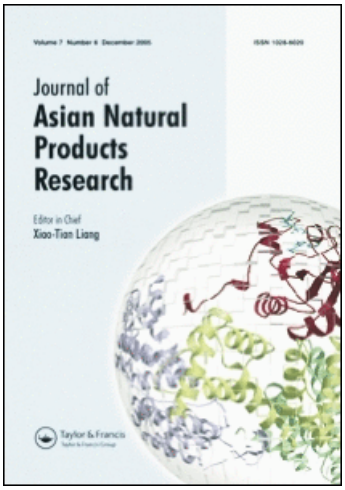

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New α-pyrrolidinonoids and glycosides from *Euphorbia humifusa*

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A phytochemical investigation on the constituents from *Euphorbia humifusa* Willd. has resulted in the isolation of three new α-pyrrolidinonoidal compounds, 5β-methoxy-4β-hydroxy-3-methylene-α-pyrrolidinone (**1**), 5β-methoxy-4α-hydroxy-3-methylene-α-pyrrolidinone (**2**), and 5β-butoxy-4α-hydroxy-3-methylene-α-pyrrolidinone (**3**), and three new glycosides including an indole glycoside, 3-(2-hydroxyethyl)-5-(1-*O*-β-glucopyranosyloxy)-indole (**4**), an ionone glycoside, 3-*oxo*-7,8-dihydro-α-ionone-11-*O*-β-glucoside (**5**), and a hemiterpene glycoside, 1-(4-hydroxy-2-methyl-2-buten-1-yl)-6- (3,4,5-trihydroxybenzoyl)-β-D-glucose (**6**), along with 10 known compounds. Their structures were elucidated by analysis of 1D and 2D NMR spectral data. The structure of **1** was further confirmed by a single-crystal X-ray diffraction analysis.

Keywords: *Euphorbia humifusa* Willd; α-pyrrolidinonoids; indole and ionone glycosides; hemiterpene glycoside

1. Introduction

Euphorbia humifusa Willd., an annual growing plant in East Asia, is used in Chinese folk medicine for the treatment of jaundice, dysentery, enteritis, poisonous snake bites, and traumatic bleeding. More than 30 flavonoids and tannins have been isolated from this plant.[1–2] In a continuing study on its constituents, we isolated three new α-pyrrolidinonoidal compounds and three new glycosides including an indole glycoside, an ionone glycoside, and a hemiterpene glycoside, along with 10 known compounds, from this plant for the first time. This paper describes the isolation and structural elucidation of these new compounds.

2. Results and discussion

Compound **1**, mp 108–109°C, $[\alpha]_D^{20}$ − 78 ($CHCl_3$, *c* 0.13), was obtained as white needles. The molecular formula was determined to be $C_6H_9NO_3$ based on the HR-EI-MS at *m/z* 143.0581 $[M]^+$. In the ^1H NMR spectrum (Table 1), the proton at δ 8.35 (1H, s, in $CDCl_3$) disappeared when determined in CD_3OD suggesting the presence of the CONH moiety, which corresponded with the presence of a carbon resonance at δ 170.2. The olefinic proton signals at δ 6.14 (1H, d, $J = 3.1$ Hz) and 5.73 (1H, d, $J = 3.1$ Hz) defined the presence of a terminal olefinic bond, which was confirmed by the ^{13}C NMR spectral data at δ 141.4 (s, C-3) and 119.2 (t, C-6). In the HMBC experiments, the

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Table 1. ^{1}H and ^{13}C NMR spectral data for compounds **1**–**3**.

	1		**2**		**3**	
	$^{1}H^{a}$	$^{13}C^{b}$	$^{1}H^{a}$	$^{13}C^{b}$	$^{1}H^{a}$	$^{13}C^{b}$
1	8.35 s		8.51 s		8.50 s	
2		170.2 s		169.9 s		169.8 s
3		141.4 s		141.4 s		141.4 s
4	4.73 m	69.9 d	4.45 m	72.5 d	4.40 m	73.0 d
5	4.78 m	84.2 d	4.66 m	91.5 d	4.69 m	90.4 d
6	6.14 d (3.1), 5.73 d (3.1)	119.2 t	6.11 d (0.6), 5.74 d(0.6)	122.2 t	6.06 d (2.1), 5.71 d (2.1)	121.7 t
7	3.44 s	55.6 q	3.30 s	54.9 q	3.39 m, *3.50* m	67.5 t
8					1.45 m	34.5 t
9					1.26 m	19.0 t
10					0.91 t (7.6)	13.6 q

