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

Toru Ishikawa, Eiko Fuiimatu, and Junichi Kitaima*<br>Showa Pharmaceutical University; 3 Higashi-Tamagawagakuen, Machida, Tokyo 194-8543, Japan. Received June 26, 2002; accepted August 10, 2002


#### Abstract

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 $\mathbf{2}^{\prime}-\boldsymbol{O}-\boldsymbol{\beta}$ - D -glucopyranoside and four stereoisomers of $1^{\prime}$-(4-hydroxyphenyl)propane-1', $2^{\prime}$-diol $2^{\prime}-O-\beta$-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', $2^{\prime}$-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 transanethole ( $80-90 \%$ ) is chiefly responsible for the taste and smell. Also, cis-anethole, estragole, $p$-anisaldehyde, anisketone, linalool and $\beta$-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, $\mathbf{2}$ and 13) and their glucosides ( $\mathbf{3}$ to 12 and $\mathbf{1 4}$ to 20). Among the glucosides, $\mathbf{5}$ to $\mathbf{9}, \mathbf{1 1}, \mathbf{1 2}, \mathbf{1 4}$ to $\mathbf{1 7}$ and $\mathbf{2 0}$ are new. All new glucosides described in this paper were $\beta$-d-glucopyranosides as shown by their ${ }^{13} \mathrm{C}$-NMR data (Table 2), and this was confirmed by hydrolysis to yield D -glucose or by a comparison of the $[\alpha]_{\mathrm{D}}$ or $[M]_{\mathrm{D}}$ values with those of their aglycones except $\mathbf{8 , 9}$ and 18. ${ }^{9,10)}$ Their molecular formulae were suggested from the accurate mass number of $[\mathrm{M}+\mathrm{H}]^{+}$or $[\mathrm{M}+\mathrm{Na}]^{+}$or $[\mathrm{M}+\mathrm{K}]^{+}$ion peaks in the high-resolution positive FAB-MS.

Phenylpropanoid $1\left(\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{O}_{3}, \mathrm{mp} 115-117^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{21}\right.$ $\left.\pm 0^{\circ}\right)$ and $2\left(\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{O}_{3}, \mathrm{mp} 62-63^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{21} \pm 0^{\circ}\right)$, glucoside $3\left(\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{O}_{8}\right.$, mp $\left.84-85^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{23}-29^{\circ}\right)$ and $4\left(\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{O}_{8}\right.$, $\mathrm{mp} 125-127^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{23}-15^{\circ}$ ) were identified as erythroanethole, threo-anethole glycol, ${ }^{11)}\left(1^{\prime} R, 2^{\prime} S\right)$-anethole glycol
$2^{\prime}-O-\beta$-d-glucopyranoside and $\left(1^{\prime} S, 2^{\prime} R\right)$-anethole glycol $2^{\prime}$ $O$ - $\beta$-D-glucopyranoside, ${ }^{12)}$ respectively.

Glucosides $5\left(\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{O}_{8}, \mathrm{mp} 80-84^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{22}-59^{\circ}\right)$ and 6 $\left(\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{O}_{8}, \mathrm{mp} 75-78^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{22}+11^{\circ}\right)$ showed $[\mathrm{M}+\mathrm{Na}]^{+}$ and $\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$ion peaks at $m / z 367$ and 165 in the positive FAB-MS. Both glucosides were hydrolyzed with $\beta$ glucosidase and, from the hydrolyzed mixtures, ( - )-threoanethole glycol (2a; $\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{O}_{3}$, mp $62-63^{\circ} \mathrm{C}$, $[\alpha]_{\mathrm{D}}^{22}-23^{\circ}$ ) and D -glucose from 5, and ( + )-threo-anethole glycol ( $\mathbf{2 b}$; $\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{O}_{3}, \mathrm{mp} 62-63^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{22}+25^{\circ}$ ) and D-glucose from 6 were obtained. The ${ }^{1} \mathrm{H}-$ and ${ }^{13} \mathrm{C}$-NMR chemical shifts (Tables 1,2 ) of 5 and $\mathbf{6}$ showed that both compounds were monoglucopyranosides of $\mathbf{2}$, and the position of the $\beta$-glucosyl units was proved to be $\mathrm{C}-2^{\prime}$ from the cross-peaks between the glucosyl $\mathrm{H}-1 / \mathrm{C}-2^{\prime}$ in the heteronuclear multiple bond connectivity (HMBC) spectrum. Thus, 5 and 6 were represented as $(-)$ - and ( + )-threo-anethole glycol $2^{\prime}$-O- $\beta$-d-glucopyranoside. As the $1 R^{\prime}, 2 R^{\prime}$ form of threo-anethole glycol was reported to have a negative $[\alpha]_{\mathrm{D}}$ value, and the $1 S^{\prime}, 2 S^{\prime}$ form of threo-anethole glycol had a positive $[\alpha]_{\mathrm{D}}$ value, ${ }^{13)}$ the absolute stereochemistry of $\mathrm{C}-1^{\prime}$ and $\mathrm{C}-2^{\prime}$ of $(-)$-threo-anethole glycol should be $R$, and that of $(+)$-threo-anethole glycol should be $S$. Furthermore, the absolute configurations at C- $2^{\prime}$ of 5 and $\mathbf{6}$ were confirmed to be $R$ and $S$ by the values of the glycosylation shift of the $\alpha$-carbon $(\mathbf{5} ;+8.5 \mathrm{ppm}, \mathbf{6}$; +11.1 ppm ), and the chemical shifts of the glucosyl aromatic carbon ( $\mathbf{5} ; \delta 103.53,6 ; \delta 106.36$ ). ${ }^{12,14-19)}$ Therefore, 5 and 6 were characterized as $\left(1^{\prime} R, 2^{\prime} R\right)$-anethole glycol $2^{\prime}-O$ - $\beta$-Dglucopyranoside and ( $1^{\prime} S, 2^{\prime} S$ )-anethole glycol $2^{\prime}-O-\beta$-d-glucopyranoside, respectively.

Glucoside $7\left(\mathrm{C}_{15} \mathrm{H}_{22} \mathrm{O}_{8}\right.$, an amorphous powder, $[\alpha]_{\mathrm{D}}^{22}$ $-38^{\circ}$ ) 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 $[\mathrm{M}+\mathrm{Na}]^{+},[\mathrm{M}+\mathrm{H}]^{+}$and $\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$ion peaks at $m / z 353,331$ and 151 , and its ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}-\mathrm{NMR}$ data suggested that 7 was built up with one $\beta$-glucopyranosyl group and one $1^{\prime}$-(4-hydroxyphenyl)propane- $1^{\prime}, 2^{\prime}$-diol moiety. Enzymatic hydrolysis of 7 gave d-glucose and an aglycone (21; $\mathrm{C}_{9} \mathrm{H}_{12} \mathrm{O}_{3}$, an amorphous powder, $[\alpha]_{\mathrm{D}}^{22} \pm 0^{\circ}$ ) which was characterized as $1^{\prime}$-(4-hydroxyphenyl)propane-1', $2^{\prime}$ diol, and the position of the $\beta$-glucosyl unit was proved to be C-4 from the HMBC correlation of the glucosyl H-1/C-4. By
comparison of the $\mathrm{H}-1^{\prime}, \mathrm{H}-2^{\prime}, \mathrm{H}-3^{\prime}$ and $\mathrm{C}-1^{\prime}, \mathrm{C}-2^{\prime}, \mathrm{C}-3^{\prime}$ chemical shifts with those of $\mathbf{1}$ and 2 (Tables 1,2 ), 7 was suggested to be an erythro form as $\mathbf{1}$. Therefore, 7 is an equivalent mixture of two stereoisomeric erythro-1'-(4-hy-droxyphenyl)propane-1', $2^{\prime}$-diol 4- $O$ - $\beta$-d-glucopyranosides.

