alpha\)-6), 4.51* (H\(_\beta\)-6), 4.35* (H\(_\gamma\)-6), 5.05* (H\(_\delta\)-6). 9: mp 93-97°C, C\(_{78}\)H\(_{142}\)O\(_{26}\), \([\alpha]_D^{24} -24.4^\circ\) (c=0.1, CHCl3). Negative FAB-MS \(m/z\): 1493 [M-H]*, 1255, 1017, 855, 709, 563. \(^1\)H-NMR (pyridine-d\(_5\), 600 MHz) \(\delta\): 2.45 (t, 7.0, H-2 of Jla), 2.37-2.48 (2 x H-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); 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); 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); 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); 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\(_\alpha\)-6), 4.23* (H\(_\beta\)-6).


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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