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Furostanol saponins from *Allium tuberosum*

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Abstract

Three new furostanol saponins, tuberoside **A**, **B** and **C**, have been isolated from the seeds of *Allium tuberosum*. On the basis of chemical reactions and spectral data, their structures were established as 26-*O*-β-D-glucopyranosyl-(25 S)-5α-furost-20(22)-ene-2α,3β,26-triol 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-*O*-β-D-glucopyranoside; 26-*O*-β-D-glucopyranosyl-(25 S)-5α-furost-20(22)-ene-2α,3β,26-triol 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-[α-L-rhamnopyranosyl-(1 → 4)]-β-D-glucopyranoside and 26-*O*-β-D-glucopyranosyl-(25 S)-5α-furost-20(22)-ene-2α,3β,26-triol 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-[β-D-glucopyranosyl-(1 → 3)]-β-D-glucopyranoside, respectively.

Keywords: *Allium tuberosum*; Liliaceae; Furostanol saponins; Tuberoside **A**; **B**; **C**

1. Introduction

Allium tuberosum Rottl. (Liliaceae) is distributed all over mainland China and used not only as food but also as medicine. The seeds of this plant are used in Chinese folk medicine as a tonic and aphrodisiac (Jiangsu New Medical Academy, 1986). Various sulfide derivatives (Mackenzie & Ferns, 1977; Meng, Wang & Cao, 1996), 3-*O*-rhamnogalactosyl-7-*O*-rhamnosylkaempferol (Kaneta, Hikichi & Endo, 1980), flavonoids (Yoshida, Saito & Kadoya, 1987), *N*-*p*-coumaroyl tyramine (Choi & Go, 1996) and bis(*p*-hydroxyphenyl) ether (Choi & Go, 1996) have also been isolated from the leaves of *A. tuberosum*. However, no chemical analysis has been carried out on the seeds of this plant. In order to clarify its bioactive compounds, we studied the chemical constituents of the seeds of *A. tuberosum* systematically. This paper deals with the isolation and structural elucidation of three new furostanol saponins, named tuberoside **A** (**1**), **B** (**2**) and **C** (**3**), respectively.

2. Results and discussion

The *n*-butanol fraction from the ethanol extract of the seeds of *A. tuberosum* was chromatographed on Diaion HP-20, and RP-18 silica gel to afford tuberoside **A** (**1**), **B** (**2**), and **C** (**3**).

Tuberoside **A** (**1**), an amorphous solid, had a molecular formula of $C_{45}H_{74}O_{18}$ determined by positive ion FAB-MS (at *m*/*z* 903 $[M+H]^+$) as well as from its ^{13}C and DEPT NMR data. Its IR spectrum showed characteristic absorptions for hydroxyl (3417 cm^{-1}) and a glycosidic linkage (1000–1100 cm^{-1}). Its spectral features and physicochemical properties suggested **1** to be a sterol saponin. Of the 45 carbons observed, 27 were assigned to the aglycone, 18 to the oligosaccharide moiety (see Tables 1 and 2). Compound **1** was shown to be a 20(22)-ene-furostanol saponin from analysis of ^1H and ^{13}C NMR spectra [δ_H 1.70 (H-21, *s*), δ_C 152.6 (C-22), and 103.8 (C-20)] (Mimaki, Takaashi & Kuroda, 1997). Comparison of the signals from the sterol part of **1** in the ^{13}C NMR spectra with those from the sterol part of 26-*O*-β-D-glucopyranosyl-(25 S)-5α-furost-20(22)-ene-1β,3α,26-triol 3*O*-β-D-glucopyranoside (**X**) (Mimaki et al., 1997) (Table 1) showed that the sterol part of **1** was the same as that of **X** except A ring. Acid hydrolysis of **1** gave **1a**, glu-

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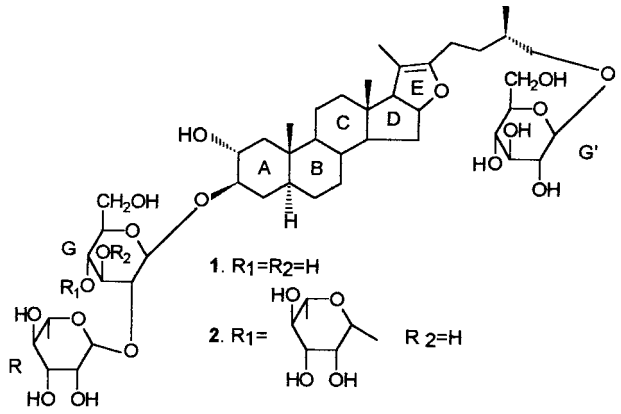

