Water-Soluble Constituents of Coriander

Toru Ishikawa, Kyoko Kondo, and Junichi Kitajima*

Showa Pharmaceutical University; 3 Higashi-Tamagawagakuen, Machida, Tokyo 194–8543, Japan.
Received July 26, 2002; accepted October 2, 2002

From the water-soluble portion of the methanol extract of coriander (fruit of *Coriandrum sativum* L.), which has been used as a spice and medicine since antiquity, 33 compounds, including two new monoterpenoids, four new monoterpenoid glycosides, two new monoterpenoid glucoside sulfates and two new aromatic compound glycosides were obtained. Their structures, were clarified by spectral investigation.

Key words coriander; *Coriandrum sativum* fruit; hydroxylinalool; monoterpenoid glycoside; phenylpropanoid glycoside

Coriander (*Coriandrum sativum* L.; Umbelliferae) is indigenous to the Mediterranean region and is now widely cultivated as a spice. Its culinary and medical uses have been documented for over 3000 years (Ebers papyrus of 1550 BC), it is an essential ingredient in curry powder, and is used in minced meat dishes, sausages, and stews.[1] The fruit is listed in the British, German, and European pharmacopoeias[2,3] and has been used as a drug for indigestion, against worms, and as a component of embrocations for rheumatism and pains in the joints.[4] It contains an essential oil (up to 1%) constituted of (3*S*)-linalool (main, 60—70%), other monoterpenoids (citronellol, geraniol, myrcene, α- and γ-terpinene, limonene, α- and β-phellandrene, *p*-cymene, α- and β-pinene (−)-borneol, and camphor), and fatty acids (oleic, linolenic, and palmitic acids *etc.*).[4] However, to the best of our knowledge no report has been published on the constituents of the water-soluble portion of this fruit. In a continuation of our studies on the water-soluble constituents of spices,[5] and to show the relationship between the essential oil and the water-soluble constituent, we undertook a detailed investigation of this fruit. In this paper, we discuss the isolation and structure elucidation of monoterpenoid alcohols and its glucosides, norcarotenoid glucosides, an aromatic compound and its glycosides, alkyl glucosides, glucides, uracil, and nucleosides.

Commercial coriander was extracted with 70% methanol, and the methanolic extract was suspended in water and successively extracted with ether and ethyl acetate. The aqueous layer was chromatographed on Amberlite XAD-II to give water and methanol eluate fractions. The methanol eluate fraction was chromatographed on Sephadex LH-20 and then subjected to a combination of silica gel, Lobar RP-8 column chromatography, and HPLC to separate two monoterpenoid triols (**4**, **5**), seven monoterpenoid glycosides (**1** to **3**, **6** to **9**), three norcarotenoid glucosides (**10** to **12**), an aromatic compound (**17**), seven aromatic compound glycosides (**13** to **16**, **18** to **20**), two alkyl glucosides (**21**, **22**), eight glucides (**23** to **30**), uracil (**31**), and two nucleosides (**32**, **33**). Among them, **2** to **9**, **18**, and **19** are new. All new glucosides described in this paper were β-D-glucopyranosides as shown by their ^{1}H- and ^{13}C-NMR data (Tables 1, 2), which was confirmed by hydrolysis yielding D-glucose and/or the comparison of the $[M]_D$ values with those of their aglycones.[6,7] Their molecular formulae were suggested from the accurate mass number of the $[M+H]^+$ or $[M+Na]^+$ or $[M+K]^+$ ion peak in the high-resolution positive FAB-MS.

Monoterpenoid glucoside **1** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{21}$ −20°) was identified as (3*S*,6*E*)-8-hydroxylinalool 3-*O*-β-D-glucopyranoside by comparison with published data.[8]

Monoterpenoid glycoside **2** ($C_{16}H_{27}KO_{10}S$, an amorphous powder, $[\alpha]_D^{21}$ −12°) showed $[2M+H]^+$, $[M+K]^+$, $[M+Na]^+$, and $[M+H]^+$ ion peaks at *m/z* 901, 489, 473, and 451 in the positive FAB-MS, and $[2M-K]^-$, $[M-H]^-$, and $[M-K]^-$ ion peaks at *m/z* 861, 449, and 411 in the negative FAB-MS. Enzymatic hydrolysis of **2** gave (3*S*,6*E*)-8-hydroxylinalool (**1a**) as an aglycone,[9] and the presence of a potassium sulfate group in **2** was suggested by a positive result in the potassium rhodizonate test.[10,11] From a comparison of its ^{1}H- and ^{13}C-NMR data with those of **1** (Tables 1, 2), **2** was concluded to be the potassium sulfate of **1**, and the position of the sulfate group was revealed to be C-3 of the glucose moiety by the downfield shift of H-3 (by 1.0 ppm) and C-3 (by 6.3 ppm) signals and the upfield shift of C-2 (by 2.0 ppm) and C-4 (by 1.6 ppm) signals of the glucosyl moiety. From these results, **2** was determined to be (3*S*,6*E*)-8-hydroxylinalool 3-*O*-β-D-(3-*O*-potassium sulfo)glucopyranoside.

Monoterpenoid glucoside **3** ($C_{16}H_{30}O_7$, an amorphous powder, $[\alpha]_D^{21}$ −8°) showed an $[M+H]^+$ ion peak at *m/z* 335 and an $[M-C_6H_{12}O_6+H]^+$ ion peak at *m/z* 155 in the positive FAB-MS. Enzymatic hydrolysis of **3** gave an aglycone (**3a**; $C_{10}H_{20}O_2$, an amorphous powder, $[\alpha]_D^{21}$ +5°) and D-glucose. Although **3** showed one peak in HPLC, this was suggested to be a mixture of two isomeric compounds in a ratio of 2 : 1 from the NMR data of **3** and **3a** (Tables 1, 2). From a comparison of its ^{1}H- and ^{13}C-NMR data with those of **1** and analysis of the heteronuclear multiple bond connectivity (HMBC) spectrum (see Experimental), the planar structure of the aglycone of **3** was suggested to be 8-hydroxy-6,7-dihydrolinalool, and the position of the glucosyl unit was found to be C-3 of the aglycone. In our previous paper,[12] we reported the isolation of (6*E*)-8-hydroxylinalool 3-*O*-β-D-glucopyranoside (**34**) which gave an aglycone with negative optical rotation (**34a**; $[\alpha]_D^{21}$ −12°) contrary to that of **1** (**1a**; $[\alpha]_D^{21}$ +16°), and **34** was found to have the 3*R* configuration. Thus the absolute configuration at C-3 of **3** was indicated to be *S*. As the glycosylation shift values of C-2, C-3, C-4, and C-10 of **3** showed identical values to those of **1** which has the 3*S* configuration [C-2 (**3**, −2.6; **1**, −2.5), C-3 (**3**, +7.8; **1**, +7.7), C-4 (**3**, −1.1; **1**, −1.1), C-10 (**3**, −5.0 and −4.9; **1**, −4.9)], and the glycosylation shift values of C-4 and C-10 of **3** showed an obvious difference between the values of **34**

* To whom correspondence should be addressed. e-mail: Kitajima@ac.shoyaku.ac.jp

which has the 3*R* configuration [C-4 (**3**, −1.1; **34**, −2.4), C-10 (**3**, −5.0 and −4.9; **34**, −4.3)], the absolute configuration at C-3 of **3** was concluded to be *S*. Therfore, **3** was characterized as an epimeric mixture of (3*S*)-8-hydroxy-6,7-dihydrolinalool 3-*O*-*β*-D-glucopyranoside at C-7.

