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Two New Steroidal Glycosides from *Caryopteris terniflora*

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Abstract: Two new steroidal glycosides were isolated from the Chinese medicinal plant *Caryopteris terniflora*. The spectroscopic and chemical evidences revealed that their structures to be 6′-(β-sitosteroyl-3-*O*-β-glucopyranosidyl) hexacosanate **1** and 6′-(stigmasteroyl-3-*O*-β-glucopyranosidyl) linolenate **2**, respectively.

Keywords: *Caryopteris terniflora,* Verbenaceae, steroidal glycoside.

Caryopteris terniflora Maxim. (Verbenaceae) is a herbaceous plant, distributed in north China. It has been used in folk medicine as antipyretic, detoxicant, expectorant, anti-inflammatory agents and treated for cold, scrofula and rheumatism[1]. The phytochemical studies of the plant have not been reported previously. In our investigation on the whole plant of this herb, two novel steroidal glycosides were isolated. Here we report the structure elucidation of them.

Compound **1** and **2** were isolated as an inseparable mixture of two acylglucosylsterols in a ratio of 3:1 from their spectral analysis. On the basis of its spectral data, the mixture was thought to consist of compounds characterized by the two different glycosylsterol moiety, bearing different acyclic chains at the C-6′ position of the glycosyl unit. The IR spectrum of the mixture showed the presence of hydroxylic (3400 cm^{-1}), ester carbonyl groups (1735 cm^{-1}), and long chain $(CH_2)_n$ rock (732 cm^{-1}). ^{1}H NMR spectrum, besides signals that agreed with those of β-sitosterol and stigmasterol, showed the anomeric H-1′ proton of the β-glycosidic unit as a doublet at δ 4.37 (J=7.5 Hz) and the H-6′ methylene as two double doublets centered at δ 4.25 (J=12.0 and 2.0 Hz) and 4.52 (J=12.0 and 5.0 Hz), while the remaining protons were partially overlapped in the 3.2-3.8 ppm range. Finally olefinic protons at δ 5.36, long chain methylenes at δ 1.26, and other signals in the high field of the spectrum attributable to saturated and unsaturated acylic chains were detected. The ^{13}C NMR spectrum of **1** confirmed the presence of β-sitosterol and indicated β-*D*-glucose as the sugar moiety owing to the presence of the

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Figure 1 The structures of **1** and **2**

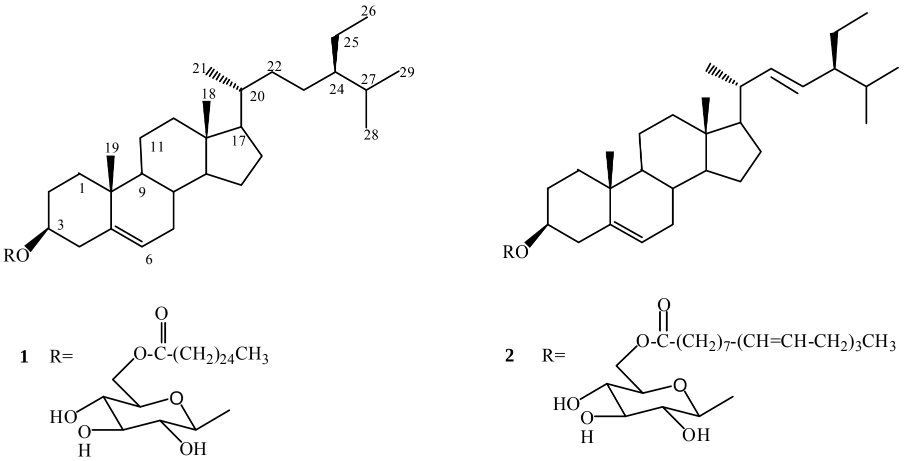

Table 1 ^{13}C NMR (100MHz) data for **1** and **2** in $CDCl_3$(δppm)