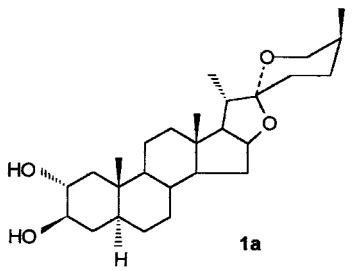

cose and rhamnose. The ^{1}H NMR, IR and EIMS spectral data of **1a** and the ^{13}C NMR spectral data of the aglycon part of **1** allowed the identification of **1a** as (25 S)-5α-spirostan-2α,3β diol (neogitogenin) (Agrawal, Jain & Gupta, 1985; Tori, Nishikawa & Seo, 1982; Gupta & Jain, 1986). Thus, based on the above spectral data and chemical evidence, the structure of the sterol part of **1** was (25 S)-5α-furost-20(22)-ene-2α,3β,26-triol substituted in the C-3 and C-26 positions. The trisaccharide nature of compound **1** was manifested by its ^{1}H [δ 6.30, *s*; δ 5.06, *d*, $J = 7.1$ Hz and δ 4.85, *d*, $J = 7.7$ Hz] and ^{13}C [δ 105.3, 102.3, 101.4] NMR data, respectively (see Table 2). The identity of the monosaccharide and the sequence of the oligosaccharide chain were determined by the analysis of a combination of DEPT, COSY, TOCSY, HMQC and HMBC NMR spectra. Starting from the anomeric proton of each sugar unit, all the hydrogens within each spin system were delineated using COSY NMR with the aid of a TOCSY spectrum. On the basis of the assigned protons the ^{13}C NMR resonances of each sugar unit were identified by HMQC and further confirmed by HMBC experiments. The α-anomeric configuration for the rhamnose was determined by its C_5 data (δ 69.7). The β-anomeric configurations for the two glucoses were determined from their large $^{3}J_{H1,H2}$ coupling constants (7–8 Hz). From the HMBC spectrum it was observed that C_3 (δ 85.5) with H_{G1} (δ 5.06), C_{G2} (δ 78.3) with H_{R1} (δ 6.30) and C_{26} (δ 75.5) with $H_{G'1}$ (δ 4.85) had cross peaks. Thus, tuberoside **A** (**1**) was 26-*O*-β-D-glucopyranosyl-(25 S)-5α-furost-20(22)-ene-2α,3β,26-triol 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-*O*-β-D-glucopyranoside.

Tuberoside **B** (**2**), an amorphous solid, was assigned a molecular formula of $C_{51}H_{84}O_{22}$ determined by positive ion FAB-MS (at *m/z* 1049 $[M+H]^{+}$) as well as from analysis of its ^{13}C and DEPT NMR data. Of the 51 carbons observed, 27 were assigned to the aglycone, 24 to the oligosaccharide moiety (see Tables 1 and 2). The spectral data of **2** showed that it possessed the same aglycon as that of **1**, but differed from the saccharide structure of **1**. The molecular weight of **2** was 146 mass units greater than that of tuberoside **A** (**1**) indicating that **2** had four sugar units. The tetrasaccharide nature of compound **2** was also manifested by its ^{1}H [δ 6.36, *s*; δ 5.82, *s*; δ 5.05, *d*, $J = 7.0$ Hz and δ 4.87, *d*, $J = 7.7$ Hz] and ^{13}C [δ 105.3, 103.1, 102.3 101.0] NMR data, respectively (see Table 2). Acid hydrolysis of **2** on a HR–TLC silica gel plate gave glucose and rhamnose. The identity of the monosaccharide and the sequence of the oligosacchar-

Table 1
^{13}C (100 MHz) spectral data for the sterol parts of **1**, **2**, **3** and **X** (C_5D_5N) (δ in ppm)