Monoterpenoid triols **4** ($C_{10}H_{20}O_3$, an amorphous powder, $[\alpha]_D^{21}$ −15°) and **5** ($C_{10}H_{20}O_3$, an amorphous powder, $[\alpha]_D^{21}$ +24°) showed $[M+H]^+$ ion peaks at *m/z* 189 in the positive FAB-MS. They revealed similar ^{1}H- and ^{13}C-NMR spectral features (Tables 1, 2) and have three *tert*-methyls, two methylenes, one oxygenated methine, two oxygenated quaternary carbons, and one vinyl group. From the results of the HMBC experiment of **4** (see Experimental), they were suggested to be 6,7-dihydroxy-6,7-dihydrolinalool, respectively. Monoterpenoid glucoside **6** ($C_{16}H_{30}O_8$, an amorphous powder, $[\alpha]_D^{21}$ −27°) and **7** ($C_{16}H_{30}O_8$, an amorphous powder, $[\alpha]_D^{21}$ +6°) also showed similar ^{1}H- and ^{13}C-NMR spectral features (Tables 1, 2) and revealed $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 351 and 171, respectively, in the positive FAB-MS. Both glucosides were hydrolyzed with hesperidinase and **4** and D-glucose from **6**, and **5** and D-glucose from **7** were obtained from the hydrolyzed mixtures. Consequently, **6** and **7** are monoglucosides of **4** and **5**. The position of the *β*-glucosyl unit of both glucosides was confirmed to be C-3 from the HMBC correlation of glucosyl H-1/C-3 in the HMBC spectrum of **6**. Previously, we reported the isolation of 6,7-dihydroxy-6,7-dihydrolinalool 3-*O*-*β*-D-glucopyranoside (**35**), which has the same planar structure as **6** and **7**.[13] Glucoside **35** gave an aglycone (**35a**; $[\alpha]_D^{23}$ −22°), which had identical ^{1}H- and ^{13}C-NMR spectra and the oppo-

Table 1. ^{1}H-NMR Chemical Shifts of **1**—**9**, **1a**, and **9a** (in Pyridine-d_5, 500 MHz)

	1	**1a**	**2**	**3**
H-1a	5.22 1H, dd (1.5, 11.0)	5.17 1H, dd (2.0, 11.0)	5.25 1H, br d (11.0)	5.20 1H, dd (1.5, 11.0)
b	5.39 1H, dd (1.5, 17.5)	5.58 1H, dd (2.0, 17.0)	5.35 1H, br d (17.5)	5.37 1H, dd (1.5, 17.5)
H-2	6.30 1H, dd (11.0, 17.5)	6.18 1H, dd (11.0, 17.0)	6.24 1H, dd (11.0, 17.5)	6.28 1H, dd (11.0, 17.5)
H_2-4	1.81 2H, m	1.81 2H, m	1.76 2H, m	1.74 2H, m
H_2-5	2.36 2H, m	2.45 2H, m	2.30 2H, m	1.60—1.71 2H, m
H-6a	5.69 1H, dd (7.0, 7.0)	5.78 1H, dd (7.0, 7.0)	5.65 1H, dd (7.0, 7.0)	1.19 1H, m
b	—	—	—	1.61 1H, m
H-7	—	—	—	1.78 1H, m
H_2-8	4.27 2H, br s	4.31 2H, d (5.0)	4.26 2H, br s	3.63 1H, dd (7.0, 9.5)
	—	—	—	3.72 1H, dd (7.0, 9.5)
H_3-9	1.76 3H, s	1.81 3H, s	1.75 3H, s	1.028 3H, d (7.0) [1.033 3H, d (7.0)]
H_3-10	1.59 3H, s	1.48 3H, s	1.51 3H, s	1.58 3H, s
Glc H-1	4.98 1H, d (7.5)	—	4.91 1H, d (8.0)	4.99 1H, d (7.5)
Glc H-3	4.24 1H, dd (8.0, 8.0)	—	5.24 1H, dd (8.0, 8.0)	4.24 1H, dd (8.0, 8.0)

	4	**5**	**6**	**7**
H-1a	5.13 1H, dd (2.0, 11.0)	5.14 1H, dd (2.0, 10.5)	5.16 1H, br d (11.0)	5.16 1H, dd (2.0, 11.0)
b	5.59 1H, dd (2.0, 17.5)	5.59 1H, dd (2.0, 17.0)	5.39 1H, br d (17.5)	5.41 1H, dd (2.0, 17.5)
H-2	6.21 1H, dd (11.0, 17.5)	6.21 1H, dd (10.5, 17.0)	6.33 1H, dd (11.0, 17.5)	6.30 1H, dd (11.0, 17.5)
H-4a	1.97 1H, ddd (3.5, 13.0, 13.0)	1.99 1H, ddd (4.5, 13.0, 13.0)	1.99 1H, ddd (3.5, 13.0, 13.0)	1.90 1H, ddd (4.0, 13.0, 13.0)
b	2.43 1H, ddd (3.5, 13.0, 13.0)	2.42 1H, ddd (4.5, 13.0, 13.0)	2.51 1H, ddd (3.5, 13.0, 13.0)	2.56 1H, ddd (4.0, 13.0, 13.0)
H-5a	1.94 1H, dddd (3.5, 9.5, 13.0, 13.0)	1.94 1H, dddd (4.5, 10.0, 13.0, 13.0)	1.92 1H, dddd (3.5, 8.5, 13.0, 13,0)	2.04 1H, dddd (4.0, 9.5, 13.0, 13,0)
b	2.20 1H, dddd (2.0, 3.5, 13.0, 13.0)	2.20 1H, dddd (2.0, 4.5, 13.0, 13.0)	2.28 1H, dddd (3.5, 6.0, 13.0, 13.0)	2.20 1H, dddd (4.0, 4.0, 13.0, 13.0)
H-6	3.79 1H, dd (2.0, 9.5)	3.78 1H, dd (2.0, 10.0)	3.77 1H, dd (6.0, 8.5)	3.73 1H, dd (4.0, 9.5)
H_3-8	1.48[a] 3H, s	1.50[a] 3H, s	1.46[a] 3H, s	1.46[a] 3H, s
H_3-9	1.51[a] 3H, s	1.51[a] 3H, s	1.50[a] 3H, s	1.49[a] 3H, s
H_3-10	1.51 3H, s	1.48 3H, s	1.62 3H, s	1.62 3H, s
Glc H-1	—	—	5.04 1H, d (8.0)	5.06 1H, d (8.5)
Glc H-3	—	—	4.22 1H, dd (8.0, 8.0)	4.24 1H, dd (8.0, 8.0)

	8		**9**	**9a**
H-1a	5.15 1H, dd (1.5, 11.0)	H-3*endo*	2.02 1H, br d (18.0)	1.98 1H, br d (18.0)
b	5.36 1H, dd (1.5, 17.5)	*exo*	2.32 1H, ddd (4.0, 4.0, 18.0)	2.33 1H, ddd (3.5, 4.5, 18.0)
H-2	6.29 1H, dd (11.0, 17.5)	H-4	1.92 1H, br dd (4.0, 4.0)	1.90 1H, br dd (4.5, 4.5)
H-4a	1.91 1H, ddd (3.5, 13.0, 13.0)	H-5*endo*	1.92 1H, br dd (4.0, 13.5)	1.85 1H, br dd (3.0, 14.0)
b	2.51 1H, ddd (3.5, 13.0, 13.0)	*exo*	2.67 1H, dddd (4.0, 4.0, 9.0, 13.5)	2.49 1H, dddd (3.5, 4.5, 10.0, 14.0)
H-5a	1.99 1H, dddd (3.5, 8.5, 13.0, 13.0)	H-6*exo*	4.37 1H, br d (9.0)	4.39 1H, dd (3.0, 10.0)
b	2.20 1H, dddd (3.5, 8.5, 13.0, 13.0)	H_3-8	0.85 3H, s	0.82 3H, s
H-6	3.74 1H, dd (3.5, 8.5)	H_3-9	0.68 3H, s	0.70 3H, s
H_3-8	1.46[a] 3H, s	H_3-10	1.20 3H, s	1.22 3H, s
H_3-9	1.48[a] 3H, s	Glc H-1	4.78 1H, d (7.5)	4.84 1H, d (8.0)
H_3-10	1.53 3H, s	Api H-1	5.81 1H, d (2.5)	—
Glc H-1	5.00 1H, d (7.5)			
Glc H-3	5.26 1H, dd (9.0, 9.0)			

δ in ppm from TMS [coupling constants (*J*) in Hz are given in parentheses]. Minor stereoisomeric components are given in brackets. *a*) Assignments may be interchanged in each column.

site optical rotation to **5**. Consequently, **5** and **35a** were both enantiomers. The absolute configuration at C-3 of **4** to **7** was determined by comparison of the glycosylation shift values of the α- and β-carbon between **1**, **3**, **6**, **7**, **34**, and **35**. The glycosylation shift values of C-2, C-3, C-4, and C-10 of **6** and **7** showed identical values to those of **1** which has the 3*S* configuration (Table 2), and the glycosylation shift values of C-4 of **6** and **7** showed an obvious difference between the values of **34** and **35** which have the 3*R* configuration (**6**, −1.6; **7**, −1.3; **34**, −2.4; **35**, −3.7). Then the absolute configuration at C-3 of **4** to **7** was concluded to be *S*. It has been reported that the (3*R*,6*R*)- and (3*R*,6*S*)-forms of 6,7-dihydroxy-6,7-dihydrolinalool show positive {$[\alpha]_D^{20}$ +25.5° ($CHCl_3$)} and negative {$[\alpha]_D^{20}$ −15.9° ($CHCl_3$)} optical rotation, respectively.[14] Because **4** and **5** showed negative and positive optical rotations, respectively, **4** and **5** should be the (3*S*,6*S*)- and (3*S*,6*R*)-forms. Therefore **4**, **5**, **6**, and **7** were characterized as (3*S*,6*S*)-6,7-dihydroxy-6,7-dihydrolinalool, (3*S*,6*R*)-6,7-dihydroxy-6,7-dihydrolinalool, (3*S*,6*S*)-6,7-dihydroxy-6,7-dihydrolinalool 3-*O*-β-D-glucopyranoside, and (3*S*,6*R*)-6,7-dihydroxy-6,7-dihydrolinalool 3-*O*-β-D-glucopyranoside, respectively.

