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Nunziatina De Tommasi, Rita Aquino, Francesco De Simone, and Cosimo Pizza

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PLANT METABOLITES. NEW SESQUITERPENE AND IONONE GLYCOSIDES FROM *ERIOBOTRYA JAPONICA*

NUNZIATINA DE TOMMASI, RITA AQUINO, FRANCESCO DE SIMONE, and COSIMO PIZZA*

Dipartimento di Chimica delle Sostanze Naturali, Università degli Studi di Napoli, via D. Montesano 49, 80131 Napoli, Italy

ABSTRACT.—In a previous paper we described the isolation of four nerolidol glycosides **1–4** from *Eriobotrya japonica* collected in China. Here we report the isolation of seven glycosides **5–11**, five of which (**5–7**, **10**, and **11**) are new natural products, from *E. japonica* collected in Southern Italy. Compounds **5–7** are sesquiterpene glycosides characterized by nerolidol (**5**) or isohumbertiol (**6** and **7**) as aglycones and by branched oligosaccharidic chains made up of one β-D-glucopyranosyl and three α-L-rhamnopyranosyl units which link *trans*-feruloyl ester moieties in compounds **5** and **7**. Analysis of the oligosaccharide structures was achieved by 2D spectral analysis including ^{1}H-^{1}H correlated spectroscopy (COSY), ^{1}H-^{13}C direct chemical shift correlations (HETCOR), and 2D-Homonuclear Hartmann-Hahn spectroscopy (HOHAHA). Compounds **8–11** were characterized as ionone-derived glycosides by chemical and spectral methods.

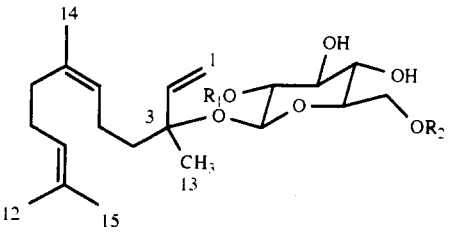
Previous chemical investigations of *Eriobotrya japonica* Lindl. (Rosaceae), a Chinese drug exhibiting hypoglycemic activity, collected in Chang-Sou province, China, afforded a series of triterpenoids (1) and sesquiterpene glycosides **1–4** (2). In assays using normoglycemic rats and genetically diabetic mice, both groups of compounds were found to produce a marked inhibition of glycosuria (3).

In the present study, using *E. japonica* collected in Southern Italy, in addition to **4**, three new sesquiterpene glycosides **5–7** and two new ionone-derived glycosides **10** and **11** were isolated from the MeOH extract of the leaves.

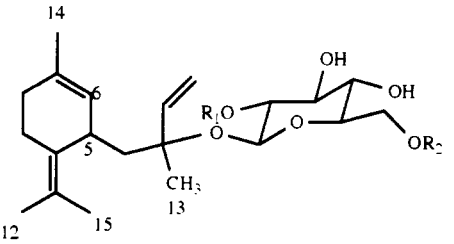
Their structures were established by 1D and 2D nmr spectroscopic methods which provided unambiguous information about the structure of the aglycone and the nature, position of the attachment, and sequence of the various substituents in the sugar moieties. Complete assignment of both the ^{1}H- and ^{13}C-nmr data of the underivatized molecules was possible.

RESULTS AND DISCUSSION

The MeOH extract of the leaves of *E. japonica* collected in Southern Italy afforded, in addition to the known glycoside **4** previously isolated from *E. japonica* collected in China (2), seven other glycosides **5–11** by Sephadex LH-20 cc, dccc, and reversed-

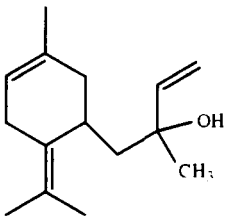


1 R_1=Rha, R_2=H
2 R_1=Rha(1↦4)Rha, R_2=H
3 R_1=H, R_2=Rha(1↦4)Rha
4 R_1=Rha(1↦4)Rha, R_2=Rha
5 R_1=Rha(1↦4)Rha, R_2=(4-*trans*-feruloyl)-Rha

