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SCAMMONIN III–VI, RESIN GLYCOSIDES OF *CONVOLVULUS SCAMMONIA**

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Key Word Index—*Convolvulus scammonia*; Convolvulaceae; Radix Scammoniae; resin glycoside; ether-soluble resin glycoside; scammonin III–VI.

Abstract—Four kinds of ether-soluble resin glycosides named scammonins III–VI were obtained as their acetates from Radix Scammoniae (scammony root), the root of *Convolvulus scammonia*. Their structures have been determined on the bases of chemical and spectral evidences. All of them have a common glycosidic acid, scammonic acid A, and a intramolecular macrocyclic ester structure.

INTRODUCTION

In the preceding paper [2], we reported a new glycosidic acid named scammonic acid A which was obtained along with three organic acids, isobutyric, 2(*S*)-methylbutyric and tiglic acids, as the components of the alkaline hydrolysate of the ether-soluble resin glycoside fraction from Radix Scammoniae (scammony root, roots of *Convolvulus scammonia* L.), and the structures of two ether-soluble genuine resin glycosides, scammonins I and II. This paper deals with the structural elucidation of four resin glycosides, scammonins III (**1**), IV (**2**), V (**3**) and VI (**4**), which were obtained in the form of peracetates.

RESULTS AND DISCUSSION

Fraction 2 previously obtained [2] as a white powder, mp 139–143° (dec.), $[\alpha]_D^{26}$ −34.5°, yielded, on alkaline hydrolysis, tiglic acid and isobutyric acid (identified by GC) together with a glycosidic acid (**5**). The latter was identical with scammonic acid A [2], 11(*S*)-jalapinolic acid [11(*S*)-hydroxyhexadeconoic acid] 11-*O*-*β*-D-quinovopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-*β*-D-glucopyranosyl-(1→2)-*β*-D-quinovopyranoside, on the bases of ^{1}H and ^{13}C NMR spectral data. Although fraction 2 seemed to be homogeneous when examined by normal and reversed phase HPLC using a variety of solvent systems, its negative ion FAB mass spectrum showed two peaks at *m/z* 1005 and 1017 in the highest region. The difference of 12 mass units between the two peaks suggested that fraction 2 is a mixture of two compounds which differ from each other in the component organic acids namely isobutyric and tiglic acids.

In spite of many attempts, separation of fraction 2 could not be achieved. However, when it was acetylated in the usual way, and subjected to low pressure preparative HPLC, it afforded two compounds, **1a** (less polar) and **2a** in the ratio of *ca* 3:1.

Compound **1a**, $C_{63}H_{96}O_{28}$, showed no hydroxyl absorption band in the IR spectrum. The $[M-H]^-$ ion peak observed at *m/z* 1299 [1005 + 7 × 42 (C_2H_2O)] in the negative ion FAB mass spectrum suggested that **1a** is the heptaacetate of a resin glycoside named scammonin III (**1**), which consists of 1 mol each of isobutyric acid, tiglic acid and scammonic acid A (**5**), and, similar to the other ether-soluble resin glycosides so far isolated [1–8], the carboxyl group of the aglycone (jalapinolic acid) of **5** combines with a hydroxy group of the sugar moiety to form an intramolecular macrocyclic ester structure. These suggestions were supported by the presence in the ^{1}H NMR of seven acetoxy methyl signals [δ1.96, 2.00, 2.01, 2.11, 2.12, 2.13, 2.39 (3H, each *s*)], the signals characteristic of 1 mol each of isobutyric acid [δ2.68, (1H, *sept*, H-2), 1.27 (3H, *d*, H_3-3), 1.29 (3H, *d*, H_3-3′)] and tiglic acid groups [δ6.95 (1H, *dq*, H-3), 1.82 (3H, *s*, H_3-5), 1.61 (3H, *dd*, H_3-4)] and the deformed signals due to the nonequivalent H_2-2 [δ2.55, 2.57 (each 1H)] of the aglycone [3]. The last signals are in contrast to the sharp triplet signal due to the equivalent H_2-2 observed in **5** [δ2.51 (3H)].

In order to specify the sites of the three ester linkages, ^{1}H signals due to the sugar moiety of **1a** were assigned with the aid of ^{1}H–^{1}H shift correlated COSY and NOESY methods as shown in Table 1. Subsequently, the long-range ^{1}H–^{13}C shift correlated 2D NMR (HETCOR) of **1a** was recorded.

Among 10 signals due to ester carbonyl carbon atoms, those at δ176.0, 166.8 and 173.3 exhibited cross peaks with H_3-3 and H_3-3′ of isobutyric acid, H_3-5 of tiglic acid, and H_2-2 of jalapinolic acid groups, respectively, and further, the former two were each correlated to H-2 (δ2.68) of rhamnose (Rha) and H-4 (δ5.22) of the terminal quinovose (Qui′) unit. Therefore, the ester linkages of tiglic and isobutyric acids had to be located at OH-2 of Rha and OH-4 of Qui′, respectively. However, the site of the ester group of the jalapinolic acid residue was still unknown because no cross peak appeared between its C-1 and the ^{1}H signals due to the sugar moiety.