Position	**1**	**2**	Position	**1**	**2**
1	37.27 t	37.27 t	28	22.67 t	25.61 t
2	29.78 t	29.78 t	29	11.83 q	12.21 q
3	79.74 d	79.74 d	1′	101.25 d	101.25 d
4	38.91 t	38.91 t	2′	73.35 d	73.35 d
5	140.33 s	140.33 s	3′	76.19 d	76.19 d
6	122.03 d	122.03 d	4′	70.41 d	70.41 d
7	31.92 t	31.92 t	5′	73.70 d	73.70 d
8	31.84 d	31.84 d	6′	63.62 t	63.62 t
9	50.13 d	50.13 d	1″	174.20 s	174.20 s
10	36.66 s	36.66 s	2″	34.27 t	34.27 t
11	21.06 t	21.06 t	3″	23.03 t	23.03 t
12	39.76 t	39.76 t	4″	29.78-29.27 t	29.69 t
13	42.30 s	42.28 s	5″	29.78-29.27 t	29.48 t
14	56.75 d	56.77 d	6″	29.78-29.27 t	29.34 t
15	24.28 t	24.30 t	7″	29.78-29.27 t	29.79 t
16	28.23 t	28.23 t	8″	29.78-29.27 t	24.97 t
17	56.16 d	55.95 d	9″	29.78-29.27 t	130.19 d
18	11.94 q	12.02 q	10″	29.78-29.27 t	128.04 d
19	19.35 q	19.35 q	11″	29.78-29.27 t	25.61 t
20	36.16 d	40.51 d	12″	29.78-29.27 t	129.67 d
21	18.76 q	21.24 q	13″	29.78-29.27 t	129.31 d
22	33.92 t	138.26 d	14″	29.78-29.27 t	25.38 t
23	26.17 t	129.96 d	15″	29.78-29.27 t	127.86 d
24	45.78 d	51.23 d	16″	29.78-29.27 t	129.96 d
25	29.12 d	31.96 d	17″-24″	29.78-29.27 t	21.24 t
26	19.79 q	21.06 q	25″	24.97 t	
27	18.99 q	18.99 q	CH_3	14.10 q	14.10 q

signals at δ 101.25, 76.19, 73.70, 73.35, 70.41, and 63.62[2]. Several carbons of saturated acyclic residues were also present. The downfield shift of C-6′, as well as the corresponding downfield shift of H-6′, suggested that the acyclic chains were linked at this position. The ^{13}C NMR spectrum of **2** showed signals in good agreement with stigmasterol with the exception of C-2, C-3, and C-4, which were shifted to δ 29.78, 79.74, and 38.91, respectively, by the presence of the glucosidic moiety at C-3[3]. Besides the glucose carbons, signals were also present attributable to a triunsaturated C_{18} acyclic residue with a carbonyl carbon at δ 174.20, six olefinic carbons at δ 130.19, 129.96, 129.67, 129.31, 128.04, and 127.86, four allylic methylene carbons at δ 24.97, 25.61, 25.38, and 21.24, six methylenes at δ 34.27, 29.79, 29.69, 29.48, 29.34, and 29.27, and a methyl carbon at δ 14.10. These signals were assigned by comparison with the data reported for analogous fatty acid methyl esters[4]. Hydrolysis of the mixture with aqueous NaOH gave β-sitosteroyl-3-*O*-β-glucopyranoside, stigmasteroyl-3-*O*-β- glucopyranoside, and a mixture of fatty acids. The fatty acids were identified as hexacosanic acid and linolenic acid by the spectral methods and the MS [*m/z* (%) 396 (M^+, 100), 278 (M^+, 5), 75 (57), 69 (62), 55 (75)]. These indicated that hexacosanyl residue was in **1** and a linolenyl one in **2**. Thus, compound **1** was elucidated as 6′-(β-sitosteroyl-3-*O*-β-gluco-pyranosidyl) hexacosanate, and compound **2** was deduced as 6′-(stigmasteroyl-3-*O*-β-gluco-pyranosidyl) linolenate.

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