Tetrahedron Letters,Vol.26,No.49,pp 6101-6102,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

TWO NOVEL AROMATIC GLYCOSIDES, PUEROSIDE-A AND -B, FROM PUERARIAE RADIX

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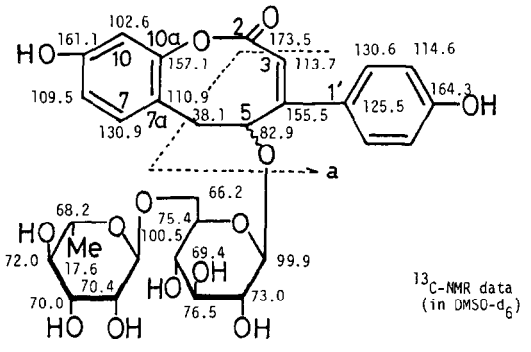
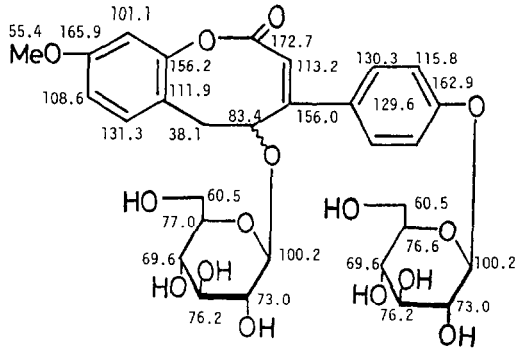
Summary: Two novel aromatic glycosides were obtained from Puerariae Radix and their chemical structures were characterized.

Two novel aromatic glycosides, named pueroside-A (1) and -B (2), with a new skeleton were isolated from Puerariae Radix, the roots of Pueraria lobata Ohwi, one of the most important oriental crude drugs. This report concerns with the structural elucidations of these two substances.

Pueroside-A (1), $C_{29}H_{34}O_{14}$, colorless needles, mp 183-185°C, $[\alpha]_D$ -107.5° (MeOH), showed maxima absorptions at 3300 (OH), 1685 (α,β-unsaturated ketone), 1605 cm^{-1} (arom. ring) in the IR (KBr), and at 313 (18600), 290 (15000), 217 (24100) nm in the UV (MeOH) spectra. The ^{13}C-NMR spectrum suggested the presence of the α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl moiety, therefore, 1 was hydrolized with crude hesperidinase to afford an aglycone (3), $C_{17}H_{14}O_5$, colorless needles, mp 226-228°C, $[\alpha]_D$ -75.8° (MeOH), IR (KBr): 3200, 1670, 1580 cm^{-1}, UV (MeOH): 325 (17500), 286 (14100), 221 (21700) nm (ε), CD [θ] (MeOH): -1.4 x 10^5 (320), -2.1 x 10^5 (285),



pueroside-A (1)



pueroside-B (2)

+1.4 x 10^5 (250), -0.6 x 10^5 (230)(nm), together with D-glucose and L-rhamnose. The aglycone 3, designated as puerol A, showed a molecular ion ($C_{17}H_{14}O_5^+$) at m/z 298 in the EI- and FD-MS, and signals due to the aromatic ABX coupling (1H, d, J=8 Hz, δ 7.36; 1H, dd, J=2, 8 Hz, δ 6.50; 1H, d, J=2 Hz, δ 6.58), aromatic A_2X_2 (2H, d, J=8 Hz, δ 6.68; 2H, d, J=8 Hz, δ 6.92), and ABMX system (1H, dd, J=7, 14 Hz, δ 2.74; 1H, dd, J=4, 14 Hz, δ 3.25; 1H, ddd, J=1, 4, 7 Hz, δ 5.88; 1H, d, J=1 Hz, δ 6.18) in the ^{1}H-NMR spectrum. The last coupling system indicated the presence of the partial structure a. Taking into account the evidence of the ^{13}C-NMR data of 3 [acetone-d_6 + D_2O, δ 175.0, 112.5, 156.7, 84.5, 39.4, 131.7, 108.9, 162.3, 103.8, 159.1, 110.2 (C-2 ~10, 10a, 7a), 127.4 (C-1'), 131.3 (C-2', 6'), 115.6 (C-3', 5'), 166.7 (C-4')], the structure of 3 could be composed as shown in the formula. Location of the sugar linkage in 1 was estimated at the secondary hydroxyl group by comparing of the ^{13}C-NMR spectrum with that of 3 (Shifts accompanied by going to 1 from 3, C-4: +1.2, C-5: +1.6, C-6: +1.3 ppm). The absolute configuration at C-5 is remained unsolved.

Pueroside-B (2), $C_{30}H_{36}O_{15}$, colorless needles, mp 227-229°C, $[\alpha]_D$ -37.6° (MeOH), IR (KBr): 3300, 1725, 1605 cm^{-1}, UV (MeOH): 313 (16900), 290 (14000), 220 (18800) nm (ε), also has a glycosidic bond. Enzymic hydrolysis of 2 yielded an aglycone (4), named puerol B, $C_{18}H_{16}O_5$, colorless plates, mp 238-240°C, $[\alpha]_D$ +68.2° (MeOH), IR (KBr): 3200, 1710, 1605, UV (MeOH): 323 (14400), 285 (11800), 220 (18000) nm (ε), MS (m/z): 312 (M^+), 268 (M^+-CO_2), 253, 206, 107 (base peak), 44, CD [Θ] (MeOH): +1.8 x 10^5 (320), +2.9 x 10^5 (285), -1.9 x 10^5 (250), +0.7 x 10^5 (230), and D-glucose. Comparative study of the ^{1}H- and ^{13}C-NMR [acetone-d_6 + D_2O, ^{1}H δ : 2.74 (1H, dd, J=7, 14 Hz, H-6), 3.25 (1H, dd, J=4, 14 Hz, H'-6), 3.84 (3H, s, 9-O-CH_3), 5.91 (1H, ddd, J=1, 4, 7 Hz, H-5), 6.22 (1H, d, J=1 Hz, H-3), 6.59 (1H, dd, J=2, 8 Hz, H-8), 6.65 (1H, d, J= 2 Hz, H-10), 6.68 (2H, d, J=8 Hz, H-3', 5'), 6.92 (2H, d, J=8 Hz, H-2', 6'), 7.46 (1H, d, J= 8 Hz, H-7); ^{13}C δ : 174.8, 113.4, 156.8, 84.5, 39.4, 131.7, 107.4, 164.1, 102.3, 159.0, 111.3, (C-2~10, 10a, 7a), 127.3 (C-1'), 131.4 (C-2', 6'), 115.7 (C-3', 5'), 166.4 (C-4'), 55.9 (OMe)] and CD spectra of 4 with those of 3 revealed that 4 was corresponding to the 9-O-methyl ether of the enantiomer of 3. Furthermore, it was suggested by the ^{13}C-NMR spectrum that each one mole of the β-D-glucopyranosyl moiety in 1 linked to 5- and 4'-hydroxyl groups (Shifts going to 2 from 4, C-5: +1.1, C-4': +3.5 ppm).

These two substances 1 and 2 obtained from the widely used crude drug offer a new framework-model among the naturally occurring compounds. These compounds, 1 and 2, might be biosynthesized from two moles of p-coumaroyl units.

Acknowledgement. We are grateful to Prof. I.Nishioka for measurements of ^{1}H- and ^{13}C-NMR, and MS spectra. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

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(Received in Japan 1 October 1985)