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NORCAROTENOID GLYCOSIDES OF *REHMANNIA GLUTINOSA* VAR. *PURPUREA**

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Key Word Index—*Rehmannia glutinosa* var. *purpurea*; Scrophulariaceae; roots; norcarotenoids; jiocarotenosides; D-quinovose; 6-*O*-*sec*-hydroxyaeginetoyl ajugol; rehmaionosides; X-ray analysis.

Abstract—Three new norcarotenoid glycosides named jiocarotenosides A_1, A_2 and 6-*O*-*sec*-hydroxyaeginetoyl ajugol, together with two known compounds, have been isolated from the dried roots of *Rehmannia glutinosa* var. *purpurea*. Their structures were determined by chemical and spectral studies, and confirmed by X-ray analysis of jiocarotenoside A_1.

INTRODUCTION

In the previous paper [1], we reported the isolation of norcarotenoids from the steamed roots of *Rehmannia glutinosa* Libosch. var. *hueichingensis* (Chao et Schih) Hsiao. The present investigation on the norcarotenoid constituents in the dried roots of *R. glutinosa* Libosch. var. *purpurea* Makino resulted in the isolation of three new glycosides named jiocarotenosides A_1 (**1**), A_2 (**2**) and 6-*O*-*sec*-hydroxyaeginetoyl ajugol (**3**), together with two known compounds, rehmaionosides A (**4**) and C (**5**) [2, 3].

RESULTS AND DISCUSSION

Compound **1** was obtained as prisms, mp 213–215°, $[\alpha]_D$ −104.8° (MeOH), whose molecular formula $C_{21}H_{34}O_9 \cdot H_2O$ was confirmed by elemental analysis and the observation of the $[M+H]^+$ ion peak at *m/z* 431 in its FAB mass spectrum. Its UV and IR spectra [λ_{max} 254 nm (log ε 4.32); ν_{max} 3464 (OH), 1692 (C=O), 1632, 1608 (C=C) cm^{-1}] as well as the ^1H and ^{13}C NMR spectral data (Tables 1 and 2) bore a resemblance to those of aeginetic acid (**6**) [1]. The ^{13}C NMR spectrum of **1** showed 15 signals due to a norcarotenoid moiety and six excess signals which were attributable to a sugar moiety. From these spectral data, **1** seemed to be a monoglycoside of a norcarotenoid.

The ^1H NMR spectrum of **1** showed an olefinic proton signal at δ5.79 (1H, *br s*), *trans*-olefinic proton signals at δ6.47 and 6.82 (each 1H, *d*, $J = 15.9$ Hz) and an olefinic methyl proton signal at δ2.29 (3H, *d*, $J = 1.0$ Hz), which were in good agreement with those of the side chain of **6**, i.e. 3-methyl-2*E*,4*E*-pentadienoic acid. Regarding the cyclohexyl end-group, three singlet methyl signals (C-1 *geminal* dimethyls and a C-5 methyl) are commonly observed in the ^1H NMR spectra of many known norcarotenoids such as **6**. By contrast two singlet methyl signals at δ1.04 and 1.08 (each 3H, *s*) were observed in the ^1H NMR spectrum of **1**. Instead of the third methyl signal, **1** exhibited *geminal* coupled methylene signals at δ3.00 and 3.63 (each 1 H, *d*, $J = 11.5$ Hz). This indicates that one methyl group out of three in the cyclohexyl end-group is replaced by a hydroxymethyl group in **1**. However, the position of this group could not be determined, because either C-1 or C-5 position gave no contradiction in spectral data of **1**. The final structure determination was made by X-ray crystallographic analysis (see below).