Ozonolysis of fraction 2 yielded **6**, $C_{44}H_{76}O_{20}$, as a major product (*ca* 65% yield). It showed a $[M-H]^-$ ion peak at *m/z* 923 [1005 − 82 (C_5H_6O)] in the negative ion

*Part 10 in the series 'Resin Glycosides'. For Part 9 see ref. [1].
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Table 1. ^{1}H NMR spectral data for compounds **1a**, **2a**, **3a**, **4a**, **5** and **6** (400 MHz, 4% soln in pyridine-d_5, TMS as int. standard)

		1a	**2a**	**3a**	**4a**	**5**	**6**
Qui	1	4.85 1H, *d* (7.5)*	4.90 1H *d* (7.5)	4.88 1H, *d* (7.5)	4.90 1H, *d* (7.5)	4.83 1H, *d* (7.5)	4.97 1H, *d* (7.5)
	2	4.07 1H, *dd* (7.5, 9.5)	4.13 1H, *dd* (7.5, 9.5)	4.07 1H, *dd* (7.5, 9.5)	4.13 1H, *dd* (7.5, 9.5)	4.26 1H, *dd* (7.5, 9.0)	4.29 1H, *dd* (7.5, 9.5)
	3	5.34 1H, *dd* (9.5, 9.5)	5.42 1H, *dd* (9.5, 9.5)	5.37 1H, *dd* (9.5, 9.5)	5.43 1H, *dd* (9.5, 9.5)	4.43 1H, *dd* (9.0, 9.0)	4.09 1H, *dd* (9.5, 9.5)
	4	4.93 1H, *dd* (9.5, 9.5)	4.96 1H, *dd* (9.5, 9.5)	4.96 1H, *dd* (9.5, 9.5)	4.96 1H, *dd* (9.5, 9.5)	3.58 1H, *dd* (9.0, 9.0)	3.54 1H, *dd* (9.5, 9.5)
	5	3.73 1H, *dq* (9.5, 6.0)	3.68 1H, *dq* (9.5, 6.0)	3.72 1H, *dq* (9.5, 6.0)	3.70 1H, *dq* (9.5, 6.0)	3.72 1H, *dq* (9.0, 6.0)	3.70 1H, *dq* (9.5, 6.0)
	6	1.27 3H, *d* (6.0)	1.26 3H, *d* (6.0)	1.27 3H, *d* (6.0)	1.27 3H, *d* (6.0)	1.53 3H, *d* (6.0)	1.59 3H, *d* (6.0)
Glc	1	5.12 1H, *d* (7.5)	5.17 1H, *d* (7.5)	5.14 1H, *d* (7.5)	5.17 1H, *d* (6.0)	5.82 1H, *d* (7.0)	5.90 1H, *d* (7.5)
	2	4.03 1H, *dd* (7.5, 9.5)	4.12 1H, *dd* (7.5, 9.5)	4.05 1H, *dd* (7.5, 9.5)	4.12 1H, *dd* (6.0, 9.0)	4.21 1H, *dd* (7.0, 9.0)	4.21 1H, *dd* (7.5, 9.5)
	3	5.77 1H, *dd* (9.5, 9.5)	5.82 1H, *dd* (9.5, 9.5)	5.80 1H, *dd* (9.5, 9.5)	5.82 1H, *dd* (9.0, 9.0)	4.19 1H, *dd* (9.0, 9.0)	4.27 1H, *dd* (9.5, 9.5)
	4	5.38 1H, *dd* (9.5, 9.5)	5.41 1H, *dd* (9.5, 9.5)	5.40 1H, *dd* (9.5, 9.5)	5.42 1H, *dd* (9.0, 9.5)	4.04 1H, *dd* (9.0, 9.0)	4.04 1H, *dd* (9.5, 9.5)
	5	4.10 1H, *ddd* (9.5, 5.0, 2.5)	4.14 1H†	4.11 1H†	4.14 1H†	3.85 1H†	3.86 1H, *ddd* (9.5, 6.0, 3.0)
	6	4.37 1H, *dd* (2.5, 12.0)	4.40 1H, *dd* (2.5, 12.0)	4.39 1H, *dd* (2.5, 12.5)	4.40 1H, *dd* (5.0, 12.0)	4.22 1H, *dd* (6.0, 11.5)	4.20 1H, *dd* (6.0, 12.0)
		4.60 1H, *dd* (5.0, 12.0)	4.63 1H, *dd* (5.0, 12.0)	4.62 1H, *dd* (5.0, 12.5)	4.63 1H, *dd* (2.5, 12.0)	4.41 1H, *dd* (2.5, 11.5)	4.40 1H, *dd* (3.0, 12.0)
Rha	1	5.58 1H, *d* (1.0)	5.76 1H, *d* (1.0)	5.59 1H, *d* (1.0)	5.76 1H, *d* (1.0)	6.28 1H, *d* (0.5)	6.32 1H, *d* (1.5)
	2	5.79 1H, *dd* (1.0, 4.5)	5.89 1H, *dd* (1.0, 4.5)	5.81 1H, *dd* (1.0, 5.5)	5.89 1H, *dd* (1.0, 3.5)	4.68 1H, *dd* (0.5, 3.0)	6.24 1H, *dd* (1.5, 3.5)
	3	5.76 1H, *dd* (4.5, 9.5)	5.84 1H, *dd* (4.5, 9.5)	5.78 1H, *dd* (5.5, 9.5)	5.84 1H, *dd* (3.5, 9.0)	4.81 1H, *dd* (3.0, 9.0)	6.38 1H, *dd* (3.5, 9.5)
	4	4.20 1H, *dd* (9.5, 9.5)	4.27 1H, *dd* (9.5, 9.5)	4.21 1H, *dd* (9.5, 9.5)	4.26 1H, *dd* (9.5, 9.5)	4.40 1H, *dd* (9.0, 9.0)	4.33 1H, *dd* (9.5, 9.5)
	5	4.23 1H, *dq* (9.5, 6.0)	4.30 1H, *dq* (9.5, 6.0)	4.22 1H, *dq* (9.5, 5.0)	4.28 1H, *dq* (9.5, 6.0)	5.03 1H, *dq* (9.0, 6.0)	4.80 1H, *dq* (9.5, 6.0)
	6	1.49 3H, *d* (6.0)	1.54 3H, *d* (6.0)	1.49 3H, *d* (5.0)	1.54 3H, *d* (6.0)	1.88 3H, *d* (6.0)	1.63 3H, *d* (6.0)