Monoterpenoid glycoside **8** ($C_{16}H_{29}KO_{11}S$, an amorphous powder, $[\alpha]_D^{22}$ −14°) showed $[M+K]^+$ and $[M+Na]^+$ ion peaks at *m*/*z* 507 and 491 in the positive FAB-MS, and $[M-H]^-$ and $[M-K]^-$ ion peaks at *m*/*z* 467 and 429 in the negative FAB-MS. Enzymatic hydrolysis of **8** gave **5** as an aglycone,[15] and the presence of a potassium sulfate group in **8** was suggested in the same manner as in **2**. From a comparison of its ^{1}H- and ^{13}C-NMR data with those of **2** and **7** (Tables 1, 2), **8** was suggested to be (3*S*,6*R*)-6,7-dihydroxy-6,7-dihydrolinalool 3-*O*-β-D-(3-*O*-potassium sulfo)glucopyranoside.

Monoterpenoid glycoside **9** ($C_{21}H_{34}O_{11}$, an amorphous powder, $[\alpha]_D^{21}$ −73°) showed an $[M+H]^+$ ion peak at *m*/*z* 463, and $[M-C_5H_8O_4+H]^+$ and $[M-C_{11}H_{20}O_{10}+H]^+$ ion peaks at *m*/*z* 331 and 151 in the positive FAB-MS. The ^{1}H- and ^{13}C-NMR spectral data (Tables 1, 2) showed the presence of one β-apiofuranosyl-(1→6)-β-glucopyranosyl,[16] three *tert*-methyls, two methylenes, two methines (one of which

Table 2. ^{13}C-NMR Chemical Shifts of **1**—**9**, **1a**, **3a**, and **9a** (in Pyridine-d_5, 125 MHz)

	1	**2**	**1a**	**3**	**3a**
C-1	114.79	115.11	111.27	114.62 [114.59]	111.04 [111.01]
C-2	144.50 (−2.5)	143.97 (−3.1)	147.04	144.80 (−2.6) [144.80] (−2.6)	147.37 [147.42]
C-3	79.99 (+7.7)	80.22 (+7.9)	72.32	80.24 (+7.8) [80.24] (+7.8)	72.46 [72.45]
C-4	41.97 (−1.1)	41.89 (−1.2)	43.11	42.67 (−1.1) [42.61] (−1.1)	43.73 [43.71]
C-5	22.62	22.49	22.95	21.73 [21.79]	22.09 [22.07]
C-6	124.88	124.78	125.11	34.34 [34.34]	34.50 [34.50]
C-7	136.36	136.28	136.24	36.54 [36.54]	36.70 [36.70]
C-8	68.08	68.01	68.11	67.53 [67.48]	67.61 [67.59]
C-9	13.94	13.87	13.88	17.36 [17.40]	17.34 [17.37]
C-10	23.58 (−4.9)	23.44 (−5.0)	28.45	23.48 (−5.0) [23.48] (−4.9)	28.48 [28.38]
Glc-1	99.79	99.10		99.60 [99.60]	
Glc-2	75.38	73.59		75.38 [75.38]	
Glc-3	78.85	85.12		78.88 [78.88]	
Glc-4	71.83	70.23		71.77 [71.77]	
Glc-5	78.11	77.13		78.20 [78.20]	
Glc-6	62.96	62.20		62.89 [62.89]	

	4	**5**	**6**	**7**	**8**	**9**	**9a**
C-1	111.11	111.19	114.25	104.06	114.19	63.36	63.42
C-2	147.44	147.49	144.91 (−2.5)	145.09 (−2.4)	144.73 (−2.8)	215.19	215.39
C-3	72.60	72.58	80.33 (+7.7)	80.21 (+7.6)	80.30 (+7.7)	43.50	43.49
C-4	41.17	41.14	39.59 (−1.6)	39.80 (−1.3)	38.68 (−2.5)	41.88	41.83
C-5	27.03	26.91	26.55	26.54	26.16	37.10	36.90
C-6	79.65	79.78	79.53	79.61	79.34	84.63	84.60
C-7	72.77	72.78	72.82	72.81	72.86	47.76	47.85
C-8	25.87[a]	25.92[a]	25.67[a]	25.99	26.01[a]	19.86	19.82
C-9	26.16[a]	26.07[a]	26.44[a]	25.99	26.38[a]	20.22	20.20
C-10	28.75	28.67	24.18 (−4.6)	24.30 (−4.4)	24.50 (−4.2)	8.28	8.31
Glc-1			99.60	99.59	99.02	106.41	106.48
Glc-2			75.38	75.40	73.47	75.03	75.23
Glc-3			78.88	78.86	84.08	78.44	78.42
Glc-4			71.77	71.93	70.33	71.63	71.44
Glc-5			78.20	78.44	77.53	77.24	78.52
Glc-6			62.89	63.18	62.35	68.87	62.85
Api-1						111.13	
Api-2						77.88	
Api-3						80.51	
Api-4						75.05	
Api-5						65.65	

δ in ppm from TMS. $\Delta\delta$ (δ glucoside − δ aglycone) are given in parentheses. Minor stereoisomeric components are given in brackets. *a*) Assignments may be interchanged in each column.

Table 3. ^{1}H-NMR Chemical Shifts of **17**—**19** and **19a** (in Pyridine-d_5, 500 MHz)

	17	18	19	19a
H-2	7.70 1H, d (8.5)	7.59 1H, d (8.0)	7.04 1H, s	7.08 1H, s
H-3	7.25 1H, d (8.5)	7.20 1H, d (8.0)	—	—
H-5	7.25 1H, d (8.5)	7.20 1H, d (8.0)	—	—
H-6	7.70 1H, d (8.5)	7.59 1H, d (8.0)	7.04 1H, s	7.08 1H, s
H-1′	5.28 1H, t (6.0)	5.33 1H, dd (3.0, 8.5)	4.87 1H, dd (6.0, 7.0)	4.91 1H, dd (6.5, 6.5)
H_2-2′	4.20 2H, br d (6.0)	4.05 1H, dd (8.5, 10.5)	1.96 2H, m	2.04 2H, m
	—	4.41 1H, dd (3.0, 10.5)	—	—
H_3-3′	—	—	1.11 3H, t (7.0)	1.15 3H, t (7.0)
3,5-OCH_3	—	—	3.78 6H, s	3.81 6H, s
Glc H-1	—	5.01 1H, d (7.5)	5.75 1H, d (7.0)	—
Api H-1	—	5.77 1H, d (2.5)		

was oxygenated), two quaternary carbons, and one carbonyl group. From the analysis of HMBC spectral data (see Experimental), **9** was suggested to be a glycoside of 6-hydroxycamphor, and partial hydrolysis of **9** with 0.5 N H_2SO_4 afforded (1*R*,4*S*,6*S*)-6-hydroxycamphor β-D-glucopyranoside (**9a**, $C_{16}H_{26}O_7$, an amorphous powder, $[\alpha]_D^{23}$ −66°), which was reported to be a biotransformation product from a cell suspension culture of *Eucalyptus prerriniana* following administration of (+)-camphor[17] and apiose. By comparison of the $[M]_D$ value between **9** and **9a** ($[M]_D$ value of **9**−$[M]_D$ value of **9a**=−119°),[6,7,18] apiose was confirmed to be the D-form. Therefore **9** was characterized as (1*R*,4*S*,6*S*)-6-hydroxycamphor β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside.

