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27-NOR-TRITERPENOID GLYCOSIDES FROM *ADINA RUBELLA*

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Key Word Index—*Adina rubella*; Rubiaceae; saponins; 3β-hydroxy-27-nor-olean-13-en-28-oic acid glycosides; pyrocincholic acid; rubelloside C and D.

Abstract—Two new 27-nor-triterpenoid glycosides, pyrocincholic acid-3β-*O*-β-D-glucopyranosyl-(1→2)-β-D-fucopyranoside, pyrocincholic acid-3β-*O*-α-L-rhamnopyranosyl-28-[β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl] ester, named rubelloside C and D, respectively, were isolated from roots of *Adina rubella*. Their structures were elucidated on the basis of spectral data.

INTRODUCTION

Adina rubella Hance, a Chinese folk medicine, has been reported to contain rubelloside A and B [1]. These compounds were isolated from the ether fraction of the ethanol extract of its roots. The ethyl acetate fraction has been shown to contain two new nor-triterpenoid glycosides, pyrocincholic acid-3β-*O*-β-D-glucopyranosyl-(1→2)-β-D-fucopyranoside (**1**), pyrocincholic acid-3β-*O*-α-L-rhamnopyranosyl-28-[β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl] ester (**2**), named rubelloside C and D, respectively.

RESULTS AND DISCUSSION

The nor-triterpenoid glycoside **1** was obtained as a powder. The molecular formula was determined as $C_{41}H_{66}O_{12}$ by ^{13}C NMR DEPT (Table 1) and FAB-mass spectral data (*m/z* 773 $[M + Na]^+$). The presence of a nor-triterpenoid glycoside containing two sugar subunits was revealed by its ^1H (Table 2) and ^{13}C NMR spectra and FAB-mass spectral data. In the ^1H NMR spectrum, there are characteristic signals of nor-triterpenoid, but no olefinic proton resonances. The ^{13}C NMR spectrum of the aglycone showed 29 carbon signals including two quaternary olefinic carbons (δ 137.1, 130.7). A comparison of the ^{13}C NMR spectra of **1** and pyrocincholic acid-3β-*O*-β-D-6-deoxy-glucopyranosyl-28-[β-D-glucopyranosyl] ester (**3**) [2] revealed that the carbon signals of the aglycones were almost identical except for the chemical shift of the carboxylic carbon of **1**, (180.0 ppm rather than 176.5 ppm) showing that it was not glycosidated. These data indicated that the aglycone of compound **1** was pyrocincholic acid (**4**) and the glycosidation site was C-3. Acid hydrolysis gave D-glucose and D-fucose. The ^1H and ^{13}C NMR spectra were assigned by ^1H–^1H COSY, TOCSY, NOESY, HMQC and HMBC experiments. The coupling constants of the ^1H NMR signals of the sugar moieties suggested a β-D-glucopyranose and β-D-fucopyranose (Table 2). The ^{13}C NMR signals of the glucose and methyl-β-D-glucopyranoside (δ 106.1, 76.6, 78.2, 71.6, 77.9, 62.5) [3] were almost identical and those of the fucose of **1** and β-D-fucopyranose (δ 106.3, 73.0, 75.5, 72.8, 71.3, 17.4) [4] were similar, except that C-1 was shifted upfield by 1.1 ppm and C-2 downfield by 8.9 ppm indicating that the fucose was attached to C-3 and the glucose was attached to C-2′. In the NOESY spectrum there were cross-peaks between H-1′ and H-3, H-1″ and H-2′, confirming the linkage mode. From these considerations, the structure of **1** was deduced to be pyrocincholic acid-3β-*O*-β-D-glucopyranosyl-(1→2)-β-D-fucopyranoside.