With respect to the sugar moiety of **1**, the ^1H and ^{13}C NMR spectral data suggest that this sugar is a methyl pentose, showing a methyl [δ_H 1.22 (3H, *d*, $J = 6.1$ Hz); δ_C 18.4 (*q*)] and an anomeric [δ_H 4.43 (1H, *d*, $J = 7.7$ Hz); δ_C 97.8 (*d*)] signal. The ^1H spin decoupling and ^1H ^1H COSY experiments of **1** or its tetraacetate (**1a**) led us to the conclusion that this sugar must be quinovose (6-deoxyglucose). Acid hydrolysis of **1** with 1 M hydrochloric acid gave the aglycone (**1b**), needles, mp 198–200° (decomp.), FABMS *m/z* 285 $[M+H]^+$) and the sugar (as an anomeric mixture). Acetylation of the latter followed by crystallization gave needles, mp 144–145°, $[\alpha]_D$ +26.3° ($CHCl_3$). This compound was proved to be tetraacetyl β-D-quinovose by direct comparison with an authentic sample prepared from commercially available D-quinovose [4]. The position of D-quinovose was resolved by comparison of the ^{13}C NMR chemical shifts for the aglycone moiety of **1** with those of its aglycone (**1b**), C-5 appeared at lower field by 7.7 ppm and the neighbouring C-4 and C-6 carbons shifted to higher field by 4.0 and 3.6 ppm, respectively, due to the well known glycosylation shifts [5]. This pointed to the D-quinovose being situated at C-5. The sugar linkage must be in the β-form as judged from the coupling constant ($J = 7.7$ Hz) of the anomeric proton signal at δ4.43.

In order to determine the complete structure of **1**, X-ray crystallographic analysis was carried out, the stereoscopic view of the molecule is shown in Fig. 1. The

*Part 9 in the series 'Chemical and Biological Studies on Rehmanniae Radix'. For Part 8 see ref. [1].

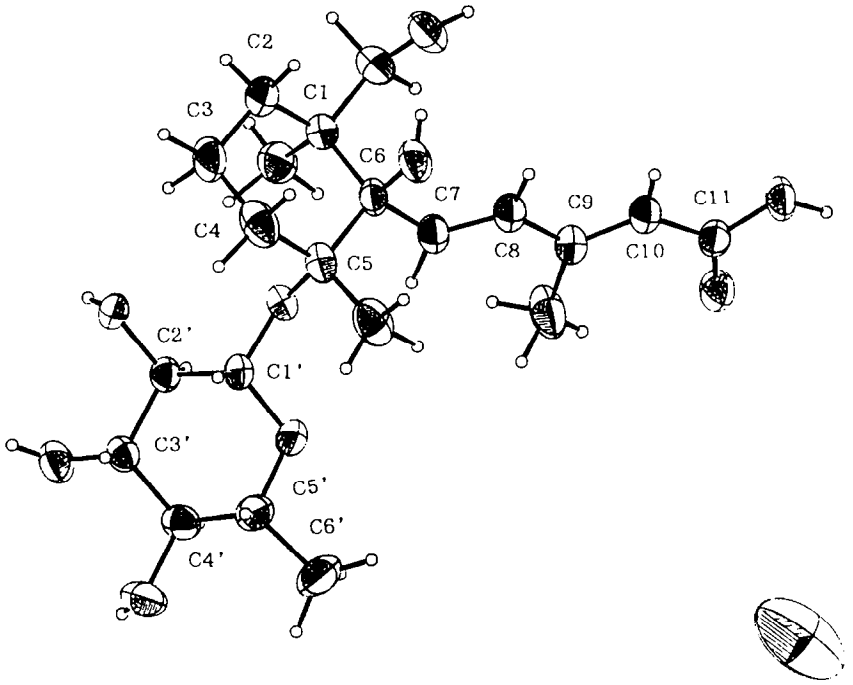


Fig. 1. X-Ray stereoscopic view of jiocarotenoside A_1 (**1**). The solvated water molucule is depicted as an oxygen atom.

hydroxymethyl group was located at C-1 in the β-equatorial configuration. The stereochemistry of **1** was confirmed to be 1*S*,5*R* and 6*R*, based on the absolute structure of D-quinovose. The cyclohexane ring is in a chair conformation ($^4C_1$) and the double bonds at C-7 and C-9 both have the *E*-configuration. The structure of jiocarotenoside A_1 was thus elucidated as **1**.