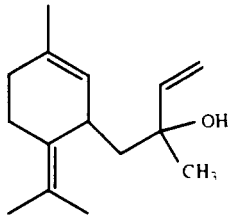


6 R_1=Rha(1↦4)Rha, R_2=Rha
7 R_1=Rha(1↦4)Rha, R_2=(4↦*trans*-feruloyl)-Rha

Rha=α-L-rhamnopyranosyl



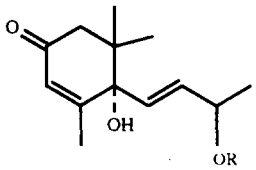
6a (humbertiol)



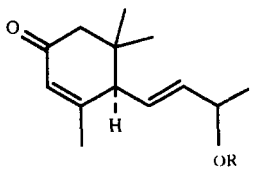
6b (isohumbertiol)

phase hplc. The molecular formulae ($C_{39}H_{66}O_{18}$ for **4**, $C_{49}H_{74}O_{21}$ for **5**, $C_{39}H_{64}O_{18}$ for **6**, and $C_{49}H_{72}O_{21}$ for **7**) were determined by ^{13}C-nmr data and fabms analysis in the negative ion mode. The fabms spectrum of **4** showed the $[M-H]^-$ ion at *m/z* 821 and the fragmentation pattern as reported by De Tommasi *et al.* (2). The fabms spectrum of **5** gave an ion $[M-H]^-$ at *m/z* 997 which was 176 mass units higher than that of **4** (2) and is compatible with an additional methoxyl-C_6-C_3 ester moiety. The fragmentation pattern of **5** was identical to that of **4** starting from *m/z* 821 $[(M-H)-176]^-$. A peak at *m/z* 221, in the spectra of **1–4** (2), was ascribable to the aglycone mass ($C_{15}H_{26}O$).

By comparison of the nmr data for **1–4** (2), **5** was determined to have nerolidol as the aglycone with a branched sugar chain made up of one D-glucose, three L-rhamnoses, and an ester moiety, linked at C-3 (Tables 1 and 2). In fact, the ^{13}C-nmr spectrum of **5** showed ten signals more than that of **4** (2), and these were ascribable to a *trans*-feruloyl moiety (4). The exact disposition of the various moieties was achieved by 2D nmr spectroscopy. Even at high field (500 MHz) the 1D sugar spectral region of **5** was complex, as most of the shifts were found between 5.37 and 3.28 ppm and were overlapped by the aglycone signals. 2D-Homonuclear Hartmann-Hahn (HOHAHA) spectroscopy (5) was used to resolve the overlapped spectra of oligosaccharides into a subset of individual monosaccharide spectra (6). In the 2D HOHAHA spectrum of **5** (Table 1), the anomeric proton signal ascribable to a β-D-glucose (H-1′, δ 4.48, d, $J=8$ Hz) shows connectivities to four methines (3.50, 3.42, 3.34, and 3.28 ppm), and a methylene (3.60 and 4.01 ppm). Because in the HOHAHA method the cross peaks represent both direct and relayed connectivities, we also recorded a COSY-90 spectrum which allowed the proton resonance sequence within this sugar fragment to be established as H-1 (δ 4.48), H-2 (δ 3.50), H-3 (δ 3.42), H-4 (δ 3.34), H-5 (δ 3.28), and H_2-6 (δ 3.60 and 4.01). Similar observations concerning the results of the HOHAHA and COSY experiments for the other sugar residues (Table 1) allowed the complete sequential assignment of all proton resonances starting from the well-isolated anomeric proton signals of the rhamnosyl units H-1″ (δ 5.19), H-1‴ (δ 5.37), H-1⁗ (δ 4.80). HETCOR (^{1}H-^{13}C direct chemical shift correlations) experiments correlated all proton resonances with those of each corresponding carbon (Table 1).



8 R=Glu
11 R=Api(1↦6)Glu



9 R=Glu
10 R=Api(1↦6)Glu

Glu=β-D-glucopyranosyl, Api=β-D-apiofuranosyl

TABLE 1. Nmr Data of the Sugar Moiety for Compound **5** (CD_3OD, 500 MHz).

