Water-Soluble Constituents of Anise: New Glucosides of Anethole Glycol and Its Related Compounds

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From the water-soluble portion of the methanolic extract of the fruit of anise (*Pimpinella anisum* L.), which has been used as a spice and medicine since antiquity, twelve new and five known glucosides of phenylpropanoids, including four stereoisomers of anethole glycol 2′-*O*-*β*-D-glucopyranoside and four stereoisomers of 1′-(4-hydroxyphenyl)propane-1′,2′-diol 2′-*O*-*β*-D-glucopyranoside were isolated together with anethole glycols and guaiacyl glycerol. The structures of the new compounds were clarified by spectral investigation.

Key words anise; *Pimpinella anisum* fruit; anethole glycol glucoside; 1′-(4-hydroxyphenyl)propane-1′,2′-diol glucoside; phenylpropanoid glucoside; stereoisomer

Anise [*Pimpinella anisum* L.; Umbelliferae] has been used as a popular aromatic herb and spice since antiquity, and is cultivated throughout Europe.[1,2] Its fruit has been used for medicine and in cooking, and is listed in British, German and European pharmacopoeia.[2—4] For medicinal purposes, it is used to treat dyspeptic complaints and catarrh of the respiratory tract, and also as a mild expectorant.[1,2] Studies on the fruit were made on the essential oil (1.5—5%), and *trans*-anethole (80—90%) is chiefly responsible for the taste and smell. Also, *cis*-anethole, estragole, *p*-anisaldehyde, aniseketone, linalool and *β*-farnesene were reported as the constituents.[5—7] However, no report has been published concerning the water-soluble portion of this fruit. In continuation of our studies on the water-soluble constituents of spices,[8] and to learn the relationship between the essential oil and the water-soluble constituents, we undertook a detailed investigation of the constituents of this fruit. In this paper, we discuss the isolation and the characterization of twelve new glycosides of phenylpropanoid related to anethole.

Commercial anise 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 subjected to a combination of silica gel, Lobar RP-8 column chromatography and HPLC to isolate phenylpropanoids (**1**, **2** and **13**) and their glucosides (**3** to **12** and **14** to **20**). Among the glucosides, **5** to **9**, **11**, **12**, **14** to **17** and **20** are new. All new glucosides described in this paper were *β*-D-glucopyranosides as shown by their ^{13}C-NMR data (Table 2), and this was confirmed by hydrolysis to yield D-glucose or by a comparison of the $[\alpha]_D$ or $[M]_D$ values with those of their aglycones except **8**, **9** and **18**.[9,10] Their molecular formulae were suggested from the accurate mass number of $[M+H]^+$ or $[M+Na]^+$ or $[M+K]^+$ ion peaks in the high-resolution positive FAB-MS.

Phenylpropanoid **1** ($C_{10}H_{14}O_3$, mp 115—117 °C, $[\alpha]_D^{21}$ ±0°) and **2** ($C_{10}H_{14}O_3$, mp 62—63 °C, $[\alpha]_D^{21}$ ±0°), glucoside **3** ($C_{16}H_{24}O_8$, mp 84—85 °C, $[\alpha]_D^{23}$ −29°) and **4** ($C_{16}H_{24}O_8$, mp 125—127 °C, $[\alpha]_D^{23}$ −15°) were identified as *erythro*-anethole, *threo*-anethole glycol,[11] (1′*R*,2′*S*)-anethole glycol 2′-*O*-*β*-D-glucopyranoside and (1′*S*,2′*R*)-anethole glycol 2′-*O*-*β*-D-glucopyranoside,[12] respectively.

Glucosides **5** ($C_{16}H_{24}O_8$, mp 80—84 °C, $[\alpha]_D^{22}$ −59°) and **6** ($C_{16}H_{24}O_8$, mp 75—78 °C, $[\alpha]_D^{22}$ +11°) showed $[M+Na]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m*/*z* 367 and 165 in the positive FAB-MS. Both glucosides were hydrolyzed with *β*-glucosidase and, from the hydrolyzed mixtures, (−)-*threo*-anethole glycol (**2a**; $C_{10}H_{14}O_3$, mp 62—63 °C, $[\alpha]_D^{22}$ −23°) and D-glucose from **5**, and (+)-*threo*-anethole glycol (**2b**; $C_{10}H_{14}O_3$, mp 62—63 °C, $[\alpha]_D^{22}$ +25°) and D-glucose from **6** were obtained. The ^{1}H- and ^{13}C-NMR chemical shifts (Tables 1, 2) of **5** and **6** showed that both compounds were monoglucopyranosides of **2**, and the position of the *β*-glucosyl units was proved to be C-2′ from the cross-peaks between the glucosyl H-1/C-2′ in the heteronuclear multiple bond connectivity (HMBC) spectrum. Thus, **5** and **6** were represented as (−)- and (+)-*threo*-anethole glycol 2′-*O*-*β*-D-glucopyranoside. As the 1*R*′,2*R*′ form of *threo*-anethole glycol was reported to have a negative $[\alpha]_D$ value, and the 1*S*′,2*S*′ form of *threo*-anethole glycol had a positive $[\alpha]_D$ value,[13] the absolute stereochemistry of C-1′ and C-2′ of (−)-*threo*-anethole glycol should be *R*, and that of (+)-*threo*-anethole glycol should be *S*. Furthermore, the absolute configurations at C-2′ of **5** and **6** were confirmed to be *R* and *S* by the values of the glycosylation shift of the *α*-carbon (**5**; +8.5 ppm, **6**; +11.1 ppm), and the chemical shifts of the glucosyl aromatic carbon (**5**; *δ* 103.53, **6**; *δ* 106.36).[12,14—19] Therefore, **5** and **6** were characterized as (1′*R*,2′*R*)-anethole glycol 2′-*O*-*β*-D-glucopyranoside and (1′*S*,2′*S*)-anethole glycol 2′-*O*-*β*-D-glucopyranoside, respectively.

Glucoside **7** ($C_{15}H_{22}O_8$, an amorphous powder, $[\alpha]_D^{22}$ −38°) showed one peak on HPLC, but it was suggested to be an equivalent mixture of two diastereomeric compounds from NMR spectral data (Tables 1, 2). Its positive FAB-MS revealed $[M+Na]^+$, $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m*/*z* 353, 331 and 151, and its ^{1}H- and ^{13}C-NMR data suggested that **7** was built up with one *β*-glucopyranosyl group and one 1′-(4-hydroxyphenyl)propane-1′,2′-diol moiety. Enzymatic hydrolysis of **7** gave D-glucose and an aglycone (**21**; $C_9H_{12}O_3$, an amorphous powder, $[\alpha]_D^{22}$ ±0°) which was characterized as 1′-(4-hydroxyphenyl)propane-1′,2′-diol, and the position of the *β*-glucosyl unit was proved to be C-4 from the HMBC correlation of the glucosyl H-1/C-4. By

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comparison of the H-1′, H-2′, H-3′ and C-1′, C-2′, C-3′ chemical shifts with those of **1** and **2** (Tables 1, 2), **7** was suggested to be an *erythro* form as **1**. Therefore, **7** is an equivalent mixture of two stereoisomeric *erythro*-1′-(4-hydroxyphenyl)propane-1′,2′-diol 4-*O*-*β*-D-glucopyranosides.