Compound **2**, needles, mp 163–169°, $[\alpha]_D$ −92.5° (MeOH), was found to have the same molecular formula as **1** by elemental analysis $C_{21}H_{34}O_9 \cdot 3/2H_2O$ and its FAB mass spectrum *m/z* 431 $[M+H]^+$. The ^1H and ^{13}C NMR spectral data of **2** were superimposable with those of **1** except for the signals due to the side chain, indicating that **2** is a geometrical isomer of **1** in its side chain. The ^1H NMR signals arising from the side chain of **2** were observed at δ5.68 (1H, *br s*, H-10), 6.82 (1H, *d*, *J* = 16.4 Hz, H-7), 7.79 (1H, *d*, *J* = 16.4 Hz, H-8) and 2.06 (3H, *d*, *J* = 1.2 Hz, Me-9). The chemical shift values of the latter two signals were considerably different from those of **1**. The H-8 olefinic proton is subjected to a pronounced downfield shift (+1.32 ppm) attributable to the diamagnetic anisotropy of the acid carbonyl group and the C-9 methyl appeared upfield (−0.23 ppm) compared to that of **1**. These shifts are in accord with those observed by other investigators in the ^1H NMR spectra of norcarotenoids having the 3-methyl-2,4-pentadienoic acid system [6, 7], that is, when the configurations of the double bonds at C-7 and C-9 changed from *trans–trans* to *trans–cis*, the H-8 proton and C-9 methyl of the *trans–cis*-isomer resonated downfield and upfield, respectively. Thus the configurations of the double bonds in the side chain of **2** were determined to be *trans–cis* (7*E*,9*Z*) and the structure of jiocarotenoside A_2 was formulated as **2**.

Compound **3**, amorphous powder, $[\alpha]_D$ −124.0° (MeOH), has the molecular formula, $C_{30}H_{46}O_{13} \cdot 3/2H_2O$, FABMS *m/z* 637 $[M+Na]^+$. The ^1H and ^{13}C NMR spectra of **3** were more complex than those of **1** and **2**. Detailed examination of these data led us to the conclusion that **3** is composed of two parts, a norcarotenoid and an iridoid glycosidic moiety. The ^1H and ^{13}C chemical shift values for the norcarotenoid moiety were in agreement with those for the methyl ester (**3a**) of *sec*-hydroxyaeginetic acid (**7**) [1]. On the other hand, the signals for the iridoid glycosidic moiety were coincident with those of 6-*O*-acylated ajugols previously reported by us [8]. Indeed, alkaline hydrolysis of **3** with sodium methoxide yielded **3a** and ajugol. The disposition of the norcarotenoid ester group was determined to be at C-6 of the ajugol moiety, based on NMR spectral data comparisons between **3** and ajugol (acylation shifts) which were previously discussed in relation to 6-*O*-acylated ajugols [8]. The structure of **3** was thus established as 6-*O*-*sec*-hydroxyaeginetoyl ajugol.

In this and previous papers, we described the isolation of 10 norcarotenoids, including five new compounds from the steamed roots of *R. glutinosa* var. *hueichingensis* and the dried roots of *R. glutinosa* var. *purpurea*. Among them, 6-*O*-*sec*-hydroxyaeginetoyl ajugol (**3**) is an interesting example composed of a monoterpenoid glucoside and a sesquiterpenoid. Moreover, jiocaroteosides A_1 (**1**) and A_2 (**2**) are rare glycosides having D-quinovose. In the plant kingdom, the occurrence of the quinovoside in *Cinchoa* sp. has been described before, but its structure has not been elucidated [9]. Several saponins including D-quinovose have been isolated from the marine starfish [10, 11]. Preliminary biological tests of norcarotenoids obtained here showed that jiocarotenoside A_1 (**1**) has an inhibitory activity against aldose reductase.