Method[a]	Sugar[b]	ppm (J_{HH}, Hz)						
^{1}H nmr . . . . . (from H-1′ to H-6′)	Glu 1,2,6[c]	4.48, (8) d	3.50,	3.42, (9.5,9.5) t	3.34,	3.28,	3.60, (12,3) dd	4.01 (12,5) dd
^{13}C nmr . . . . . (from C-1′ to (C-6′)		98.2,	81.6,	77.7,	72.2,	76.2,	68.1	
^{1}H nmr . . . . . (from H-1″ to H-6″)	Rha 1,4	5.19, (1.5) d	3.68,	4.05, (3.2,9.5) dd	3.42, (9.5) t	4.00, (9.5,6.2) dq	1.26 (6.2) d	
^{13}C nmr . . . . . (from C-1″ to C-6″)		103.4,	72.5,	72.4,	79.9,	67.7,	17.8	
^{1}H nmr . . . . . (from H-1‴ to H-6‴)	Rha 1	5.37, (1.5) d	3.94, (1.5,3.4) dd	3.88,	3.55,	4.28, (9.5,6.2) dq	1.28 (6.2) d	
^{13}C nmr . . . . . (from C-1‴ to C-6‴)		102.4,	72.6,	72.6,	74.1,	70.5,	17.9	
^{1}H nmr . . . . . (from H-1⁗ to H-6⁗)	Rha 1,4 ester	4.80, (1.5) d	3.88,	3.50,	5.10, (9.0) t	3.70, (9.0,6.2) dq	1.30 (6.2) d	
^{13}C nmr . . . . . (from C-1⁗ to C-6⁗)		101.9,	73.1,	71.7,	75.5,	70.5,	18.1	

[a]Assignments confirmed by HOHAHA, COSY-90, and HETCOR experiments.
[b]Glu = glucose, Rha = rhamnose.
[c]Sugar bond to C-3 of the aglycone.

Chemical shifts, multiplicity of the signals, absolute values of coupling constants and their magnitude from the shape of cross peaks in the 2D COSY spectrum, as well as ^{13}C nmr data (Table 1), indicated that the sugars must be in the β-D-glucopyranosyl and in the α-L-rhamnopyranosyl forms. The combined use of the techniques mentioned above with HETCOR experiments, as well as comparison with literature data (2,7), showed the oligosaccharidic moiety of **5** to be formed by a glucose branched at C-2′ and C-6′ with a 4-acyl-rhamnosyl as one of the branches and rhamnosyl-(1→4)-rhamnosyl as the second branch. In fact, positions of the interglycosidic linkages at C-2′ (81.6 ppm) and C-6′ (68.2 ppm) of the glucose and at C-4″ (79.9 ppm) of a rhamnose unit were assigned by comparison of these carbon shifts with respective shifts in unglycosidated model compounds (8).

Of the three signals due to anomeric protons of rhamnose, the one at δ 5.19 (correlated to the C-1″ resonance at 103.4 ppm by HETCOR) was assigned to the rhamnose linked to a tertiary alcoholic carbon (C-2′ of glucose) (2,7). By HOHAHA, this proton showed connectivities with a signal at δ 3.42 (t, J = 9.2, H-4″ by COSY) which was correlated by HETCOR to the carbon resonance at 79.9 ppm (C-4″). Therefore, it was assigned to a 1,4-glycosylated central rhamnose unit.

The signal at δ 5.37 (correlated to C-1‴ at 102.4 ppm by HETCOR) was assigned to another rhamnose unit linked to a tertiary alcoholic carbon (C-4″ of the central rhamnose) which was determined to be terminal by analysis of ^{13}C chemical shifts (2,7). The anomeric proton at higher field (δ 4.80), correlating to the C-1⁗ resonance at 101.9 ppm, indicated a rhamnose linked to a secondary alcoholic carbon (C-6′ of glucose) (2,7). By HOHAHA this proton showed a cross peak with a signal at δ 5.10 (1H, t, J = 9.0 Hz, H-4⁗ by COSY) which was correlated to a carbon resonance at 75.5 ppm (C-4⁗). The low field shifts of H-4⁗ (5.10 ppm) and C-4⁗ (75.5 ppm) in this rham-

TABLE 2. Nmr Data of Compounds **6** and **7**.[a]