Glucosides **8** ($C_{15}H_{22}O_8$, an amorphous powder, $[\alpha]_D^{21}$ −33°) and **9** ($C_{15}H_{22}O_8$, an amorphous powder, $[\alpha]_D^{21}$ −16°) showed $[M+Na]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 353 and 151 in the positive FAB-MS. The ^{1}H- and ^{13}C-NMR spectral data (Tables 1, 2) and the results of HMBC experiment showed that they were 2′-*O*-*β*-glucopyranoside of 1′-(4-hydroxyphenyl)propane-1′,2′-diol. The stereochemical relation between C-1′ and C-2′ of the two compounds was deduced from comparison of their ^{1}H- and ^{13}C-NMR spectra with those of stereoisomeric pairs of anethole glycol (**3** to **6**; Tables 1, 2). As the chemical shifts of the aglycone parts (H-2,6, H-1′, H-2′, H_2-3′, C-1, C-2,6, C-1′, C-2′, C-3′) of **8** showed good similarity with those of **3**, and **9** revealed similarity with those of **4**, **8** was suggested to be an *erythro* form with the 1′*R*,2′*S* configuration [(−) form] and **9** was indicated to be an *erythro* form with the 1′*S*,2′*R* configuration [(+) form], respectively. This was also supported by their $[M]_D$ values (**8**; −109°, **9**; −53°), which showed minus and plus $\Delta[M]_D$ values when calculated using {$[M]_D$−methyl *β*-D-glucopyranoside (−62°)} [$\Delta[M]_D$ (**8**; Δ−47°, **9**; Δ+9°)].[9,10] Therefore, **8** and **9** were characterized as (1′*R*,2′*S*)-1′-(4-hydroxyphenyl)propane-1′,2′-diol 2′-*O*-*β*-D-glucopyranoside and (1′*S*,2′*R*)-1′-(4-hydroxyphenyl)propane-1′,2′-diol 2′-*O*-*β*-D-glucopyranoside, respectively.

Glucoside **10** ($C_{15}H_{22}O_8$, an amorphous powder, $[\alpha]_D^{23}$ −49°) was identified as an equivalent mixture of two stereoisomeric *threo*-1′-(4-hydroxyphenyl)propane-1′,2′-diol 4-*O*-*β*-D-glucopyranosides which has been reported as a constituent of fennel.[12]

Glucosides **11** ($C_{15}H_{22}O_8$, an amorphous powder, $[\alpha]_D^{22}$ −51°) and **12** ($C_{15}H_{22}O_8$, an amorphous powder, $[\alpha]_D^{22}$ +21°) were also *β*-glucopyranosides of 1′-(4-hydroxyphenyl)-propane-1′,2′-diol and, hydrolyzed with *β*-glucosidase gave the (−)-form and the (+)-form of 1′-(4-hydroxyphenyl)-propane-1′,2′-diol [**22a** ($C_9H_{12}O_3$, an amorphous powder, $[\alpha]_D^{22}$ −19°) and **22b** ($C_9H_{12}O_3$, an amorphous powder, $[\alpha]_D^{22}$ +19°)], respectively, together with D-glucose. The position of the *β*-glucosyl units was proved to be C-2′ from the HMBC correlation of the glucosyl H-1/C-2′ signals. The stereochemical relation between C-1′ and C-2′ of **11** and **12** was revealed by comparison of their ^{1}H- and ^{13}C-NMR spectra with those of stereoisomeric pairs of anethole glycol (**3** to **6**; Tables 1, 2) in the same way as described for **8** and **9**. As the chemical shifts of the aglycone parts of **11** and **12** showed good similarity with those of **5** and **6**, they were suggested to be glucosides of *threo*-1′-(4-hydroxyphenyl)-propane-1′,2′-diol with the 1′*R*,2′*R* configuration [(−) form] for **11** and the 1′*S*,2′*S* configuration [(+) form] for **12**. Therefore, **11** and **12** were characterized as (1′*R*,2′*R*)-1′-(4-hydroxyphenyl)propane-1′,2′-diol 2′-*O*-*β*-D-glucopyranoside and (1′*S*,2′*S*)-1′-(4-hydroxyphenyl)propane-1′,2′-diol 2′-*O*-*β*-D-glucopyranoside, respectively.

Consequently, we have isolated all four anethole glycol 2′-*O*-*β*-D-glucopyranosides and all four 1′-(4-hydroxyphenyl)-propane 2′-*O*-*β*-D-glucopyranosides from the fruit of anise.

Phenylpropanoid **13** ($C_{10}H_{14}O_5$, an amorphous powder, $[\alpha]_D^{25}$ −26°) was identified as (1′*R*,2′*R*)-guaiacyl glycerol which has been isolated from *Zantedeschia aethiopica*.[20]

Glucosides **14** ($C_{16}H_{24}O_{10}$, an amorphous powder, $[\alpha]_D^{21}$ −50°) and **15** ($C_{16}H_{24}O_{10}$, an amorphous powder, $[\alpha]_D^{22}$ −13°) showed $[M+K]^+$, $[M+Na]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 415, 399 and 197 in the positive FAB-MS, respectively. Both glucosides were hydrolyzed with *β*-glucosidase, and the same aglycone was obtained, which was identical to **13**, together with D-glucose. The position of the *β*-glucosyl unit was proved to be C-4 for **14**, and C-3′ for **15**, from the HMBC correlations of the glucosyl H-1/C-4 and glucosyl H-1/C-3′ of their HMBC spectra. Their ^{13}C-NMR data suggested that they were *β*-glucopyranosides, and **14** and **15** were characterized as (1′*R*,2′*R*)-guaiacyl glycerol 4-*O*-*β*-D-glucopyranoside and (1′*R*,2′*R*)-guaiacyl glycerol 3′-*O*-*β*-D-glucopyranoside, respectively.