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

Glucoside $10\left(\mathrm{C}_{15} \mathrm{H}_{22} \mathrm{O}_{8}\right.$, an amorphous powder, $[\alpha]_{\mathrm{D}}^{23}$ $-49^{\circ}$ ) was identified as an equivalent mixture of two stereoisomeric threo-1'-(4-hydroxyphenyl)propane-1', $2^{\prime}$-diol $4-O-\beta$-D-glucopyranosides which has been reported as a constituent of fennel. ${ }^{12)}$

Glucosides $11\left(\mathrm{C}_{15} \mathrm{H}_{22} \mathrm{O}_{8}\right.$, an amorphous powder, $[\alpha]_{\mathrm{D}}^{22}$ $\left.-51^{\circ}\right)$ and $12\left(\mathrm{C}_{15} \mathrm{H}_{22} \mathrm{O}_{8}\right.$, an amorphous powder, $\left.[\alpha]_{\mathrm{D}}^{22}+21^{\circ}\right)$ were also $\beta$-glucopyranosides of $1^{\prime}$-(4-hydroxyphenyl)-propane- $1^{\prime}, 2^{\prime}$-diol and, hydrolyzed with $\beta$-glucosidase gave the $(-)$-form and the $(+)$-form of $1^{\prime}$-(4-hydroxyphenyl)-propane-1', $2^{\prime}$-diol [22a $\left(\mathrm{C}_{9} \mathrm{H}_{12} \mathrm{O}_{3}\right.$, an amorphous powder, $\left.[\alpha]_{\mathrm{D}}^{22}-19^{\circ}\right)$ and 22b $\left(\mathrm{C}_{9} \mathrm{H}_{12} \mathrm{O}_{3}\right.$, an amorphous powder, $[\alpha]_{\mathrm{D}}^{22}$ $\left.+19^{\circ}\right)$ ], respectively, together with d-glucose. The position of the $\beta$-glucosyl units was proved to be $\mathrm{C}-2^{\prime}$ from the HMBC correlation of the glucosyl $\mathrm{H}-1 / \mathrm{C}-2^{\prime}$ signals. The stereochemical relation between $\mathrm{C}-1^{\prime}$ and $\mathrm{C}-2^{\prime}$ of $\mathbf{1 1}$ and $\mathbf{1 2}$ was revealed by comparison of their ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}$-NMR spectra with those of stereoisomeric pairs of anethole glycol (3 to 6; Tables 1,2 ) in the same way as described for $\mathbf{8}$ and 9 . As the chemical shifts of the aglycone parts of $\mathbf{1 1}$ and $\mathbf{1 2}$ showed good similarity with those of 5 and $\mathbf{6}$, they were suggested to be glucosides of threo-1'-(4-hydroxyphenyl)-propane- $1^{\prime}, 2^{\prime}$-diol with the $1^{\prime} R, 2^{\prime} R$ configuration [( - form] for 11 and the $1^{\prime} S, 2^{\prime} S$ configuration $[(+)$ form] for 12. Therefore, $\mathbf{1 1}$ and $\mathbf{1 2}$ were characterized as $\left(1^{\prime} R, 2^{\prime} R\right)-1^{\prime}-(4-$ hydroxyphenyl)propane-1', $2^{\prime}$-diol $2^{\prime}-O-\beta$-d-glucopyranoside and ( $1^{\prime} S, 2^{\prime} S$ )-1'-(4-hydroxyphenyl)propane-1', $2^{\prime}$-diol $2^{\prime}-O$ -$\beta$-d-glucopyranoside, respectively.
Consequently, we have isolated all four anethole glycol 2'-$O-\beta$-d-glucopyranosides and all four 1'-(4-hydroxyphenyl)propane $2^{\prime}-O-\beta$ - D -glucopyranosides from the fruit of anise.

Phenylpropanoid $13\left(\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{O}_{5}\right.$, an amorphous powder,
$\left.[\alpha]_{\mathrm{D}}^{25}-26^{\circ}\right)$ was identified as $\left(1^{\prime} R, 2^{\prime} R\right)$-guaiacyl glycerol which has been isolated from Zantedeschia aethiopica. ${ }^{20}$ )

Glucosides $14\left(\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{O}_{10}\right.$, an amorphous powder, $[\alpha]_{\mathrm{D}}^{21}$ $\left.-50^{\circ}\right)$ and $15\left(\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{O}_{10}\right.$, an amorphous powder, $[\alpha]_{\mathrm{D}}^{22}$ $-13^{\circ}$ ) showed $[\mathrm{M}+\mathrm{K}]^{+},[\mathrm{M}+\mathrm{Na}]^{+}$and $\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$ ion peaks at $m / z 415,399$ and 197 in the positive FAB-MS, respectively. Both glucosides were hydrolyzed with $\beta$-glucosidase, and the same aglycone was obtained, which was identical to $\mathbf{1 3}$, together with d-glucose. The position of the $\beta$-glucosyl unit was proved to be C-4 for 14, and C-3' for 15 , from the HMBC correlations of the glucosyl $\mathrm{H}-1 / \mathrm{C}-4$ and glucosyl $\mathrm{H}-1 / \mathrm{C}-3^{\prime}$ of their HMBC spectra. Their ${ }^{13} \mathrm{C}-\mathrm{NMR}$ data suggested that they were $\beta$-glucopyranosides, and 14 and 15 were characterized as $\left(1^{\prime} R, 2^{\prime} R\right)$-guaiacyl glycerol 4$O$ - $\beta$-d-glucopyranoside and $\left(1^{\prime} R, 2^{\prime} R\right)$-guaiacyl glycerol $3^{\prime}$ $O$ - $\beta$-d-glucopyranoside, respectively.

Glucoside $16\left(\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{O}_{10}\right.$, an amorphous powder, $[\alpha]_{\mathrm{D}}^{22}$ $-20^{\circ}$ ) showed $[\mathrm{M}+\mathrm{K}]^{+},[\mathrm{M}+\mathrm{Na}]^{+}$and $\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$ ion peaks at $m / z 415,399$ and 197 in the positive FAB-MS. The ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}-\mathrm{NMR}$ spectral data (Tables 1, 2) for $\mathbf{1 6}$ showed good similarity to those of $\mathbf{1 5}$, but obvious differences were seen in the chemical shifts of $\mathrm{H}-1^{\prime}, \mathrm{H}-2^{\prime}, \mathrm{H}_{2}-3^{\prime}$ and C-1', C-2', C-3'. So, $\mathbf{1 6}$ was considered to be an erythro form of 15 , and the results of HMBC experiment supported this conclusion. Enzymatic hydrolysis of $\mathbf{1 6}$ gave an aglycone (23; $\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{O}_{5}$, an amorphous powder, $[\alpha]_{\mathrm{D}}^{22}+11^{\circ}$ ) and D-glucose, and aglycone 23 was suggested to be an erythro form by comparison of the chemical shifts of $\mathrm{H}-1^{\prime}, \mathrm{H}-2^{\prime}$ and $\mathrm{H}_{2}-3$ with $13 .{ }^{21)}$ The positive $[\alpha]_{\mathrm{D}}$ value suggested that $\mathbf{2 3}$ has the $1^{\prime} S, 2^{\prime} R$ configuration as $4\left[1^{\prime} S, 2^{\prime} R ;(+)\right.$ form]. So, 16 was characterized as $\left(1^{\prime} S, 2^{\prime} R\right)$-guaiacyl glycerol $3^{\prime}-O-\beta$ -D-glucopyranoside.

Glucoside $17\left(\mathrm{C}_{17} \mathrm{H}_{26} \mathrm{O}_{10}\right.$, an amorphous powder, $[\alpha]_{\mathrm{D}}^{22}$ $\left.-15^{\circ}\right)$ showed $[\mathrm{M}+\mathrm{K}]^{+},[\mathrm{M}+\mathrm{Na}]^{+}$and $\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$ ion peaks at $m / z 429,413$ and 211 in the positive FAB-MS. Enzymatic hydrolysis of $\mathbf{1 7}$ gave an aglycone $\left(\mathbf{2 4} ; \mathrm{C}_{11} \mathrm{H}_{16} \mathrm{O}_{5}\right.$, $\mathrm{mp} 86-88^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{24}-24^{\circ}$ ) and d-glucose. As the ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}$-NMR spectra of $\mathbf{1 7}$ (Tables 1,2 ) showed good similarity with those of $\mathbf{1 5}$ except for having one more methoxyl proton and a carbon signal, 17 was indicated to be a mono-methylate of $\mathbf{1 5}$. 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 $\mathrm{H}-1^{\prime}, \mathrm{H}-2^{\prime}, \mathrm{H}_{2}-3^{\prime}$, and chemical shifts of $\mathrm{C}-1^{\prime}$, C-2', C-3' between 24 and $\mathbf{1 3}$ (Tables 1, 2) also supported this conclusion. Therefore, $\mathbf{1 7}$ was characterized as $\left(1^{\prime} R, 2^{\prime} R\right)$ -4-O-methylguaiacyl glycerol $3^{\prime}$ - $O$ - $\beta$-d-glucopyranoside. Glucoside $18\left(\mathrm{C}_{17} \mathrm{H}_{26} \mathrm{O}_{10}\right.$, an amorphous powder, $\left.[\alpha]_{\mathrm{D}}^{22}-33^{\circ}\right)$ was identified as $4-O$-methylguaiacyl glycerol $2^{\prime}-O-\beta$-d-glucopyranoside which was isolated from the aerial parts of Chrozophora obliqua. ${ }^{22)}$ However, the absolute configuration of the aglycone of $\mathbf{1 8}$ could not be assigned.