[a] 400 MHz, $CDCl_3$; chemical shifts in ppm relative to TMS; coupling constants (*J*) in Hz.
[b] 100 MHz, $CDCl_3$; multiplicities from the DEPT spectrum.

proton signals at δ 6.14 and 5.73 (H-6) correlated with the carbon signals at δ 170.2 (C-2), 141.4 (C-3), and 69.9 (C-4), and the proton signal at δ 4.78 (H-5) correlated with the carbon signals at δ 170.2 (C-2), 141.4 (C-3), and 69.9 (C-4), revealing the presence of an α,β-unsaturated γ-lactam ring. The correlation of the proton signal at δ 3.44 (H-7) with the carbon signal at δ 84.2 (C-5) suggested that the methoxy was located at C-5. The NOESY spectrum showed no correlation between H-4 and the methoxy signal indicating a *cis* configuration between H-4 and H-5. The X-ray diffraction analysis of compound **1** verified the above deduction. Compound **1** was assigned as 5β-methoxy-4β-hydroxy-3-methylene-α-pyrrolidinone (Figure 1).

Compound **2**, $[\alpha]_D^{20}$ − 19 ($CHCl_3$, *c* 0.14), was obtained as a yellow oil. The molecular formula of **2** was determined as $C_6H_9NO_3$ based on the HR-EI-MS at *m/z* 143.0587 $[M]^+$. The ^{1}H and ^{13}C NMR spectral data of **2** (Table 1) coincided with those of **1**, and its HMQC and HMBC experiments showed that **2** has the same structure as **1**. The NOESY spectrum exhibited correlation between the H-4 and the methoxy signals indicating a *trans* configuration between H-4 and H-5. According to the above evidence, the structure of **2** was determined as 5β-methoxy-4α-hydroxy-3-methylene-α-pyrrolidinone.

Compound **3**, $[\alpha]_D^{20}$ + 2.4 ($CHCl_3$, *c* 0.53), was obtained as a yellow oil, whose molecular formula was determined as $C_9H_{15}NO_3$ from the HR-EI-MS at *m/z* 185.1050 $[M]^+$. The ^{1}H NMR spectrum of **3** (Table 1) revealed a great similarity to that of compound **2** except for the signals of a butoxy at δ 3.39, 3.50 (each 1H, m, H-7), 1.45 (2H, m, H-8), 1.26 (2H, m, H-9), and 0.91 (3H, t, $J = 7.6$ Hz, H-10), corresponding to the carbon signals at δ 67.5 (t, C-7), 34.5 (t, C-8), 19.0 (t, C-9), and 13.6 (q, C-10), instead of the methoxy in **2**. The ^{1}H NMR spectral data also showed the presence of a β-hydroxy-α,β-unsaturated-γ-lactam structure that was confirmed by the HMBC experiment. The NOESY spectrum showed correlation between the signals of H-4 and H-7 indicating a *trans* configuration between H-4 and H-5. Therefore, the structure of compound **3** was assigned as 5β-butoxy-4α-hydroxy-3-methylene-α-pyrrolidinone.

Compound **4**, $[\alpha]_D^{20}$ − 25.0 (CH_3OH, *c* 0.24), was obtained as a yellow amorphous powder, whose molecular formula was determined to be $C_{16}H_{21}NO_7$ according to the HR-EI-MS at *m/z* 362.1206 $[M + Na]^+$. The UV absorption maxima at 224 and 276 nm indicated the presence of indole ring.

