*Phytochemistry*, Vol 28, No 10, pp 2787–2791, 1989
Printed in Great Britain

0031-9422/89 $3.00+0.00
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# STEROIDAL SAPONINS FROM A CULTIVATED FORM OF *AGAVE SISALANA*

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(*Received* 9 *December* 1988)

**Key Word Index**—*Agave sisalana*, Agavaceae; steroidal saponin; dongnoside C, D, E.

**Abstract**—Three new steroidal saponins, dongnosides C–E, were isolated from the methanol extracts of the fermented residues of leave-juices of *Agave sisalana* form Dong No 1. On the basis of chemical and spectral evidence, the structures of dongnosides E, D and C were determined as tigogenin-3-*O*-β-D-xylopyranosyl(1→2)[β-D-glucopyranosyl(1→3)]β-D-glucopyranosyl(1→4)β-D-galactopyranoside, tigogenin-3-*O*-β-D-xylopyranosyl(1→3)β-D-xylopyranosyl(1→2)[β-D-glucopyranosyl (1→3)]β-D-glucopyranosyl(1→4)β-D-galactopyranoside and tigogenin-3-*O*-α-L-rhamnopyranosyl (1→4)β-D-xylopyranosyl(1→2)[β-D-glucopyranosyl (1→3)]β-D-glucopyranosyl(1→4)β-D-galactopyranoside, respectively.

## INTRODUCTION

*Agave sisalana* is a very important resource of hard fibre and steroidal material, which was introduced from abroad and has been cultivated in the south of China. Several sapogenins have been isolated from Dong No 1, a cultivated form of this plant [1, 2]. In the present paper, we report the isolation and structure elucidation of three new steroidal saponins, dongnoside E(**1**), D(**2**) and C(**3**) from this plant.

## RESULTS AND DISCUSSION

The methanol extract of fermented residues of leaf-juices were subjected to repeated column chromatography and preparative TLC on silica gel to afford three saponins, all of which were positive in the Liebermann–Burchard reaction, but negative to the Ehrlich reagent [3]. They were predicted to be glycosides of a (25*R*)-spirostanol steroid based on the characteristic absorption band in the IR spectra [4].

On mineral acid hydrolysis, all three saponins yielded a common aglycone. By comparing mp, mmp, optical rotation, IR, EIMS, $R_f$ value on TLC and NMR spectra, the aglycone was determined to be tigogenin.

Saponin **1** was hydrolysed with acid to yield D-galactose (Gal), D-glucose (Glc) and D-xylose (Xyl). The negative ion FAB mass spectrum of **1** exhibited a molecular ion peak at *m/z* 1033 $[M-H]^-$ and fragment ions at *m/z* 901 [1033 − pentose]$^-$, 871 [1033 − hexose]$^-$, 739 [1033 − pentose − hexose]$^-$ and 577 [1033 − pentose − 2 hexose]$^-$. The $^1$H NMR spectrum of **1** ($C_5D_5N$ + $CF_3COOH$) exhibited four anomeric proton signals at δ4.85 (1H, *d*, *J* = 7.3 Hz), 5.12 (1H, *d*, *J* = 7.8 Hz), 5.18 (1H, *d*, *J* = 7.8 Hz) and 5.50 (1H, *d*, *J* = 7.3 Hz), respectively. EIMS of acetylated **1** showed fragment ions at *m/z* 835 [(hexose–hexose–pentose) $Ac_9]^+$, 331 [(terminal hexose) $Ac_4]^+$ and 259 [(terminal pentose) $Ac_3]^+$. These data indicated **1** to contain 1 mol of Xyl and 3 mol of hexose (Glc and Gal).

When saponin **1** was partially hydrolysed with dilute hydrochloric acid in ethanol, three prosapogenins, **4**–**6**, were obtained. From acid hydrolysis test on TLC [5], both **4** and **5** gave Glc and Gal, **6** only gave Gal.

The positive ion FAB mass spectrum of **6** showed a molecular ion peak at *m/z* 579 $[M+H]^+$ and fragment ions at *m/z* 417 $[M-Gal]^+$, suggesting that **6** should be a tigogenin-3-*O*-β-D-galactopyranoside.

$^{13}$C NMR spectra of **1**, **4** and **5** (Table 1) showed a common downfield shift (+6.9 ppm) for C-3 of the aglycone moeity comparing with tigogenin [6], therefore the sugar chain must be attached at the C-3 position of the aglycone. Prosapogenin **5** exhibited peaks at *m/z* 763 $[M+Na]^+$ and 740 $[M]^+$ in FDMS and showed the signals of a terminal Glc and a inner Gal besides the aglycone in the $^{13}$C NMR spectrum (Table 2). According to the glycosylation shift effect [7], the downfield shift (+9.6 ppm) of C-4 of Gal suggested that the Glc should attach to C-4 of the Gal. It had the same chemical shifts for the sugar moiety as **7** which is a saponin of diosgenin isolated from *Aspitistra elatior* [8] Thus, compound **5** was established as tigogenin-3-*O*-β-D-glucopyranosyl (1→4)β-D-galactopyranoside.

Prosapogenin **4** showed peaks at *m/z* 903 $[M+H]^+$ and 902 $[M]^+$ upon FDMS and only added signals originating from a Glc unit more than **5** in the $^{13}$C NMR spectrum. The chemical shifts of the inner Glc showed a downfield shift (+9.6 ppm) for C-3, suggesting the terminal Glc should attach to C-3 of the inner Glc. Therefore, the structure of **4** was deduced as tigogenin-3-*O*-β-D-glucopyranosyl(1→3)β-D-glucopyranosyl(1→4)β-D-galactopyranoside.