Glucoside **16** ($C_{16}H_{24}O_{10}$, an amorphous powder, $[\alpha]_D^{22}$ −20°) showed $[M+K]^+$, $[M+Na]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 415, 399 and 197 in the positive FAB-MS. The ^{1}H- and ^{13}C-NMR spectral data (Tables 1, 2) for **16** showed good similarity to those of **15**, but obvious differences were seen in the chemical shifts of H-1′, H-2′, H_2-3′ and C-1′, C-2′, C-3′. So, **16** was considered to be an *erythro* form of **15**, and the results of HMBC experiment supported this conclusion. Enzymatic hydrolysis of **16** gave an aglycone (**23**; $C_{10}H_{14}O_5$, an amorphous powder, $[\alpha]_D^{22}$ +11°) and D-glucose, and aglycone **23** was suggested to be an *erythro* form by comparison of the chemical shifts of H-1′, H-2′ and H_2-3 with **13**.[21] The positive $[\alpha]_D$ value suggested that **23** has the 1′*S*,2′*R* configuration as **4** [1′*S*,2′*R*; (+) form]. So, **16** was characterized as (1′*S*,2′*R*)-guaiacyl glycerol 3′-*O*-*β*-D-glucopyranoside.

Glucoside **17** ($C_{17}H_{26}O_{10}$, an amorphous powder, $[\alpha]_D^{22}$ −15°) showed $[M+K]^+$, $[M+Na]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 429, 413 and 211 in the positive FAB-MS. Enzymatic hydrolysis of **17** gave an aglycone (**24**; $C_{11}H_{16}O_5$, mp 86—88 °C, $[\alpha]_D^{24}$ −24°) and D-glucose. As the ^{1}H- and ^{13}C-NMR spectra of **17** (Tables 1, 2) showed good similarity with those of **15** except for having one more methoxyl proton and a carbon signal, **17** was indicated to be a mono-methylate of **15**. It was supported by the observed cross-peak between the methoxyl group proton and the C-4 carbon of the benzene ring in its HMBC spectrum. The cross-peak between the glucosyl H-1 and C-3′ carbon in the HMBC spectrum, and comparison of the chemical shifts and the coupling constants of H-1′, H-2′, H_2-3′, and chemical shifts of C-1′, C-2′, C-3′ between **24** and **13** (Tables 1, 2) also supported this conclusion. Therefore, **17** was characterized as (1′*R*,2′*R*)-4-*O*-methylguaiacyl glycerol 3′-*O*-*β*-D-glucopyranoside. Glucoside **18** ($C_{17}H_{26}O_{10}$, an amorphous powder, $[\alpha]_D^{22}$ −33°) was identified as 4-*O*-methylguaiacyl glycerol 2′-*O*-*β*-D-glucopyranoside which was isolated from the aerial parts of *Chrozophora obliqua*.[22] However, the absolute configuration of the aglycone of **18** could not be assigned.

Glucoside **19** ($C_{15}H_{20}O_7$, an amorphous powder, $[\alpha]_D^{22}$ −56°) was identified as (*E*)-4-hydroxycinnamyl alcohol 4-*O*-*β*-D-glucopyranoside, which was isolated from the leaves of *Lilium cordatum*.[23] Glucoside **20** ($C_{15}H_{20}O_7$, an amorphous powder, $[\alpha]_D^{22}$ −63°) showed $[M+Na]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 335 and 133 in the positive FAB-MS, and its ^{1}H- and ^{13}C-NMR spectra (Tables 1, 2) showed simi-

Table 1. ^{1}H-NMR Chemical Shifts of **1**—**24** (in Pyridine-d_5, 270[a] and 500 MHz)

	1[a]	**2**[a]	**3**	**4**
H-2,6	7.72 d (8.5)	7.63 d (8.5)	7.68 d (8.5)	7.64 d (8.5)
H-3,5	7.03 d (8.5)	7.03 d (8.5)	7.02 d (8.5)	6.99 d (8.5)
H-1′	5.08 d (5.0)	4.84 d (7.0)	5.35 d (3.0)	5.43 d (3.0)
H-2′	4.40 dq (5.0, 6.0)	4.28 dq (6.0, 7.0)	4.52 dq (3.0, 6.5)	4.49 dq (3.0, 6.5)
H_3-3′	1.54 d (6.0)	1.32 d (6.0)	1.37 d (6.5)	1.36 d (6.5)
OCH_3	3.68 s	3.68 s	3.66 s	3.67 s
Glc H-1	—	—	5.28 d (7.5)	5.08 d (7.5)

	5	**6**	**7**[b]	
H-2,6	7.59 d (8.5)	7.62 d (8.5)	7.70 d (8.5)	[7.70 d (8.5)]
H-3,5	6.99 d (8.5)	7.02 d (8.5)	7.42 d (8.5)	[7.42 d (8.5)]
H-1′	5.02 d (7.0)	4.95 d (8.0)	5.06 d (4.5)	[5.05 d (4.5)]
H-2′	4.42 dq (6.5, 7.0)	4.30 dq (6.5, 8.0)	4.38 dq (4.5, 6.0)	[4.38 dq (4.5, 6.0)]
H_3-3′	1.22 d (6.5)	1.25 d (6.5)	1.51 d (6.0)	[1.51 d (6.0)]
OCH_3	3.67 s	3.67 s	—	—
Glc H-1	5.09 d (8.0)	5.34 d (8.0)	5.63 d (7.5)	[5.63 d (7.5)]

	8	**9**	**21**[a]	**22**[a]
H-2,6	7.67 d (8.5)	7.63 d (8.5)	7.73 d (8.5)	7.64 d (8.5)
H-3,5	7.22 d (8.5)	7.20 d (8.5)	7.25 d (8.5)	7.25 d (8.5)
H-1′	5.35 d (3.0)	5.43 d (3.0)	5.10 d (4.5)	4.84 d (7.0)
H-2′	4.53 dq (3.0, 6.5)	4.51 dq (3.0, 6.5)	4.45 dq (4.5, 6.5)	4.30 dq (6.5, 7.0)
H_3-3′	1.40 d (6.5)	1.38 d (6.5)	1.57 d (6.5)	1.35 d (6.5)
Glc H-1	5.28 d (7.5)	5.07 d (7.5)	—	—

	10[b]		**11**	**12**
H-2,6	7.61 d (8.5)	[7.61 d (8.5)]	7.58 d (8.5)	7.60 d (8.5)
H-3,5	7.42 d (8.5)	[7.42 d (8.5)]	7.19 d (8.5)	7.23 d (8.5)
H-1′	4.82 d (7.0)	[4.82 d (7.0)]	5.02 d (7.0)	4.94 d (8.0)
H-2′	4.25 m	[4.25 m]	4.44 dq (6.5, 7.0)	4.31 dq (6.5, 8.0)
H_3-3′	1.29 d (6.5)	[1.30 d (6.5)]	1.25 d (6.5)	1.29 d (6.5)
Glc H-1	5.64 d (7.5)	[5.65 d (7.5)]	5.11 d (7.5)	5.36 d (8.0)