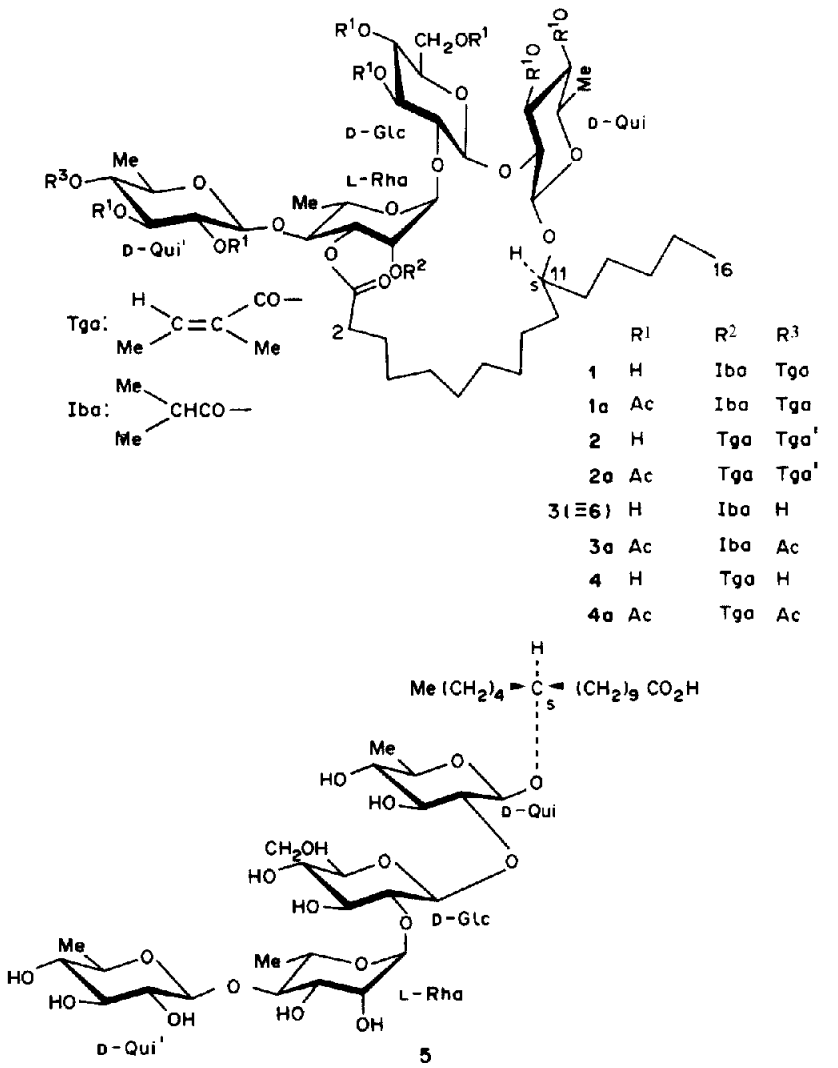
Qui′	1	5.16 1H, *d* (8.0)	5.21 1H *d* (8.0)	5.16 1H, *d* (8.0)	5.14 1H, *d* (8.0)	5.23 1H, *d* (8.0)	4.99 1H, *d* (7.5)
	2	5.35 1H, *dd* (8.0, 9.5)	5.36 1H, *dd* (8.0, 9.5)	5.34 1H, *dd* (8.0, 9.5)	5.34 1H, *dd* (8.0, 9.5)	3.99 1H, *dd* (8.0, 9.0)	3.84 1H, *dd* (7.5, 9.5)
	3	5.70 1H, *dd* (9.5, 9.5)	5.70 1H, *dd* (9.5, 9.5)	5.64 1H, *dd* (9.5, 9.5)	5.63 1H, *dd* (9.5, 9.5)	4.07 1H, *dd* (9.0, 9.0)	4.06 1H, *dd* (9.5, 9.5)
	4	5.22 1H, *dd* (9.5, 9.5)	5.24 1H, *dd* (9.5, 9.5)	5.14 1H, *dd* (9.5, 10.0)	5.14 1H, *dd* (9.5, 9.5)	3.62 1H, *dd* (9.0, 9.0)	3.69 1H, *dd* (9.5, 9.5)
	5	3.74 1H, *dq* (9.5, 6.0)	3.74 1H, *dq* (9.5, 6.0)	3.75 1H, *dq* (10.0, 6.0)	3.68 1H, *dq* (9.5, 6.0)	3.60 1H†	3.70 1H, *dq* (9.5, 6.0)
	6	1.23 3H, *d* (6.0)	1.25 3H, *d* (6.0)	1.21 3H, *d* (6.0)	1.23 3H, *d* (6.0)	1.52 3H, *d* (6.0)	1.56 3H, *d* (6.0)
Jla	2	2.55 1H† 2.57 1H†	2.55 2H, *br t*	2.52 1H† 2.54 1H†	2.52 2H, *br t*	2.51 2H, *t* (7.5)	2.57 1H, *ddd* (3.0, 10.0, 16.0) 2.76 1H, *ddd* (3.0, 8.0, 16.0)
