

A Further Furostanol Glycoside From *Smilax china*

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Abstract—A furostanol glycoside, mp 190~198°, was isolated from the MeOH extract of *Smilax china* rhizomes. The structure was established as a mixture of 26-O- β -D-glucopyranosyl-(25R)-22-methoxy-furost-5-en-3 β , 26-diol 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside and its 22-hydroxy derivative on the basis of spectral data and chemical correlations.

Keywords—*Smilax china* • Liliaceae • furostanol glycoside

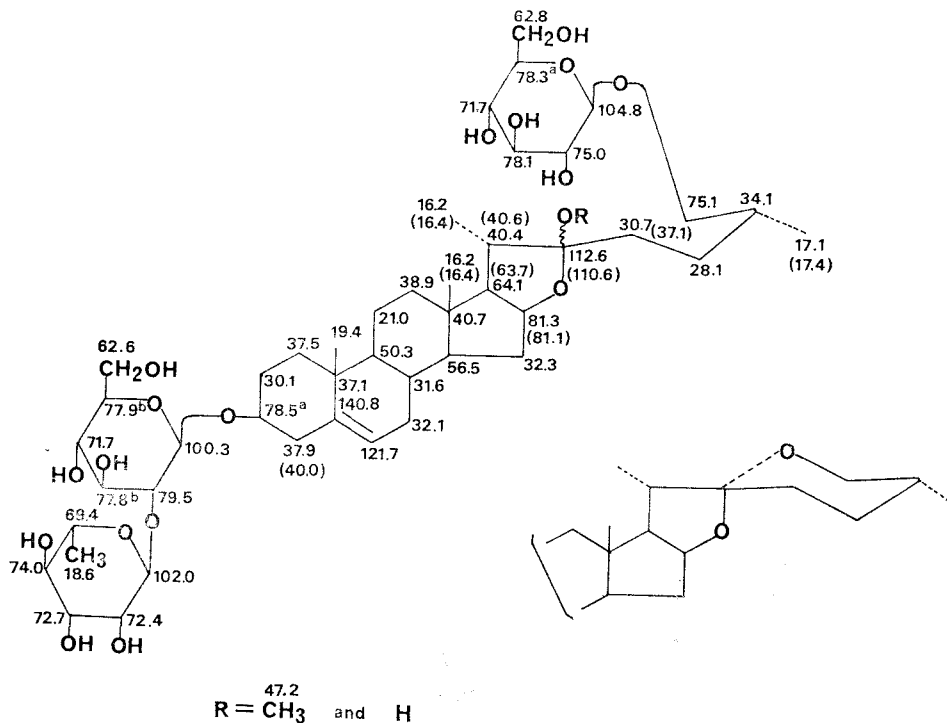
In a previous paper¹⁾, the structures of five steroidal glycosides were described from the rhizomes of *Smilax china* L.(Liliaceae). The presence of a further proto type prosapogenin A of dioscin was also postulated. A further experiment on the same species has led to the isolation of the aforementioned furostanol glycoside. This paper deals with the structure elucidation of this compound.

The BuOH fraction obtained from the MeOH extract of the rhizomes of *Smilax china* followed by fractionation was chromatographed on silica gel to afford a minor furostanol glycoside (1), mp 190~198°, which was positive to Ehrlich reagent²⁾ and exhibited no spiroketal absorptions in its IR spectrum. On enzymatic hydrolysis with β -glucosidase (almond emulsin), 1 gave a glycoside (2), mp 238~240°, which was identified as diosgenin 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside (=prosapogenin A of dioscin) by direct comparison with an authentic sample.¹⁾ Accordingly, the structure of 1 was deduced as a furostanol glycoside corresponding to prosapogenin A of dioscin.

However, a closer inspection of the ¹H-NMR spectrum (Table I) showed that compound 1 was a mixture of 22-methoxy and 22-hydroxy derivatives. In this mixture the 22-methoxy derivative was the more abundant with the corresponding 22-hydroxy one. ¹³C-NMR spectral data as shown in figure supported the above observations. Based on the above data 1 was elucidated as a mixture of 26-O- β -D-glucopyranosyl-(25R)-22-methoxy-furost-5-en-3 β , 16-diol 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside (=methyl proto-prosapogenin A of dioscin) and the corresponding 22-hydroxy one (=proto-prosapogenin A of dioscin). Very recently, Nakano *et al.*³⁾ reported the isolation of methyl proto-prosapogenin A of dioscin from the same genus *Lilium cordatum*. Therefore this is the second report of the isolation.

Experimental

Mps: uncor.; ¹H- and ¹³C-NMR: Bruker AM-300, pyridine-d₅ with TMS as an internal standard; optical rotation: Rudolph Autopol III; IR: Perkin-Elmer 283B.



^{a, b}) Assignments may be reversed.

Chemical shifts for 22-hydroxy derivative(R=H) in parentheses.

Table I. Partial ¹H-NMR spectral data for 1 in pyridine-d₅*

Proton	22-OCH ₃ derivative	22-OH derivative
H-18	0.78 s	0.86 s
H-19	1.02 s	1.01 s
H-21	1.16 d (6.9)	1.30 d (6.8)
H-27	0.96 d (6.3)	0.94 d (6.0)
OCH ₃	3.23 s	—
H-6	5.29br d(4.8)	
rha-CH ₃	1.73 d (6.1)	
Anomeric protons	4.98 d (7.1)	
	6.31 s	

*Data are δ(ppm), multiplicity, and *J*(in parentheses) in Hz.

Plant material and isolation of saponin

...see previous report.¹⁾

Compound 1...amorphous white from MeOH.

Mp 190~198°; [α]_D²² = -58.3°(c, 0.06, pyridine); IR ν_{max}^{KBr} cm⁻¹ 3400, 1650, 1130, 1070, 1045, 905, 887, 833, 807; ¹H-NMR: see Table

I; ¹³C-NMR: see figure.

Enzymatic hydrolysis of 1...It was performed as described in the previous paper¹⁾. The compound thus obtained(2) was identical with prosapogenin A of dioscin by direct comparison with an authentic specimen(TLC, mmp and ¹³C-NMR).

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