	13	**14**	**15**	**23**
H-2	7.50 d (1.5)	7.53 d (1.5)	7.56 d (1.5)	7.53 d (1.5)
H-5	7.25 d (8.0)	7.58 d (8.5)	7.25 d (8.0)	7.26 d (8.0)
H-6	7.33 dd (1.5, 8.0)	7.29 dd (1.5, 8.5)	7.38 dd (1.5, 8.0)	7.38 dd (1.5, 8.0)
H-1′	5.33 d (6.0)	5.32 d (5.5)	5.37 d (6.0)	5.40 d (6.0)
H-2′	4.43 ddd (4.5, 6.0, 6.0)	4.38 ddd (4.5, 5.5, 6.0)	4.50 ddd (4.0, 6.0, 6.0)	4.53 ddd (5.0, 6.0, 6.0)
H-3′a	4.11 dd (6.0, 11.0)	4.10 dd (6.0, 11.0)	4.03 dd (6.0, 10.5)	4.43 dd (6.0, 10.5)
H-3′b	4.25 dd (4.5, 11.0)	4.24 dd (4.5, 11.0)	4.60 dd (4.0, 10.5)	4.45 dd (5.0, 10.5)
3-OCH_3	3.70 s	3.67 s	3.74 s	3.69 s
Glc H-1	—	5.65 d (7.5)	4.97 d (7.5)	—

	16	**24**	**17**	**18**
H-2	7.48 d (1.5)	7.49 d (2.0)	7.54 d (1.5)	7.47 d (1.5)
H-5	7.23 d (8.0)	6.96 d (8.0)	6.95 d (8.0)	6.93 d (8.5)
H-6	7.33 dd (1.5, 8.0)	7.35 dd (2.0, 8.0)	7.40 dd (1.5, 8.0)	7.28 dd (1.5. 8.5)
H-1′	5.29 d (6.5)	5.35 d (6.0)	5.39 d (5.5)	5.30 d (7.5)
H-2′	4.62 ddd (3.0, 6.5, 6.5)	4.41 ddd (4.5, 6.0, 6.0)	4.48 ddd (4.0, 5.5, 5.5)	4.56 ddd (3.0, 7.5, 7.5)
H-3′a	4.41 dd (6.5, 10.5)	4.11 dd (6.0, 11.0)	4.03 dd (5.5, 10.5)	3.94 dd (7.5, 10.0)
H-3′b	4.78 dd (3.0, 10.5)	4.25 dd (4.5, 11.0)	4.60 dd (4.0, 10.5)	4.06 dd (3.0, 10.0)
3-OCH_3	3.68 s	3.70 s	3.74 s	3.69 s
4-OCH_3	—	3.75 s	3.74 s	3.74 s
Glc H-1	5.09 d (8.0)	—	4.98 d (8.0)	5.33 d (8.0)

	19	**20**
H-2,6	7.44 d (8.5)	7.32 d (9.0)
H-3,5	7.35 d (8.5)	7.35 d (9.0)
H-1′	6.86 dt (1.5, 16.0)	6.55 dt (1.5, 12.0)
H-2′	6.54 dt (5.0, 16.0)	6.18 dt (6.0, 12.0)
H_2-3′	4.55 dt (1.5, 5.0)	4.75 dt (1.5, 6.0)
Glc H-1	5.65 d (7.5)	5.65 d (7.5)

δ in ppm from TMS [coupling constants (J) in Hz are given in parentheses]. *b*) Stereoisomeric components are given in brackets.

Table 2. ^{13}C-NMR Chemical Shifts of **1**—**24** (in Pyridine-d_5, 67.5[a] and 125 MHz)

	1[a]	**2**[a]	**3**	**4**	**5**	**6**
C-1	136.61	136.17	134.92 (−1.7)	135.36 (−1.3)	134.78 (−1.4)	134.43 (−1.7)
C-2,6	128.78	128.91	128.61	128.47	129.28	129.22
C-3,5	113.77	113.92	113.88	113.76	113.88	114.03
C-4	159.15	159.40	159.18	159.05	159.53	159.65
C-1′	78.09	79.19	74.77 (−3.3)	75.73 (−2.4)	77.28 (−1.9)	78.77 (−0.4)
C-2′	72.12	72.49	80.64 (+8.5)	80.42 (+8.3)	81.00 (+8.5)	83.59 (+11.1)
C-3′	18.98	19.70	16.25 (−2.7)	14.15 (−4.8)	16.90 (−2.8)	18.63 (−1.1)
OCH_3	55.14	55.14	55.13	55.13	55.15	55.16
Glc-1			104.24	103.82	103.53	106.36
Glc-2			75.78	75.10	74.91	75.92
Glc-3			78.79	78.59	78.55	78.73
Glc-4			71.64	71.86	71.71	71.64
Glc-5			78.58	78.53	78.72	78.73
Glc-6			62.78	62.88	62.73	62.79

	7[b]		**8**	**9**	**21**[a]
C-1	138.00	[138.00]	133.24 (−1.7)	133.66 (−1.3)	134.97
C-2,6	128.77	[128.77]	128.83	128.69	129.02
C-3,5	116.39	[116.38]	115.83	115.71	115.75
C-4	157.73	[157.73]	158.01	157.86	157.98
C-1′	78.04	[78.11]	75.01 (−3.3)	75.92 (−2.4)	78.31
C-2′	72.06	[72.09]	80.86 (+8.7)	80.47 (+8.3)	72.19
C-3′	18.95	[18.90]	16.33 (−2.7)	14.16 (−4.8)	18.99
Glc-1	102.40	[102.40]	104.30	103.74	
Glc-2	75.00	[75.00]	75.80	75.10	
Glc-3	78.81	[78.81]	78.74	78.56	
Glc-4	71.25	[71.25]	71.66	71.87	
Glc-5	78.54	[78.54]	78.56	78.51	
Glc-6	62.31	[62.31]	62.79	62.87	