Carbon	**1**	**2**	**3**	**X** (Mimaki et al., 1997)
1	46.0 *t*	46.0 *t*	46.0 *t*	73.7 *d*
2	70.9 *d*	70.8 *d*	70.8 *d*	37.1 *t*
3	85.5 *d*	85.2 *d*	85.0 *d*	73.8 *d*
4	33.8 *t*	33.7 *t*	33.6 *t*	35.1 *t*
5	44.9 *d*	44.9 *d*	44.8 *d*	39.2 *d*
6	28.4 *t*	28.4 *t*	28.3 *t*	28.7 *t*
7	32.7 *t*	32.7 *t*	32.6 *t*	32.7 *t*
8	34.8 *d*	34.6 *d*	34.5 *d*	35.8 *d*
9	54.6 *d*	54.6 *d*	54.6 *d*	55.1 *d*
10	37.1 *s*	37.1 *s*	37.1 *s*	42.6 *s*
11	21.8 *t*	21.9 *t*	21.8 *t*	21.3 *t*
12	40.0 *t*	40.1 *t*	40.0 *t*	40.6 *t*
13	44.0 *s*	44.0 *s*	43.9 *s*	43.4 *s*
14	54.9 *d*	54.9 *d*	54.8 *d*	55.1 *d*
15	34.6 *t*	34.7 *t*	34.6 *t*	34.7 *t*
16	84.7 *d*	84.7 *d*	84.8 *d*	84.4 *d*
17	64.8 *d*	64.8 *d*	64.9 *d*	64.8 *d*
18	14.6 *q*	14.7 *q*	14.6 *q*	14.6 *q*
19	13.7 *q*	13.7 *q*	13.7 *q*	6.5 *q*
20	103.8 *s*	103.9 *s*	103.8 *s*	103.7 *s*
21	12.0 *q*	12.1 *q*	12.0 *q*	11.8 *q*
22	152.6 *s*	152.6 *s*	152.6 *s*	152.3 *s*
23	31.6 *t*	31.6 *t*	31.6 *t*	31.4 *t*
24	23.9 *t*	23.9 *t*	23.8 *t*	23.6 *t*
25	33.9 *d*	33.9 *d*	33.9 *d*	33.7 *d*
26	75.5 *t*	75.5 *t*	75.4 *t*	75.2 *t*
27	17.4 *q*	17.4 *q*	17.4 *q*	17.2 *q*

Table 2
^{13}C (100 MHz) and ^{1}H (400 MHz) NMR spectral data for the sugar moieties of **1**, **2**, and **3** (C_5D_5N) (δ in ppm, *J* in Hz)

	1		**2**		**3**	
	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
Glucose						
1	101.4 *d*	5.06, *d, J* = 7.1	101.0 *d*	5.05, *d, J* = 7.0	100.6 *d*	5.05, *d, J* = 7.6
2	78.3 *d*	4.20, *m*	78.2 *d*	4.22, *m*	77.8 *d*	4.21, *m*
3	79.7 *d*	4.25, *m*	78.0 *d*	3.99, *m*	82.0 *d*	4.22, *m*
4	72.1 *d*	4.05, *m*	78.9 *d*	4.35, *m*	71.4 *d*	4.30, *m*
5	78.5 *d*	4.03, *m*	77.2 *d*	3.83, *m*	76.6 *d*	4.02, *m*
6	62.8 *t*	4.32, *m*	61.4 *t*	4.12, *m*	61.9 *t*	4.52, *m*
		4.40, *m*		4.32, *m*		5.58, *m*
1′	105.3 *d*	4.85, *d, J* = 7.7	105.3 *d*	4.87, *d, J* = 7.7	105.3 *d*	4.89, *d, J* = 7.7
2′	75.3 *d*	4.02, *m*	75.4 *d*	4.05, *m*	75.4 *d*	4.08, *m*
3′	78.7 *d*	4.21, *m*	78.7 *d*	4.22, *m*	78.6 *d*	4.31, *m*
4′	71.9 *d*	4.22, *m*	71.9 *d*	4.22, *m*	71.9 *d*	4.30, *m*
5′	78.6 *d*	3.95, *m*	78.6 *d*	3.99, *m*	78.7 *d*	4.02, *m*
6′	63.0 *t*	4.40, *m*	63.0 *t*	4.41, *m*	63.0 *t*	4.45, *m*
		4.55, *m*		4.56, *m*		4.58, *m*
1″					105.3 *d*	5.17, *d, J* = 7.8
2″					75.1 *d*	4.11, *m*
3″					78.4 *d*	4.24, *m*
4″					71.4 *d*	4.30, *m*
5″					77.8 *d*	4.05, *m*
6″					62.3 *t*	4.38, *m*
						4.52, *m*
Rhamnose						
1	102.3 *d*	6.30, *s*	102.3 *d*	6.36, *s*	102.1 *d*	6.25, *s*
2	72.6 *d*	4.81, *m*	72.8 *d*	4.85, *m*	72.9 *d*	4.81, *m*
3	72.9 *d*	4.57, *m*	72.6 *d*	4.60, *m*	72.5 *d*	4.60, *m*
4	74.3 *d*	4.33, *m*	74.0 *d*	4.36, *m*	74.2 *d*	4.38, *m*
5	69.7 *d*	4.88, *m*	69.7 *d*	4.89, *m*	69.6 *d*	4.90, *m*
6	18.8 *q*	1.73, *d, J* = 6.8	18.7 *q*	1.72, *d, J* = 6.1	18.7 *q*	1.80, *d, J* = 6.2
1′			103.1 *d*	5.82, *s*		
2′			72.9 *d*	4.69, *m*		
3′			72.7 *d*	4.52, *m*		
4′			74.2	4.36, *m*		
5′			70.6 *d*	4.90, *m*		
6′			18.7 *q*	1.66, *d, J* = 6.1		