Glucoside $19\left(\mathrm{C}_{15} \mathrm{H}_{20} \mathrm{O}_{7}\right.$, an amorphous powder, $[\alpha]_{\mathrm{D}}^{22}$ $-56^{\circ}$ ) was identified as ( $E$ )-4-hydroxycinnamyl alcohol 4-O-$\beta$-d-glucopyranoside, which was isolated from the leaves of Lilium cordatum. ${ }^{23)}$ Glucoside $20\left(\mathrm{C}_{15} \mathrm{H}_{20} \mathrm{O}_{7}\right.$, an amorphous powder, $[\alpha]_{\mathrm{D}}^{22}-63^{\circ}$ ) showed $[\mathrm{M}+\mathrm{Na}]^{+}$and $\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\right.$ $\mathrm{H}]^{+}$ion peaks at $m / z 335$ and 133 in the positive FAB-MS, and its ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}$-NMR spectra (Tables 1,2 ) showed simi-

Table 1. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ Chemical Shifts of $\mathbf{1 - 2 4}$ (in Pyridine- $d_{5}, 270^{a}$ and 500 MHz )

|  | $1^{\text {a) }}$ | $2^{\text {a }}$ | 3 | 4 |
| :---: | :---: | :---: | :---: | :---: |
| H-2,6 | $7.72 \mathrm{~d}(8.5)$ | $7.63 \mathrm{~d}(8.5)$ | 7.68 d (8.5) | $7.64 \mathrm{~d}(8.5)$ |
| H-3,5 | $7.03 \mathrm{~d}(8.5)$ | $7.03 \mathrm{~d}(8.5)$ | $7.02 \mathrm{~d}(8.5)$ | 6.99 d (8.5) |
| H-1 | $5.08 \mathrm{~d}(5.0)$ | 4.84 d (7.0) | $5.35 \mathrm{~d}(3.0)$ | 5.43 d (3.0) |
| H-2' | $4.40 \mathrm{dq}(5.0,6.0)$ | $4.28 \mathrm{dq}(6.0,7.0)$ | $4.52 \mathrm{dq}(3.0,6.5)$ | $4.49 \mathrm{dq}(3.0,6.5)$ |
| $\mathrm{H}_{3}-3^{\prime}$ | 1.54 d (6.0) | 1.32 d (6.0) | 1.37 d (6.5) | 1.36 d (6.5) |
| $\mathrm{OCH}_{3}$ | 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 | $7{ }^{\text {b) }}$ |  |
| H-2,6 | $7.59 \mathrm{~d}(8.5)$ | $7.62 \mathrm{~d}(8.5)$ | $7.70 \mathrm{~d}(8.5)$ | [7.70 d (8.5)] |
| H-3,5 | 6.99 d (8.5) | 7.02 d (8.5) | $7.42 \mathrm{~d}(8.5)$ | [7.42 d (8.5)] |
| H-1' | $5.02 \mathrm{~d}(7.0)$ | 4.95 d (8.0) | 5.06 d (4.5) | [ $5.05 \mathrm{~d}(4.5)$ ] |
| H-2' | $4.42 \mathrm{dq}(6.5,7.0)$ | $4.30 \mathrm{dq}(6.5,8.0)$ | $4.38 \mathrm{dq}(4.5,6.0)$ | [4.38 dq (4.5, 6.0)] |
| $\mathrm{H}_{3}-3^{\prime}$ | 1.22 d (6.5) | 1.25 d (6.5) | 1.51 d (6.0) | [1.51 d (6.0)] |
| $\mathrm{OCH}_{3}$ | $3.67 \mathrm{~s}$ | 3.67 s | - ${ }^{\text {d }}$ | [1.51 (6.0)] |
| 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 | $21{ }^{\text {a) }}$ | $22^{\text {a) }}$ |
| H-2,6 | 7.67 d (8.5) | 7.63 d (8.5) | $7.73 \mathrm{~d}(8.5)$ | 7.64 d (8.5) |
| H-3,5 | 7.22 d (8.5) | 7.20 d (8.5) | $7.25 \mathrm{~d}(8.5)$ | 7.25 d (8.5) |
| H-1 | 5.35 d (3.0) | $5.43 \mathrm{~d}(3.0)$ | 5.10 d (4.5) | 4.84 d (7.0) |
| H-2' | $4.53 \mathrm{dq}(3.0,6.5)$ | $4.51 \mathrm{dq}(3.0,6.5)$ | $4.45 \mathrm{dq}(4.5,6.5)$ | $4.30 \mathrm{dq}(6.5,7.0)$ |
| $\mathrm{H}_{3}-3^{\prime}$ | $1.40 \mathrm{~d}(6.5)$ | $1.38 \mathrm{~d}(6.5)$ | 1.57 d (6.5) | 1.35 d (6.5) |
| Glc H-1 | 5.28 d (7.5) | 5.07 d (7.5) | - | - |


| $10^{\text {b) }}$ |  |  | 11 | 12 |
| :---: | :---: | :---: | :---: | :---: |
| H-2,6 | $7.61 \mathrm{~d}(8.5)$ | [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 ] | $4.44 \mathrm{dq}(6.5,7.0)$ | $4.31 \mathrm{dq}(6.5,8.0)$ |
| $\mathrm{H}_{3}-3^{\prime}$ | 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) | [ $5.65 \mathrm{~d}(7.5)$ ] | 5.11 d (7.5) | 5.36 d (8.0) |


|  | 13 | 14 | 15 | 23 |
| :---: | :---: | :---: | :---: | :---: |
| H-2 | $7.50 \mathrm{~d}(1.5)$ | $7.53 \mathrm{~d}(1.5)$ | $7.56 \mathrm{~d}(1.5)$ | $7.53 \mathrm{~d}(1.5)$ |
| H-5 | 7.25 d (8.0) | 7.58 d (8.5) | 7.25 d (8.0) | 7.26 d (8.0) |
| H-6 | $7.33 \mathrm{dd}(1.5,8.0)$ | $7.29 \mathrm{dd}(1.5,8.5)$ | 7.38 dd (1.5, 8.0) | 7.38 dd (1.5, 8.0) |
| H-1 | 5.33 d (6.0) | $5.32 \mathrm{~d}(5.5)$ | 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 | $4.11 \mathrm{dd}(6.0,11.0)$ | $4.10 \mathrm{dd}(6.0,11.0)$ | $4.03 \mathrm{dd}(6.0,10.5)$ | $4.43 \mathrm{dd}(6.0,10.5)$ |
| H-3'b | $4.25 \mathrm{dd}(4.5,11.0)$ | 4.24 dd (4.5, 11.0) | $4.60 \mathrm{dd}(4.0,10.5)$ | $4.45 \mathrm{dd}(5.0,10.5)$ |
| $3-\mathrm{OCH}_{3}$ | 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) | $6.93 \mathrm{~d}(8.5)$ |
| H-6 | $7.33 \mathrm{dd}(1.5,8.0)$ | $7.35 \mathrm{dd}(2.0,8.0)$ | $7.40 \mathrm{dd}(1.5,8.0)$ | 7.28 dd (1.5. 8.5) |
| H-1 | 5.29 d (6.5) | 5.35 d (6.0) | $5.39 \mathrm{~d}(5.5)$ | $5.30 \mathrm{~d}(7.5)$ |
| 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 | $4.41 \mathrm{dd}(6.5,10.5)$ | $4.11 \mathrm{dd}(6.0,11.0)$ | $4.03 \mathrm{dd}(5.5,10.5)$ | $3.94 \mathrm{dd}(7.5,10.0)$ |
| H-3'b | 4.78 dd (3.0, 10.5) | 4.25 dd (4.5, 11.0) | $4.60 \mathrm{dd}(4.0,10.5)$ | 4.06 dd (3.0, 10.0) |
| $3-\mathrm{OCH}_{3}$ | 3.68 s | 3.70 s | 3.74 s | 3.69 s |
| $4-\mathrm{OCH}_{3}$ | - | 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) |


|  | $\mathbf{1 9}$ | $\mathbf{2 0}$ |
| :--- | :--- | :--- |
| $\mathrm{H}-2,6$ | $7.44 \mathrm{~d}(8.5)$ | $7.32 \mathrm{~d}(9.0)$ |
| $\mathrm{H}-3,5$ | $7.35 \mathrm{~d}(8.5)$ | $7.35 \mathrm{~d}(9.0)$ |
| $\mathrm{H}-1^{\prime}$ | $6.86 \mathrm{dt}(1.5,16.0)$ | $6.55 \mathrm{dt}(1.5,12.0)$ |
| $\mathrm{H}^{\prime}$ | $6.54 \mathrm{dt}(5.0,16.0)$ | $6.18 \mathrm{dt}(6.0,12.0)$ |
| $\mathrm{H}_{2} \mathbf{3}^{\prime}$ | $4.55 \mathrm{dt}(1.5,5.0)$ | $4.75 \mathrm{dt}(1.5,6.0)$ |
| Glc H-1 | $5.65 \mathrm{~d}(7.5)$ | $5.65 \mathrm{~d}(7.5)$ |

[^0]Table 2. ${ }^{13} \mathrm{C}$-NMR Chemical Shifts of $\mathbf{1 - 2 4}$ (in Pyridine- $d_{5}, 67.5^{a}$ ) and 125 MHz )

|  | $1^{\text {a) }}$ | $2^{\text {a }}$ | 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 |
| $\mathrm{C}-1^{\prime}$ | 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) |
| $\mathrm{OCH}_{3}$ | 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 |
|  | $7{ }^{\text {b) }}$ |  | 8 | 9 | $21^{\text {a) }}$ |  |
| 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 |  |
| $\mathrm{C}-1^{\prime}$ | 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 |  |  |


|  | $10^{\text {b) }}$ |  | 11 | 12 | $22^{\text {a) }}$ | 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 ${ }^{\prime}$ | 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 |
| $3-\mathrm{OCH}_{3}$ | 55.80 | 55.77 | 55.81 | 55.76 | 55.80 | 55.77 | 55.82 | 55.78 |
| $4-\mathrm{OCH}_{3}$ |  |  |  |  |  | 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 |

[^1]

1: $\mathrm{R}_{1}=\mathrm{CH}_{3}, \mathrm{R}_{2}=\mathrm{H}$ (rel.)
3: $\mathrm{R}_{1}=\mathrm{CH}_{3}, \mathrm{R}_{2}=\beta$-D-glc
7: $R_{1}=\beta-\mathrm{d}-\mathrm{glc}, R_{2}=\mathrm{H}$ (rel.)
8: $R_{1}=H, R_{2}=\beta-\mathrm{d}-\mathrm{glc}$
21: $\mathrm{R}_{1}=\mathrm{H}, \mathrm{R}_{2}=\mathrm{H}$ (rel.)