Compound **2** was obtained as a powder whose molecular formula, $C_{47}H_{76}O_{17}$ was determined by ^{13}C NMR DEPT and FAB mass spectral data (*m/z* 935 $[M + Na]^+$). The ^{13}C NMR signals of the aglycone were very similar to those of **3**, indicating that the aglycone and the glycosidation sites were identical. Acid hydrolysis gave L-rhamnose and D-glucose. In the ^{13}C NMR spectrum, the carbon signals of the rhamnose were consistent with those of methyl rhamnopyranoside (δ 102.1, 71.2, 71.5, 73.3, 69.5, 17.9) [3]. There were two glucose units. A comparison of their carbon signals with those of methyl-β-D-glucopyranoside (δ 106.1, 76.6, 78.2, 71.6, 77.9, 62.5) [3] revealed that one of them (δ 95.7, 74.2, 78.8 or 78.4, 69.8, 78.0, 69.8) was attached to the aglycone at C-28 while the other glucose (δ 105.3, 75.2, 78.4 or 78.8, 71.0, 78.4 or 78.8, 62.9) or the rhamnose was attached to it at C-6″. The

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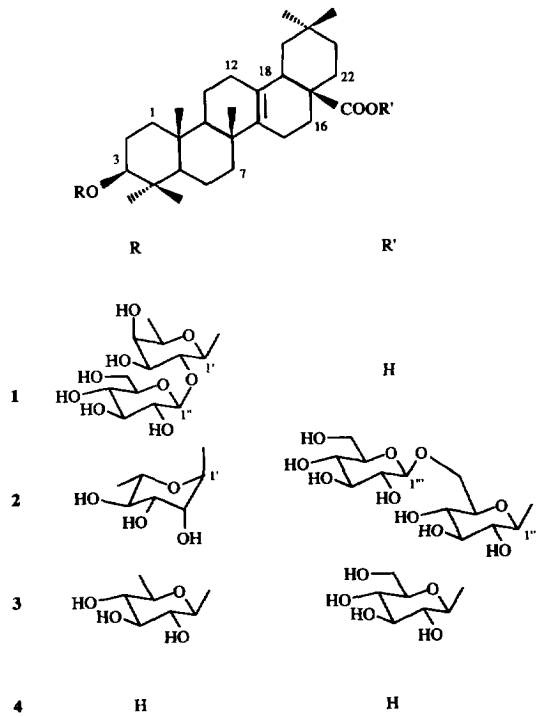
Table 1. ^{13}C NMR spectral data for compounds **1** and **2**

C	1	2
1	38.7	38.5
2	27.0	26.1
3	89.2	88.9
4	40.0	39.6
5	56.1	55.6
6	18.9	19.0
7	39.8	39.4
8	38.1	38.2
9	56.7	56.9
10	37.4	37.4
11	18.3	18.1
12	32.3	32.1
13	130.7	130.4
14	137.1	137.0
15	21.3	21.0
16	24.4	24.3
17	45.3	45.8
18	39.8	39.6
19	41.8	41.6
20	30.9	30.7
21	34.8	34.5
22	31.8	31.4
23	28.3	28.3
24	16.7	16.7
25	16.7	16.7
26	20.3	21.0
28	180.0	176.7
29	32.6	32.4
30	25.3	25.1
1′	105.2	104.4
2′	81.9	72.5
3′	75.4	73.0
4′	72.5	74.2
5′	71.0	69.8
6′	17.4	18.5
1″	106.1	95.7
2″	76.8	74.2
3″	77.7	78.8*
4″	71.9	69.8
5″	78.1	78.0
6″	62.9	69.8
1‴		105.3
2‴		75.2
3‴		78.4*
4‴		71.0
5‴		78.4*
6‴		62.9

*Assignments may be interchanged within each column.



proton signals of the sugar moieties were assigned from the ^1H–^1H COSY spectrum. The coupling constants were consistent with the above results. On irradiation of H-3 a NOE was observed at H-1′, a *vice versa* effect also indicating that it was the rhamnose that was attached to C-3. Thus, the terminal glucose was attached to the inner glucose at C-6″. This was consistent with the data for a reported 28-*O*-gentiobiosyl moiety (inner glucose: δ 95.7, 74.0, 78.7*, 71.4, 77.3, 69.7; terminal glucose: δ 105.1, 75.2, 78.4*, 71.9, 78.7*, 62.9*; assignments may be interchanged) [5]. From these results, the structure of **2** was established as pyrocincholic acid-3β-*O*-α-L-rhamnopyranosyl-28-[β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl] ester.