	10[b]		**11**	**12**	**22**[a]	**19**	**20**
C-1	137.56	[137.61]	133.15 (−1.5)	132.81 (−1.8)	134.62	131.87	131.39
C-2,6	128.90	[128.90]	129.50	129.42	129.14	127.91	130.62
C-3,5	116.47	[116.52]	115.87	116.01	115.90	117.11	116.69
C-4	157.94	[157.96]	158.43	158.56	158.30	157.99	157.64
C-1′	79.16	[79.08]	77.61 (−1.9)	79.17 (−0.4)	79.55	129.00	128.98
C-2′	72.42	[72.42]	81.15 (+8.5)	83.90 (+11.3)	72.63	129.84	133.18
C-3′	19.68	[19.70]	17.07 (−2.7)	18.80 (−4.8)	19.78	62.95	59.41
Glc-1	102.33	[102.33]	103.50	106.49		102.13	102.09
Glc-2	75.00	[75.00]	74.88	75.96		74.96	74.95
Glc-3	78.55	[78.55]	78.56	78.74		78.53	78.53
Glc-4	71.27	[71.27]	71.72	71.62		71.26	71.29
Glc-5	78.85	[78.85]	78.75	78.74		78.93	78.96
Glc-6	62.33	[62.32]	62.74	62.78		62.35	62.38

	13	**14**	**15**	**23**	**16**	**24**	**17**	**18**
C-1	135.43	138.47 (+3.0)	135.02	135.52	135.41	137.34	136.94	134.90
C-2	111.72	112.08	111.78	111.83	111.95	111.81	111.89	111.94
C-3	148.51	149.79 (+1.3)	148.33	148.43	148.40	149.83	149.72	149.88
C-4	147.34	147.03 (−0.3)	147.21	147.34	147.30	149.12	149.02	149.43
C-5	116.09	115.84	116.03	116.02	116.00	112.30	112.26	112.14
C-6	120.49	119.92	120.30	120.70	120.79	119.85	119.70	120.28
C-1′	74.89	74.56	74.40	76.17	75.40	74.71	74.20	74.19
C-2′	77.85	77.63	76.09 (−1.8)	76.52	75.81 (−0.7)	77.76	76.01 (−1.8)	88.09
C-3′	64.34	64.26	72.27 (+7.9)	64.31	73.28 (+9.0)	64.37	72.23 (+7.9)	62.66
3-OCH_3	55.80	55.77	55.81	55.76	55.80	55.77	55.82	55.78
4-OCH_3						56.01	55.94	55.93
Glc-1		102.38	105.41		105.87		105.49	105.35
Glc-2		74.85	75.22		75.48		75.28	75.60
Glc-3		78.46	78.38		78.56		78.48	78.45
Glc-4		71.17	71.51		71.63		71.61	71.63
Glc-5		78.71	78.42		78.56		78.53	78.79
Glc-6		62.26	62.52		62.65		62.63	62.61

δ in ppm from TMS. $\Delta\delta$ ($\delta_{glucoside} - \delta_{aglycone}$) are given in parentheses. *b*) Stereoisomeric components are given in brackets.

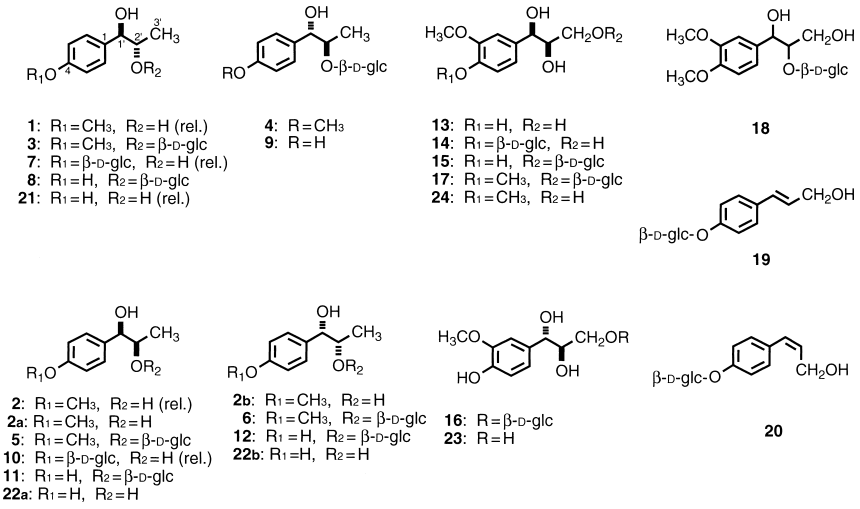

Fig. 1. Structures of **1**—**24**, **2a**, **2b**, **22a** and **22b**

larity with those of **19**. The structure of **20** was confirmed to be 4-hydroxycinnamyl 4-*O*-*β*-D-glucopyranoside by comparison of the results of the HMBC experiment with those of **19**, and the stereochemistry of the propenyl double bond was suggested to be *Z* by the value of the coupling constant between H-1′ and H-2′ (J=12.0 Hz).[24] Therefore, **20** was characterized as (*Z*)-4-hydroxycinnamyl alcohol 4-*O*-*β*-D-glucopyranoside.

The ingredient relationship between the essential oil and the water-soluble constituent was confirmed by the isolation of these anethole glycol glucosides. It is worthy of note that, in anise fruit, oxidation of the propenyl double bond of anethole may proceed by a non-stereospecific route.

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 taken on JEOL JNM GX-270 and A-500 spectrometers with tetramethylsilane as an internal standard, and chemical shifts were recorded in δ value. ^{1}H–^{13}C correlation spectroscopy (COSY), HMBC and nuclear Overhauser effect spectroscopy (NOESY) spectra were obtained with the usual pulse sequence, and data processing was performed with standard JEOL software. Column chromatography (C. C.) was carried out under TLC monitoring using Kieselgel 60 (70—230 mesh, Merck), Sephadex LH-20 (25—100 μm, Pharmacia), 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 a JASCO chromatograph (980-system) with a JASCO RI-930 detector, and Symmetryprep C18 7 μm [Waters; column size, 7.8×300 mm; ODS], Carbohydrate analysis [Waters; column size, 3.9×300 mm; CHA] were used as columns.