EXPERIMENTAL

General and plant material. See ref. [8].

Isolation. As previously described [8, 12], the MeOH extract of the dried roots of *R. glutinosa* var. *purpurea* (50 kg) was

Table 1. ^{1}H NMR spectral data for norcarotenoids **1**–**5**, **1a** and **1b** (200 MHz in CD_3OD)

H	1*	1a†	1b*	2	3*‡	4	5
2	1.05 *m* 2.19 *m*		1.08 *m* 2.19 *td* (13.9, 3.9)	1.06 *m* 2.18 *m*	3.73 *dd* (11.5, 4.1)		
3	1.38 *m* 1.72 *m*	1.1–2.2 *m* [6H]	1.48 *m* 1.98 *qt* (13.4, 3.9)	1.37 *m* 1.70 *m*	1.54 *m* 1.94 *m*	1.13 [2H] *m* 1.77 [3H] *m* 2.06 [1H] *m*	1.24 [2H] *m* 1.72 [3H] *m* 2.09 [1H] *m*
4	1.72 *m* 2.19 *m*		1.45 *m* 1.91 *td* (13.4, 3.9)	1.70 *m* 2.18 *m*	1.54 *m* 1.94 *m*		
7	6.82 *d* (15.9)	6.70 *d* (16.1)	6.71 *d* (15.9)	6.82 *d* (16.4)	6.72 *d* (16.1)	6.22 *dd* (15.9, 1.2)	6.31 *d* (16.2)
8	6.47 *br d* (15.9)	6.33 *d* (16.1)	6.52 *br d* (15.9)	7.79 *d* (16.4)	6.40 *d* (16.1)	5.69 *dd* (15.9, 6.5)	7.53 *d* (16.2)
9	—	—	—	—	—	4.33 *br quin* (6.5)	—
10	5.79 *br s*	5.84 *br s*	5.81 *br s*	5.68 *br s*	5.86 *br s*	1.26 *d* (6.6)	2.31 *s*
Me_2-1 (β)	—	—	—	—	0.88 *s*	0.81 *s*	0.83 *s*
Me_2-1 (α)	1.04 *s*	1.14 *s*[a]	1.01 *s*[a]	1.04 *s*	1.11 *s*	1.16 *s*[a]	1.22 *s*
$\underline{CH_2}OH$-1	3.00 *d* (11.5) 3.63 *d* (11.5)	3.71 *d* (11.5) 4.06 *d* (11.5)	3.01 *d* (11.1) 3.61 *d* (11.1)	2.99 *d* (11.0) 3.68 *d* (11.0)	—	—	—
Me-5	1.08 *s*	1.15 *s*[a]	1.06 *s*[a]	1.09 *s*	1.04 *s*	1.19 *s*[a]	1.19 *s*
Me-9	2.29 *d* (1.0)	2.32 *br s*	2.32 *d* (1.0)	2.06 *d* (1.2)	2.34 *d* (1.0)	—	—
Sugar moiety	Qui	Qui		Qui	Glc	Glc	Glc
1	4.43 *d* (7.7)	4.65 *d* (7.5)		4.43 *d* (7.3)	4.67 *d* (7.9)	4.44 *d* (7.6)	4.47 *d* (7.3)
2	3.21 *dd* (9.1, 7.7)	5.04 *t* (8.4)		3.2–3.4 *m*	3.21 *dd* (9.2, 7.9)	3.2–3.4 *m*	3.2–3.4 *m*
3	3.29 *t* (9.0)	5.15 *t* (9.3)		3.2–3.4 *m*	3.38 *t* (8.9)	3.2–3.4 *m* 3.2–3.4 *m*	3.2–3.4 *m* 3.2–3.4 *m*
4	3.00 *t* (8.7)	4.84 *t* (9.3)		2.99 *t* (8.8)	3.28 *t* (9.0)		
5	3.23 *m*	3.48 *m*		3.2–3.4 *m*	3.35 *m*	3.2–3.4 *m*	3.2–3.4 *m*
6	1.22 *d* (6.1)	1.16 *d* (6.0)		1.22 *d* (6.1)	3.66 *dd* (11.9, 5.8) 3.90 *dd* (11.9, 2.1)	3.61 *dd* (12.0, 5.6) 3.81 *dd* (12.0, 2.2)	3.62 *dd* (11.7, 5.6) 3.81 *dd* (11.7, 2.2)