EXPERIMENTAL

General procedures were carried out as described in our previous paper [1]. The EtOAc fr. (143.5 g) was chromatographed on a silica gel column using $CHCl_3$–MeOH as eluent. The frs eluted with $CHCl_3$–MeOH (1:2) were further chromatographed on a silica gel column eluting with EtOAc–MeOH (7:1), **1** (21 mg) and **2** (18 mg) were obtained consecutively.

Rubelloside C (**1**). Powder, mp 232–235°, $[\alpha]_D^{20}$ −99.4° (MeOH; *c* 0.053). IR ν_{max} cm^{-1}: 3400, 2940, 1700, 1650, 1460, 1380, 1360, 1300, 1180, 1070. FAB-MS *m/z*: 773 $[M + Na]^+$. ^{13}C and ^1H NMR: Tables 1 and 2.

Rubelloside D (**2**). Powder, mp 225–226°. $[\alpha]_D^{20}$ −47.1° (MeOH; *c* 0.034). IR ν_{max} cm^{-1}: 3400, 2940, 1730, 1640, 1450, 1380, 1250, 1060. FAB-MS *m/z*: 935 $[M + Na]^+$. ^{13}C and ^1H NMR: Tables 1 and 2.

Acid hydrolysis of **1** *and* **2**. **1** and **2** (10 mg, respectively) were submitted to acid hydrolysis in the usual way. The sugars were identified with authentic samples by PC.

Table 2. ^{1}H NMR spectral data for compounds **1** and **2**

H	**1**	**2**
3	3.31 *dd* (11.6, 4.2)	3.28 *dd* (11.5, 4.2)
18	2.85 *dd* (11.7, 3.9)	2.71 *dd* (11.6, 3.3)
23	1.30 *s*	1.25 *s**
24	1.10 *s*	0.98 *s**
25	0.77 *s*	0.94 *s**
26	0.95 *s*	0.91 *s**
29	0.99 *s*	0.82 *s**
30	1.00 *s*	0.78 *s**
1′	4.78 *d* (7.5)	5.33 *br s*
2′	4.54 *dd* (9.3, 7.5)	4.54 *br s*
3′	4.15 *dd* (9.3, 3.3)	4.48 *overlap*
4′	4.00 *br d* (3.3)	4.30 *overlap*
5′	3.75 *overlap*	4.30 *overlap*
6′	1.53 *d* (6.3)	1.69 *d* (5.5)
1″	5.21 *d* (7.6)	6.24 *d* (8.0)
2″	4.10 *dd* (9.1, 7.6)	4.11 *t* (8.0)
3″	4.15 *t* (9.1)	4.30 *overlap*
4″	4.30 *t* (9.1)	4.15 *overlap*
5″	3.75 *overlap*	3.90 *overlap*
6″	4.40 *d* (3.4), 4.40 *d* (3.4)	4.48 *overlap*, 4.30 *m*
1‴		5.00 *d* (7.7)
2‴		4.00 *t* (7.7)
3‴		4.15 *overlap*
4‴		4.30 *overlap*
5‴		4.08 *overlap*
6‴		4.30 *overlap*, 4.72 *d* (10.2)

Coupling constants (J in Hz) are given in parentheses; the assignments were based on ^{1}H-COSY (**1**, **2**), NOESY (**1**), TOCSY (**1**), HMQC (**1**) and HMBC (**1**).

*Assignments may be interchanged within each column.

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