4: $\mathrm{R}=\mathrm{CH}_{3}$
9: $R=H$


2: $\mathrm{R}_{1}=\mathrm{CH}_{3}, \mathrm{R}_{2}=\mathrm{H}$ (rel.) 2a: $\mathrm{R}_{1}=\mathrm{CH}_{3}, \mathrm{R}_{2}=\mathrm{H}$
5: $R_{1}=C_{3}, R_{2}=\beta-\mathrm{D}$-glc
10: $R_{1}=\beta$-D-glc, $R_{2}=H$ (rel.)
$\begin{array}{ll}\text { 10: } & R_{1}=\beta-D-g l c, R_{2}=H(r \\ \text { 11: } & R_{1}=H, R_{2}=\beta-o-g l c\end{array}$
11: $R_{1}=H, R_{2}=\beta-D-g$
22a: $R_{1}=H, R_{2}=H$


2b: $\mathrm{R}_{1}=\mathrm{CH}_{3}, \mathrm{R}_{2}=\mathrm{H}$
6: $\mathrm{R}_{1}=\mathrm{CH}_{3}, \mathrm{R}_{2}=\beta-\mathrm{o}-\mathrm{g}$
$\begin{array}{ll}\text { 6: } & R_{1}=C_{3}, R_{2}=\beta \text {-D-glc } \\ \text { 12: } & R_{1}=H, R=\beta \text { R } \\ R_{2}=\beta \text {-D-glc } & \text { 23: }: \\ R=H\end{array}$
22b: $R_{1}=H, R_{2}=H$
23: $R=H$


13: $R_{1}=H, R_{2}=H$
14: $R_{1}=\beta$-D-glc, $R_{2}=H$
15: $\mathrm{R}_{1}=\mathrm{H}, \mathrm{R}_{2}=\beta$-d-glc
17: $\mathrm{R}_{1}=\mathrm{CH}_{3}, \mathrm{R}_{2}=\beta$-d-glc
24: $\mathrm{R}_{1}=\mathrm{CH}_{3}, \mathrm{R}_{2}=\mathrm{H}$