Coupling constants (Hz) are given in parentheses.
*Measured at 500 MHz.
†In chloroform-*d*. Acetyl signals are at δ2.00, 2.01, 2.03 and 2.04 (each 3H, *s*).
‡Data of the aglycone moiety of ajugol: see Experimental.
[a]Interchangeable in each column.

fractionated. Fr. A-4 (5.4 g) [13] was subjected to a combination of CC on Fuji gel by eluting with a mixt. of H_2O–MeOH (9:1→1:1), silica gel by developing with a mixt. of EtOAc–MeOH–H_2O (40:2:1→20:3:2), and prep. HPLC by eluting with EtOAc–MeOH–H_2O (30:2:1), to give **4** (460 mg) and **5** (43 mg).

Fr. B-2 (10.1 g) [12], after removal of phenolic glycosides, was applied to a combination of CC on MCI gel CHP20P eluting with a mixt. of H_2O–MeOH (19:1→1:1), μBondapak C_{18} developing with a mixt. of H_2O–MeOH (4:1→3:2), Sephadex LH-20 eluting with H_2O–MeOH (3:2), and prep. HPLC developing with a mixt. of $CHCl_3$–MeOH–H_2O (70:10:1), to afford, **1** (202 mg), **2** (38 mg) and **3** (31 mg).

Jiocarotenoside A_1 (**1**). Prisms, mp 213–215°, $[\alpha]_D^{28}$ −104.8° (MeOH; *c* 0.43). UV λ_{max}^{EtOH} nm (log ε): 254 (4.32). IR ν_{max}^{KBr} cm^{-1}: 3464 (OH), 1692 (C=O), 1632, 1608 (C=C). ^{1}H and ^{13}C NMR (CD_3OD): see Tables 1 and 2. FABMS *m/z* 431 $[M+H]^+$, 453 $[M+Na]^+$, 469 $[M+K]^+$. (Found: C, 56.34; H, 8.10. $C_{21}H_{34}O_9 \cdot H_2O$ requires: C, 56.24; H, 8.09%).

Jiocarotenoside A_1 *tetraacetate* (**1a**). Prisms, mp 199°, $[\alpha]_D^{26}$ −140.5° ($CHCl_3$; *c* 0.12). IR ν_{max}^{KBr} cm^{-1}: 1744, 1724 (acetyl C=O), 1706 (C=O), 1632, 1612 (C=C). ^{1}H NMR ($CDCl_3$): see Table 1. FABMS *m/z* 599 $[M+H]^+$.

Acid hydrolysis of compound **1**. A soln of **1** (60 mg) in 1 M HCl–MeOH (12:1) (13 ml) was heated at 85° for 1 hr. The reaction mixt. was extracted with $CHCl_3$ (20 ml, ×2). The

Table 2. ^{13}C NMR spectral data for norcarotenoids **1**–**5** and **1b** (50 MHz in CD_3OD)