Extraction and Isolation Commercial anise (the fruit of *Pimpinella anisum* L.; purchased from Asaoka Spices, Ltd., Lot. No. 99012001; 2.0 kg) was extracted with 70% methanol (5 l×4) at room temperature for two weeks. After evaporation of the solvent, the residue (346.7 g) was partitioned into ether–water and ethyl acetate–water. Removal of the solvent from each phase gave the ether (145.3 g), ethyl acetate (7.5 g) and aqueous (193.9 g) extract. The aqueous extract was chromatographed over Amberlite XAD-II (H_2O→MeOH). The methanol eluate (52.1 g) was subjected to Sephadex LH-20 (MeOH) to give six fractions (frs. A—F). Fraction B (40.9 g) was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (17 : 3 : 0.2→4 : 1 : 0.1→15 : 5 : 0.4→7 : 3 : 0.5)→MeOH] to give thirteen fractions (frs. B_1—B_{13}). Fraction B_2 (0.83 g) was subjected to a Lobar RP-8 column [MeCN–H_2O (3 : 17)] and HPLC [ODS; MeCN–H_2O (9 : 11)] to give **1** (43 mg) and **2** (103 mg). Fraction B_6 (0.91 g) was subjected to a Lobar RP-8 column [MeCN–H_2O (3 : 17)], HPLC [CHA; MeCN–H_2O (97 : 3)] and silica gel column chromatography to give **13** (4 mg). Fraction B_7 (1.15 g) was also subjected to a Lobar RP-8 column [MeCN–H_2O (3 : 17)] and HPLC [ODS, MeCN–H_2O (3 : 37) and CHA; MeCN–H_2O (24 : 1)] to give **3** (18 mg), **4** (9 mg), **5** (8 mg) and **6** (4 mg). Fraction B_9 (1.81 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give eighteen fractions (frs. $B_{9\text{-}1}$—$B_{9\text{-}18}$) and fr. $B_{9\text{-}4}$ was subjected to Sephadex LH-20 (MeOH) and HPLC [CHA; MeCN–H_2O (14 : 1)] to give **18** (1 mg). Fraction B_{10} (7.29 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give ten fractions (frs. $B_{10\text{-}1}$—$B_{10\text{-}10}$) and fr. $B_{10\text{-}2}$ was subjected to a combination of HPLC [ODS; MeCN–H_2O (1 : 19) and CHA; MeCN–H_2O (14 : 1) to give **11** (8 mg), **12** (10 mg), **8** (1 mg) and **9** (3 mg), respectively. Fraction $B_{10\text{-}3}$ was passed through HPLC [ODS; MeCN–H_2O (3 : 37)] to give **17** (68 mg), **19** (283 mg) and fr. $B_{10\text{-}3c}$. Fraction $B_{10\text{-}3c}$ was passed through HPLC [CHA; MeCN–H_2O (14 : 1)] to give **20** (3 mg). Fraction B_{11} (4.37 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give ten fractions (frs. $B_{11\text{-}1}$—$B_{11\text{-}10}$) and fr. $B_{10\text{-}3}$ was subjected to HPLC [ODS; MeCN–H_2O (3 : 197)] to give **7** (12 mg), **16** (9 mg), **10** (54 mg) and **15** (73 mg), respectively. A part of the water eluate fraction (50.4 g) was subjected to Sephadex LH-20 (MeOH) to give three fractions (frs. G—I). Fraction H (41.5 g) was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1→15 : 5 : 0.4→7 : 3 : 0.5→6 : 4 : 1→1 : 1 : 0.1→4 : 6 : 0.5)→MeOH] to give twenty fractions (frs. H_1—H_{20}). Fraction H_{13} (4.68 g) was subjected to Lobar RP-8 column (H_2O) to give ten fractions (frs. $H_{3\text{-}1}$—$H_{3\text{-}10}$), and fr. $H_{13\text{-}8}$ was subjected to HPLC [CHA; MeCN–H_2O (14 : 1)] to give **14** (6 mg).

***erythro*-Anethole Glycol (1)** Colorless needles (MeOH–H_2O), mp 115—117 °C, $[\alpha]_D^{21}$ ±0° (c=1.0, $CHCl_3$). ^{1}H-NMR (pyridine-d_5, 270 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 67.5 MHz) δ: Table 2.

***threo*-Anethole Glycol (2)** Colorless needles (MeOH–H_2O), mp 62—63 °C, $[\alpha]_D^{21}$ ±0° (c=1.0, $CHCl_3$). ^{1}H-NMR (pyridine-d_5, 270 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 67.5 MHz) δ: Table 2.

(1′*R*,2′*S*)-Anethole Glycol 2′-*O*-*β*-D-Glucopyranoside (3) Colorless needles (MeOH), mp 84—85 °C, $[\alpha]_D^{23}$ −29° (c=0.3, MeOH). Positive FAB-MS *m/z*: 689 $[2M+H]^+$, 367.1367 $[M+Na]^+$, (Calcd for $C_{16}H_{24}NaO_8$; 367.1369), 327 $[M-H_2O+H]^+$, 165 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2.

(1′*S*,2′*R*)-Anethole Glycol 2′-*O*-*β*-D-Glucopyranoside (4) Colorless needles (MeOH), mp 125—127 °C, $[\alpha]_D^{23}$ −15° (c=0.5, MeOH). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2.

(1′*R*,2′*R*)-Anethole Glycol 2′-*O*-*β*-D-Glucopyranoside (5) Colorless needles (MeOH), mp 80—84 °C, $[\alpha]_D^{22}$ −59° (c=0.4, MeOH). Positive FAB-MS *m/z*: 383 $[M+K]^+$, 367.1382 $[M+Na]^+$, (Calcd for $C_{16}H_{24}NaO_8$; 367.1369), 327 $[M-H_2O+H]^+$, 165 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2. HMBC correlations: H-2/C-3, 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-5, C-1′; H-1′/C-1, C-2, C-6, C-2′; H-2′/C-1, C-1′, Glc-1; H-3′/C-1′, C-2′; O-CH_3/C-4; Glc-1/C-2′.

Enzymatic Hydrolysis of 5 A mixture of **5** (5 mg) and *β*-glucosidase (5 mg, TOYOBO CO., Lot. 93240) in water (5 ml) was shaken in a water bath at 37 °C for 2 d. The mixture was evaporated *in vacuo* to dryness and the residue was chromatographed over silica gel [$CHCl_3$–MeOH (19 : 1 and

1 : 1)] to afford **2a** (2 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, solv.; 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.

(1′*R*,2′*R*)-Anethole Glycol (2a) Colorless needles (MeOH), mp 62—63 °C, $[\alpha]_D^{22}$ −23° (*c*=0.2, MeOH). ^{1}H-NMR (pyridine-d_5, 270 MHz) δ: same as **2**. ^{13}C-NMR (pyridine-d_5, 67.5 MHz) δ: same as **2**.

(1′*S*,2′*S*)-Anethole Glycol 2′-*O*-β-D-Glucopyranoside (6) Colorless needles (MeOH), mp 75—78 °C, $[\alpha]_D^{22}$ +11° (*c*=0.3, MeOH). Positive FAB-MS *m/z*: 367.1364 [M+Na]$^+$, (Calcd for $C_{16}H_{24}NaO_8$; 367.1369), 327 [M−H_2O+H]$^+$, 165 [M−$C_6H_{12}O_6$+H]$^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2. HMBC correlations: H-2/C-3, 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-5, C-1′; H-1′/C-1, C-2, C-6, C-2′; H-2′/C-1, C-1′, Glc-1; H-3′/C-1′, C-2′; O-CH_3/C-4; Glc-1/C-2′.