ide chain were determined as described under compound **1** above. The α-anomeric configuration for the rhamnoses were judged by their C_5 data (δ 69.7 and 70.6). The β-anomeric configurations for the two glucoses were judged from their large $^{3}J_{H1,H2}$ coupling constants (7–8 Hz). From the HMBC spectrum cross peaks were observed between C_3 (δ 85.2) and H_{G1} (δ 5.05), C_{G2} (δ 78.2) and H_{R1} (δ 6.36), C_{G4} (δ 78.9) and $H_{R'1}$ (δ 5.82), and C_{26} (δ 75.5) and $H_{G'1}$ (δ 4.87). Thus tuberoside **B** (**2**) was established as 26-*O*-β-D-glucopyranosyl-(25 S)-5α-furost-20(22)-ene-2α,3β,26-triol 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-[α-L-rhamnopyranosyl-(1 → 4)]-β-D-glucopyranoside.

Tuberoside **C** (**3**) was obtained as an amorphous solid with the molecular formula $C_{51}H_{84}O_{23}$, which was deduced from the ESIMS (at *m/z* 1088 $[M+Na]^+$) as well as its ^{13}C and DEPT NMR data. Of the 51 carbons observed, 27 were assigned to the aglycone, 24 to the oligosaccharide moiety (see Tables 1 and 2). The spectral data of **3** showed that the aglycone and the number of sugar units were the same as those of **2**. Acid hydrolysis of **3** on a HR–TLC silica gel plate gave glucose and rhamnose. The tetrasaccharide nature of the compound **3** was also determined from its ^{1}H [δ 6.25, *s*; δ 5.17, *d, J* = 7.8; δ 5.05, *d, J* = 7.6 Hz and δ 4.89, *d, J* = 7.7 Hz] and ^{13}C [δ 105.3, 105.3, 102.1, 100.6] NMR data, respectively (see Table 2). The identity of the monosaccharide and the sequence of the oligosaccharide chain were determined from the DEPT, COSY, TOCSY, HMQC and HMBC

spectra as described for compound **1** above. An α-anomeric configuration for the rhamnose unit was concluded from its C_5 data (δ 69.6). The β-anomeric configurations for the three glucoses were judged from their large $^3J_{H1,H2}$ coupling constants (7–8 Hz). From the HMBC spectrum we can see that C_3 (δ 85.0) with H_{G1} (δ 5.05), C_{G2} (δ 77.8) with H_{R1} (δ 6.25), C_{G3} (δ 82.0) with H_{G*1} (δ 5.17) and C_{26} (δ 75.4) with $H_{G'1}$ (δ 4.89) have cross peaks. Thus, tuberoside **C** (**3**) was characterized as 26-*O*-β-D-glucopyranosyl-(25 S)-5α-furost-20(22)-ene-2α,3β,26-triol 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-[β-D-glucopyranosyl-(1 → 3)]-β-D-glucopyranoside.