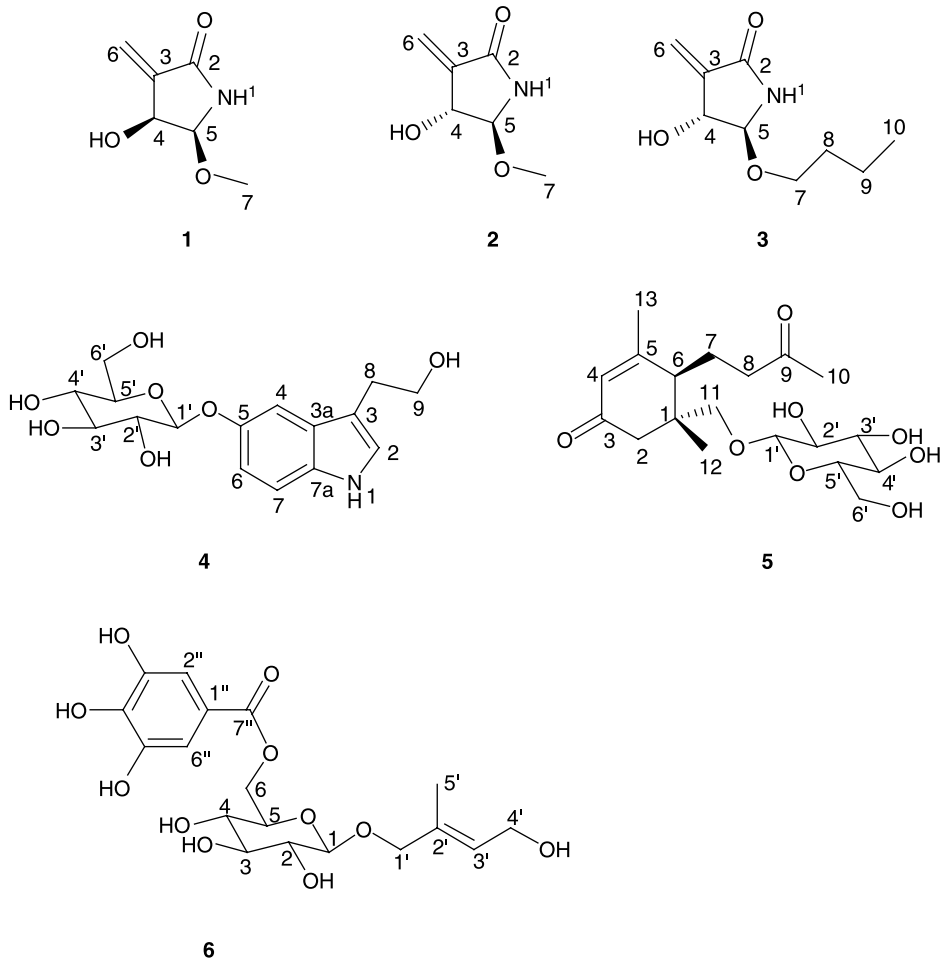

Figure 1. Structures of compounds **1**–**6**.

The ^{1}H NMR (Table 2) signals at δ 7.06 (1H, s, H-2), 7.32 (1H, d, $J = 2.3$ Hz, H-4), 7.22 (1H, d, $J = 8.7$ Hz, H-7), and 6.95 (1H, dd, $J = 8.7$, 2.3 Hz, H-6) revealed a 3,5-disubstituted indole ring that was further confirmed by four quaternary aromatic carbon signals at δ 113.4 (C-3), 129.7 (C-3a), 153.3 (C-5), and 135.0 (C-7a), and four methine peaks at δ 125.2 (C-2), 107.4 (C-4), 114.8 (C-6), and 112.9 (C-7). The signals at δ 2.91 (2H, t, $J = 7.1$ Hz, H-8) and 3.78 (2H, t, $J = 7.1$ Hz, H-9) exhibited the presence of a CH_2CH_2OH moiety in **4**, supported by the carbon signals at δ 30.3 (C-8) and 64.1 (C-9). The glucosyl moiety was identified by enzymatic hydrolysis of **4**, and in comparison with an authentic sample. The β-stereochemistry of the anomeric carbon was determined according to the J value 7.9 Hz of the anomeric proton.[3] In the HMBC experiment, the correlation between H-8 (δ 2.91) and C-3 (δ 113.4) indicated that the side chain CH_2CH_2OH was linked to C-3. The correlation between H-1′ (δ 4.83) and C-5 (δ 153.3) suggested that the glucosyl moiety was linked to C-5. Consequently, compound **4** was elucidated as 3-(2-hydroxyethyl)-5-*O*-β-D-glucopyranosyl indole.

Compound **5**, $[\alpha]_D^{20} + 24.0$ (CH_3OH, c 0.20), was obtained as a yellow oil, whose molecular formula was determined to be

Table 2. ^{1}H and ^{13}C NMR spectral data for compound **4**.