Enzymatic Hydrolysis of 6 A mixture of **6** (3 mg) and β-glucosidase (3 mg) in water (5 ml) was shaken in a water bath at 37 °C for 2 d. The mixture was treated in the same way described for **5** to afford **2b** (1 mg) and a sugar fraction. From the sugar fraction, the presence of D-glucose was revealed as **5**.

(1′*S*,2′*S*)-Anethole Glycol (2b) Colorless needles (MeOH), mp 62—63 °C, $[\alpha]_D^{22}$ +25° (*c*=0.1, MeOH). ^{1}H-NMR (pyridine-d_5, 270 MHz) δ: same as **2**. ^{13}C-NMR (pyridine-d_5, 67.5 MHz) δ: same as **2**.

***erythro*-1′-(4-Hydroxyphynyl)propane-1′,2′-diol 4-*O*-β-D-Glucopyranoside (7)** An amorphous powder, $[\alpha]_D^{22}$ −38° (*c*=0.7, MeOH). Positive FAB-MS *m/z*: 353 [M+Na]$^+$, 331.1388 [M+H]$^+$ (Calcd for $C_{15}H_{23}O_8$; 331.1393), 313 [M−H_2O+H]$^+$, 151 [M−$C_6H_{12}O_6$+H]$^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2. HMBC correlations: H-2/C-3, 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-5, C-1′; H-1′/C-1, C-2, C-6, C-2′, C-3′; H-2′/C-1, C-1′, C-3′; H_3-3′/C-1′, C-2′; Glc-1/C-4.

Enzymatic Hydrolysis of 7 A mixture of **7** (8 mg) and β-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 14 d. The mixture was evaporated *in vacuo* to dryness and the residue was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (15 : 5 : 0.4) and $CHCl_3$–MeOH (1 : 1)] to afford **21** (2 mg) and a sugar fraction. From the sugar fraction, the presence of D-glucose was revealed as **5**.

***erythro*-1′-(4-Hydroxyphynyl)propane-1′,2′-diol (21)** An amorphous powder, $[\alpha]_D^{22}$ ±0° (*c*=0.2, MeOH). ^{1}H-NMR (pyridine-d_5, 270 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 67.5 MHz) δ: Table 2.

(1′*R*,2′*S*)-1′-(4-Hydroxyphynyl)propane-1′,2′-diol 2′-*O*-β-D-Glucopyranoside (8) An amorphous powder, $[\alpha]_D^{21}$ −33° (*c*=0.3, MeOH). Positive FAB-MS *m/z*: 369 [M+K]$^+$, 353.1215 [M+Na]$^+$, (Calcd for $C_{15}H_{22}NaO_8$; 353.1212), 313 [M−H_2O+H]$^+$, 151 [M−$C_6H_{12}O_6$+H]$^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: 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′, C-3′; H-2′/C-1, C-3′, Glc-1; H-3′/C-1′, C-2′; Glc-1/C-2′.

(1′*S*,2′*R*)-1′-(4-Hydroxyphynyl)propane-1′,2′-diol 2′-*O*-β-D-Glucopyranoside (9) An amorphous powder, $[\alpha]_D^{21}$ −16° (*c*=0.2, MeOH). Positive FAB-MS *m/z*: 369 [M+K]$^+$, 353.1211 [M+Na]$^+$, (Calcd for $C_{15}H_{22}NaO_8$; 353.1212), 313 [M−H_2O+H]$^+$, 151 [M−$C_6H_{12}O_6$+H]$^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: 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′, C-3′; H-2′/C-1, C-3′, Glc-1; H-3′/C-1′, C-2′; Glc-1/C-2′.

***threo*-1′-(4-Hydroxyphynyl)propane-1′,2′-diol 4-*O*-β-D-Glucopyranoside (10)** An amorphous powder, $[\alpha]_D^{23}$ −49° (*c*=0.2, MeOH). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2.

(1′*R*,2′*R*)-1′-(4-Hydroxyphynyl)propane-1′,2′-diol 2′-*O*-β-D-Glucopyranoside (11) An amorphous powder, $[\alpha]_D^{22}$ −51° (*c*=0.8, MeOH). Positive FAB-MS *m/z*: 369.0935 [M+K]$^+$ (Calcd for $C_{15}H_{22}KO_8$; 369.0951), 353 [M+Na]$^+$, 313 [M−H_2O+H]$^+$, 151 [M−$C_6H_{12}O_6$+H]$^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: 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-2, C-6, C-2′, C-3′; H-2′/C-1, Glc-1; H-3′/C-1′, C-2′; Glc-1/C-2′.

Enzymatic Hydrolysis of 11 A mixture of **11** (6 mg) and β-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 2 d. The mixture was treated in the same way described for **7** to afford **22a** (3 mg) and a sugar fraction. From the sugar fraction, the presence of D-glucose was revealed as **5**.

(1′*R*,2′*R*)-1′-(4-Hydroxyphynyl)propane-1′,2′-diol (22a) An amorphous powder, $[\alpha]_D^{22}$ −19° (*c*=0.3, MeOH). ^{1}H-NMR (pyridine-d_5, 270 MHz) δ: Table 1 (**22**). ^{13}C-NMR (pyridine-d_5, 67.5 MHz) δ: Table 2 (**22**).

(1′*S*,2′*S*)-1′-(4-Hydroxyphynyl)propane-1′,2′-diol 2′-*O*-β-D-Glucopyranoside (12) An amorphous powder, $[\alpha]_D^{22}$ +21° (*c*=1.0, MeOH). Positive FAB-MS *m/z*: 369 [M+K]$^+$, 353.1215 [M+Na]$^+$ (Calcd for $C_{15}H_{22}NaO_8$; 353.1212), 313 [M−H_2O+H]$^+$, 151 [M−$C_6H_{12}O_6$+H]$^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: 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′, C-3′; H-2′/C-1, C-1′, Glc-1; H-3′/C-1′, C-2′; Glc-1/C-2′.

Enzymatic Hydrolysis of 12 A mixture of **12** (5 mg) and β-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 2 d. The mixture was treated in the same way described for **7** to afford **22b** (3 mg) and a sugar fraction. From the sugar fraction, the presence of D-glucose was revealed as **5**.

(1′*S*,2′*S*)-1′-(4-Hydroxyphynyl)propane-1′,2′-diol (22b) An amorphous powder, $[\alpha]_D^{22}$ +19° (*c*=0.2, MeOH). ^{1}H-NMR (pyridine-d_5, 270 MHz) δ: Table 1 (**22**). ^{13}C-NMR (pyridine-d_5, 67.5 MHz) δ: Table 2 (**22**).