	11	3.82 1H, *m*	3.86 1H, *m*	3.83 1H, *m*	3.86 1H, *q* (5.0)	3.88 1H, *q* (5.5)	3.96 1H, *q* (5.5)
	16	0.89 3H, *t* (7.0)	0.90 3H, *t* (7.0)	0.90 3H, *t* (7.0)	0.91 3H, *t* (7.0)	0.87 3H, *t* (7.5)	0.84 3H, *t* (7.0)
Iba	2	2.68 1H, *sept* (7.0)		2.67 1H, *sept* (7.0)			2.53 1H, *sept* (7.0)
	3	1.27 3H, *d* (7.0)		1.27 3H, *d* (7.0)			1.15 3H, *d* (7.0)
	4	1.29 3H, *d* (7.0)		1.29 3H, *d* (7.0)			1.21 3H, *d* (7.0)
Tga	3	6.95 1H, *dq* (1.5, 7.5)	6.95 1H, *dq* (1.5, 7.5)		7.14 1H, *dq* (1.5, 7.0)		
	4	1.61 3H, *dd* (7.5, 1.0)	1.61 3H, *dd* (7.5, 1.0)		1.54 3H, *dd* (7.0, 1.0)		
	5	1.82 3H, *s*	1.82 3H, *s*		1.90 3H, *s*		
Tga′	3		7.14 1H, *dq* (1.5, 7.5)				
	4		1.54 3H, *d* (7.0, 1.0)				
	5		1.91 3H, *s*				
$MeCO_2$		1.96, 2.00, 2.01, 2.11, 2.12, 2.13, 2.39 each 3H, *s*	1.96, 1.98, 2.01, 2.10, 2.11, 2.12, 2.41 each 3H, *s*	1.98, 2.00, 2.01, 2.03, 2.11, 2.12, 2.40 each 3H, *s*	2.00, 2.00, 2.01, 2.03, 2.11, 2.12, 2.13, 2.39 each 3H, *s*		