19


18






20

Fig. 1. Structures of $\mathbf{1 - 2 4}, \mathbf{2 a}, \mathbf{2 b}, \mathbf{2 2} \mathbf{a}$ and 22b
larity with those of $\mathbf{1 9}$. The structure of $\mathbf{2 0}$ was confirmed to be 4-hydroxycinnamyl 4-O- $\beta$-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' $\left.(J=12.0 \mathrm{~Hz}) .{ }^{24}\right)$ Therefore, 20 was characterized as ( $Z$ )-4-hydroxycinnamyl alcohol $4-O$ - $\beta$-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. ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}$-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 $\delta$ value. ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ 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 $\mu \mathrm{m}$, 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- $\mathrm{H}_{2} \mathrm{SO}_{4}$ reagent. HPLC separation was carried out on a JASCO chromatograph ( 980 -system) with a JASCO RI-930 detector, and Symmetryprep C18 $7 \mu \mathrm{~m}$ [Waters; column size, $7.8 \times 300 \mathrm{~mm}$; ODS], Carbohydrate analysis [Waters; column size, $3.9 \times 300 \mathrm{~mm}$; 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 $(51 \times 4)$ 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 $\left(\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{MeOH}\right)$. The methanol eluate ( 52.1 g ) was subjected to Sephadex $\mathrm{LH}-20(\mathrm{MeOH})$ to give six fractions (frs. A-F). Fraction B ( 40.9 g ) was chromatographed over silica gel $\left[\mathrm{CHCl}_{3}-\mathrm{MeOH}-\mathrm{H}_{2} \mathrm{O}(17: 3: 0.2 \rightarrow 4: 1\right.$ : $0.1 \rightarrow 15: 5: 0.4 \rightarrow 7: 3: 0.5) \rightarrow \mathrm{MeOH}]$ to give thirteen fractions (frs. $\mathrm{B}_{1}-$ $\left.\mathrm{B}_{13}\right)$. Fraction $\mathrm{B}_{2}(0.83 \mathrm{~g})$ was subjected to a Lobar RP-8 column [MeCN$\mathrm{H}_{2} \mathrm{O}(3: 17)$ ] and HPLC [ODS; $\mathrm{MeCN}-\mathrm{H}_{2} \mathrm{O}(9: 11)$ ] to give $\mathbf{1}(43 \mathrm{mg})$ and 2 $(103 \mathrm{mg})$. Fraction $\mathrm{B}_{6}(0.91 \mathrm{~g})$ was subjected to a Lobar RP-8 column $\left[\mathrm{MeCN}-\mathrm{H}_{2} \mathrm{O}(3: 17)\right]$, HPLC [CHA; $\left.\mathrm{MeCN}-\mathrm{H}_{2} \mathrm{O}(97: 3)\right]$ and silica gel column chromatography to give $\mathbf{1 3}$ ( 4 mg ). Fraction $\mathrm{B}_{7}(1.15 \mathrm{~g})$ was also sub-
jected to a Lobar RP-8 column $\left[\mathrm{MeCN}-\mathrm{H}_{2} \mathrm{O}(3: 17)\right]$ and HPLC [ODS, $\mathrm{MeCN}-\mathrm{H}_{2} \mathrm{O}(3: 37)$ and CHA; $\left.\mathrm{MeCN}-\mathrm{H}_{2} \mathrm{O}(24: 1)\right]$ to give 3 ( 18 mg ), 4 $(9 \mathrm{mg}), 5(8 \mathrm{mg})$ and $\mathbf{6}(4 \mathrm{mg})$. Fraction $\mathrm{B}_{9}(1.81 \mathrm{~g})$ was passed through a Lobar RP-8 column [MeCN- $\left.\mathrm{H}_{2} \mathrm{O}(3: 17)\right]$ to give eighteen fractions (frs. $\mathrm{B}_{9}$ $\left.{ }_{1}-\mathrm{B}_{9-18}\right)$ and fr. $\mathrm{B}_{9-4}$ was subjected to Sephadex LH-20 (MeOH) and HPLC [CHA; MeCN- $\left.\mathrm{H}_{2} \mathrm{O}(14: 1)\right]$ to give $\mathbf{1 8}(1 \mathrm{mg})$. Fraction $\mathrm{B}_{10}(7.29 \mathrm{~g})$ was passed through a Lobar RP-8 column $\left[\mathrm{MeCN}-\mathrm{H}_{2} \mathrm{O}(3: 17)\right]$ to give ten fractions (frs. $\mathrm{B}_{10-1}-\mathrm{B}_{10-10}$ ) and fr. $\mathrm{B}_{10-2}$ was subjected to a combination of HPLC [ODS; $\mathrm{MeCN}-\mathrm{H}_{2} \mathrm{O}(1: 19)$ and CHA; $\mathrm{MeCN}-\mathrm{H}_{2} \mathrm{O}(14: 1)$ to give $\mathbf{1 1}$ $(8 \mathrm{mg}), \mathbf{1 2}(10 \mathrm{mg}), \mathbf{8}(1 \mathrm{mg})$ and $9(3 \mathrm{mg})$, respectively. Fraction $\mathrm{B}_{10-3}$ was passed through HPLC [ODS; MeCN- $\mathrm{H}_{2} \mathrm{O}(3: 37)$ ] to give $\mathbf{1 7}(68 \mathrm{mg}), \mathbf{1 9}$ $(283 \mathrm{mg})$ and fr. $\mathrm{B}_{10-3 \mathrm{c}}$. Fraction $\mathrm{B}_{10-3 \mathrm{c}}$ was passed through HPLC [CHA; $\left.\mathrm{MeCN}-\mathrm{H}_{2} \mathrm{O}(14: 1)\right]$ to give $20(3 \mathrm{mg})$. Fraction $\mathrm{B}_{11}(4.37 \mathrm{~g})$ was passed through a Lobar RP-8 column [MeCN- $\mathrm{H}_{2} \mathrm{O}$ (3:17)] to give ten fractions (frs. $\mathrm{B}_{11-1}-\mathrm{B}_{11-10}$ ) and fr. $\mathrm{B}_{10-3}$ was subjected to HPLC [ODS; MeCN- $\mathrm{H}_{2} \mathrm{O}$ $(3: 197)]$ to give $7(12 \mathrm{mg}), \mathbf{1 6}(9 \mathrm{mg}), \mathbf{1 0}(54 \mathrm{mg})$ and $15(73 \mathrm{mg})$, respectively. A part of the water eluate fraction $(50.4 \mathrm{~g})$ was subjected to Sephadex $\mathrm{LH}-20(\mathrm{MeOH})$ to give three fractions (frs. G-I). Fraction H ( 41.5 g ) was chromatographed over silica gel $\left[\mathrm{CHCl}_{3}-\mathrm{MeOH}-\mathrm{H}_{2} \mathrm{O} \quad(4: 1: 0.1 \rightarrow 15\right.$ : $5: 0.4 \rightarrow 7: 3: 0.5 \rightarrow 6: 4: 1 \rightarrow 1: 1: 0.1 \rightarrow 4: 6: 0.5) \rightarrow \mathrm{MeOH}]$ to give twenty fractions (frs. $\mathrm{H}_{1}-\mathrm{H}_{20}$ ). Fraction $\mathrm{H}_{13}(4.68 \mathrm{~g})$ was subjected to Lobar RP-8 column $\left(\mathrm{H}_{2} \mathrm{O}\right)$ to give ten fractions (frs. $\left.\mathrm{H}_{3-1}-\mathrm{H}_{3-10}\right)$, and fr. $\mathrm{H}_{13-8}$ was subjected to HPLC [CHA; $\mathrm{MeCN}-\mathrm{H}_{2} \mathrm{O}(14: 1)$ ] to give $\mathbf{1 4}(6 \mathrm{mg})$.
erythro-Anethole Glycol (1) Colorless needles $\left(\mathrm{MeOH}-\mathrm{H}_{2} \mathrm{O}\right), \mathrm{mp}$ $115-117^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{21} \pm 0^{\circ}\left(c=1.0, \mathrm{CHCl}_{3}\right) .{ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 270 \mathrm{MHz}$ ) $\delta$ : Table $1 .{ }^{13} \mathrm{C}$-NMR (pyridine- $\left.d_{5}, 67.5 \mathrm{MHz}\right) \delta$ : Table 2.
threo-Anethole Glycol (2) Colorless needles $\left(\mathrm{MeOH}-\mathrm{H}_{2} \mathrm{O}\right)$, mp 62$63{ }^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{21} \pm 0^{\circ}\left(c=1.0, \mathrm{CHCl}_{3}\right) .{ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $\left.d_{5}, 270 \mathrm{MHz}\right) \delta$ : Table 1. ${ }^{13} \mathrm{C}$-NMR (pyridine- $d_{5}, 67.5 \mathrm{MHz}$ ) $\delta$ : Table 2.
( $\mathbf{1}^{\prime} \boldsymbol{R}, \mathbf{2}^{\prime} \boldsymbol{S}$ )-Anethole Glycol $\mathbf{2}^{\prime}$ - $\boldsymbol{O}$ - $\boldsymbol{\beta}$-d-Glucopyranoside (3) Colorless needles $(\mathrm{MeOH})$, mp $84-85^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{23}-29^{\circ}(c=0.3, \mathrm{MeOH})$. Positive FAB-MS $m / z: 689[2 \mathrm{M}+\mathrm{H}]^{+}, 367.1367[\mathrm{M}+\mathrm{Na}]^{+},\left(\right.$Calcd for $\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{NaO}_{8}$; 367.1369), $327\left[\mathrm{M}-\mathrm{H}_{2} \mathrm{O}+\mathrm{H}\right]^{+}, 165\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$(base). ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500 \mathrm{MHz}$ ) $\delta$ : Table $1 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : Table 2.
( $\mathbf{1}^{\prime} \boldsymbol{S}, \mathbf{2}^{\prime} \boldsymbol{R}$ )-Anethole Glycol $\mathbf{2}^{\prime}$ - $\boldsymbol{O}$ - $\boldsymbol{\beta}$-d-Glucopyranoside (4) Colorless needles (MeOH), mp $125-127^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{23}-15^{\circ}(c=0.5, \mathrm{MeOH}) .{ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500 \mathrm{MHz}$ ) $\delta$ : Table $1 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : Table 2.
( $\mathbf{1}^{\prime} \boldsymbol{R}, \mathbf{2}^{\prime} \boldsymbol{R}$ )-Anethole Glycol $\mathbf{2}^{\prime}$ - $\boldsymbol{O}$ - $\boldsymbol{\beta}$-d-Glucopyranoside (5) Colorless needles $(\mathrm{MeOH}), \mathrm{mp} 80-84^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{22}-59^{\circ}(c=0.4, \mathrm{MeOH})$. Positive FAB-MS m/z: $383[\mathrm{M}+\mathrm{K}]^{+}, 367.1382[\mathrm{M}+\mathrm{Na}]^{+},\left(\mathrm{Calcd}\right.$ for $\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{NaO}_{8}$; 367.1369), $327\left[\mathrm{M}-\mathrm{H}_{2} \mathrm{O}+\mathrm{H}\right]^{+}, 165\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$(base). ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500 \mathrm{MHz}$ ) $\delta$ : Table 1. ${ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $\left.d_{5}, 125 \mathrm{MHz}\right) \delta$ : Table 2. HMBC correlations: H-2/C-3, C-4, C-6, C-1'; H-3/C-1, C-4, C-5; $\mathrm{H}-5 / \mathrm{C}-1, \mathrm{C}-3, \mathrm{C}-4 ; \mathrm{H}-6 / \mathrm{C}-2, \mathrm{C}-4, \mathrm{C}-5, \mathrm{C}-1^{\prime} ; \mathrm{H}-1^{\prime} / \mathrm{C}-1, \mathrm{C}-2, \mathrm{C}-6, \mathrm{C}-2^{\prime} ; \mathrm{H}-$ $2^{\prime} / \mathrm{C}-1, \mathrm{C}-1^{\prime}$, Glc-1; $\mathrm{H}-3^{\prime} / \mathrm{C}-1^{\prime}, \mathrm{C}-2^{\prime}$; $\mathrm{O}-\mathrm{CH}_{3} / \mathrm{C}-4$; Glc-1/C-2'.

Enzymatic Hydrolysis of 5 A mixture of $\mathbf{5}(5 \mathrm{mg})$ and $\beta$-glucosidase ( 5 mg , TOYOBO CO., Lot. 93240) in water ( 5 ml ) was shaken in a water bath at $37^{\circ} \mathrm{C}$ for 2 d . The mixture was evaporated in vacuo to dryness and the residue was chromatographed over silica gel $\left[\mathrm{CHCl}_{3}-\mathrm{MeOH}(19: 1\right.$ and
$1: 1)$ ] to afford $\mathbf{2 a}(2 \mathrm{mg})$ 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.; $\mathrm{MeCN}-\mathrm{H}_{2} \mathrm{O}(17: 3), 2 \mathrm{ml} / \mathrm{min} ; t_{\mathrm{R}} 4.50 \mathrm{~min}$ (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$63^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{22}-23^{\circ}(c=0.2, \mathrm{MeOH}) .{ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $\left.d_{5}, 270 \mathrm{MHz}\right) \delta$ : same as $2 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 67.5 \mathrm{MHz}$ ) $\delta$ : same as 2 .
( $\mathbf{1}^{\prime} \boldsymbol{S}, \mathbf{2}^{\prime} \boldsymbol{S}$ )-Anethole Glycol $\mathbf{2}^{\prime}$ - $\boldsymbol{O}$ - $\boldsymbol{\beta}$-d-Glucopyranoside (6) Colorless needles (MeOH), mp $75-78^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{22}+11^{\circ}(c=0.3, \mathrm{MeOH})$. Positive FAB-MS $m / z: 367.1364[\mathrm{M}+\mathrm{Na}]^{+}$, (Calcd for $\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{NaO}_{8} ; 367.1369$ ), 327 $\left[\mathrm{M}-\mathrm{H}_{2} \mathrm{O}+\mathrm{H}\right]^{+}, 165\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$(base). ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}$, 500 MHz ) $\delta$ : Table $1 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : 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, C4; 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', Glc1; H-3'/C-1', C-2'; O-CH3/C-4; Glc-1/C-2'
Enzymatic Hydrolysis of 6 A mixture of $6(3 \mathrm{mg})$ and $\beta$-glucosidase $(3 \mathrm{mg})$ in water $(5 \mathrm{ml})$ was shaken in a water bath at $37^{\circ} \mathrm{C}$ for 2 d . The mixture was treated in the same way described for $\mathbf{5}$ to afford $\mathbf{2 b}(1 \mathrm{mg})$ and a sugar fraction. From the sugar fraction, the presence of d-glucose was revealed as 5 .
( $\mathbf{1}^{\prime} \boldsymbol{S}, \mathbf{2}^{\prime} \boldsymbol{S}$ )-Anethole Glycol (2b) Colorless needles (MeOH), mp 62$63{ }^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{22}+25^{\circ}(c=0.1, \mathrm{MeOH}) .{ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 270 \mathrm{MHz}$ ) $\delta$ : same as $2 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 67.5 \mathrm{MHz}$ ) $\delta$ : same as $\mathbf{2}$.
erythro-1'-(4-Hydroxyphynyl)propane-1', $\mathbf{2}^{\prime}$-diol $\mathbf{4 - O}$ - $\boldsymbol{\beta}$-d-Glucopyranoside (7) An amorphous powder, $[\alpha]_{\mathrm{D}}^{22}-38^{\circ}(c=0.7, \mathrm{MeOH})$. Positive FAB-MS m/z: $353[\mathrm{M}+\mathrm{Na}]^{+}, 331.1388[\mathrm{M}+\mathrm{H}]^{+}$(Calcd for $\mathrm{C}_{15} \mathrm{H}_{23} \mathrm{O}_{8}$; 331.1393), $313\left[\mathrm{M}-\mathrm{H}_{2} \mathrm{O}+\mathrm{H}\right]^{+}, 151\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$(base). ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500 \mathrm{MHz}$ ) $\delta$ : Table $1 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : 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'; $\mathrm{H}_{3}-3^{\prime} / \mathrm{C}-1^{\prime}, \mathrm{C}-2^{\prime}$; Glc-1/C-4.