(1′*R*,2′*R*)-Guaiacyl Glycerol (13) An amorphous powder, $[\alpha]_D^{25}$ −26° (*c*=0.3, MeOH). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2.

(1′*R*,2′*R*)-Guaiacyl Glycerol 4-*O*-β-D-Glucopyranoside (14) An amorphous powder, $[\alpha]_D^{21}$ −50° (*c*=0.5, MeOH). Positive FAB-MS *m/z*: 415.0999 [M+K]$^+$ (base, Calcd for $C_{16}H_{24}KO_{10}$; 415.1007), 399 [M+Na]$^+$, 197 [M−$C_6H_{12}O_6$+H]$^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2. HMBC correlations: H-2/C-1, C-3, C-4, C-6, C-1′; 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′, C-3′; H-2′/C-1, C-1′, C-3′; H-3′a/C-1′, C-2′; H-3′b/C-1′, C-2′; O-CH_3/C-3; Glc-1/C-4.

Enzymatic Hydrolysis of 14 A mixture of **14** (6 mg) and β-glucosidase (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 described for **7** to afford **13** (3 mg) and a sugar fraction. From the sugar fraction, the presence of D-glucose was revealed as **5**.

(1′*R*,2′*R*)-Guaiacyl Glycerol 3′-*O*-β-D-Glucopyranoside (15) An amorphous powder, $[\alpha]_D^{22}$ −13° (*c*=1.0, MeOH). Positive FAB-MS *m/z*: 415.1019 [M+K]$^+$ (Calcd for $C_{16}H_{24}KO_{10}$; 415.1007), 399 [M+Na]$^+$ (base), 197 [M−$C_6H_{12}O_6$+H]$^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2. HMBC correlations: H-2/C-1, C-3, C-4, C-6, C-1′; 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′, C-3′; H-2′/C-1, C-1′, C-3′; H-3′a/C-1′, C-2′, Glc-1; H-3′b/C-1′, C-2′, Glc-1; O-CH_3/C-3; Glc-1/C-3′.

Enzymatic Hydrolysis of 15 A mixture of **15** (13 mg) and β-glucosidase (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 described for **7** to afford **13** (3 mg) and a sugar fraction. From the sugar fraction, the presence of D-glucose was revealed as **5**.

(1′*S*,2′*R*)-Guaiacyl Glycerol 3′-*O*-β-D-Glucopyranoside (16) An amorphous powder, $[\alpha]_D^{22}$ −20° (*c*=0.8, MeOH). Positive FAB-MS *m/z*: 415 [M+K]$^+$, 399.1281 [M+Na]$^+$ (base, Calcd for $C_{16}H_{24}NaO_{10}$; 399.1268), 197 [M−$C_6H_{12}O_6$+H]$^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2. HMBC correlations: H-2/C-1, C-3, C-4, C-6, C-1′; 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′, C-3′; H-2′/C-1, C-1′, C-3′; H-3′a/C-1′, C-2′, Glc-1; H-3′b/C-1′, C-2′, Glc-1; O-CH_3/C-3; Glc-1/C-3′.

Enzymatic Hydrolysis of 16 A mixture of **16** (8 mg) and β-glucosidase (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 described for **7** to afford **23** (5 mg) and a sugar fraction. From the sugar fraction, the presence of D-glucose was revealed as **5**.

(1′*S*,2′*R*)-Guaiacyl Glycerol (23) An amorphous powder, $[\alpha]_D^{22}$ +11° (*c*=0.2, MeOH). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2.

(1′*R*,2′*R*)-4-*O*-Methylguaiacyl Glycerol 3′-*O*-β-D-Glucopyranoside (17) An amorphous powder, $[\alpha]_D^{22}$ −15° (*c*=1.2, MeOH). Positive FAB-MS *m/z*: 429 [M+K]$^+$, 413.1442 [M+Na]$^+$ (base, Calcd for $C_{17}H_{26}NaO_{10}$; 413.1424), 373 [M−H_2O+H]$^+$, 211 [M−$C_6H_{12}O_6$+H]$^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2. HMBC correlations: H-2/C-3, C-4, C-6, C-1′; H-5/C-1, C-3, C-4; H-6/C-2, C-4, C-5, C-1′; H-1′/C-1, C-2, C-6, C-2′, C-3′; H-2′/C-1, C-1′, C-3′; H-3′a/C-1′, C-2′, Glc-1; H-3′b/C-1′, C-2′, Glc-1; 3-O-CH_3/C-3; 4-O-CH_3/C-4; Glc-1/C-3′.

Enzymatic Hydrolysis of 17 A mixture of **17** (10 mg) and β-glucosi-

dase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 5 d. The mixture was evaporated *in vacuo* to dryness and the residue was chromatographed over silica gel [$CHCl_3$–MeOH (17 : 3 to 1 : 1)] to afford **24** (5 mg) and a sugar fraction. From the sugar fraction, the presence of D-glucose was revealed as **5**.

(1′*R*,2′*R*)-4-*O*-Methylguaiacyl Glycerol (24) Colorless needles (MeOH), mp 86—88 °C, $[\alpha]_D^{24}$ −24° (*c*=1.2, MeOH). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2.

4-*O*-Methylguaiacyl Glycerol 2′-*O*-β-D-Glucopyranoside (18) An amorphous powder, $[\alpha]_D^{22}$ −33° (*c*=0.1, MeOH). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2. HMBC correlations: H-2/C-1, C-3, C-4, C-6, C-1′; H-5/C-1, C-3, C-4; H-6/C-2, C-4, C-5, C-1′; H-1′/C-1, C-2, C-6, C-2′, C-3′; H-2′/C-1, C-1′, C-3′, Glc-1; 3-O-CH_3/C-3; 4-O-CH_3/C-4; Glc-1/C-2′.

(*E*)-4-Hydroxycinnamyl Alcohol 4-*O*-β-D-Glucopyranoside (19) An amorphous powder, $[\alpha]_D^{22}$ −56° (*c*=1.0, MeOH). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: 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-3′; H-2′/C-1, C-3′; H-3′/C-1′, C-2′; Glc-1/C-4.

(*Z*)-4-Hydroxycinnamyl Alcohol 4-*O*-β-D-Glucopyranoside (20) An amorphous powder, $[\alpha]_D^{22}$ −63° (*c*=0.2, MeOH). Positive FAB-MS *m*/*z*: 335.1099 $[M+Na]^+$ (Calcd for $C_{15}H_{20}NaO_7$; 335.1107), 295 $[M-H_2O+H]^+$, 133 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: 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-3′; H-2′/C-1; H-3′/C-1′, C-2′; Glc-1/C-4.

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