Position	Compound						Position	Compound		
	5 Aglycone			**6** and **7** Aglycone				**5** and **7** Feruloyl acid moiety		
	δC	DEPT	δH (J_{HH}, Hz)	δC	DEPT	δH (J_{HH}, Hz)		δC	DEPT	δH (J_{HH}, Hz)
1	115.49	CH_2	5.21 dd (17,1) 5.25 dd (11,1)	115.70	CH_2	5.20 dd (17,1) 5.25 dd (10,1)	1‴″	168.9	C	—
2	144.72	CH	6.00 dd (17,11)	144.38	CH	6.00 dd (17,10)	2‴″	116.9	CH	6.55 d (16)
3	82.4	C		81.53	C		3‴″	147.1	CH	7.68 d (16)
4	42.70	CH_2	1.96–2.10	43.43	CH_2	1.96–2.10	1‴″	127.6	C	
5	25.93	CH_2	" "	29.84	CH	2.72 br t	6‴″	124.4	CH	7.09 dd (8,2)
6	125.59	CH	5.21 br s	126.0	CH	5.62 br s	5‴″	116.5	CH	6.81 d (8)
7	136.24	C	"	136.59	C		4‴″	149.4	C	
8	40.83	CH_2	1.96–2.10	42.41	CH_2	1.96–2.10	3‴″	150.8	C	
9	27.89	CH_2	"	23.53	CH_2	" "	2‴″	111.8	CH	7.19 d (2)
10	124.17	CH	5.24 br s	129.8	C		-OMe	56.46	Me	3.89 s
11	131.99	C		140.21	C					
12	16.30	Me	1.67 s	16.07	Me	1.67 s				
13	22.75	Me	1.40 br s	22.68	Me	1.40 br s				
14	18.81	Me	1.67 br s	18.81	Me	1.67 br s				
15	23.58	Me	1.72 br s	24.81	Me	1.72 br s				

[a]s = singlet, d = doublet, dd = double doublet, m = multiplet, br = broad. Data for the sugar moiety of **6** are superimposable to those of **4** (see literature data); data for the sugar moiety of **7** are identical to those of **5** (see Table 1).

nose unit, with respect to the corresponding signals in the spectrum of **4** (H-4'''' 3.6–3.7 ppm, submerged by other signals; C-4'''' 74.0 ppm) (2) and the upfield shift of C-3'''' (71.7 ppm in **5** vs. 72.2 ppm in **4**) are evidence of esterification shifts. From the same 1D and 2D nmr spectra the ester moiety was confirmed to be *trans*-feruloyl acid (4).

Thus, **5** is nerolidol-3-*O*- α-L-rhamnopyranosyl (1↦4)-α-L-rhamnopyranosyl-(1↦2)-[α-L-(4-*trans*-feruloyl)-rhamnopyranosyl-(1↦6)] -β-D-glucopyranoside.

In the fabms spectrum of **6** we observed a quasi-molecular anion at *m/z* 819 $[M-H]^-$, prominent fragment due to the loss of three rhamnose and one glucose units (see Experimental) from the aglycone (mass peak *m/z* 219). The molecular formula of the aglycone was therefore $C_{15}H_{24}O$, which required a rearranged monocyclofarnesyl skeleton. ^{13}C-nmr data of **6** (after subtraction of signals attributed to the sugar moiety which were identical with those of **4**) indicated that **6** contained 15 signals which were sorted by DEPT ^{13}C nmr into four Me, three CH_2, a CH_2=CH group (115.70 and 144.38 ppm), three quaternary sp^2 carbons (136.59, 129.80, 140.21 ppm, respectively), one oxygenated quaternary carbon (81.53 ppm), an aliphatic CH (29.84 ppm), and an olefinic CH (126.0 ppm).

Comparison with nerolidol and several monocyclic sesquiterpenes (2,9) suggested the aglycone to be formed by an oxygenated isoprenyl chain linked to a 1,4 menthadiene partial structure. The ^{1}H-nmr spectrum (in addition to the sugar signals identical with those of **4** to ± 0.02 ppm) confirmed the presence of four methyl groups, one attached to a quaternary carbon bearing an oxygen atom (δ 1.40, 3H, s) and three methyls on trisubstituted double bonds (δ 1.67, 6H, br s; δ 1.72, 3H, br s). The olefinic region showed three signals that formed an AMX pattern [δ 5.20 (J = 17 and 1 Hz), 5.25 (J = 10 and 1 Hz), 6.00 (J = 17 and 10 Hz)] indicative of CH_2=CH group linked to a quaternary carbon and only one broad multiplet appearing at δ 5.62 (H-6) indicative of an olefinic CH. A well-isolated signal resonating at δ 2.72 was assigned by spin decoupling experiments to an aliphatic CH (H-5, br t). Of the two possible structures for the aglycone of **6**, humbertiol [**6a**] (10) or isohumbertiol [**6b**], structure **6b** was established by COSY experiments. The broad one-proton multiplet at δ 5.62 (1H, H-6) has a long range coupling to one of the olefinic methyl signals (Me-14, δ 1.67, 3H, br s) and a direct coupling to the well-isolated methine proton signal at δ 2.72 (H-5). This led to a fragment with the partial structure Me-C=CH-CH- which is compatible only with structure **6b**.