C	1	1b	2	3*	4	5
1	42.2	42.1	42.3	44.7	39.3	39.8
2	31.0	31.5	31.2	74.5	37.2	37.0
3	17.9	18.4	18.0	27.7	18.7	18.6
4	32.6	36.6	32.7	35.9	32.6	32.6
5	83.2	75.5	83.3	75.5	83.6	83.4
6	81.9	82.5	82.1	82.2	79.5	80.3
7	140.7	139.7	142.1	139.9	134.6	153.7
8	134.2	135.0	128.5	134.4	132.5	131.2
9	154.0	153.4	152.6	154.2	69.7	201.8
10	119.2	119.9	117.4	119.3	24.3	27.2[a]
11	170.7	170.9	170.1	168.6		-
Me_2-1 (α)	20.5	20.4	20.6	18.0	25.8	25.8
(β)				22.9	27.3	27.4[a]
CH_2OH-1	72.0	72.0	72.0			
Me-5	21.2	26.6	21.3	27.0	22.3	22.4
Me-9	14.5	14.5	21.8	14.5		
Sugar moiety						
	Qui		Qui	Glc	Glc	Glc
1	97.8		97.9	99.4	98.2	98.2
2	75.6		75.7	74.7	75.5	75.4
3	78.7		78.8	78.1	79.1	79.0
4	72.4		72.5	71.7	71.8	71.7
5	76.9		77.0	78.0	77.4	77.4
6	18.4		18.5	62.9	62.9	62.9

*Measured at 125 MHz. Data of the aglycone moiety of ajugol: see Experimental.
[a]Interchangeable in each column.

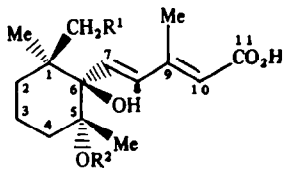
organic layer was conc to dryness and the product subjected to prep. HPLC with $CHCl_3$–MeOH (23:2) as an eluent, to yield the aglycone (**1b**) (8 mg) as needles, mp 198–200° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1684 (C=O), 1632, 1610 (C=C). ^1H and ^{13}C NMR (CD_3OD): see Tables 1 and 2. FABMS *m/z* 285 $[M+H]^+$, 307 $[M+Na]^+$.

The aq. layer was conc to dryness, and the material acetylated in the usual way. Prep. HPLC of the reaction mixt. with *n*-hexane–Me_2CO (17:3) gave an α- and β-anomeric mixt. of the acetylated sugar in the proportion of *ca* 4:3. Crystallization of the mixt. with Et_2O yielded tetraacetyl β-D-quinovose (8 mg) as needles, mp 144–145°. $[\alpha]_D^{26}+26.3$ ($CHCl_3$; *c* 0.16). IR ν_{max}^{KBr} cm^{-1}: 1758 (acetyl C=O), 1252, 1228, 1084, 1036. ^1H NMR (200 MHz, $CDCl_3$): δ 1.25 (3H, *d*, *J* = 6.1 Hz, H-6), 2.01, 2.03, 2.05, 2.11 (each 3H, *s*, OAc × 4), 3.72 (1H, *m*, H-5), 4.86 (1H, *t*, *J* = 8.5 Hz, H-4), 5.10 (1H, *t*, *J* = 8.5 Hz, H-2), 5.21 (1H, *t*, *J* = 9.2 Hz, H-3), 5.68 (1H, *d*, *J* = 8.1 Hz, H-1). EIMS *m/z* (rel. int.): 273 $[M-OAc]^+$ (9), 184 (59), 157 (100), 142 (31), 115 (98), 103 (22). This compound was identified as tetraacetyl β-D-quinovose by direct comparison with an authentic sample prepared from commercially available D-quinovose [4].

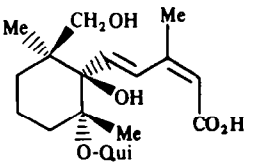
X-Ray crystallographic analysis of compound **1**. The crystal size of **1** was 0.35 × 0.30 × 0.15 mm. Unit cell dimension was obtained by least-squares refinement using 25 centered reflections for which $20° < \theta < 28°$ (graphite monochromatized CuK_α, $\lambda = 1.54184$ Å). Intensity data were collected at $\omega/2\theta$ scans on Enraf–Nonius CAD-4 with three check reflection at intervals of 200 reflections. Other crystal data were: $C_{21}H_{34}O_9 \cdot H_2O$, monoclinic, space group *C* 2, $z = 4$, $a = 22.822$ (2), $b = 8.019$ (9), $c = 16.745$ (2) Å, $\beta = 129.554$ (7)°, $V = 2363$ (19) Å^3, $D_{calc} = 1.21$ g cm^{-3} and μ (CuK_α) = 7.5 cm^{-1}. Intensities were measured for 2432 reflections in the range $2 \leqq 2\theta \leqq 140°$ with 2353 considered as observed by the criterions $I > 3\sigma(I)$. The data were corrected for Lorents and polarization effects. No absorption correction was applied. The structure was solved by the direct-methods program Multan [14] and was refined by full-matrix least-squares, using the Enraf Nonius SDP programs [15]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference maps. The last difference Fourier map was essentially featureless with no peaks greater than 0.21 eÅ^{-3}. The final discrepancy index was $R = 0.036$. The ORTEP drawing is given in Fig. 1. Full crystal data are deposited at the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