*Coupling constants (*J*) in Hz are given in parentheses.

†Signals are overlapping.

Qui, quinovopyranosyl; Glc, glucopyranosyl; Rha, rhamnopyranosyl; Jla, jalapinoyl; Iba, isobutyryl; Tga, tiglyl.

All assignments are based on ^1H–^1H COSY and NOESY data.



	R^1	R^2	R^3
1	H	Iba	Tga
1a	Ac	Iba	Tga
2	H	Tga	Tga'
2a	Ac	Tga	Tga'
3 (≡6)	H	Iba	H
3a	Ac	Iba	Ac
4	H	Tga	H
4a	Ac	Tga	Ac

FAB mass spectrum, and the typical ^{1}H NMR signals of an isobutyric acid group at δ2.53, 1.21 and 1.15. However, no signals due to a tiglic acid group were present. These findings indicated that **6** is produced by solvolysis of the intermediary pyruvic acid ester generated by ozonolysis of the tiglic acid group in the major compound (**1**).

Compared with the ^{1}H signals due to the sugar moiety of **5**, compound **6** exhibited remarkable downfield shifts at H-2 (1.56 ppm) and H-3 (1.57 ppm) of Rha (Table 1). The cross peak observed among three signals assignable to C-1 (δ175.9) and H-2 (δ2.53) of isobutyric acid and H-2 (δ6.24) of Rha in the HETCOR spectrum, showed the location of the intramolecular ester group to be at OH-3 of Rha.

Accordingly, the structure of **6** was defined as 11(*S*)-jalapinolic acid 11-*O*-β-D-quinovopyranosyl-(1→4)-*O*-2-*O*-isobutylyl-α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranosyl-(1→2)-β-D-quinovopyranosyl, intramol. 1,3‴-ester. Taking the absence of acetoxy methyl signal in the ^{1}H NMR spectrum of fraction 2 into account, **1** and **1a** are characterized as a derivative of **6** acylated by tiglic acid at the OH-4 of terminal quinovose unit (Qui') and its heptaacetate, respectively.

Compound **2a**, $C_{64}H_{96}O_{28}$, exhibited a $[M-H]^-$ ion peak at *m/z* 1311 [1017 + 7 × 42 (C_2H_2O)] in the negative FAB mass spectrum and a quite similar ^{1}H NMR spectrum to that of **1a** except for the absence of the signals due to isobutyric acid group, suggesting that **2a** is a heptaacetate of the minor resin glycoside named scammonin IV (**2**), an analogue of **1** possessing 2 mol of tiglic acid as the component organic acids.

The ^{13}C NMR spectrum of **2a** showed three ester cabonyl carbon signals at δ166.8, 166.9 and 173.3 besides seven acetoxy carbonyl carbon signals. In the long range HETCOR spectrum, the former two signals correlated with the ^{1}H signals of Me-2 of tiglic acid groups (δ1.82 and 1.91) and exhibited cross peaks with the signals of H-4 (δ5.24) of Qui' and H-2 (δ5.89) of Rha, respectively. The counterpart for the third signal (δ173.3) could not be seen apart for the H_2-2 signal (δ2.55) of the jalapinolic acid moiety, hence the location of the ester group of the jalapinolic acid moiety remains unsolved.

In the lower field of the ^{1}H NMR spectrum of fraction 2 (Fig. 1), two sets of three methyne signals, which were shifted downfield by acylation, were observed in the ratio of *ca* 3:1. The signals at δ5.33 (*dd*, J = 9.0, 9.0 Hz), 6.27

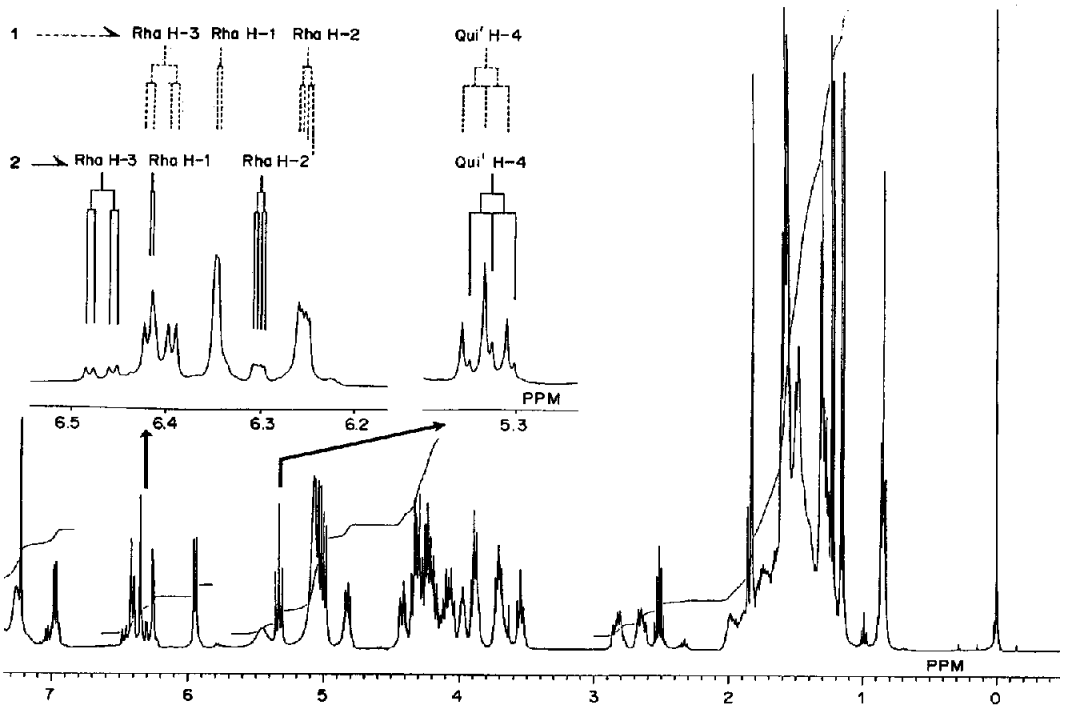


Fig. 1. ^{1}H NMR spectrum of fraction 2 (in pyridine-d_5, 400 MHz).