Thus, **6** is isohumbertiol-3-*O*-{α-L-rhamnopyranosyl-(1↦4)-α-L-rhamnopyranosyl-(1↦2)-[α-L-rhamnopyranosyl-(1↦6)]}-β-D-glucopyranoside. This is the first report of isohumbertiol glycosides in nature.

The fabms of **7** gave a quasi molecular anion at *m/z* 995 $[M-H]^-$, shifted 176 mass units with respect to **6**, and a fragmentation pattern identical to that of **6** starting from the peak at *m/z* 819 $[(M-H)-176]^-$. Nmr data (Table 2) showed **7** to be a *trans*-feruloyl ester derivative of **6** at the C-4'''' position. As observed in **5** with respect to **4**, the esterification induced a downfield shift of H-4'''' and C-4'''' and an upfield shift of C-3'''' in **7** with respect to **6**. Thus, **7** is isohumbertiol-3-*O*-{α-L-rhamnopyranosyl-(1↦4)-α-L-rhamnopyranosyl-(1↦2)-[α-L-(4-*trans*-feruloyl)-rhamnopyranosyl-(1↦6)]}-β-D-glucopyranoside.

Compounds **8** and **9** were identified as vomifoliol-9-*O*-β-D-glucopyranoside (roseoside) and 3-oxo-α-ionyl-9-*O*-β-D-glucopyranoside, respectively, by comparison of nmr data with reported values (11,12).

Compounds **10** and **11** were identified as 3-oxo-α-ionyl-9-*O*-β-D-apiofuranosyl-(1↦6)-β-D-glucopyranoside and vomifoliol-9-*O*-β-D-apiofuranosyl-(1↦6)-β-D-glucopyranoside, respectively, from chemical and spectral data. The molecular formulas,

deduced by DEPT ^{13}C, $^{13}\bar{C}$ nmr, and fabms analysis, were $C_{24}H_{38}O_{11}$ for **10** and $C_{24}H_{38}O_{12}$ for **11**. Acid methanolysis of both **10** and **11** liberated methyl apioside and methyl glucoside in the ratio 1:1. Fabms data (**10** *m/z* 501 $[M-H]^-$, 469 $[501-132]^-$, 307 $[469-162]^-$; **11** *m/z* 517 $[M-H]^-$, 485 $[517-132]^-$, 323 $[485-162]^-$) established the sequence to be (terminal) apiose-glucose-aglycone for both compounds and the aglycone formulae as $C_{13}H_{20}O_2$ for **10** and $C_{13}H_{20}O_3$ for **11**. The ^1H- and ^{13}C-nmr spectra (Table 3) of **10** and **11** showed signals for the aglycone moiety superimposable to those of **8** and **9**, respectively, and led to identification of the aglycone of **10** as 3-oxo-α-ionol and of the aglycone of **11** as vomifoliol. The downfield shifts (β effect) observed for the C-9 resonance (76.9 ppm in **10** and 77.0 ppm in **11**) and the upfield shifts (γ effect) experienced by the C-10 resonance (21.0 ppm in **10** and 20.9 ppm in **11**), as compared with those reported for vomifoliol (11), revealed that the sugar is attached at C-9 both in **10** and **11**.