Enzymatic Hydrolysis of 7 A mixture of $7(8 \mathrm{mg})$ and $\beta$-glucosidase $(5 \mathrm{mg})$ in water ( 5 ml ) was shaken in a water bath at $37^{\circ} \mathrm{C}$ for 14 d . The mixture was evaporated in vacuo to dryness and the residue was chromatographed over silica gel $\left[\mathrm{CHCl}_{3}-\mathrm{MeOH}-\mathrm{H}_{2} \mathrm{O}(15: 5: 0.4)\right.$ and $\mathrm{CHCl}_{3}-$ $\mathrm{MeOH}(1: 1)]$ to afford $21(2 \mathrm{mg})$ and a sugar fraction. From the sugar fraction, the presence of d-glucose was revealed as 5 .
erythro-1'-(4-Hydroxyphynyl)propane-1', $\mathbf{2}^{\prime}$-diol (21) An amorphous powder, $[\alpha]_{\mathrm{D}}^{22} \pm 0^{\circ}(c=0.2, \mathrm{MeOH}) .{ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 270 \mathrm{MHz}$ ) $\delta$ : Table $1 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 67.5 \mathrm{MHz}$ ) $\delta$ : Table 2.
( $\mathbf{1}^{\prime} R, 2^{\prime} S$ )-1'-(4-Hydroxyphynyl)propane-1', $\mathbf{2}^{\prime}$-diol $\mathbf{2}^{\prime}$ - $\boldsymbol{O}$ - $\boldsymbol{\beta}$-d-Glucopyranoside (8) An amorphous powder, $[\alpha]_{\mathrm{D}}^{21}-33^{\circ}(c=0.3, \mathrm{MeOH})$. Positive FAB-MS m/z: $369[\mathrm{M}+\mathrm{K}]^{+}, 353.1215[\mathrm{M}+\mathrm{Na}]^{+}$, (Calcd for $\mathrm{C}_{15} \mathrm{H}_{22} \mathrm{NaO}_{8}$; 353.1212), $313\left[\mathrm{M}-\mathrm{H}_{2} \mathrm{O}+\mathrm{H}\right]^{+}, 151\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$(base). ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500 \mathrm{MHz}$ ) $\delta$ : Table $1 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : 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$2^{\prime} / \mathrm{C}-1, \mathrm{C}-3^{\prime}, \mathrm{Glc}-1$; H-3'/C-1', C-2'; Glc-1/C-2'
( $\mathbf{1}^{\prime} S, 2^{\prime} R$ )-1'-(4-Hydroxyphynyl)propane-1', $\mathbf{2}^{\prime}$-diol $\mathbf{2}^{\prime}$ - $\boldsymbol{O}$ - $\boldsymbol{\beta}$-d-Glucopyranoside (9) An amorphous powder, $[\alpha]_{\mathrm{D}}^{21}-16^{\circ}(c=0.2, \mathrm{MeOH})$. Positive FAB-MS $m / z: 369[\mathrm{M}+\mathrm{K}]^{+}, 353.1211[\mathrm{M}+\mathrm{Na}]^{+}$, (Calcd for $\mathrm{C}_{15} \mathrm{H}_{22} \mathrm{NaO}_{8}$; 353.1212), $313\left[\mathrm{M}-\mathrm{H}_{2} \mathrm{O}+\mathrm{H}\right]^{+}, 151\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$(base). ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500 \mathrm{MHz}$ ) $\delta$ : Table $1 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : Table 2. HMBC correlations: $\mathrm{H}-2 / \mathrm{C}-4, \mathrm{C}-6, \mathrm{C}-1^{\prime} ; \mathrm{H}-3 / \mathrm{C}-1, \mathrm{C}-4, \mathrm{C}-5$; 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$2^{\prime} / \mathrm{C}-1, \mathrm{C}-3^{\prime}$, Glc-1; $\mathrm{H}-3^{\prime} / \mathrm{C}-1^{\prime}, \mathrm{C}-2^{\prime}$; Glc-1/C-2'
threo-1'-(4-Hydroxyphynyl)propane- $\mathbf{1}^{\prime}, 2^{\prime}$-diol 4-O- $\beta$-d-Glucopyranoside (10) An amorphous powder, $[\alpha]_{\mathrm{D}}^{23}-49^{\circ}(c=0.2, \mathrm{MeOH}) .{ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500 \mathrm{MHz}$ ) $\delta$ : Table $1 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $\left.d_{5}, 125 \mathrm{MHz}\right) \delta$ : Table 2.
$\left(1^{\prime} R, 2^{\prime} R\right)-1^{\prime}$-(4-Hydroxyphynyl)propane-1', $\mathbf{2}^{\prime}$-diol $\mathbf{2}^{\prime}$ - $\boldsymbol{O}$ - $\boldsymbol{\beta}$-d-Glucopyranoside (11) An amorphous powder, $[\alpha]_{\mathrm{D}}^{22}-51^{\circ}(c=0.8, \mathrm{MeOH})$. Positive FAB-MS m/z: $369.0935[\mathrm{M}+\mathrm{K}]^{+}$(Calcd for $\mathrm{C}_{15} \mathrm{H}_{22} \mathrm{KO}_{8} ; 369.0951$ ), 353 $[\mathrm{M}+\mathrm{Na}]^{+}, 313\left[\mathrm{M}-\mathrm{H}_{2} \mathrm{O}+\mathrm{H}\right]^{+}, 151\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$(base). ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500 \mathrm{MHz}$ ) $\delta$ : Table $1 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : 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; $\mathrm{H}-3^{\prime} / \mathrm{C}-1^{\prime}, \mathrm{C}-2^{\prime}$; Glc-1/C-2 ${ }^{\prime}$
Enzymatic Hydrolysis of 11 A mixture of $\mathbf{1 1}(6 \mathrm{mg})$ and $\beta$-glucosidase $(5 \mathrm{mg})$ in water $(5 \mathrm{ml})$ was shaken in a water bath at $37^{\circ} \mathrm{C}$ 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 .
( $\mathbf{1}^{\prime} R, \mathbf{2}^{\prime} R$ )-1'-(4-Hydroxyphynyl)propane-1', $\mathbf{2}^{\prime}$-diol (22a) An amorphous powder, $[\alpha]_{\mathrm{D}}^{22}-19^{\circ}(c=0.3, \mathrm{MeOH}) .{ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 270$ $\mathrm{MHz}) \delta$ : Table $1(\mathbf{2 2}) .{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\right.$ pyridine $\left.-d_{5}, 67.5 \mathrm{MHz}\right) \delta$ : Table $2(\mathbf{2 2})$.
( $\mathbf{1}^{\prime} \boldsymbol{S}, \mathbf{2}^{\prime} S$ )-1'-(4-Hydroxyphynyl)propane-1', $\mathbf{2}^{\prime}$-diol $\mathbf{2}^{\prime}$ - $\boldsymbol{O}$ - $\boldsymbol{\beta}$-d-Glucopyranoside (12) An amorphous powder, $[\alpha]_{\mathrm{D}}^{22}+21^{\circ}(c=1.0, \mathrm{MeOH})$. Positive FAB-MS m/z: $369[\mathrm{M}+\mathrm{K}]^{+}, 353.1215[\mathrm{M}+\mathrm{Na}]^{+}$(Calcd for $\mathrm{C}_{15} \mathrm{H}_{22} \mathrm{NaO}_{8} ; 353.1212$ ), $313\left[\mathrm{M}-\mathrm{H}_{2} \mathrm{O}+\mathrm{H}\right]^{+}, \quad 151\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$ (base). ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500 \mathrm{MHz}$ ) $\delta$ : Table $1 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}$, $125 \mathrm{MHz}) \delta$ : Table 2. HMBC correlations: $\mathrm{H}-2 / \mathrm{C}-4, \mathrm{C}-6, \mathrm{C}-1^{\prime} ; \mathrm{H}-3 / \mathrm{C}-1, \mathrm{C}-$ 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$3^{\prime}$; $\mathrm{H}-2^{\prime} / \mathrm{C}-1, \mathrm{C}-1^{\prime}$, Glc-1; $\mathrm{H}-3^{\prime} / \mathrm{C}-1^{\prime}, \mathrm{C}-2^{\prime}$; Glc-1/C-2'.