(*dd*, J = 1.0, 3.5 Hz) and 6.41 (*dd*, J = 3.5, 10.0 Hz) of the major set were each assigned as H-4 of Qui', H-2 and H-3 of Rha of **1** with the aid of COSY and NOESY experiments. Similarly, another (minor) set of signals at δ5.32 (*dd*, J = 9.0, 9.0 Hz), 6.30 (*dd*, J = 1.5, 3.0 Hz) and 6.47 (*dd*, J = 3.0, 10.0 Hz) could be assigned as H-4 of Qui', H-2 and H-3 of Rha of **2**, respectively, hence the ester group of jalapinolic acid moiety was defined to be at OH-3 of Rha.

Consequently, the structure of **2a** is determined as shown, and further, taking the absence of an acetyl signal in the ^{1}H NMR spectrum of fraction 2 into consideration, scammonin IV (**2**) is characterized as 11(*S*)-jalapinolic acid 11-*O*-4-*O*-tiglyl-β-D-quinovopyranosyl-(1→4)-*O*-2-*O*-tiglyl-α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranosyl-(1→2)-β-D-quinovopyranosyl, intramol. 1,3‴-ester.

Fraction 4 (more polar than fraction 2) obtained previously [2] seemed to be homogeneous on normal and reversed phase HPLC as in the case of fraction 2. It gave, on alkaline hydrolysis, isobutyric acid, tiglic acid and scammonic acid A (**5**). The negative ion FAB mass spectrum exhibited two pseudomolecular ions, $[M-H]^-$, at m/z 923 (major) and 935, which are respectively 82 mass units less than those of **1** and **2** (m/z 1005 and 1017) observed in the spectrum of fraction 2. These data indicated that fraction 4 is a mixture of two compounds named scammonins V (**3**) and VI (**4**), each of which contains 1 mol less of tiglic acid than **1** and **2**, respectively. Acetylation of fraction 4 and subsequent preparative HPLC afforded two acetates, **3a** and **4a**.

Compound **3a**, $C_{60}H_{92}O_{28}$, exhibited a $[M-H]^-$ ion peak at m/z 1259 [923 + 8 × 42 (C_2H_2O)] in the negative ion FAB mass spectrum, and the signals due to the nonequivalent H_2-2 of the aglycone (δ2.52, 2.54) along with that characteristic of H-2 of isobutyric acid group (δ2.67) in the ^{1}H NMR spectrum. From these data, **3a** is presumed to be the octaacetate of **6** obtained by ozonolysis of fraction 2 (*vide supra*).

Acetylation of compound **6** yielded a powder, negative ion FAB mass spectrum m/z 1259. Its ^{1}H NMR spectrum was superimposable on that of **3a**. Accordingly, scammonin V (**3**) and **3a** are concluded to be **6** and its octaacetate.

Compound **4a**, $C_{61}H_{92}O_{28}$, negative ion FAB mass spectrum m/z 1271 [935 + 8 × 42 (C_2H_2O)], exhibited the ^{1}H NMR signals due to eight acetyl groups together with the typical signals (δ7.14, 1.90, 1.54) of a tiglic acid group (Table 1). The long range HETCOR spectrum revealed cross peaks between the carbonyl carbon signal (δ166.9), H_3-5 of tiglic acid group (δ1.90) and H-2 of Rha (δ5.89), hence the tiglic acid group was concluded to be attached at OH-2 of Rha. However, the C-1 signal (δ173.3) of jalapinolic acid moiety showed no cross peak with any ^{1}H-signals of a sugar moiety.

In the low field region of the ^{1}H NMR spectrum, fraction 4 (Fig. 2) showed two minor proton signals at δ6.26 (*dd*, J = 1.5, 3.0 Hz) and 6.39 (*dd*, J = 3.0, 10.0 Hz) along with major signals at δ6.22 (*dd*, J = 1.5, 3.0 Hz) and 6.33 (*dd*, J = 3.0, 10.0 Hz). In comparison with the spectrum of **6** (≡ **3**), the former two signals were assigned as those of H-2 and H-3 of Rha of **4** and the latter two as those of **3**. Therefore, it was clear that the carboxyl group of the jalapinolic acid moiety is linked with the OH-3 of Rha. Consequently, the structures of scammonin VI (**4**) and **4a** were determined as depicted.