	$^{1}H^{a}$	$^{13}C^{b}$	HMBC (H → C)
1			
2	7.06 s	125.2 d	C-3, C-8, C-3a, C-7a
3		113.4 s	
3a		129.7 s	
4	7.32 d (2.3)	107.4 d	C-5, C-6, C-7a
5		153.3 s	
6	6.95 dd (8.7, 2.3)	114.8 d	C-5, C-7a
7	7.22 d (8.7)	112.9 d	C-5, C-3a
7a		135.0 s	
8	2.91 t (7.1)	30.3 t	C-2, C-3, C-9, C-3a
9	3.78 t (7.1)	64.1 t	C-3
1′	4.83 d (7.9)	104.8 d	C-5′
2′	3.45 dd (9.1, 7.9)	75.7 d	C-1′, C-3′
3′	3.41 dd (8.7, 9.1)	78.7 d	C-2′
4′	3.39 dd (9.3,8.7)	72.1 d	
5′	3.47 m	78.6 d	C-1′, C-4′
6′	3.71 dd (12.0, 5.4), 3.90 d (12.0)	63.2 t	C-4′, C-5′

[a] 400 MHz, CD_3OD; chemical shifts in ppm relative to TMS; coupling constants (J) in Hz.
[b] 100 MHz, CD_3OD; multiplicities from the DEPT spectrum.

$C_{19}H_{30}O_8$ according to the HR-ESI-MS at m/z 409.1812 $[M + Na]^+$. The ^{1}H NMR spectrum (Table 3) showed the presence of three methyls at δ 1.11 (3H, *s*, H-12), 2.05 (3H, s, H-13), and 2.15 (3H, s, H-10); four methylenes at δ 3.72 and 3.29 (each 1H, d, $J = 9.3$ Hz, H-11), 2.66 (2H, m, H-8), 2.33 (2H, s, H-2), 1.99, and 1.70 (each 1H, m, H-7); a methine at δ 2.38 (1H, t, $J = 5.6$ Hz, H-6); an olefinic proton at δ 5.83 (1H, s, H-4); and an anomeric proton at δ 4.15 (1H, d, $J = 7.7$ Hz, H-1′). The ^{13}C NMR spectrum revealed the presence of 19 carbons including two carbonyls at δ 211.4 and 202.1, two olefinic carbons at δ 126.7 and 169.4, and typical glucosyl carbons (δ 105.2, 78.6, 78.4,

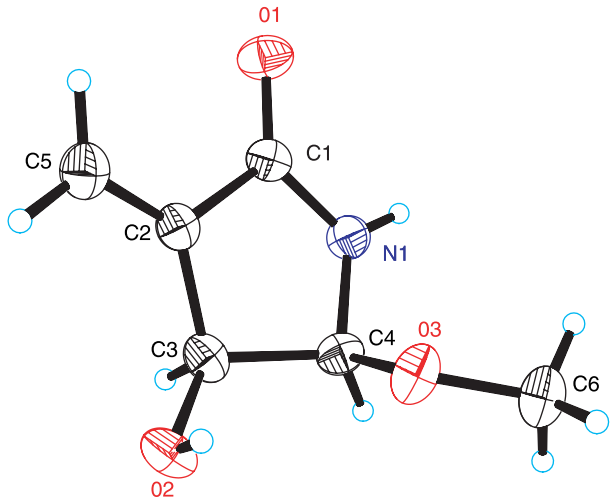

Figure 2. Perspective ORTEP drawing for compound **1**.

75.6, 72.1, and 63.2). Enzymatic hydrolysis of **5** gave glucopyranose, which was confirmed by comparing with an authentic sample. The *J* value of 7.7 Hz of the anomeric proton indicated a β-configuration at C-1′ (δ 105.2). The $^{1}H-^{1}H$ COSY and HMBC spectral data (Table 3) exhibited the presence of an ionone moiety in compound **5**. In the HMBC spectrum, the correlation between proton signal at δ 4.15 (H-1′) and carbon signal at δ 77.2 (C-11) suggested that the glucosyl moiety was linked to C-11 of the ionone moiety. In the ROESY spectrum of **5**, the NOE correlation at H-7/H-12 showed an α-configuration for H-6 and H-11, respectively. Thus, **5** was identified as 3-*oxo*-7,8-dihydro-α-ionol-11-*O*-β-glucopyranoside.