Jiocarotenoside A_2 (**2**). Needles, mp 163–169°, $[\alpha]_D^{28}-92.5°$ (MeOH; *c* 0.13). UV λ_{max}^{EtOH} nm (log ε): 253 (4.28). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1678 (C=O), 1634, 1602 (C=C). ^1H and ^{13}C NMR (CD_3OD): see Tables 1 and 2. FABMS *m/z* 431 $[M+H]^+$, 453 $[M+Na]^+$.

6-O-*sec*-*Hydroxyaeginetoyl ajugol* (**3**). Amorphous powder, $[\alpha]_D^{28}-124.0°$ (MeOH; *c* 0.10). UV λ_{max}^{EtOH} nm (log ε): 270.5 (4.41). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1694 (C=O), 1662, 1612 (C=C). ^1H and ^{13}C NMR (CD_3OD) of the norcarotenoid and glucosyl moieties: see Tables 1 and 2; ^1H NMR (500 MHz, CD_3OD) of the aglycone moiety of ajugol: δ 1.37 (3H, *s*, H-10), 1.96 (1H, *dd*, *J* = 14.2, 4.5 Hz, H-7), 2.22 (1H, *dd*, *J* = 14.2, 6.5 Hz, H-7), 2.55 (1H, *dd*, *J* = 9.3, 2.4 Hz, H-9), 2.88 (1H, *dd*, *J* = 9.3, 2.4 Hz, H-5), 4.80–4.95 (1H, *m*, H-6), 4.97 (1H, *dd*, *J* = 6.4, 2.6 Hz, H-4), 5.49 (1H, *d*, *J* = 2.4 Hz, H-1), 6.21 (1H, *dd*, *J* = 6.4, 2.4 Hz, H-3); ^{13}C NMR (125 MHz, CD_3OD): δ 26.0 (*q*, C-10), 39.2 (*d*, C-5), 47.9



1 R^1 = OH, R^2 = Qui
1a R^1 = OAc, R^2 = Qui(OAc)$_3$
1b R^1 = OH, R^2 = H
6 R^1 = R^2 = H



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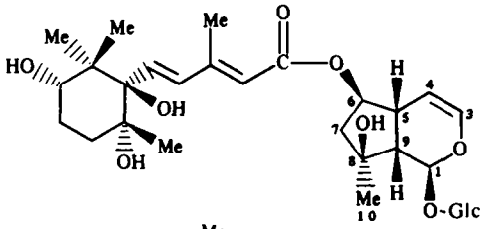

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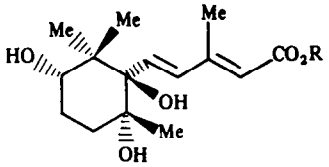
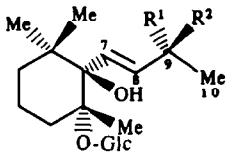


3a R = Me
7 R = H



4 R^1 = H, R^2 = OH
5 R^1 = R^2 = O

(*t*, C-7), 51.5 (*d*, C-9), 79.1 (*s*, C-8), 79.7 (*d*, C-6), 93.4 (*d*, C-1), 104.7 (*d*, C-4), 140.9 (*d*, C-3). FABMS *m/z* 637 $[M+Na]^+$, 653 $[M+K]^+$. (Found: C, 56.41; H, 7.49. $C_{30}H_{46}O_{13}\cdot 3/2H_2O$ requires: C, 56.15; H, 7.70%).

