Cardiac Glycosides from Erysimum cheiranthoides

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Three new cardiac glycosides named cheiranthoside VIII (1), cheiranthoside IX (2) and cheiranthoside X (3) were isolated from the seeds of Erysimum cheiranthoides. Based on spectroscopic data, the structures of 1—3 were characterized as strophanthidin 3-O-β-D-glucopyranosyl-(1→4)-β-D-antiaropyranoside, cheiranthidin 3-O-β-D-glucopyranosyl-(1→4)-β-D-boiviopyranoside and cheiranthidin 3-O-α-L-rhamnopyranosyl-(1→4)-β-D-digitoxopyranoside, respectively. The aglycone moiety possessing a carboxyl group at C-10 of 2 and 3 was regarded to be determined for the first time.

Key words Erysimum cheiranthoides; Cruciferae; 19-carboxylated cardiac glycoside; cheiranthoside; strophanthidin

Erysimum cheiranthoides L. (Cruciferae) is a Chinese crude drug used for treating cardiac diseases, weak cardialpalmus, edema, dyspepsia, etc.1 In previous papers,2—4) we reported seven new cardenolides. As a continuing study on the constituents in the seeds, three additional new glycosides named cheiranthosides VIII, IX and X were isolated, and their chemical structures are described here.

Cheiranthoside VIII (1), obtained as a white powder, [α]D

−5.2° (MeOH), showed a quasimolecular ion at m/z 711 [M−H]− in the negative FAB-MS. Its 1H-NMR spectrum displayed signals due to H2-18 (3H, s) at δ 1.00, H-17 (1H, br d, J=8.5 Hz) at δ 2.78, H2-21 (each 1H, br d, J=18.3 Hz) at δ 4.98 and 5.28, H-22 (1H, s) at δ 6.12, CHO-19 at δ 10.37 on the cardiac steroidal framework, and two anomeric protons at δ 4.57 (1H, d, J=7.3 Hz) and 5.38 (1H, d, J=8.5 Hz), and H1-6 at δ 1.52 (3H, d, J=6.1 Hz) representing of one 6-deoxyxugar in the sugar moiety. The 13C-NMR spectrum showed signals due to a total of 35 carbons, among which 23 carbon signals were originated from the steroidal aglycone part and were coincident with those of strophanthinid; the remaining 12 carbons should be assigned to a sugar moiety. Comparative studies of the 1H- and 13C-NMR spectra with those of the glycosidic linkages of cheiranthosides already obtained from the seeds of the title plant resulted in the identification of 1 with that of the sugar linkage, β-D-glucopyranosyl-(1→4)-β-D-antiaropyranosylαιςς moieties, of cheiranthoside VII.4) Heteronuclear multiplebonds correlation (HMBC) spectrum of 1 showed the connectivities between C-3 (δ1374.8) of the aglycone and the H-1 (δ1953.8) of antiarose, and between the H-1 (δ1345.7) of glucose and the C-4 (δ1379.1) of antiarose. Therefore, 1 was characterized as 3-O-β-D-glucopyranosyl-(1→4)-β-D-antiaropyranosyl strophanthidin, as shown in the Formulæ.

Cheiranthoside IX (2), obtained as a white powder, [α]D

+16.3° (MeOH), showed a quasimolecular ion peak at m/z 695 [M−H]− in the negative FAB-MS. The 1H-NMR spectrum showed signals due to H2-18 at δ 1.04, H-17 (1H, br d,
cone, cheiranthidin, 6 to a terminal rhamnopyranosyl moiety carbon signals, among which 23 were assigned to the agly-
cones, cheiranthidin, 6 to a terminal rhamnopyranosyl moiety and the H-1, H-5 and H-2 of β-D-digitoxopyra-
osyl, and the H-1, H-5 and H-6 of α-L-rhamnopyranosyl residues. The $^{13}$C-NMR spectrum of 2 showed a total of 35 carbon signals, among which 23 were assigned to the agly-
cone, cheiranthidin, 6 to a terminal rhamnopyranosyl moiety and the remaining 6 (δ 104.1, 72.5, 73.8, 79.0, 70.4, 18.6) to a 4-O-substituted-β-D-digitoxopyranosyl moiety, by compari-
son with those of cheiranthoside II. Therefore, the chemical structure of 3 was characterized as 3-O-$\alpha$-L-rhamnopyra-
osyl-(1→4)-β-D-digitoxopyranosyl cheiranthidin, as shown in the Formulae.

Although much attention has focused on the change in Na$^+$, K$^+$-ATPase inhibiting activity, the introduction of car-
boxylic acid at C-10 resulted in a decrease of their activities in 2 and 3.

It is worth noting that the cardiac glycosides having a novel aglycone, cheiranthidin, were isolated from Cruciferae
plant.

**Experimental**

**General** Optical rotations were determined on a JASCO DIP-1000 digi-
ttoral polarimeter. FAB-MS were obtained in a glycerol matrix in the negative

**Extraction and Isolation** The seeds of E. cheiranthoides L. were extracted with MeOH, and the extract (189 g) was partitioned between hexane and water. The aqueous layer (123 g) was subjected to MCI gel CHP 20P (75—150 μm, Mitsubishi Chemical Ind.), Sephadex LH-20 (25—100 μm, Pharmacia Fine Chemicals) and Chromatorex ODS (30—5 μm, Fuji Silycia Chemical Ltd.).

**Plant Material** The seeds of E. cheiranthoides were harvested at Harbin, Heilongjiang Province, in China.

**References**

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