Like the ether-soluble resin glycosides so far isolated from various convolvulaceae plants [1, 3–8], scammonins III–VI as well as the previously reported scammonins I and II have in common a macrocyclic ester structure in which the carboxyl group of the jalapinolic acid moiety of

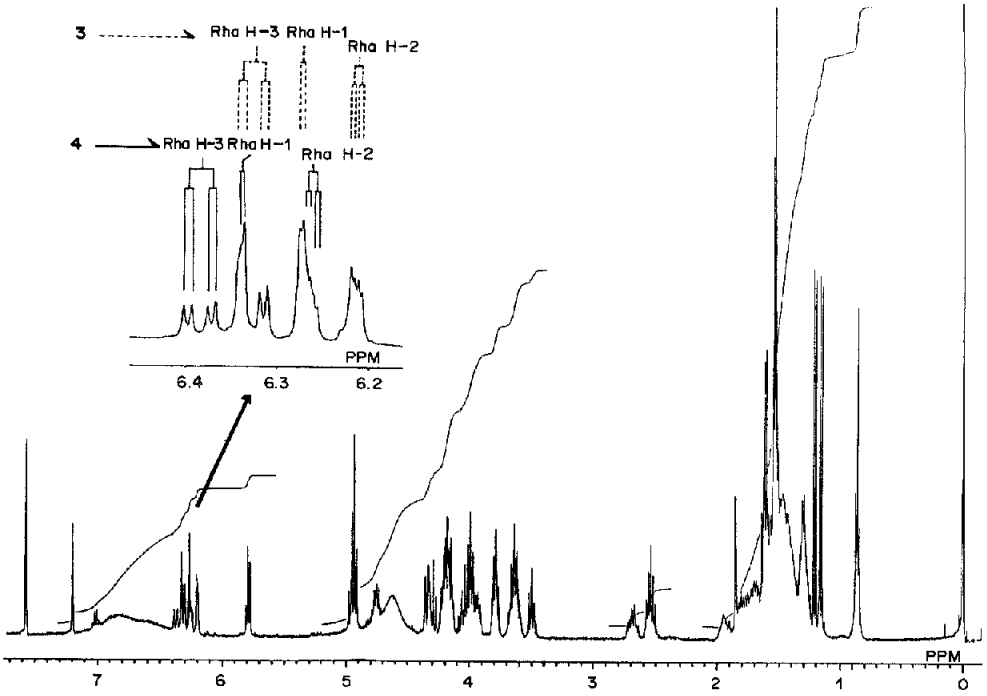


Fig. 2. ^{1}H NMR spectrum of fraction 4 (in pyridine-d_5, 400 MHz).

scammonic acid A combines with the OH-3 of the rhamnose unit in itself. Scammonin II, V and VI correspond respectively to deacyl derivatives lacking the tiglyl group at OH-4 of the terminal quinovose of scammonins I, III and IV.

EXPERIMENTAL

The instruments and materials generally used are cited in the preceding report [2] unless otherwise specified.

Isolation of **1a** and **2a**. A soln of Fr. 2 (30 mg) in Ac_2O–pyridine (1:1) (2 ml) was allowed to stand at room temp. overnight. The reaction mixt. was added into ice H_2O (30 ml) and the ppt. was collected, washed with H_2O and dried. The product (30 mg) was subjected to prep. HPLC (prepacked silica gel column, 5 μm, 22 mm × 10 cm) using *n*-hexane–EtOAc (7:3) as the solvent to give **1a** (22 mg) and **2a** (8 mg).

Scammonin III acetate (**1a**). Powder, mp 91–93° (dec.), $[\alpha]_D^{26}$ −13.0° (MeOH: *c*0.8). Found: C, 58.48; H, 7.62. $C_{63}H_{96}O_{28}$ requires: C, 58.14; H, 7.44%. Negative ion FABMS *m/z* 1299 $[M-H]^-$. IR ν_{max}^{KBr} cm^{-1}: no hydroxyl band, 1740 (C=O). ^{13}C NMR (pyridine-d_5): δ95.4 (C-1 of Rha), 100.4 (C-1 of Qui), 101.2 (C-1 of Glc), 102.7 (C-1 of Qui'), 166.8 [C-1 of tiglic acid group (Tga)], 173.3 [C-1 of isobutyric acid group (Iba)], 176.0 [C-1 of jalapinolic acid moiety (Jla)], 169.7, 169.8, 170.2, 170.3, 170.4, 170.5, 170.7 (each C-1 of acetyl groups). ^{1}H NMR (pyridine-d_5): see Table 1.

Scammonin IV acetate (**2a**). Powder, mp 85–88° (dec.), $[\alpha]_D^{26}$ −2.5° (MeOH; *c*0.8). Found: C, 58.77; H, 7.61. $C_{64}H_{96}O_{28}$ requires: C, 58.53; H, 7.37%. Negative ion FABMS *m/z* 1311 $[M-H]^-$. IR ν_{max}^{KBr} cm^{-1}: no hydroxyl band, 1740 (C=O). ^{13}C NMR (pyridine-d_5): δ95.7 (C-1 of Rha), 100.4 (C-1 of Qui), 101.3 (C-1 of Glc), 102.8 (C-1 of Qui'), 166.8 (C-1 of Tga'), 166.9 (C-1 of Tga), 173.3 (C-1 of Jla), 169.7, 169.9, 170.1, 170.3, 170.4, 170.5, 170.7 (each C-1 of acetyl groups). ^{1}H NMR (pyridine-d_5): see Table 1.