Alkaline hydrolysis of compound **3**. A soln of **3** (18 mg) in 2% NaOMe was kept stirring at room temp. for 3 hr. The reaction mixt. was added with H_2O (10 ml) and was extracted with $CHCl_3$ (10 ml). The $CHCl_3$ layer was concd and subjected to prep. HPLC. Elution with C_6H_6–Me_2CO (17:3) yielded **3a** (3 mg) as needles, mp 148–150°, which was identical to authentic *sec*-hydroxyaeginetic acid methyl ester in all respects (IR, $[\alpha]_D$, ^1H, ^{13}C NMR, MS and TLC) [1]. In the aq. layer, ajugol was detected and was identified with an authentic sample by co-TLC [silica gel, R_f 0.13, $CHCl_3$–MeOH–H_2O (40:10:1); R_f 0.15, EtOAc–MeOH–H_2O (20:3:2)] [8].

Rehmaionoside A (**4**). Amorphous powder, $[\alpha]_D^{28}-73.6°$ (MeOH; *c* 0.49). IR ν_{max}^{KBr} cm^{-1}: 3416 (OH), 1640 (C=C). ^1H and ^{13}C NMR (CD_3OD): see Tables 1 and 2. ^1H NMR (200 MHz, pyridine-d_5): δ 1.16, 1.55, 1.65 (each 3H, *s*, Me_2-1 and Me-5), 1.42 (3H, *d*, *J* = 6.3 Hz, H-10), 1.3–1.6 (2H, *m*), 2.08 (3H, *m*), 2.60 (1H, *m*) (H-2–H-4), 3.82 (1H, *m*, Glc H-5), 3.9–4.3 (4H, *m*, Glc H-2, H-3, H-4 and H-6), 4.37 (1H, *dd*, *J* = 12.0, 2.9 Hz, Glc H-6), 4.62 (1H, *br quin*, *J* = 6.1 Hz, H-9), 5.02 (1H, *d*, *J* = 7.3 Hz, Glc H-1), 6.30 (1H, *dd*, *J* = 16.1, 6.1 Hz, H-8), 6.79 (1H, *dd*, *J* = 1.1 Hz). ^{13}C NMR (50 MHz, pyridine-d_5): δ 18.5 (*t*, C-3), 22.8 (*q*, Me-5), 25.1 (*q*, C-10), 25.8, 27.9 (each *q*, Me_2-1), 32.3 (*t*, C-4), 37.0 (*t*, C-2), 39.1 (*s*, C-1), 63.0 (*t*, Glc C-6), 68.4 (*d*, C-9), 72.0 (*d*, Glc C-4), 75.4 (*d*, Glc C-2), 77.8 (*d*, Glc C-5), 78.8 (*d*, Glc C-3), 79.5 (*s*, C-6), 82.9 (*s*, C-5), 98.4 (*d*, Glc C-1), 131.2 (*d*, C-8), 135.7 (*d*, C-7). FDMS *m/z* 390 $[M]^+$. FABMS *m/z* 413 $[M+Na]^+$, 429 $[M+K]^+$. These data were coincident with those of rehmaionoside A described in the literature [3].

Rehmaionoside C (**5**). Prisms, mp 222°, $[\alpha]_D^{28}-60.5°$ (MeOH; *c* 0.35). IR ν_{max}^{KBr} cm^{-1}: 3280 (OH), 1680 (C=O), 1652 (C=C). ^1H and ^{13}C NMR (CD_3OD): see Tables 1 and 2. FABMS *m/z* 389 $[M+H]^+$, 411 $[M+Na]^+$. This compound was identified as rehmaionoside C (= dihydroxy-β-ionone glucoside) by direct comparison with an authentic sample [2, 3].

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