Compound **6**, obtained as a yellow amorphous powder, displayed a molecular ion at *m/z* 439.1219 $[M + Na]^+$ in HR-ESI-MS, corresponding to the molecular formula $C_{18}H_{24}O_{11}$. The IR spectrum of **6** showed the presence of hydroxyl groups (3415 cm^{-1}) and the carbonyl group (1697 cm^{-1}). The UV spectrum exhibited absorption maxima at 217 and 275 nm, assignable to a phenyl group. The ^{1}H NMR spectrum showed resonances at δ 7.09 (2H, s, H-2″, 6″), 5.63 (1H, t, $J = 6.5$ Hz, H-3′), two oxymethylenes at δ 4.15, 4.03 (each 1H, br d, $J = 12.0$ Hz, H-1′), and 4.10 (2H, overlapped, H-4′), one olefinic methyl at δ 1.60 (1H, s, H-5′) and glucosyl signals. The ^{13}C NMR and DEPT spectral data revealed the presence of 18 carbons in the molecule, corresponding to a galloyl at δ 168.8, 147.0 × 2, 140.4, 121.9, 110.6 × 2, a hemiterpene unit at δ 135.9, 128.9, 75.6, 59.6 and 14.5, and a glucosyl moiety at δ 103.2, 78.5, 75.9, 75.6, 72.3, and 65.3. The ^{1}H and ^{13}C NMR spectral data were assigned on the basis of the HMQC and HMBC experiments (Table 4). The sugar moiety was determined

Table 3. ^{1}H and ^{13}C NMR spectral data for compound **5**.

	^{1}H[a]	^{13}C[b]	HMBC (H → C)
1		42.3 s	
2	2.33 s	44.8 t	C-1, C-3, C-6, C-11, C-12
3		202.1 s	
4	5.83 s	126.7 d	C-2
5		169.4 s	
6	2.38 t (5.6)	46.2 d	C-1, C-2, C-4, C-7, C-8, C-11
7	1.99 m, 1.70 m	24.2 t	C-1, C-5, C-6, C-8, C-9
8	2.66 m	43.9 t	C-7, C-9
9		211.4 s	
10	2.15 s	30.5 q	C-8, C-9
11	3.72 d (9.3), 3.29 d (9.3)	77.2 t	C-2, C-12, C-1′
12	1.11 s	22.6 q	C-1, C-2, C-3, C-6
13	2.05 s	25.1 q	C-4, C-5, C-6
1′	4.15 d (7.7)	105.2 d	C-11, C-2′
2′	3.17 d (7.7, 4.3)	75.6 d	C-1′
3′	3.33	78.4 d	C-2′, C-4′
4′	3.25 dd (8.4, 5.4)	72.1 d	C-3′
5′	3.47 dd (5.4, 2.0)	78.6 d	
6′	3.71 dd (12.0, 2.0), 3.90 d (12.0)	63.2 t	C-5′

[a] 400 MHz, CD_3OD; chemical shifts in ppm relative to TMS; coupling constants (*J*) in Hz.
[b] 100 MHz, CD_3OD; multiplicities from the DEPT spectrum.

as glucose by cellulase hydrolysis and comparison with an authentic sample. The stereochemistry of the anomeric carbon was determined as β-form based on the coupling constant $J = 7.9$ Hz. In the HMBC experiment, the proton signals at δ 4.03 and 4.15 (H-1′) correlated with carbon signal at δ 103.2 (C-1) suggesting that the glucose was linked to C-1′ in the hemiterpene moiety. The proton signals at δ 4.39 and 4.51 (H-6) correlated with carbonyl signal at δ 168.8 (C=O) indicating that the carboxyl of the galloyl group was linked to C-6 in the glucose. Moreover, the NOE between the allylic methyl (H-5′) and the methylene at H-4′ was observed, indicating *E*-configuration of the hemiterpene moiety. Thus, the structure of **6** was established as 1-(4-hydroxy-2-methyl-2-buten-1-yl)-6-(3,4,5-trihydroxybenzoyl)-β-D-glucose.