Norcarotenoid glucosides **10** ($C_{19}H_{30}O_8$, an amorphous powder, $[\alpha]_D^{23}$ −117°), **11** ($C_{19}H_{30}O_8$, an amorphous powder, $[\alpha]_D^{23}$ −51°), **12** ($C_{19}H_{30}O_{18}$, mp 173—174 °C, $[\alpha]_D^{25}$ −100°), aromatic compound glycosides **13** ($C_{13}H_8O_6$, mp 120—121 °C, $[\alpha]_D^{21}$ −53°), **14** ($C_{18}H_{26}O_{10}$, mp 133—135 °C, $[\alpha]_D^{21}$ −98°), **15** ($C_{14}H_{20}O_9$, mp 232—234 °C, $[\alpha]_D^{23}$ −21°), **16** ($C_{15}H_{22}O_9$, mp 175—177 °C, $[\alpha]_D^{21}$ −21°) and **20** ($C_{19}H_{28}O_{10}$, an amorphous powder, $[\alpha]_D^{25}$ −86°) were identified as citroside A,[19] citroside B,[19] and icariside B_2,[20] benzyl β-D-glucopyranoside,[21] icariside F_2,[21,22] leonuriside A,[23] 4-hydroxy-3,5-dimethoxybenzyl alcohol 4-*O*-β-D-glucopyranoside,[21] and icariside D_1,[22] respectively, by comparison with authentic compounds or published physical and spectral data.

Aromatic compound **17** ($C_8H_{10}O_3$, mp 128—132 °C, $[\alpha]_D^{24}$ +10°) was identified as 1′-(4-hydroxyphenyl)ethane-1′,2′-diol, which was reported to be isolated from whole plants of *C. sativum*.[24] Aromatic compound glycosides **18** ($C_{19}H_{28}O_{12}$, an amorphous powder, $[\alpha]_D^{22}$ −38°) gave **17**, D-glucose, and D-apiose upon enzymatic hydrolysis and showed an $[M+H]^+$ ion peak at *m*/*z* 449 in the positive FAB-MS. Glycoside **18** was suggested to be a β-apiofuranosyl-(1→6)-β-glucopyranoside of **17** based on the ^{1}H- and ^{13}C-NMR spectral data (Tables 1, 2), and the position of the sugar unit was indicated to be C-2′ by the HMBC correlation of glucosyl H-1/C-2′ in the HMBC spectrum. Thus **18** was characterized as 1′-(4-hydroxyphenyl)ethane-1′,2′-diol 2′-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside. As **17** showed a positive optical rotation value that was the same as that of synthetic (1′*S*)-1′-phenylethane-1′,2′-diol,[25] the absolute configuration at C-1′ of **17** and **18** was considered to be *S*.

Aromatic compound glycoside **19** ($C_{17}H_{26}O_9$, an amorphous powder, $[\alpha]_D^{23}$ −10°) showed $[M+K]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m*/*z* 413 and 195 in the positive FAB-MS. The ^{1}H- and ^{13}C-NMR data for **19** (Tables 3, 4) showed the presence of one β-glucopyranosyl, one 1,2,4,5-tetrasubstituted benzene, one ethyl group, one hydroxylated methine, and two methoxyl groups. Enzymatic hydrolysis of **19** gave an aglycone (**19a**; $C_{11}H_{16}O_4$, an amorphous powder, $[\alpha]_D^{22}$ +5°) and D-glucose. From the analysis of the HMBC spectrum (see Experimental), the aglycone of **19** was indicated to be 1′-(4-hydroxy-3,5-dimethoxyphenyl)propan-1′-ol, and the position of the glucosyl unit was C-4. As **19a** showed a positive optical rotation value that was the same as that of (1*R*)-1-phenyl-1-propanol,[26,27] the absolute configuration at C-1′ of **19** was suggested to be *R*. Therefore **19** was represented as (1′*R*)-1′-(4-hydroxy-3,5-dimethoxyl)propan-1′-ol 4-*O*-β-D-glucopyranoside.

Alkyl glucosides **21** (an amorphous powder, $[\alpha]_D^{21}$ −8°) and **22** (an amorphous powder, $[\alpha]_D^{21}$ −20°), glucides **23** (an amorphous powder, $[\alpha]_D^{21}$ −7°), **24** (an amorphous powder, $[\alpha]_D^{21}$ −72°), **25** [an amorphous powder, $[\alpha]_D^{21}$ ±0° (H_2O)], **26** [mp 168—169 °C, $[\alpha]_D^{22}$ −30° (pyridine)], **27** [a colorless syrup, $[\alpha]_D^{22}$ −93° (H_2O)], **28** (a colorless syrup, $[\alpha]_D^{22}$ −33°), **29** [mp 80—83 °C, $[\alpha]_D^{22}$ +49° (H_2O)], and **30** [an amorphous powder, $[\alpha]_D^{22}$ +66° (H_2O)], and nucleosides **32**

Table 4. ^{13}C-NMR Chemical Shifts of **17**—**19** and **19a** (in Pyridine-d_5, 125 MHz)

	17	18	19	19a
C-1	134.85	133.35	143.46 (+5.9)	137.52
C-2,6	128.40	128.39	104.80	104.51
C-3,5	116.00	116.06	153.61 (+4.6)	149.04
C-4	158.17	158.28	134.90 (−1.6)	136.47
C-1′	75.25	73.31 (−1.9)	75.08	75.38
C-2′	69.41	77.20 (+7.8)	33.18	33.33
C-3′			10.81	10.92
3,5-OCH_3			56.57	56.35
Glc-1		105.53	105.25	
Glc-2		75.26	76.10	
Glc-3		78.47	78.37	
Glc-4		71.76	71.58	
Glc-5		77.18	78.67	
Glc-6		68.91	62.61	
Api-1		111.13		
Api-2		77.79		
Api-3		80.45		
Api-4		75.04		
Api-5		65.56		

δ in ppm from TMS [coupling constants (*J*) in Hz are given in parentheses]. $\Delta\delta$ (δ glucoside−δ aglycone) are given in parentheses.