Isolation of **3a** *and* **4a**. Fr. 4 (72 mg) was acetylated in a similar manner to Fr. 2 and the product sepd by use of prep. silica gel HPLC (solvent; *n*-hexane–EtOAc, 3:2) to afford **3a** (38 mg) and **4a** (14 mg).

Scammonin V acetate (**3a**). Powder, mp 94–97° (dec.), $[\alpha]_D^{26}$ −8.9° (MeOH; *c*0.8). Found: C, 57.43; H, 7.51. $C_{60}H_{92}O_{28}$ requires: C, 57.13; H, 7.35%. IR ν_{max}^{KBr} cm^{-1}: no hydroxyl band, 1740 (C=O). Negative ion FABMS *m/z* 1259 $[M-H]^-$. ^{1}H NMR (pyridine-d_5): see Table 1.

Scammonin VI acetate (**4a**). Powder, mp 88–92° (dec.), $[\alpha]_D^{26}$ −1.9° (MeOH; *c*0.8). Found: C, 57.79; H, 7.50. $C_{61}H_{92}O_{28}$ requires: C, 57.54; H, 7.28%. IR ν_{max}^{KBr} cm^{-1}: no hydroxyl band, 1740 (C=O). Negative ion FABMS *m/z* 1271 $[M-H]^-$. ^{13}C NMR (pyridine-d_5): δ95.7 (C-1 of Rha), 100.4 (C-1 of Qui), 101.2 (C-1 of Glc), 102.8 (C-1 of Qui'), 166.9 (C-1 of Tga), 173.3 (C-1 of Jla), 169.7, 169.8, 169.9, 170.1, 170.3, 170.4, 170.5, 170.7 (each C-1 of acetyl groups). ^{1}H NMR (pyridine-d_5): see Table 1.

Alkaline hydrolysis of Frs 2 and 4. A soln of Fr. 2 (16 mg) in 3% KOH (1 ml) was refluxed for 1 hr. The reaction mixt. was made acidic to pH 4.0 with 1 M HCl, and extracted with Et_2O (5 ml). The organic layer was dried over $MgSO_4$ and evapd to afford an brown syrup (1 mg). It was examined by GC (5% Unisol 30T, 4 mm i.d. × 2 m, glass column; column temp., 120°; N_2, 1.5 kg cm^{-2}). R_t (min): 6.72 (isobutyric acid), 15.67 (tiglic acid). The aq. phase was placed on an MCI gel CHP 20P (20 mm × 25 cm) column and the column was washed with H_2O (100 ml) and then eluted with Me_2CO (30 ml). The Me_2CO eluate was evapd *in vacuo* to afford a glycosidic acid (**5**, 12 mg), powder, mp 154–157° (dec.), $[\alpha]_D^{26}$ −51.1° (MeOH; *c*1.0). Its ^{1}H and ^{13}C NMR spectra were superimposable on those of scammonic acid A [2].

Fr. 4 (15 mg) was subjected to alkaline hydrolysis under the same conditions as those described for Fr. 2 to provide an oil (1 mg) and a powder (8 mg), which were respectively proved to be a mixt. of isobutyric acid and tiglic acid by GC as in the case of Fr. 2, and scammonic acid A (**5**) on the basis of ^{13}C NMR.

Ozonolysis of Fr. 2. O_3 was passed into a soln of Fr. 2 (30 mg) in MeOH (10 ml) for 20 min at room temp. and then the reaction

mixt. allowed to stand overnight. After removal of the solvent, the residue (28 mg) was subjected to low pressure prep. HPLC on a reversed phase C-8 prepacked column (Kusano) using 85% MeOH as the solvent to give **6** (18 mg).

(11S)-*Jalapinolic acid* 11-O-β-D-*quinovopyranosyl*-(1→4)-O-2-O-*isopropionyl*-α-L-*rhamnopyranosyl*-(1→2)-O-β-D-*glucopyranosyl*-(1→2)-α-D-*quinovopyranosyl*, *intramol.* 1,3‴-*ester* (**6**). An amorphous powder, mp 161–164° (dec.), $[\alpha]_D^{26}$ −21.9° (MeOH; *c* 0.9). Found: C, 57.14; H, 8.30. $C_{44}H_{76}O_{20}$ requires: C, 57.13; H, 8.28%. Negative ion FABMS *m/z* (rel. int.): 923 $[M-H]^-$ (72), 579 (93), 561 (100), 417 (99), 271 (98). ^{1}H NMR (pyridine-d_5); see Table 1. Usual acetylation of **6** (12 mg) in Ac_2O–pyridine (each 1 ml) yielded peracetate (13 mg) and its ^{1}H NMR spectrum was superimposable on that of **3a**.

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