The other constituents isolated from *E. humifusa* were identified as diisobutyl phthalate **7**,[4] bis-(2-ethylhexyl) phthalate **8**,[5] kaempferol-3-*O*-α-L-arabinofuranoside **9**,[6] avicularin **10**,[6] 3,3′-di-*O*-methyl ellagic acid **11**,[7] stenophyllin H **12**,[8] 3,3′-di-*O*-methyl ellagic acid-4-*O*-β-D-xylopyranoside **13**,[9] 3,3′-di-*O*-methyl ellagic acid-4-*O*-β-D-glucoside **14**,[7] isorhoifolin **15**,[10] and leucoside **16**[11] by comparison of their spectral data with those reported in literature.

Compounds **1**–**6** were tested for their cytotoxic activity against P388 and HL-60 leukemia, A-549 human lung adenocarcinoma, and SGC-7901 gastric adenocarcinoma tumor cell lines *in vitro*, but the inhibition was less than 50% (10^{-5} mol/l).

3. Experimental

3.1 General experimental procedures

Melting points were determined on a Fisher–Johns melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin–Elmer 241 automatic digital polarimeter, whereas the UV spectra were obtained on a Shimadzu UV-260 instrument. The IR spectra were acquired on a Perkin–Elmer 599B instrument with KBr disks, whereas the ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, with TMS as an internal standard. The EI-MS were obtained on a MAT-711 mass spectrometer and measured on a Micromass Quattro mass spectrometer.

3.2 Plant material

The aerial parts of *E. humifusa* Willd. were collected in July 2003 at Shangrao, Jiangxi Province, China, and authenticated by Professor Shui-sheng Deng. A voucher specimen has been deposited in the Herbarium of Shanghai Institute of Materia Medica (No. SIMMP04068).

3.3 Extraction and isolation

The dried aerial parts of *E. humifusa* (10 kg) were extracted with EtOH–H_2O (95:5, 50 l) for three times at room temperature. The solvent was removed *in vacuo* to yield a gummy residue (640 g) that was dissolved in 3 l EtOH–H_2O (18:92) to remove chlorophyll and the concentrated filtrate (1.5 l) was extracted with ether (1.5 l × 5), EtOAc (1.5 l × 10), and *n*-BuOH saturated with H_2O (1.5 l × 10), successively. The EtOAc extract (154 g) was subjected to silica gel CC (15 × 100 cm) and eluted with a gradient of EtOAc–petroleum ether (1:5) at a flow rate of 10 ml/min to obtain compounds **7** (15 mg), **8** (125 mg), **9** (1.6 g) and **10** (2.4 g), respectively. The *n*-BuOH extract (177 g) was subjected to silica gel CC (15 × 100 cm) and eluted with a gradient of $CHCl_3$–CH_3OH at a flow rate of 10 ml/min to obtain fractions I [2.0 l, $CHCl_3$–CH_3OH (100:1)], II [5.0 l, $CHCl_3$–CH_3OH (60:1)], III [5.0 l, $CHCl_3$–CH_3OH (40:1)], IV [5.0 l, $CHCl_3$–CH_3OH (20:1)], V [5.0 l, $CHCl_3$–CH_3OH (10:1)], VI [5.0 l, $CHCl_3$–CH_3OH (5:1)], and VII [5.0 l, $CHCl_3$–CH_3OH (3:1)]. Fraction IV (23 g) was subjected to silica gel CC (8 × 50 cm) using $CHCl_3$–CH_3OH (25:1) as an eluent to obtain six fractions IVA–IVF (eluent volume: 600 ml/fraction). Fraction IVA (1.8 g) was applied to Sephadex LH-20 CC

(eluted with MeOH) to give compound **1** (50 mg). Fractions IVC and IVD were isolated using procedures similar to give compounds **2** (120 mg) and **3** (80 mg). Fraction V (14 g) was subjected to silica gel CC (8 × 50 cm) using $CHCl_3$–CH_3OH (15:1) as an eluent to obtain compounds **6** (8 mg), **11** (40 mg) and **12** (20 mg). Fraction VI (27 g) was subjected to additional silica gel CC (8 × 50 cm) using $CHCl_3$–CH_3OH (8:1) as an eluent to obtain compounds **4** (30 mg), **13** (65 mg) and **14** (24 mg). Fraction VII (33 g) was subjected to silica gel CC (8 × 50 cm) using $CHCl_3$–CH_3OH (8:1) as an eluent to obtain compounds **5** (25 mg), **15** (45 mg), and **16** (175 mg). Compounds **4** (6 mg), **5** (6 mg), and **6** (6 mg) were heated with cellulase (6 mg) in water (10 ml) at 37°C for 48 h. The reaction mixtures were extracted with ethyl acetate (20 ml × 2) and the water layers were subjected to TLC analysis by comparison with authentic sugars showing glucose from **4**, **5** and **6**. TLC condition: Kieselgel 60 F_{254} plate (Merck) [eluent: $CHCl_3$–MeOH–H_2O (14:6:1)], $R_f = 0.13$ (glucose), and cellulose 60F plate [eluent: *n*-BuOH–pyridine–H_2O (6:4:3)], $R_f = 0.37$ (glucose).