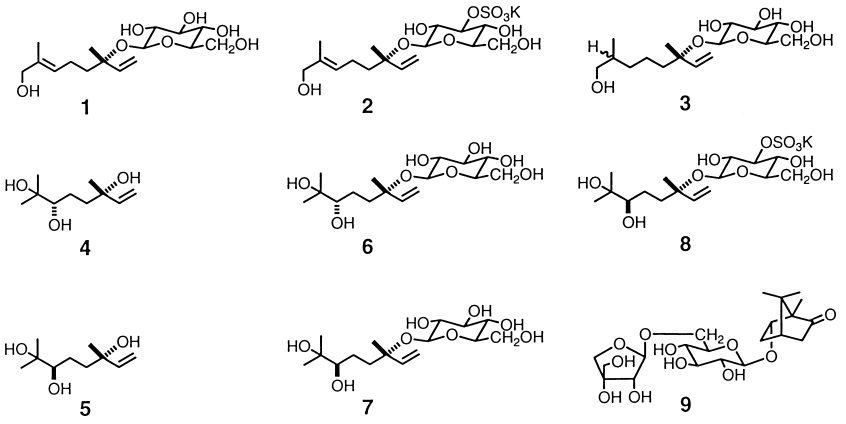

Fig. 1. Structures of **1**—**9**

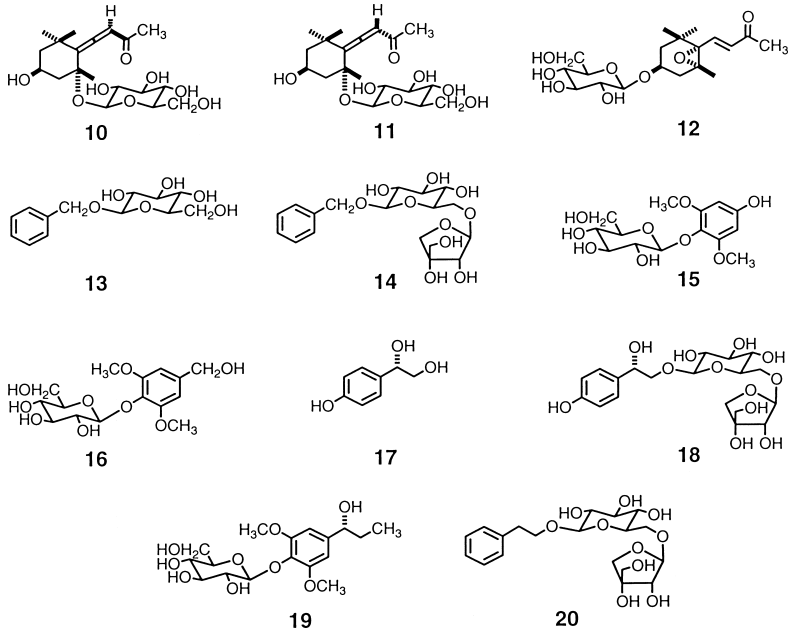

Fig. 2. Structures of **10**—**20**

(mp 164—166 °C, $[\alpha]_D^{23}$ +4°) and **33** [mp 233—235 °C, $[\alpha]_D^{21}$ −62° (H_2O)] were identified as (2*S*)-propane-1,2-diol 1-*O*-*β*-D-glucopyranoside,[28] butane-2,3-diol 2-*O*-*β*-D-glucopyranoside,[28] D-arabinitol, methyl *α*-L-arabinofuranoside,[29] glycerol, D-mannitol, D-fructose, methyl *β*-D-fructofuranoside,[30] D-glucose, sucrose, uridine, and adenosine, respectively.

The ingredient relationship between the essential oil and the water-soluble constituent was confirmed by the isolation of glucosides of (3*S*)-linalool derivatives from the polar fractions.

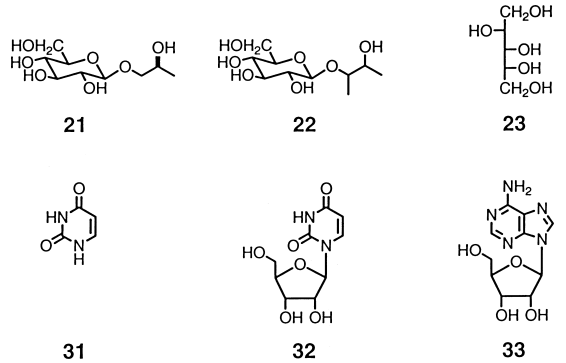

Fig. 3. Structures of **21**—**23** and **31**—**33**

Experimental

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-370 digital polarimeter. FAB-MS were recorded with a JEOL HX-110 spectrometer using glycerol as matrix. ^{1}H- and ^{13}C-NMR spectra were recorded on JEOL A-500 spectrometers with tetramethylsilane as an internal standard, and chemical shifts were recorded in δ values. Column chromatography was carried out under TLC monitoring using Kieselgel 60 (70—230 mesh, Merck), Sephadex LH-20 (25—100 μm, Pharmacia), a Lobar RP-8 column (Merck), and Amberlite XAD-II (Organo). TLC was performed on silica gel (Merck 5721), and spots were detected with *p*-anisaldehyde–H_2SO_4 reagent. HPLC separation was carried out on Symmetryprep C_{18} 7 μm [Waters, column size, 7.8×300 mm, ODS] and carbohydrate analysis [Waters; column size 3.9×300 mm, CHA] columns. Acetylation

was done in the usual way using Ac_2O and pyridine. No acetoxyl group was detected by NMR spectral analysis of the materials prior to acetylation.

Extraction and Separation Commercial coriander (the fruit of *C. sativum* L., purchased from Asaoka Spices Ltd., lot no. 99012001, 7.0 kg) was extracted with 70% methanol (10 l×4) for 2 weeks, and the extract (363.6 g) was partitioned into ether–water and ethyl acetate–water, respectively. The aqueous portion (278.1 g) was chromatographed over Amberlite XAD-II (H_2O→MeOH) to give water eluate (238.1 g) and methanol eluate (40.0 g) fractions.

The methanol fraction was subjected to Sephadex LH-20 [MeOH–H_2O (9 : 1)] to give seven fractions (frs. A—G). Fraction C (30.0 g) was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (17 : 3 : 0.2→4 : 1 : 0.1→7 : 3 : 0.5)→MeOH] to give 14 fractions (frs. C_1—C_{14}). Fraction C_2 (1.54 g) was passed through a Lobar RP-8 column [MeOH–H_2O (1 : 1)] to give 12 fractions (frs. $C_{2\text{-}1}$—$C_{2\text{-}12}$), and fr. $C_{2\text{-}5}$ was subjected to HPLC [ODS, MeOH–H_2O (1 : 1)] and silica gel column chromatography [$CHCl_3$–MeOH (14 : 1)→MeOH] to give **4** (6 mg) and **5** (8 mg). Fraction C_3 (0.83 g) was passed through a Lobar RP-8 column [MeOH–H_2O (1 : 1)] to give 10 fractions (frs. $C_{3\text{-}1}$—$C_{3\text{-}10}$), and fr. $C_{3\text{-}2}$ was subjected to HPLC [ODS, MeOH–H_2O (1 : 19)] to give **17** (10 mg). Fraction $C_{3\text{-}6}$ was subjected to HPLC [ODS, MeOH–H_2O (3 : 7)] and silica gel column chromatography [$CHCl_3$–MeOH (15 : 1)] to give **12** (36 mg). Fraction C_4 (1.03 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give 12 fractions (frs. $C_{4\text{-}1}$—$C_{4\text{-}12}$), and fr. $C_{4\text{-}7}$ was subjected to HPLC [CHA, MeCN–H_2O (19 : 1)] to give **13** (79 mg). Fraction C_5 (0.57 g) was subjected to a Lobar RP-8 column [MeCN–H_2O (3 : 17)] and HPLC [CHA, MeCN–H_2O (97 : 3)] to give **19** (12 mg). Fraction C_6 (0.85 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give 15 fractions (frs. $C_{6\text{-}1}$—$C_{6\text{-}15}$), and fr. $C_{6\text{-}10}$ was subjected to HPLC [ODS, MeCN–H_2O (1 : 7)] and silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.5)] to give **1** (80 mg). Fraction $C_{6\text{-}11}$ was subjected to HPLC [ODS, MeCN–H_2O (3 : 17)] to give **3** (7 mg). Fraction C_7 (2.00 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give 15 fractions (frs. $C_{7\text{-}1}$—$C_{7\text{-}15}$), and fr. $C_{7\text{-}3}$ was subjected to HPLC [CHA, MeCN–H_2O (19 : 1)] to give **16** (16 mg) and **15** (25 mg). Fraction $C_{7\text{-}7}$ and fr. $C_{7\text{-}9}$ were subjected to HPLC [CHA, MeCN–H_2O (19 : 1)] to give **10** (58 mg) from fr. $C_{7\text{-}7}$, and **11** (7 mg) and **9** (8 mg) from fr. $C_{7\text{-}9}$. Fraction C_8 (2.57 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give 17 fractions (frs. $C_{8\text{-}1}$—$C_{8\text{-}17}$). Fraction $C_{8\text{-}3}$ was subjected to HPLC [CHA, MeCN–H_2O (24 : 1)] to give **33** (32 mg), and fr. $C_{8\text{-}11}$ was subjected to HPLC [CHA, MeCN–H_2O (19 : 1)] to give **20** (150 mg). Fraction C_9 (0.48 g) was subjected to a Lobar RP-8 column [MeCN–H_2O (3 : 17)] and HPLC [ODS, MeCN–H_2O (1 : 9)] to give **14** (370 mg). Fraction C_{10} (0.89 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give 12 fractions (frs. $C_{10\text{-}1}$—$C_{10\text{-}12}$), and fr. $C_{10\text{-}5}$ was subjected to HPLC [ODS, MeCN–H_2O (1 : 9)], silica gel column chromatography [$CHCl_3$–MeOH–H_2O (3 : 1 : 0.1)] and HPLC [CHA, MeCN–H_2O (19 : 1)], to give **7** (8 mg) and **6** (13 mg), respectively. Fraction C_{12} (1.33 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give 12 fractions (frs. $C_{12\text{-}1}$—$C_{12\text{-}12}$), and fr. $C_{12\text{-}5}$ was subjected to HPLC [ODS, MeCN–H_2O (1 : 39)] to give **18** (9 mg). Fraction $C_{12\text{-}8}$ (146 mg) was suggested to be rich in the sulfate of **1** by NMR spectra, and the sulfate fraction thus obtained was purified by silica gel column chromatography [$CHCl_3$–MeOH–H_2O (3 : 1 : 0.1)] and HPLC [ODS, MeCN–H_2O (1 : 9)] to give **2** (44 mg). Fraction C_{13} (3.31 g) was subjected to a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give a fraction of the sulfate of **7** (120 mg), and the sulfate fraction thus-obtained was purified by silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.2)], HPLC [CHA, MeCN–H_2O (9 : 1), and ODS, MeCN–H_2O (1 : 39)] to give **8** (10 mg). A part of the water eluate fraction (45.0 g) was subjected to Sephadex LH-20 (80% MeOH) to give three fractions (frs. H—J). Fraction I (38.7 g) was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (17 : 3 : 0.2→4 : 1 : 0.1→7 : 3 : 0.5)→MeOH] to give 24 fractions (frs. I_1—I_{24}). Fraction I_2 (0.06 g) was subjected to a Lobar RP-8 column (H_2O), silica gel column chromatography [$CHCl_3$–MeOH–H_2O (17 : 3 : 0.2)], and HPLC [CHA, MeCN–H_2O (49 : 1)] to give **31** (2 mg) and **24** (17 mg). Fraction I_9 (3.14 g) was passed through a Lobar RP-8 column (H_2O) and HPLC [CHA, MeCN–H_2O (49 : 1) and (19 : 1)] to give **25** (115 mg), **28** (130 mg), **32** (47 mg), **22** (9 mg), and **21** (3 mg). Fraction I_{14} (0.93 g) was passed through a Lobar RP-8 column (H_2O) and HPLC [CHA, MeCN–H_2O (19 : 1)] to give **23** (76 mg), **27** (82 mg), **29** (20 mg), and **26** (11 mg). Fraction I_{23} (5.96 g) was passed through a Lobar RP-8 column (H_2O) and HPLC [CHA, MeCN–H_2O (3 : 1)] to give **30** (225 mg).