^1H-nmr spectra for the sugar moiety of both **10** and **11** showed an anomeric hydrogen signal at δ 4.35 (H-1′, d, $J=7.5$ Hz) ascribable to a β-D-glucopyranose and a second one at δ 5.01 (H-1″, d, $J=2$ Hz), correlated by ^1H selective decoupling experiments to a signal at δ 3.92 (H-2″, d, $J=2$ Hz), both characteristic of a β-D-apiofuranosyl (13). The DEPT ^{13}C and ^{13}C-nmr spectra of both **10** and **11** gave 11 carbon signals for the sugar moiety, ascribable to an inner β-D-glucopyranosyl and to a terminal β-D-apiofuranosyl (13) of which three were CH_2 [75.1 ppm (C-4″), 65.9 ppm(C-5″), and 68.7 ppm (C-6′)]. C-6′ was shifted downfield by ca. 6 ppm, with respect to C-6′ in a methyl glucopyranoside model (8), demonstrating that the interglycosidic linkage between glucose and apiose must be at C-6′.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—For nmr, a Bruker WH-250 Spectroscopin or Bruker AMX-500 spectrometer equipped with a Bruker X-32 computer was used, with the UXNMR software package. 2D homonuclear proton chemical shift correlation (COSY) experiments employed the conventional pulse sequence. COSY spectra were obtained using a data set ($t_1 \times t_2$) of 1024 × 1024 points for a spectral width of 1165 Hz (relaxation delay 1 sec). The data matrix was processed using an unshifted sine bell window function, following transformation to give a magnitude spectrum with symmetrization (digital resolution in both F2 and F1 dimensions 1.13 Hz/point). The 2D HOHAHA experiment was performed in the phase-sensitive mode (TPPI) using an MLEV-17 sequence for mixing (14). The spectral width (t_2) was 1002 Hz; 512 experiments of 40 scans each (relaxation delay 1.5 sec, mixing time 100 msec) were acquired in both dimensions before transformation. The resulting digital resolution in F2 was 0.48 Hz/point. The HETCOR experiment was performed on a data matrix 512 × 1024, using a CH coupling of 135 Hz and relaxation delay 1.5 sec. The data matrix was processed using a q sine window function.

Optical rotations were measured on a Perkin-Elmer 141 polarimeter using a sodium lamp operating at 589 nm. Fabms were recorded in a glycerol matrix in the negative ion mode on a VG ZAB instrument (XE atoms of energy of 2–6 kV).

Droplet counter current chromatography (dccc) was performed on a Buchi apparatus equipped with 300 tubes. Glc analyses were performed on a Supelco SP200 capillary column (30 m, i.d. 0.32 mm, film thickness 0.25 mm, carrier gas He, 5 ml·min^{-1}, 156°C).

PLANT MATERIAL.—The plant was collected in April 1990 at Benevento, Southern Italy and identified by Dr. V. De Feo, Dipartimento di Chimica delle Sostanze Naturali, Università degli Studi di Napoli. A voucher specimen is deposited at the herbarium of this department.

EXTRACTION AND ISOLATION.—The air-dried leaves (2 kg) were defatted with petroleum ether and $CHCl_3$ and extracted with MeOH to give 38 g of residue. Part of the MeOH extract (8 g) was chromatographed on a Sephadex LH-20 column (100 × 5 cm) with MeOH as eluent.

Fractions of 10 ml were collected and combined according to tlc [Si gel plates, *n*-BuOH–HOAc–H_2O (60:15:25)].

Fractions 13–20 (1.2 g) from Sephadex were purified by dccc [$CHCl_3$-MeOH-H_2O (7:13:8)]. The stationary phase consisted of the lower phase, ascending mode, flow 12 ml/h. About 300 fractions (5 ml) were collected. Dccc fractions 100–200 (400 mg), containing a mixture of sesquiterpene glycosides **4–7**, were separated by hplc (on C_{18} μ-Bondapak column 30 cm × 8 mm), MeOH-H_2O (65:35), flow rate 3

TABLE 3. ^{13}C and ^{1}H nmr of **10** and **11** (CD_3OD).[a]