*3.3.1 5β-Methoxy-4β-hydroxy-3-methylene-α-pyrrolidinone (**1**)*

White needles (methanol); mp 108–109°C; $[\alpha]_D^{20}$ − 78.0 ($CHCl_3$; *c* 0.13); UV (MeOH) λ_{max} (nm) (log ε): 207 (4.22); IR (KBr) ν_{max} (cm^{-1}): 3367, 3217, 2949, 1697, 1686, 1670, 1436, 1390, 1251, 1192, 1124, 1093, 1037, 943, 797; For the ^1H and ^{13}C NMR spectral data, see Table 1; EI-MS *m/z* (rel. int.): 143 $[M]^+$(1), 112 (8), 60 (100), 56 (12); HR-EI-MS *m/z*: 143.0581 $[M]^+$ (calcd for $C_6H_9NO_3$, 143.0583).

*3.3.2 X-ray crystal structure of **1***

$C_6H_9NO_3$, mol. wt = 143.14, triclinic space group *P-6*, $a = 13.5532(13)$, $b = 13.5532(13)$, $c = 6.6908(10)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $V = 1064.4$ (2) $Å^3$, $Z = 6$, $d = 1.340\ g/cm^3$, $F(000) = 456$, $\mu = 0.108\ mm^{-1}$. A single crystal of dimensions 0.321 × 0.113 × 0.055 mm was used for X-ray measurements. The intensity data of all unique reflections within the θ range of 1.73–28.22° were collected at 293 (2) K in a SMART APEX CCD diffractometer, using graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. A total of 6501 independent reflections were measured, and 927 were considered to be observed ($|F|^2 \geq 2\sigma|F|^2$). Hydrogen atoms were fixed at calculated positions. The structure was solved by the direct method SHELX-97 and expanded using difference Fourier techniques, refined by the program and full-matrix least-squares calculations. CCDC 630681 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; . Email: deposit@ccdc.cam.ac.uk).

*3.3.3 5β-Methoxy-4α-hydroxy-3-methylene-α-pyrrolidinone (**2**)*

Yellow oil; $[\alpha]_D^{20}$ − 19 ($CHCl_3$; *c* 0.14); UV (MeOH) λ_{max} (nm) (log ε): 202.5 (4.20); IR (KBr) ν_{max} (cm^{-1}): 3273, 2935, 1695, 1668, 1435, 1281, 1194, 1097, 1064, 970, 808, 636; For the ^1H and ^{13}C NMR spectral data, see Table 1; EI-MS *m/z* (rel. int.): 143 $[M]^+$(1), 112 (8), 60 (100), 56 (12); HR-EI-MS *m/z*: 143.0587 $[M]^+$ (calcd for $C_6H_9NO_3$, 143.0583).

*3.3.4 5β-Butoxy-4α-hydroxy-3-methylene-α-pyrrolidinone (**3**)*

Yellow oil; $[\alpha]_D^{20}$ + 2.4 ($CHCl_3$; *c* 0.53); UV (MeOH) λ_{max} (nm) (log ε): 202 (3.85); IR (KBr) ν_{max} (cm^{-1}): 3261, 2958, 2874, 1709, 1662, 1437, 1329, 1279, 1192, 1076, 958, 808; For the ^1H and ^{13}C NMR spectral data, see Table 3; EI-MS *m/z* (rel. int.): 185 $[M]^+$(2), 112 (100), 56 (46); HR-EI-MS *m/z*: 185.1050 $[M]^+$ (calcd for $C_9H_{15}NO_3$, 185.1052).