3. Experimental

3.1. General

CC: Silica gel 60H, TLC: silica gel $HSGF_{254}$ (Qingdao Haiyang Chemical Group Co., Qingdao, People's Republic of China). RP-18 CC: LiChroprep RP-18 (25–40 μm, Merck). GLC analysis: Shimadzu GC-9A, glass column (300 × 0.32 cm) packed with OV 225, carrier gas, N_2, flow rate, 30 ml/min. Optical rotations: JASCO DIP-181 polarimeter. IR: Perkin-Elmer model 599 infrared spectrometer. ^1H (400 Hz), ^{13}C (100 Hz) NMR and all 2-D spectra: Bruker AM-400 NMR spectrometer, with TMS as internal standard. FABMS: MAT-95 mass spectrometer. ESIMS: Quattro mass spectrometer.

3.2. Plant material

The seeds of *A. tuberosum* were purchased in Shanghai (China) in September 1997. The botanical identification was made by Professor Xuesheng Bao (Shanghai Institute of Drug Control). A voucher specimen (No. 334) has been deposited at the Herbarium of the Department of Phytochemistry, Shanghai Institute of Materia Media, Chinese Academy of Sciences.

3.3. Extraction and isolation

The powdered seeds of *A. tuberosum* (50 kg) were extracted successively with petroleum either × 2 and 95% EtOH × 3. After evaporation of ethanol in vacuo, the residue was suspended in water and then extracted successively with petroleum ether, EtOAc and *n*-BuOH. The *n*-BuOH fr. (270 g) was subjected to Diaion HP-20 using an EtOH–H_2O gradient system (0–100%). The fr. (60 g) eluted by 70 + 30% EtOH was subjected to silica gel CC with a CH_2Cl_2–MeOH–H_2O solvent system (5:1:0.15–1:1:0.3). The fr. eluted by CH_2Cl_2–MeOH–H_2O (4:1:0.2) was subjected to RP-18 silica gel CC with 70 and 75% MeOH to get compounds **1** (170 mg) and **2** (250 mg); the fr. eluted by CH_2Cl_2–MeOH–H_2O (3:1:0.2) was subjected to RP-18 silica gel CC with 70% MeOH to afford compound **3** (250 mg).

3.4. Compound *1*

Amorphous solid, $[\alpha]_D^{22}$ −29.5° (MeOH, *c* 0.27). IR_{max}^{KBr} cm^{-1}: 3417, 1450, 1381, 1000–1100. FABMS: *m/z* 903 $[M+H]^+$, 741 $[M+H-162]^+$, 595 $[M+H-162-146]^+$, 433 $[M+H-162\times2-146]^+$. ^1H NMR (C_5D_5N) of the sterol part of **1**: δ 0.76 (H-18, *s*, 0.96 (H-19, *s*), 1.10 (H-27, *d*, *J* = 6.3 Hz), 1.70 (H-21, *s*), 2.54 (H-17, *d*, *J* = 9.6 Hz), 3.52 (H-26a, *m*), 3.94 (H-3, *m*), 4.10 (H-26b, *m*), 4.12 (H-2, *m*), 4.89 (H-16, *m*). ^{13}C NMR (C_5D_5N) of the sterol part of **1** (see Table 1); ^1H NMR (C_5D_5N) and ^{13}C NMR (C_5D_5N) of the sugar moieties of **1** (see Table 2).

3.5. Acid hydrolysis of *1*

A solution of **1** (30 mg) in 2 N aqueous CF_3COOH (5 ml) was refluxed on a water bath for 3 h. After this period, the reaction mixture was diluted with H_2O (15 ml) and extracted with CH_2Cl_2 (3 × 5 ml). The combined CH_2Cl_2 extracts were washed with H_2O and dried with Na_2SO_4. Evaporation of the solvent gave compound **1a** (7 mg). After repeated evaporations of the solvent of the aqueous layer by adding MeOH to remove the acid, the sugars were analyzed by silica gel TLC in comparison with standard sugars [*n*-BuOH–Me_2CO–H_2O (4:5:1) and $CHCl_3$–MeOH–H_2O (7:3:0.5)], detected by spraying with aniline–phthalic acid reagent [aniline:phthalic acid:*n*-BuOH (2:3:200)] and then heating to 110°C.