The following compounds were identified by comparison with authentic compounds or published physical and spectral data. (3*S*,6*E*)-8-hydroxylinalool 3-*O*-*β*-D-glucopyranoside (**1**, the ^{1}H- and ^{13}C-NMR spectral data are described in Tables 1 and 2), citroside A (**10**), citroside B (**11**), icariside B_2 (**12**), benzyl *β*-D-glucopyranoside (**13**), icariside F_2 (**14**), leonuriside A (**15**), 4-hydroxy-3,5-dimethoxybenzyl alcohol 4-*O*-*β*-D-glucopyranoside (**16**), (1*S*)-1′-(4-hydroxyphenyl)ethane-1′,2′-diol (**17**, the ^{1}H- and ^{13}C-NMR spectral data are described in Tables 1 and 2), icariside D_1 (**20**), (2*S*)-propane-1,2-diol 1-*O*-*β*-D-glucopyranoside (**21**), butane-2,3-diol 2-*O*-*β*-D-glucopyranoside (**22**), D-arabinitol (**23**), methyl *α*-L-arabinofuranoside (**24**), glycerol (**25**), D-mannitol (**26**), D-fructose (**27**), methyl *β*-D-fructofuranoside (**28**), D-glucose (**29**), sucrose (**30**), uracil (**31**), uridine (**32**), and adenosine (**33**).

Enzymatic Hydrolysis of 1 A mixture of **1** (10 mg) and *β*-glucosidase (5 mg, TOYOBO Co. Ltd., lot 93240) in water (5 ml) was shaken in a water bath at 37 °C for 5 d. The mixture was concentrated *in vacuo* to dryness and the residue was chromatographed over silica gel [$CHCl_3$–MeOH (9 : 1)] to afford the aglycone **1a** (3 mg).

(3*S*,6*E*)-8-Hydroxylinalool (1a) An amorphous powder, $[\alpha]_D^{21}$ +17° (*c*=0.4, $CHCl_3$), $[\alpha]_D^{21}$ +16° (*c*=0.4, MeOH). ^{1}H-NMR (pyridine-d_5, 500 MHz): Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz): Table 2.

(3*S*,6*E*)-8-Hydroxylinalool 3-*O*-*β*-D-(3-*O*-Potassium sulfo)glucopyranoside (2) An amorphous powder, $[\alpha]_D^{21}$ −12° (*c*=0.9, MeOH). Positive FAB-MS *m/z*: 901 $[2M+H]^+$, 489.0602 $[M+K]^+$ (Calcd for $C_{16}H_{27}K_2O_{10}S$: 489.0600), 473.0874 $[M+Na]^+$ (Calcd for $C_{16}H_{27}KNaO_{10}S$: 473.0860), 451.1021 $[M+H]^+$ (base, Calcd for $C_{16}H_{28}KO_{10}S$: 451.1041), 433 $[M-H_2O+H]^+$. Negative FAB-MS *m/z*: 861 $[2M-K]^-$, 449 $[M-H]^-$, 411 $[M-K]^-$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz): Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz): Table 2.

Enzymatic Hydrolysis of 2 A mixture of **2** (6 mg) and cellulase (5 mg; Tokyo Kasei Kogyo Co. Ltd., lot FGG01) in water (5 ml) was shaken in a water bath at 37 °C for 14 d. The mixture was treated in the same way as described for **1** to afford the aglycone **1a** (1 mg).

Detection of the Sulfate Group in 2 and 8 A solution of **2** and **8** (2 mg of each) in aqueous 2 N HCl (1 ml) was heated for 2 h, neutralized with diluted NaOH, and evaporated to dryness under reduced pressure. The residue was subjected to paper partition chromatography and developed with a MeOH–H_2O (9 : 1) mixture. After drying in air, the paper was sprayed with a solution of $BaCl_2$ (20 mg) in 70% methanol (10 ml) and dried again in air. The paper was then sprayed with a solution of potassium rhodizonate (5 mg) in 50% methanol (25 ml) to develop the positive coloration (yellow).

(3*S*)-8-Hydroxy-6,7-dihydrolinallol 3-*O*-*β*-D-Glucopyranoside (3) An amorphous powder, $[\alpha]_D^{21}$ −8° (*c*=0.5, MeOH). Positive FAB-MS *m/z*: 669 $[2M+H]^+$, 357.1897 $[M+Na]^+$ (Calcd for $C_{16}H_{30}NaO_7$: 357.1890), 317 $[M-H_2O+H]^+$, 155 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz): Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz): Table 2. HMBC Correlations: H_2-1/C-2, C-3; H-2/C-3, C-4, C-10; H_2-4/C-2, C-3, C-5, C-6, C-10; H_2-5/C-3, C-4, C-6; H_2-6/C-4, C-5, C-7, C-8, C-9; H_2-8/C-6, C-7, C-9; H_3-9/C-6, C-7, C-8; H_3-10/C-2, C-3, C-4; Glc H-1/C-3.

Enzymatic Hydrolysis of 3 A mixture of **3** (5 mg) and hespiridinase (5 mg; ICN Biomedicals Inc., lot 72635) in water (5 ml) was shaken in a water bath at 37 °C for 3 d. The mixture was concentrated *in vacuo* to dryness and the residue was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (9 : 1 : 0.1 and 1 : 1 : 0.1)] to afford **3a** (1 mg) and a sugar fraction. The sugar fraction was passed through Sephadex LH-20 (MeOH) to give a syrup, and HPLC [carbohydrate analysis (Waters); detector, JASCO RI-930 detector and JASCO OR-990 chiral detector; solvent, MeCN–H_2O (17 : 3), 2 ml/min; t_R 4.50 min (same location as that of D-glucose)] showed the presence of D-glucose.

(3*S*)-8-Hydroxy-6,7-dihydrolinalool (3a) An amorphous powder, $[\alpha]_D^{21}$ +5° (*c*=0.1, MeOH). ^{1}H-NMR (pyridine-d_5, 500 MHz) *δ*: 6.171 (1H, dd, *J*=11.0, 17.5 Hz, H-2), [6.174 (1H, dd, *J*=11.0, 17.5 Hz, H-2)], 5.56 (1H, dd, *J*=2.0, 17.5 Hz, H-1b), 5.14 (1H, dd, *J*=2.0, 11.0 Hz, H-1a), 3.76 (1H, dd, *J*=6.0, 10.0 Hz, H-8b), 1.84 (1H, m, H-7), 1.59—1.80 (5H, m, H-4a, -4b, -5a, -5b, -6b), 1.46 (3H, s, H-10), 1.28 (1H, m, H-6a), 1.082 (3H, d, *J*=7.0 Hz, H-9), [1.076 (3H, d, *J*=7.0 Hz, H-9)], minor stereoisomeric component is given in brackets. ^{13}C-NMR (pyridine-d_5, 125 MHz): Table 2.