Position	Compound						Position	Compound		
	10 Aglycone			**11** Aglycone				Oligosaccaride residue of **10** and **11**		
	δC	DEPT	δH (J_{HH}, Hz)	δC	DEPT	δH (J_{HH}, Hz)		δC	DEPT	δH (J_{HH}, Hz)
1	201.9	C	—	201.1	C	—	G-1′	102.7	CH	4.35 d (7.5)
2	123.6	CH	5.92 br s	126.9	CH	5.90 br s	G-2′	75.3	CH	
3	165.6	C	—	168.0	C	—	G-3′	78.3	CH	
4	56.9	CH	2.70 d (8.7)	78.0	C	—	G-4′	71.9	CH	
5	37.2	C	—	43.0	C	—	G-5′	78.2	CH	
6	49.00	CH_2	2.10 d (17)	50.4	CH_2	2.20 d (17)	G-6′	68.7	CH_2	
			2.48 d (17)			2.55 d (17)				
7	129.0	CH	5.65 dd (16,8.7)	131.2	CH	5.92 br m	A-1″	111.1	CH	5.01 d (2)
8	138.1	CH	5.80 dd (16,6)	135.0	CH	5.95 br m	A-2″	77.0	CH	3.92 d (2)
9	76.9	CH	4.40 q (6)	77.0	CH	4.45 q (6)	A-3″	80.5	C	
10	21.0	Me	1.32 d (6)	20.9	Me	1.32 d (6)	A-4″	75.1	CH_2	3.78 d (10)
11	28.1	Me	1.96 d (1.5)	19.3	Me	1.95 d (1.5)				4.00 d (10)
12	27.4	Me	1.05 s	24.4	Me	1.05 s	A-5″	65.9	CH_2	3.6 br s
13	23.7	Me	1.08 s	23.2	Me	1.05 s				

[a]s = singlet, d = doublet, dd = double doublet, m = multiplet, br = broad, q = quintet. All assignments were performed by HETCOR experiments.

$ml \cdot min^{-1}$, to yield pure **4** (80 mg, Rt 6 min), **6** (21 mg, Rt 7.8 min), **5** (39 mg, Rt 25 min) and **7** (15 mg, Rt 28 min).

Fractions 20–27 (800 mg) from Sephadex LH-20 were purified by dccc [*n*-BuOH–Me_2CO–H_2O (60:18:22), ascending mode; the lower phase was the stationary phase]. Dccc fractions 120–195 (140 mg), containing a mixture of ionone glycosides, were further purified by hplc [flow rate 2 $ml \cdot min^{-1}$, MeOH-H_2O (4:6)] to give pure **11** (10.5 mg, Rt 5.5 min), **10** (3 mg, Rt 6.5 min), **8** (11 mg, Rt 10 min), and **9** (6 mg, Rt 12.5 min).

^1H- and ^{13}C-nmr data of **5–7**, and **10**, and **11** are given in Tables 1–3. For fabms of **10** and **11**, see text.

Compound **4** was identified as nerolidol-3-*O*-{α-L-rhamnopyranosyl-(1↦4)-α-L-rhamnopyranosyl-(1↦2)-[α-L-ramnopyranosyl-(1↦6)]-β-D-glucopyranoside}, previously isolated from *E. japonica* collected in China, by nmr and fabms data (2).

Compound **5**.—$[\alpha]^{25}D$ −70 (*c* = 1, MeOH); negative fabms *m/z* $[M-H]^-$ 997, $[(M-H)-176]^-$ 821, $[821-146]^-$ 675, $[821-162]^-$ 659, $[821-(146\times2)]^-$ 529, $[821-(146\times3)]^-$ 383, $[821-(3\times146+162)]^-$ 221.

Compound **6**.—$[\alpha]^{25}D$ −40 (*c* = 1, MeOH); negative fabms *m/z* $[M-H]^-$ 819, $[(M-H)-146]^-$ 673, $[(M-H)-162]^-$ 657, $[(M-H)-(146\times2)]^-$ 527, $[(M-H)-(146\times3)]^-$ 381, $[(M-H)-(146\times3+162)]^-$ 219.

Compound **7**.—$[\alpha]^{25}D$ −72 (*c* = 1, MeOH); negative fabms *m/z* $[M-H]^-$ 995, $[(M-H)-176]^-$ 819, $[819-146]^-$ 673, $[819-162]^-$ 657, $[819-(146\times2)]^-$ 527, $[819-(146\times3)]^-$ 381, $[819-(146\times3)+162)]^-$ 219.

ACID METHANOLYSIS.—Methanolysis and subsequent glc analysis of the persilylated methylsugar of the glycosides **8–11** (ca. 1 mg) was achieved as described earlier (15).

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