A 2 mg quantity of saponin **1** was refluxed in 2 N aqueous CF_3COOH (2 ml) in a sealed serum vial at 120°C for 2 h and the solution evaporated to dryness with MeOH. The residue was dissolved in 5 ml H_2O and the mixture was reduced with $NaBH_4$ at room temp. for 3 h. After neutralization by adding HOAc, the mixture was evapd to dryness by repeated co-distillation with MeOH. The resulting alditol mixture was refluxed with Ac_2O for 1 h, after which the soln was evapd to dryness. A sample was subjected to GLC to give the alditol acetates of rhamnose and glucose in a molar ratio 1:2.

3.6. Compound *1a*

Amorphous solid, IR_{max}^{KBr} cm^{-1}: 3410, 1452, 1379, 1057, 987, 922, 890, 865. EIMS: *m/z* 432 $[M]^+$, 360, 318, 139. ^1H NMR ($CDCl_3$): δ 4.40 (H-16, *m*), 3.93 (H-2, *m*), 3.55 (H-3, *m*), 3.38 (H-26a, *m*), 3.26 (H-26b, *m*), 1.05 (H-21, *d*, *J* = 7.1 Hz), 0.97 (H-27, *d*, *J* = 6.5 Hz), 0.84 (H-19, *s*), 0.73 (H-18, *s*).

3.7. Compound 2

Amorphous solid, $[\alpha]_D^{23}$ −29.5° (MeOH, *c* 0.30). IR_{max}^{KBr} cm^{-1}: 3417, 1452, 1383, 1000–1100. FABMS: *m/z* 1049 $[M+H]^+$, 903 $[M+H-146]^+$, 741 $[M+H-162-146]^+$, 595 $[M+H-162-146\times2]^+$, 433 $[M+H-162\times2-146\times2]^+$. ^1H NMR (C_5D_5N) of the sterol part of **2**: δ 0.78 (H-18, *s*), 0.96 (H-19, *s*), 1.10 (H-27, *d*, J = 6.5 Hz), 1.70 (H-21, *s*), 2.51 (H-17, *d*, J = 9.9 Hz), 3.52 (H-26a, *dd*, J = 7.1, 9.1 Hz), 3.92 (H-3, *m*), 4.10 (H-26b, *m*), 4.12 (H-2, *m*), 4.87 (H-16, *m*). ^{13}C NMR (C_5D_5N) of the sterol part of **2** (see Table 1); ^1H NMR (C_5D_5N) and ^{13}C NMR (C_5D_5N) of the sugar moieties of **2** (see Table 2).

3.8. Compound 3

Amorphous solid, $[\alpha]_D^{23}$ −19.8° (MeOH, *c* 0.51). IR_{max}^{KBr} cm^{-1}: 3400, 1450, 1381, 1000–1100. ESIMS: *m/z* 1088 $[M+Na]^+$. ^1H NMR (C_5D_5N) of the sterol part of **3**: δ 0.75 (H-18, *s*), 0.98 (H-19, *s*), 1.10 (H-27, *d*, J = 6.6 Hz), 1.69 (H-21, *s*), 2.51 (H-17, *d*, J = 10.0 Hz), 3.55 (H-26a, *dd*, J = 6.8, 9.3 Hz), 3.92 (H-3, *m*), 4.10 (H-26b, *m*), 4.15 (H-2, *m*), 4.87 (H-16, *m*). ^{13}C NMR (C_5D_5N) of the sterol part of **3** (see Table 1); ^1H NMR (C_5D_5N) and ^{13}C NMR (C_5D_5N) of the sugar moieties of **3** (see Table 2).

3.9. Acid hydrolysis of 2 and 3

MeOH soln of compounds **2** and **3** together with standard sugar samples were applied at point ca 1 cm from the bottom of an HR–TLC silica gel plate and hydrolysed with HCl vapour for 2 h at 50°C, the plate was then heated at 60°C for 4 h to remove residual HCl, sugar identification was performed as described for compound **1** above.

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