Enzymatic Hydrolysis of 34 A mixture of **34** [(6*E*)-8-hydroxylinallol 3-*O*-*β*-D-glucopyranoside, the ^{1}H- and ^{13}C-NMR spectral data are described in Tables 1 and 2; 13 mg] and *β*-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 7 d. The mixture was treated in the same way as described for **1** to afford the aglycone **34a** (6 mg).

(3*R*,6*E*)-8-Hydroxylinalool (34a) An amorphous powder, $[\alpha]_D^{21}$ −14° (*c*=0.5, $CHCl_3$), $[\alpha]_D^{21}$ −12° (*c*=0.5, MeOH). ^{1}H- and ^{13}C-NMR spectral data were identical to those of **1a**.

(3*S*,6*S*)-6,7-Dihydroxy-6,7-dihydrolinalool (4) An amorphous powder, $[\alpha]_D^{21}$ −29° (*c*=0.3, $CHCl_3$), $[\alpha]_D^{21}$ −15° (*c*=0.3, MeOH). Positive FAB-MS *m/z*: 377 $[2M+H]^+$, 227.1041 $[M+K]^+$ (Calcd for $C_{10}H_{21}KO_3$: 227.1049),

211 [M+Na]$^+$, 189.1487 [M+H]$^+$ (Calcd for $C_{10}H_{21}O_3$: 189.1490), 171 [M−H_2O+H]$^+$, 153 [M−$2H_2O$+H]$^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz): Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz): Table 2. HMBC correlations: H-1a/C-3; H-1b/C-2, C-3; H-2/C-3, C-4, C-10; H_2-4/C-2, C-3, C-5, C-6, C-10; H_2-5/C-3, C-4, C-6, C-7; H-6/C-4, C-5, C-8, C-9; H_3-8/C-6, C-7, C-9; H_3-9/C-6, C-7, C-8; H_3-10/C-2, C-3, C-4.

(3*S*,6*R*)-6,7-Dihydroxy-6,7-dihydrolinalool (5) An amorphous powder, $[\alpha]_D^{21}$ +22° (*c*=0.1, $CHCl_3$), $[\alpha]_D^{21}$ +24° (*c*=0.2, MeOH). Positive FAB-MS *m/z*: 377 [2M+H]$^+$, 227.1040 [M+K]$^+$ (Calcd for $C_{10}H_{21}KO_3$: 227.1049), 211 [M+Na]$^+$, 189.1482 [M+H]$^+$ (Calcd for $C_{10}H_{21}O_3$: 189.1490), 171 [M−H_2O+H]$^+$, 153 [M−$2H_2O$+H]$^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz): Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz): Table 2.

(3*S*,6*S*)-6,7-Dihydroxy-6,7-dihydrolinalool 3-*O*-β-D-Glucopyranoside (6) An amorphous powder, $[\alpha]_D^{21}$ −27° (*c*=1.0, MeOH). Positive FAB-MS *m/z*: 701 [2M+H]$^+$, 389 [M+K]$^+$ (base), 373 [M+Na]$^+$, 351.2022 [M+H]$^+$ (Calcd for $C_{16}H_{31}O_8$: 351.2019), 333 [M−H_2O+H]$^+$, 171 [M−$C_6H_{12}O_6$+H]$^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz): Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz): Table 2. HMBC correlations: H_2-1/C-2, C-3; H-2/C-3, C-4, C-10; H_2-4/C-2, C-3, C-5, C-6, C-10; H-5a/C-3, C-4, C-6; H-5b/C-4; H-6/C-4, C-5, C-7, C-8, C-9; H_2-8/C-6, C-7, C-9; H_3-9/C-6, C-7, C-8; H_3-10/C-2, C-3, C-4; Glc H-1/C-3.

Enzymatic Hydrolysis of 6 A mixture of **6** (6 mg) and hesperidinase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 5 d. The mixture was treated in the same way as described for **3** to afford the aglycone **4** (2 mg) and a sugar fraction. D-Glucose was detected from the sugar fraction as described for **3**.

(3*S*,6*R*)-6,7-Dihydroxy-6,7-dihydrolinalool 3-*O*-β-D-Glucopyranoside (7) An amorphous powder, $[\alpha]_D^{21}$ +6° (*c*=0.1, MeOH). Positive FAB-MS *m/z*: 701 [2M+H]$^+$, 389 [M+K]$^+$ (base), 373 [M+Na]$^+$, 351.2024 [M+H]$^+$ (Calcd for $C_{16}H_{31}O_8$: 351.2019), 333 [M−H_2O+H]$^+$, 171 [M−$C_6H_{12}O_6$+H]$^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz): Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz): Table 2.

Enzymatic Hydrolysis of 7 A mixture of **7** (3 mg) and hesperidinase (3 mg) in water (5 ml) was shaken in a water bath at 37 °C for 10 d. The mixture was treated in the same way as described for **3** to afford an aglycone **4** (2 mg) and a sugar fraction. D-Glucose was indicated from the sugar fraction by HPLC [carbohydrate analysis (Waters), detector; JASCO RI-930 detector] analysis.

Enzymatic Hydrolysis of 35 A mixture of **35** [(3*R*,6*S*)-6,7-dihydroxy-6,7-dihydrolinalool 3-*O*-β-D-glucopyranoside for which the ^{1}H- and ^{13}C-NMR spectral data are described in Tables 1 and 2, 3 mg] and hesperidinase in water (5 ml) was shaken in a water bath at 37 °C for 5 d. The mixture was treated in the same way as described for **1** to afford the aglycone **35a** (1 mg).

(3*R*,6*S*)-6,7-Dihydroxy-6,7-dihydrolinalool (**35a**): An amorphous powder, $[\alpha]_D^{23}$ −22° (*c*=0.5, MeOH). ^{1}H- and ^{13}C-NMR spectral data were identical to those of **5**.

(3*S*,6*R*)-6,7-Dihydroxy-6,7-dihydrolinalool 3-*O*-β-D-(3-*O*-Potassium sulfo)-glucopyranoside (8) An amorphous powder, $[\alpha]_D^{22}$ −14° (*c*=0.3, MeOH). Positive FAB-MS *m/z*: 507.0697 [M+K]$^+$ (Calcd for $C_{16}H_{29}K_2O_{11}S$: 507.0705), 491.0982 [M+Na]$^+$ (base, Calcd for $C_{16}H_{29}KNaO_{11}S$: 491.0966). Negative FAB-MS *m/z*: 467 [M−H]$^-$ 429 [M−K]$^-$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz): Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz): Table 2.

Enzymatic Hydrolysis of 8 A mixture of **8** (4 mg) and naringinase (5 mg; ICN Biomedicals Inc., lot 2421C) in water (5 ml) was shaken in a water bath at 37 °C for 14 d. The mixture was treated in the same way as described for **1** to afford the aglycone **5** (1 mg).

(1*R*,4*S*,6*S*)-6-Hydroxycamphor β-D-Apiofuranosyl-(1→6)-β-D-glucopyranoside (9) An amorphous powder, $[\alpha]_D^{21}$ −73° (*c*=0.5, MeOH). Positive FAB-MS *m/z*: 925 [2M+K]$^+$, 501 [M+K]$^+$, 485.2002 [M+Na]$^+$ (Calcd for $C_{21}H_{34}NaO_{11}$: 485.1999), 463 [M+H]$^+$, 331 [M−$C_5H_8O_4$+H]$^+$, 151 [M−$C_{11}H_{20}O_{10}$+H]$^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz): Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz): Table 2. HMBC correlations: H-3*endo*/C-1, C-2, C-4, C-5, C-7; H-3*exo*/C-2, C-4, C-5; H-4/C-1, C-2, C-3, C-6, C-7, C-8, C-9; H_2-5/C-1, C-3, C-4, C-6; H-6/C-1, C-2, C-4, C-5, C-10, Glc C-1; H_3-8/C-1, C-4, C-7, C-9; H_3-9/C-1, C-4, C-7, C-8; H_3-10/C-1, C-2, C-6, C-7; Glc H-1/C-6; Api H-1/Glc C-6.