Table 4. ^{1}H and ^{13}C NMR spectral data of compound **6**.

	$^{1}H^{a}$	$^{13}C^{b}$	HMBC (H → C)
1′a	4.03 br d (12.0)	75.6 t	C-2′, C-3′, C-5′
1′b	4.15 br d (12.0)		C-2′, C-3′, C-5′
2′		135.9 s	
3′	5.63 t (6.5)	128.9 d	C-1′, C-5′
4′	4.10 (overlapped)	59.6 t	C-2′, C-3′
5′	1.60 s	14.5 q	C-1′
1	4.29 d (7.9)	103.2 d	C-1′, C-5
2	3.23 dd (9.5, 7.9)	75.6 d	C-3, C-6
3	3.42 dd (8.5, 9.5)	78.5 d	C-1, C-3, C-5
4	3.36 dd (9.4, 8.5)	72.3 d	C-2
5	3.52 m	75.9 d	
6a	4.39 dd (11.5, 4.7)	65.3 t	C-4, C-7″
6b	4.51 dd (11.5, 1.8)		C-4, C-7″
1″		121.9 s	
2″	7.09 s	110.6 d	C-1″, C-5″, C-6″
3″		147.0 s	
4″		140.4 s	
5″		147.0 s	
6″	7.09 s	110.6 d	C-1″, C-2″, C-4″, C-7″
−CO		168.8 s	

[a] 400 MHz, CD_3OD; chemical shifts in ppm relative to TMS; coupling constants (*J*) in Hz.
[b] 100 MHz, CD_3OD; multiplicities from the DEPT spectrum.

*3.3.5 3-(2-Hydroxyethyl)-5-O-β-D-glucopyranosyl indole (**4**)*

Yellow amorphous powder; $[\alpha]_D^{20}$ − 25.0 (MeOH, *c* 0.24); UV (MeOH) λ_{max} (nm) (log ε): 224 (4.16), 276 (3.69); IR (KBr) ν_{max} (cm^{-1}): 3356, 2920, 2852, 1612, 1481, 1385, 1202, 1072, 1040, 617; For the ^{1}H and ^{13}C NMR spectral data, see Table 2; EI-MS *m/z* (rel. int.): 339 $[M]^+$(1), 176 (100); ESI-MS *m/z*: 362 $[M + Na]^+$, 338 $[M - H]^+$; HR-ESI-MS *m/z*: 362.1206 $[M + Na]^+$ (calcd for $C_{16}H_{21}NO_7Na$, 362.1216).

*3.3.6 3-Oxo-7,8-dihydro-α-ionol-11-O-β-glucopyranoside (**5**)*

Yellow oil; $[\alpha]_D^{20}$ + 24.0 (MeOH, *c* 0.20); UV (CH_3OH) λ_{max} (nm) (log ε): 241 (2.28); IR (film) ν_{max} (cm^{-1}): 3383, 2929, 2881, 1707, 1649, 1416, 1379, 1080, 1041, 885, 631, 580, 528; For the ^{1}H and ^{13}C NMR spectral data, see Table 3; ESI-MS *m/z*: 409 $[M + Na]^+$, 385 $[M - H]^-$; HR-ESI-MS *m/z*: 409.1812 $[M + Na]^+$ (calcd for $C_{19}H_{30}O_8Na$, 409.1838).

*3.3.7 1-(4-Hydroxy-2-methyl-2-buten-1-yl)-6-(3,4,5-trihydroxybenzoyl)-β-D-glucose (**6**)*

Yellow amorphous powder; $[\alpha]_D^{20}$ + 4.0 (CH_3OH, *c* 0.17); UV (H_2O) λ_{max} (nm) (log ε): 217 (2.85), 275 (3.79); IR (KBr) ν_{max} (cm^{-1}): 3415, 2924, 1697, 1616, 1450, 1348, 1236, 1076, 1040, 770 (cm^{-1}); For the ^{1}H and ^{13}C NMR spectral data, see Table 4; EI-MS *m/z*: 398 $[M - H_2O]^+$(8), 153 (100), 126 (72), 73 (52); ESI-MS *m/z*: 455 $[M + K]^+$, 415 $[M - H]^+$; HR-ESI-MS *m/z*: 439.1219 $[M + Na]^+$ (calcd for $C_{18}H_{24}O_{11}Na$, 439.1216).

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