Enzymatic Hydrolysis of $\mathbf{1 2}$ A mixture of $\mathbf{1 2}(5 \mathrm{mg})$ and $\beta$-glucosidase $(5 \mathrm{mg})$ in water $(5 \mathrm{ml})$ was shaken in a water bath at $37^{\circ} \mathrm{C}$ for 2 d . The mixture was treated in the same way described for $\mathbf{7}$ to afford $\mathbf{2 2 b}(3 \mathrm{mg})$ and a sugar fraction. From the sugar fraction, the presence of d-glucose was revealed as 5 .
( $\mathbf{1}^{\prime} \boldsymbol{S}, \mathbf{2}^{\prime} \boldsymbol{S}$ )-1'-(4-Hydroxyphynyl)propane-1', $\mathbf{2}^{\prime}$-diol (22b) An amorphous powder, $[\alpha]_{\mathrm{D}}^{22}+19^{\circ}(c=0.2, \mathrm{MeOH}) .{ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $\left.d_{5}, 270 \mathrm{MHz}\right) \delta$ : Table $1(\mathbf{2 2}) .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $\left.d_{5}, 67.5 \mathrm{MHz}\right) \delta$ : Table $2(\mathbf{2 2})$.
( $\mathbf{1}^{\prime} \boldsymbol{R}, \mathbf{2}^{\prime} R$ )-Guaiacyl Glycerol (13) An amorphous powder, $[\alpha]_{\mathrm{D}}^{25}-26^{\circ}$ $\left(c=0.3\right.$, MeOH). ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $\left.d_{5}, 500 \mathrm{MHz}\right) \delta$ : Table 1. ${ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : Table 2.
( $\mathbf{1}^{\prime} \boldsymbol{R}, \mathbf{2}^{\prime} \boldsymbol{R}$ )-Guaiacyl Glycerol 4- $\boldsymbol{O}$ - $\boldsymbol{\beta}$-d-Glucopyranoside (14) An amorphous powder, $[\alpha]_{\mathrm{D}}^{21}-50^{\circ}(c=0.5, \mathrm{MeOH})$. Positive FAB-MS $m / z: 415.0999$ $[\mathrm{M}+\mathrm{K}]^{+}$(base, Calcd for $\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{KO}_{10} ; 415.1007$ ), $399[\mathrm{M}+\mathrm{Na}]^{+}, 197$ $\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500 \mathrm{MHz}$ ) $\delta$ : Table 1. ${ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $\left.d_{5}, 125 \mathrm{MHz}\right) \delta$ : Table 2. HMBC correlations: $\mathrm{H}-2 / \mathrm{C}-1, \mathrm{C}-3, \mathrm{C}-4$, 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', $\mathrm{C}-3^{\prime} ; \mathrm{H}-2^{\prime} / \mathrm{C}-1, \mathrm{C}-1^{\prime}, \mathrm{C}-3^{\prime} ; \mathrm{H}-3^{\prime} \mathrm{a} / \mathrm{C}-1^{\prime}, \mathrm{C}-2^{\prime} ; \mathrm{H}-3^{\prime} \mathrm{b} / \mathrm{C}-1^{\prime}, \mathrm{C}-2^{\prime} ; \mathrm{O}^{\prime} \mathrm{CH}_{3} / \mathrm{C}-3$; Glc-1/C-4.

Enzymatic Hydrolysis of 14 A mixture of $\mathbf{1 4}(6 \mathrm{mg})$ and $\beta$-glucosidase $(5 \mathrm{mg})$ in water $(5 \mathrm{ml})$ was shaken in a water bath at $37^{\circ} \mathrm{C}$ for 5 d . The mixture was treated in the same way described for $\mathbf{7}$ to afford $\mathbf{1 3}(3 \mathrm{mg})$ and a sugar fraction. From the sugar fraction, the presence of d-glucose was revealed as 5 .
( $\mathbf{1}^{\prime} \boldsymbol{R}, \mathbf{2}^{\prime} \boldsymbol{R}$ )-Guaiacyl Glycerol $\mathbf{3}^{\prime}$ - $\boldsymbol{O}$ - $\boldsymbol{\beta}$-d-Glucopyranoside (15) An amorphous powder, $[\alpha]_{D}^{22}-13^{\circ}(c=1.0, \mathrm{MeOH})$. Positive FAB-MS $m / z: 415.1019$ $[\mathrm{M}+\mathrm{K}]^{+}$(Calcd for $\left.\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{KO}_{10} ; 415.1007\right), 399[\mathrm{M}+\mathrm{Na}]^{+}$(base), 197 $\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500 \mathrm{MHz}$ ) $\delta$ : Table 1. ${ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : 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', Glc1; $\mathrm{O}-\mathrm{CH}_{3} / \mathrm{C}-3$; Glc-1/C-3'.

Enzymatic Hydrolysis of 15 A mixture of $\mathbf{1 5}(13 \mathrm{mg})$ and $\beta$-glucosidase $(5 \mathrm{mg})$ in water $(5 \mathrm{ml})$ was shaken in a water bath at $37^{\circ} \mathrm{C}$ for 5 d . The mixture was treated in the same way described for $\mathbf{7}$ to afford $\mathbf{1 3}(3 \mathrm{mg})$ and a sugar fraction. From the sugar fraction, the presence of d-glucose was revealed as 5 .
( $\mathbf{1}^{\prime} \boldsymbol{S}, \mathbf{2}^{\prime} \boldsymbol{R}$ )-Guaiacyl Glycerol $\mathbf{3}^{\prime}$ - $\boldsymbol{O}$ - $\boldsymbol{\beta}$-d-Glucopyranoside (16) An amorphous powder, $[\alpha]_{\mathrm{D}}^{22}-20^{\circ}(c=0.8, \mathrm{MeOH})$. Positive FAB-MS $m / z: 415$ $[\mathrm{M}+\mathrm{K}]^{+}, 399.1281[\mathrm{M}+\mathrm{Na}]^{+}$(base, Calcd for $\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{NaO}_{10} ; 399.1268$ ), $197\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+} .{ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500 \mathrm{MHz}$ ) $\delta$ : Table 1. ${ }^{13} \mathrm{C}-$ NMR (pyridine- $\left.d_{5}, 125 \mathrm{MHz}\right) \delta$ : Table 2. HMBC correlations: $\mathrm{H}-2 / \mathrm{C}-1, \mathrm{C}-3$, 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, $\mathrm{C}-2^{\prime}, \mathrm{C}-3^{\prime} ; \mathrm{H}^{\prime} 2^{\prime} / \mathrm{C}-1, \mathrm{C}-1^{\prime}, \mathrm{C}-3^{\prime} ; \mathrm{H}-3^{\prime} \mathrm{a} / \mathrm{C}-1^{\prime}, \mathrm{C}-2^{\prime}$, Glc-1; H-3'b/C-1', C-2', Glc-1; O-CH ${ }_{3} / \mathrm{C}-3$; Glc-1/C-3'