Saponin **1** only had additional signals of a terminal Xyl more than **4** in the $^{13}$C NMR spectrum The chemical shifts of the inner Glc showed a downfield shift (+4.4 ppm) for C-2, suggesting that **1** should consist of a

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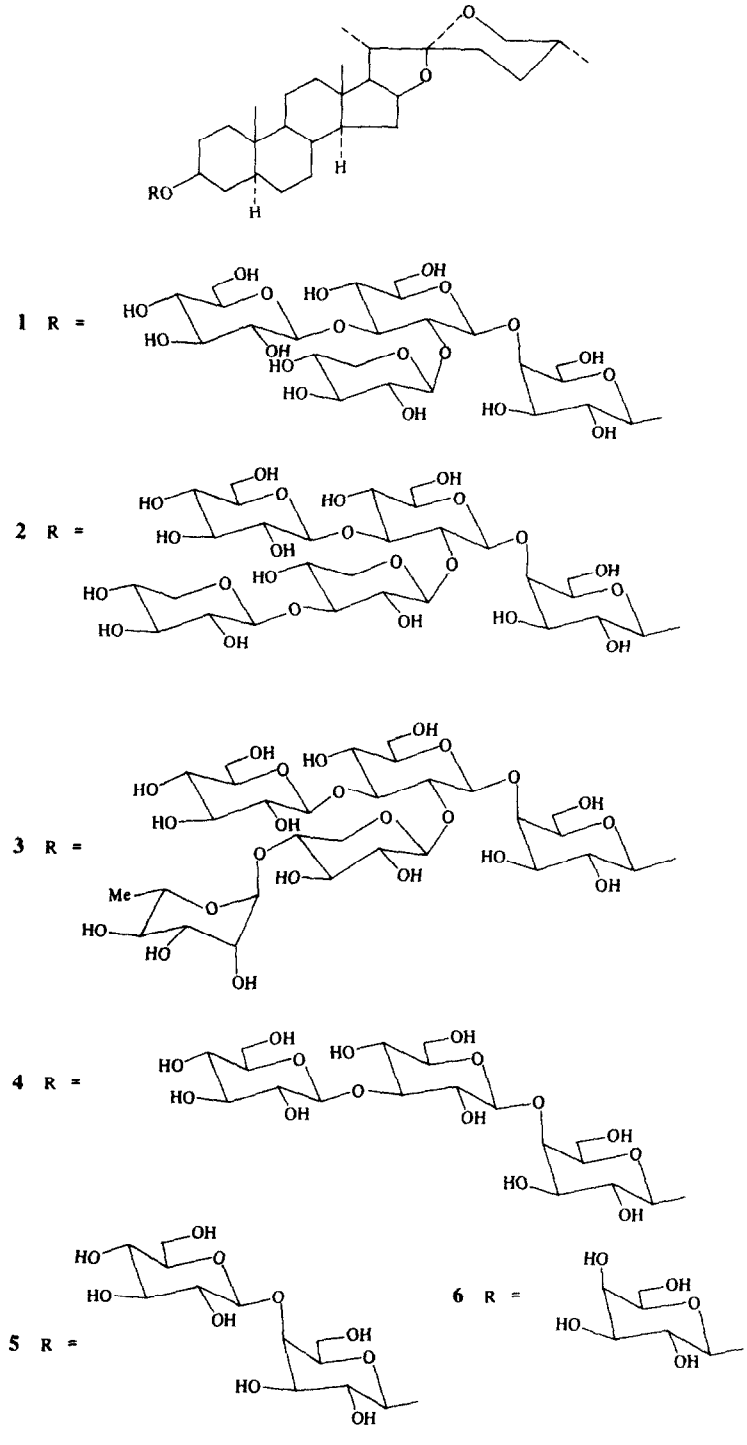


branch sugar moiety and the terminal Xyl should attach to C-2 of the inner Glc. On the basis of the above findings, the structure of **1** was concluded to be tigogenin-3-*O*-*β*-D-xylopyranosyl(1→2)[*β*-D-glucopyranosyl(1→3)]*β*-D-glucopyranosyl(1→4)*β*-D-galactopyranoside.

Saponin **2** yielded Gal, Glc and Xyl by hydrolysis with acid, and yielded compounds **1**, **4**–**6** as prosapogenin by partial hydrolysis with dilute hydrochloric acid. The negative ion FAB mass spectrum exhibited a molecular ion peak at *m/z* 1165 $[M-H]^-$ and fragment ions at *m/z* 1033 $[1165-Xyl]^-$, 901 $[1165-2Xyl]^-$, 871 $[1165-Xyl-Glc]^-$, 739 $[1165-2Xyl-Glc]^-$ and 577 $[1165-2Xyl-2Glc]^-$. The $^1H$ NMR spectrum of **2** $[C_5D_5N+CF_3COOH]$ exhibited the presence of five anomeric proton signals at 4.86 (1H, *d*, *J* = 7.4 Hz), 5.06 (1H, *d*, *J* = 7.4 Hz), 5.10 (1H, *d*, *J* = 7.8 Hz), 5.14 (1H, *d*, *J* = 7.8 Hz), 5.54 (1H, *d*, *J* = 6.4 Hz). EIMS of the acetylated **2** showed fragment ions at *m/z* 331 $[(\text{terminal Glc})Ac_4]^+$ and 259

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