Partial Acid Hydrolysis of 9 Glycoside **9** (5 mg) was dissolved in aqueous 0.5 N H_2SO_4 and heated at 55 °C for 2 h. The reaction mixture of the hydrolysate was neutralized with $NaHCO_3$, the salt was filtered off, and the filtrate passed through Sephadex LH-20 (MeOH) to afford a monoglucoside fraction and a sugar fraction. The monoglucoside fraction was chromatographed on silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1 and 1 : 1 : 0.1)] to afford **9a** (3 mg). The sugar fraction was subjected to silica gel TLC [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.5)] to show the presence of apiose (*Rf* 0.29).

(1*R*,4*S*,6*S*)-6-Hydroxycamphor β-D-Glucopyranoside (9a) An amorphous powder, $[\alpha]_D^{23}$ −66° (*c*=0.4, MeOH). Positive FAB-MS *m/z*: 661 [2M+H]$^+$, 369 [M+K]$^+$, 353 [M+Na]$^+$, 331 [M+H]$^+$, 151 [M−$C_6H_{12}O_6$+H]$^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz): Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz): Table 2.

(1′*S*)-1′-(4-Hydroxyphenyl)ethane-1′,2′-diol 2′-*O*-β-D-Apiofuranosyl-(1→6)-β-D-glucopyranoside (18) An amorphous powder, $[\alpha]_D^{22}$ −38° (*c*=0.5, MeOH). Positive FAB-MS *m/z*: 471.1481 [M+Na]$^+$ (base, Calcd for $C_{19}H_{28}NaO_{12}$: 471.1478), 449 [M+H]$^+$, 431 [M−H_2O+H]$^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz): Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz): Table 2. HMBC correlations: H-2/C-4, C-6, C-1′; H-3/C-1, C-4, C-5; H-5/C-1, C-3, C-4; H-6/C-2, C-4, C-1′; H-1′/C-1, C-2, C-6, C-2′; H_2-2′/Glc C-1, Glc H-1/C-2; Glc H_2-6/Api C-1.

Enzymatic Hydrolysis of 18 A mixture of **18** (5 mg) and β-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 7 d. The mixture was treated in the same way as described for **3** to afford the aglycone **17** (2 mg) and a sugar fraction. D-Glucose and D-apiose (t_R 7.95 min; same location as that of D-apiose) were detected from the sugar fraction in the same way as described for **3**.

(1′*R*)-1′-(4-Hydroxy-3,5-dimethoxyphenyl)propan-1′-ol 4-*O*-β-D-Glucopyranoside (19) An amorphous powder, $[\alpha]_D^{23}$ −10° (*c*=1.0, MeOH). Positive FAB-MS *m/z*: 413 [M+K]$^+$, 397.1473 [M+Na]$^+$ (Calcd for $C_{17}H_{26}NaO_9$: 397.1475), 195 [M−$C_6H_{12}O_6$+H]$^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz): Table 3. ^{13}C-NMR (pyridine-d_5, 125 MHz): Table 4. HMBC correlations: H-2/C-1, C-3, C-4, C-6, C-1′; H-6/C-1, C-2, C-4, C-5, C-1′; H-1′/C-2, C-6, C-2′, C-3′; H_2-2′/C-1′, C-3′; H_3-3′/C-1′, C-2′; 3-O-CH_3/C-3; 5-O-CH_3/C-5; Glc H-1/C-4.

Enzymatic Hydrolysis of 19 A mixture of **19** (10 mg) and naringinase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 15 d. The mixture was treated in the same way as described for **3** to afford the aglycone **19a** (5 mg) and a sugar fraction. D-Glucose was detected from the sugar fraction as described for **3**.

(1′*R*)-1′-(4-Hydroxy-3,5-dimethoxyphenyl)propan-1′-ol (19a) An amorphous powder, $[\alpha]_D^{22}$ +5° (*c*=0.4, $CHCl_3$). ^{1}H-NMR (pyridine-d_5, 500 MHz): Table 3. ^{13}C-NMR (pyridine-d_5, 125 MHz): Table 4.

Acknowledgments The authors thank Mr. Y. Takase and Dr. H. Suzuki of the Analytical Center of our university for NMR and MS measurements.

References and Notes

1) Norman J., "The Complete Book of Spices," Dorling Kindersley, 1990, p. 32.
2) British Pharmacopoeia 1, The Stationery Office, 1999, pp. 466—467.
3) European Pharmacopoeia, 3rd edition, Council of Europe Publishing, 1997, p. 672.
4) "Herbal Drugs and Phytopharmaceuticals," ed. by Wichtl M., CRC Press, Stuttgart, 1994, pp. 159—160.
5) Ishikawa T., Kudo M., Kitajima J., *Chem. Pharm. Bull.*, **50**, 501—507 (2002).
6) Klyne W., "Determination of Organic Structure by Physical Methods," ed. by Braude E. A., Nachod F. C., Academic Press, New York, 1975, p. 73.
7) Klyne W., *Biochem. J.*, **47**, XIi—XIii (1950).
8) Uchiyama T., Miyase T., Ueno A., Usmanghani K., *Phytochemistry*, **28**, 3369—3372 (1989).
9) Enzymatic hydrolysis of **2** proceeded with cellulase, but **2** was not hydrolyzed with β-glucosidase, hesperidinase, and naringinase.
10) Kitagawa I., Kobayashi M., Sugawara T., *Chem. Pharm. Bull.*, **26**, 1582—1863 (1978).
11) Schneider J. J., Lewbart M. L., *J. Biol. Chem.*, **222**, 787—794 (1966).
12) Kitajima J., Tanaka Y., *Chem. Pharm. Bull.*, **41**, 1667—1669 (1993).
13) Kitajima J., Aoki Y., Ishikawa T., Tanaka Y., *Chem. Pharm. Bull.*, **47**, 639—642 (1993).
14) Vidari G., Giori A., Dapiaggi A., Lanfranchi G., *Tetrahedron Lett.*, **1993**, 6925—6928 (1993).
15) Enzymatic hydrolysis of **8** proceeded with naringinase, but **8** was not hydrolyzed with β-glucosidase, hesperidinase, and cellulase.
16) Kitajima J., Okamura C., Ishikawa T., Tanaka Y., *Chem. Pharm. Bull.*, **46**, 1404—1407 (1998).
17) Orihara Y., Noguchi T., Furuya T., *Phytochemistry*, **35**, 941—945 (1994).
18) Hulyalkar R. K., Jones J. K. N., Perry M. B., *Can. J. Chem.*, **43**, 2085—2091 (1965).

19) Umehara K., Hattori I., Miyase T., Ueno A., Hara S., Kageyama C., *Chem. Pharm. Bull.*, **36**, 5004—5008 (1988).
20) Miyase T., Ueno A., Takizawa N., Kobayashi H., Karasawa H., *Chem. Pharm. Bull.*, **35**, 1109—1117 (1987).
21) Kitajima J., Ishikawa T., Tanaka Y., Ono M., Ito Y., Nohara T., *Chem. Pharm. Bull.*, **46**, 1587—1590 (1998).
22) Miyase T., Ueno A., Takizawa N., Kobayashi H., Oguchi H., *Chem. Pharm. Bull.*, **35**, 3713—3719 (1987).
23) Otsuka H., Takeuchi M., Inoshiri S., Sato T., Yamasaki K., *Phytochemistry*, **28**, 883—886 (1989).
24) Taniguchi M., Yanai M., Xiao Y. Q., Kido T., Baba K., *Phytochemistry*, **42**, 843—846 (1996).
25) Commercial (*R*)-1′-phenylethane-1′,2′-diol (purchased from Aldrich Chemical Co.) showed positive optical rotation ($[\alpha]_D^{22}$ +45° (MeOH) for the *S*-form; $[\alpha]_D^{22}$ −45° (MeOH) for the *R*-form).
26) Landor S. R., Miller B. J., Tatchell A. R., *J. Chem. Soc.*, 2280—2282 (1966).
27) Zoorob H. H., *Ind. J. Chem.*, **24B**, 1218—1220 (1985).
28) Kitajima J., Ishikawa T., Tanaka Y., *Chem. Pharm. Bull.*, **46**, 1643—1646 (1998).
29) Green J. W., Pacsu E., *J. Am. Chem. Soc.*, **60**, 2056—2057 (1938).
30) Agrawal P. K., *Phytochemistry*, **31**, 3307—3330 (1992).