Enzymatic Hydrolysis of 16 A mixture of $\mathbf{1 6}(8 \mathrm{mg})$ and $\beta$-glucosidase $(5 \mathrm{mg})$ in water $(5 \mathrm{ml})$ was shaken in a water bath at $37^{\circ} \mathrm{C}$ for 5 d . The mixture was treated in the same way described for 7 to afford $\mathbf{2 3}(5 \mathrm{mg})$ and a sugar fraction. From the sugar fraction, the presence of d-glucose was revealed as 5 .
( $\mathbf{1}^{\prime} \boldsymbol{S}, \mathbf{2}^{\prime} \boldsymbol{R}$ )-Guaiacyl Glycerol (23) An amorphous powder, $[\alpha]_{\mathrm{D}}^{22}+11^{\circ}$ $\left(c=0.2, \mathrm{MeOH}\right.$ ). ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $\left.d_{5}, 500 \mathrm{MHz}\right) \delta$ : Table 1. ${ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : Table 2.
( $\mathbf{1}^{\prime} \boldsymbol{R}, \mathbf{2}^{\prime} \boldsymbol{R}$ )-4-O-Methylguaiacyl Glycerol $\mathbf{3}^{\prime}$ - $\boldsymbol{O}$ - $\boldsymbol{\beta}$-d-Glucopyranoside (17) An amorphous powder, $[\alpha]_{\mathrm{D}}^{22}-15^{\circ}(c=1.2, \mathrm{MeOH})$. Positive FAB-MS $m / z$ : $429[\mathrm{M}+\mathrm{K}]^{+}, 413.1442[\mathrm{M}+\mathrm{Na}]^{+}$(base, Calcd for $\mathrm{C}_{17} \mathrm{H}_{26} \mathrm{NaO}_{10}$; 413.1424), $373\left[\mathrm{M}-\mathrm{H}_{2} \mathrm{O}+\mathrm{H}\right]^{+}, 211\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+} .{ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyri-dine- $d_{5}, 500 \mathrm{MHz}$ ) $\delta$ : Table 1. ${ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : 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, $\mathrm{C}-4, \mathrm{C}-5, \mathrm{C}-1^{\prime} ; \mathrm{H}-1^{\prime} / \mathrm{C}-1, \mathrm{C}-2, \mathrm{C}-6, \mathrm{C}-2^{\prime}, \mathrm{C}-3^{\prime} ; \mathrm{H}-2^{\prime} / \mathrm{C}-1, \mathrm{C}-1^{\prime}, \mathrm{C}-3^{\prime} ; \mathrm{H}-$ $3^{\prime} \mathrm{a} / \mathrm{C}-1^{\prime}, \mathrm{C}-2^{\prime}$, Glc-1; H-3'b/C-1', C-2', Glc-1; 3-O-CH $/ \mathrm{C}-3 ; 4-\mathrm{O}-\mathrm{CH}_{3} / \mathrm{C}-4$; Glc-1/C-3'.

Enzymatic Hydrolysis of 17 A mixture of $\mathbf{1 7}(10 \mathrm{mg})$ and $\beta$-glucosi-
dase $(5 \mathrm{mg})$ in water $(5 \mathrm{ml})$ was shaken in a water bath at $37^{\circ} \mathrm{C}$ for 5 d . The mixture was evaporated in vacuo to dryness and the residue was chromatographed over silica gel $\left[\mathrm{CHCl}_{3}-\mathrm{MeOH}(17: 3\right.$ to $\left.1: 1)\right]$ to afford 24 $(5 \mathrm{mg})$ and a sugar fraction. From the sugar fraction, the presence of d-glucose was revealed as 5 .
( $\mathbf{1}^{\prime} \boldsymbol{R}, \mathbf{2}^{\prime} \boldsymbol{R}$ )-4-O-Methylguaiacyl Glycerol (24) Colorless needles (MeOH), $\mathrm{mp} 86-88^{\circ} \mathrm{C},[\alpha]_{\mathrm{D}}^{24}-24^{\circ}(c=1.2, \mathrm{MeOH}) .{ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500$ $\mathrm{MHz}) \delta$ : Table $1 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine $-d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : Table 2.

4-O-Methylguaiacyl Glycerol $\mathbf{2}^{\prime}$ - $\boldsymbol{O}$ - $\boldsymbol{\beta}$-d-Glucopyranoside (18) An amorphous powder, $[\alpha]_{\mathrm{D}}^{22}-33^{\circ}(c=0.1, \mathrm{MeOH})$. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500$ $\mathrm{MHz}) \delta$ : Table $1 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : 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, $\mathrm{C}-5, \mathrm{C}-1^{\prime} ; \mathrm{H}-1^{\prime} / \mathrm{C}-1, \mathrm{C}-2, \mathrm{C}-6, \mathrm{C}-2^{\prime}, \mathrm{C}-3^{\prime} ; \mathrm{H}-2^{\prime} / \mathrm{C}-1, \mathrm{C}-1^{\prime}, \mathrm{C}-3^{\prime}$, Glc-1; 3-O$\mathrm{CH}_{3} / \mathrm{C}-3$; 4-O-CH3$/ \mathrm{C}-4$; Glc-1/C-2 ${ }^{\prime}$.
(E)-4-Hydroxycinnamyl Alcohol 4-O- $\boldsymbol{\beta}$-d-Glucopyranoside (19) An amorphous powder, $[\alpha]_{\mathrm{D}}^{22}-56^{\circ}(c=1.0, \mathrm{MeOH}) .{ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}$, 500 MHz ) $\delta$ : Table $1 .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : 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', C2'; Glc-1/C-4.
(Z)-4-Hydroxycinnamyl Alcohol 4-O- $\boldsymbol{\beta}$-D-Glucopyranoside (20) An amorphous powder, $[\alpha]_{\mathrm{D}}^{22}-63^{\circ}(c=0.2, \mathrm{MeOH})$. Positive FAB-MS $m / z$ : $335.1099[\mathrm{M}+\mathrm{Na}]^{+}$(Calcd for $\mathrm{C}_{15} \mathrm{H}_{20} \mathrm{NaO}_{7} ; 335.1107$ ), $295\left[\mathrm{M}-\mathrm{H}_{2} \mathrm{O}+\right.$ $\mathrm{H}]^{+}, 133\left[\mathrm{M}-\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}\right]^{+}$(base). ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (pyridine- $d_{5}, 500 \mathrm{MHz}$ ) $\delta$ : Table 1. ${ }^{13} \mathrm{C}-\mathrm{NMR}$ (pyridine- $d_{5}, 125 \mathrm{MHz}$ ) $\delta$ : 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$1^{\prime}$; $\mathrm{H}-1^{\prime} / \mathrm{C}-1, \mathrm{C}-2, \mathrm{C}-6, \mathrm{C}-3^{\prime} ; \mathrm{H}-2^{\prime} / \mathrm{C}-1 ; \mathrm{H}-3^{\prime} / \mathrm{C}-1^{\prime}, \mathrm{C}-2^{\prime} ; \mathrm{Glc}-1 / \mathrm{C}-4$.

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

## References and Notes

1) Norman J., "The Complete Book of Spices," Doerling Kindersley, 1990, p. 51.
2) "Herbal Drugs and Phytopharmaceuticals," ed. by Wichtl M., CRC Press, Stuttgart, 1994, pp. 73-75.
3) British Pharmacopoeia 1., The Stationary Office, 1999, pp. 260-261.
4) European Pharmacopoeia 3rd edition, Council of Europe Publishing, 1997, pp. 536-537.
5) Harborne J. B., Heywood V. H., Weisleder D., Phytochemistry, 8, 1729-1732 (1969)
6) Becker H., Plant Med., 18, 336-346 (1970).
7) Kleimann R., Plattner R. D., Weisleder D., J. Nat. Prod., 51, 249-256 (1988).
8) Ishikawa T., Kudo M., Kitajima J., Chem. Pharm. Bull., 50, 501-507 (2002).
9) Klyne W., "Determination of Organic Structure by Physical Methods," ed. by Braude E. A., Nachod F. C., Academic Press, New York, 1975, p. 73.
10) Klyne W., Biochem. J., 47, XIi—XIii (1950).
11) Ono M., Ito Y., Ishikawa T., Kitajima J., Tanaka Y., Niiho Y., Nohara T., Chem. Pharm. Bull., 44, 337-342 (1996).
12) Kitajima J., Ishikawa T., Tanaka Y., Chem. Pharm. Bull., 46, 15911594 (1998).
13) Takeshita M., Taguchi R., Akutsu N., Tetrahedron: Asymmetry, 3, 1369-1372 (1992).
14) Kasai R., Suzuo M., Asakawa J., Tanaka O., Tetrahedron Lett., 1977, 175-178 (1977).
15) Tori K., Seo S., Yoshimura Y., Arita Y., Tomita Y., Tetrahedron Lett., 1977, 179-182 (1977).
16) Kasai R., Okihara M., Asakawa J., Mizutani K., Tanaka O., Tetrahedron, 35, 1427-1432 (1979).
17) Mizutani K., Kasai R., Tanaka O., Carbohydr. Res., 87, 19-26 (1980).
18) Ishikawa T., Kitajima J., Tanaka Y., Ono M., Ito Y., Nohara T., Chem. Pharm. Bull., 46, 1738-1742 (1998).
19) Kitajima J., Kimizuka K, Tanaka Y., Chem. Pharm. Bull., 48, 77-80 (2000).
20) Greca D. M., Ferrara M., Fiorentino A., Monaco P., Previtera L., Phytochemistry, 49, 1299-1304 (1998).
21) Lundgren L. N., Popoff T., Theander O., Acta Chem. Scand. B, 36, 695-699 (1982).
22) Mohaned K. M., Phytochemistry, 58, 615-618 (2001).
23) Nakano K., Nishizawa K, Takemoto I., Murakami K., Tomimatsu T., Phytochemistry, 28, 301-303 (1989).
24) Dahmen J., Leander K., Rosenblom J., Acta Chem. Scand. B, 29, 627-628 (1975).

[^0]:    $\delta$ in ppm from TMS [coupling constants ( $J$ ) in Hz are given in parentheses]. b) Stereoisomeric components are given in brackets.

[^1]:    $\delta$ in ppm from TMS. $\Delta \delta\left(\delta_{\text {glucoside }}-\delta_{\text {aglycone }}\right)$ are given in parentheses. b) Stereoisomeric components are given in brackets.

