New Acyclic Bis-phenylpropanoids from the Aril of Myristica fragrans

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From a methanolic extract of the aril of Myristica fragrans HOUTT. (mace), the following new threo and erythro acyclic bis-phenylpropanoids were isolated: threo-2-(4-allyl-2,6-dimethoxy-phenoxy)-1-(4-hydroxy-3-methoxyphenyl)propan-1-ol (1a), erythro-2-(4-allyl-2,6-dimethoxy-phenoxy)-1-(4-hydroxy-3-methoxyphenyl)-1-methoxypropane (2b), erythro-2-(4-allyl-2,6-dimethoxyphenoxy)-1-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-ol (3b), 2-(4-allyl-2,6-dimethoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)propane (4), erythro-2-(4-allyl-2-methoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)propan-1-ol (5b), threo-2-(4-allyl-2-methoxyphenoxy)-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-[2-methoxy-4-(1(E)-propenyl)phenoxy]propan-1-ol (6a) and erythro-2-(4-allyl-2,6-dimethoxyphenoxy)-1-(3-hydroxy-4,5-dimethoxyphenyl)propan-1-ol (7b). Contrary to a previous finding that Myristica species contain only an erythro type of acyclic bis-phenylpropanoids, we isolated both threo and erythro derivatives.

Keywords—acyclic bis-phenylpropanoid; mace; Myristicaceae; Myristica fragrans; neolignan

The aril of Myristica fragrans HOUTT. (Myristicaceae), mace, has been widely used as a spice and a valuable remedy in Ayurvedic medicine for treatment in the low stage of fever, in consumptive complaints, humoral asthma, and when mixed with aromatics, in wasting and long-term bowel complaints. There have been numerous reports on the constituents of mace as well as nutmeg (the seed kernels of Myristica fragrans) in the literature. These include essential oils, fats, glycerides, cyclic and acyclic bis-phenylpropanoids and a pigment. Pharmacological studies have also been conducted by many workers as to hallucinogenic effect, and inhibitory effects on the growth of silkworm larvae, Bombyx mori, and on prostaglandin biosynthesis. Recently, we have reported that dehydrodiisoeugenol and 5'-methoxydehydrodiisoeugenol from mace have antibacterial action against a primary cariogenic bacterium, Streptococcus mutans. In a continuation of this investigation, we report the isolation of both threo and erythro diastereomers of acyclic bis-phenylpropanoids (1a, 2b, 3b, 5b, 6a and 7b; but with a = threo and b = erythro), as well as 4.

Results and Discussion

A methanolic extract of the aril of Myristica fragrans was subjected to solvent fractionation and silica gel column chromatography. This procedure led to the isolation of new compounds (1a, 2b, 3b, 4, 5b, 6a and 7b) along with the known 4-propenylphenols, dehydrodiisoeugenol derivatives, guaiacin, and acyclic bis-phenylpropanoids. The structures of the new compounds were determined as follows:

Compound 1a was isolated as an oily substance with the molecular formula C21H26O6. The proton nuclear magnetic resonance (1H-NMR) spectrum (in CD3COOD) showed signals
of one sec-methyl (δ 1.16, J = 6.3 Hz), three methoxyls (δ 3.83 and 3.86; 3H and 6H, respectively), one allyl group (δ 3.35, 2H, d, J = 6.7 Hz; 5.06—5.15, 2H, m; 5.80—6.03, 1H, m), one methine substituted by oxygen (β-methine; δ 4.02, br dq, J = 6.3 and 8.4 Hz), one benzylic methine substituted by oxygen (α-methine; δ 4.66, d, J = 8.4 Hz), and five aromatic protons (δ 6.50, 2H, s; 6.82—6.93, 3H). On irradiation at δ 4.02, the two doublets at δ 4.66 (α-H) and 1.16 (β-H) each became singlets. On irradiation at δ 4.66, the double quartet at δ 4.02 (β-H) became a sharp quartet (J = ca. 6 Hz). Further, the carbon-13 nuclear magnetic resonance (13C-NMR) spectrum (Table I) showed the presence of 4-allyl-2,6-dimethoxyphenoxy and 4-hydroxy-3-methoxyphenyl groups in the molecule. These findings indicate that 1a is an acyclic bis-phenylpropanoid. The molecular ion peak and mass fragmentation pattern (Table II) were identical with those of a known constituent of mace, erythro-2-(4-allyl-2,6-dimethoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)propan-1-ol (1b).5) The coupling constant between the α- and β-methine protons in 1a (Jα,β = 8.4 Hz in CD3COOD) was, however,
larger than that in 1b ($J_{\alpha,\beta} = 2.9$ Hz). Consequently, 1a was concluded to be threo-2-(4-allyl-2,6-dimethoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)propan-1-ol. This is the second example of the isolation of threo acyclic bis-phenylpropanoids from Myristica fragrans. 11) Compound 2b was isolated as an oily substance with the molecular formula $C_{22}H_{28}O_{6}$. The $1H$-NMR spectrum (in CDCl$_3$) showed signals due to one sec-methyl ($\delta 1.25$, d, $J=6.6$ Hz), one aliphatic methoxyl ($\delta 3.37$), five aromatic methoxyls ($\delta 3.79$ and $3.87$; 6H and 3H, respectively), two methines substituted by oxygen ($\delta 4.16$, dq, $J=3.4$ and $6.6$ Hz; $\delta 4.40$, d, $J=3.4$ Hz), one allyl group, and five aromatic protons ($\delta 6.38$ and $6.72-6.93$, 2H and 3H, respectively). The spectral features were similar to those of 1b except for the aliphatic methoxyl signal, suggesting that 2b is an alpha-(O)-methyl ether of 1b. The molecular ion peak at $m/z$ 388 and the mass fragmentation pattern of 2b (Table II) were identical with those of a known constituent of mace, threo-2-(4-allyl-2,6-dimethoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)-1-methoxypropane (2a), which we have previously isolated from mace. 9) The $1H$-NMR spectrum of 2b was, however, not identical with that of 2a, but in both chemical shifts and coupling constants was similar to that of a synthetic erythro-isomer as reported by Nishiyama et al. 12); the $J_{\alpha,\beta}$ value was smaller in 2b ($J_{\alpha,\beta} = 3.4$ Hz) than in 2a ($J_{\alpha,\beta} = 6.6$ Hz in CD$_3$COOD), indicating that 2b is erythro-2-(4-allyl-2,6-dimethoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)-1-methoxypropane.

Compound 3b was isolated as an oily substance with the molecular formula $C_{22}H_{28}O_{7}$. The mass spectrum (MS) showed a characteristic pattern ascribed to an acyclic bis-phenylpropanoid (Table II). The molecular ion peak was 30 mass units higher than that of 1a and 1b, suggesting a monomethoxylated derivative of either 1a or 1b. The $13C$-NMR spectrum showed the presence of 4-allyl-2,6-dimethoxyphenoxyl and 4-hydroxy-3,5-dimethoxyphenyl groups (Table I), which were also confirmed by the observation of two distinct singlet signals ($\delta 6.46$ and $6.55$, 2H each) and four methoxyl signals ($\delta 3.870$ and $3.874$, $6H$ each) in the $1H$-NMR spectrum. Based on the above evidence together with the small $J_{\alpha,\beta}$ value (2.8 Hz),
3b was concluded to be erythro-2-(4-allyl-2,6-dimethoxyphenoxy)-1-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-ol. This compound was first suggested to occur in mace by Davis et al.13) and Harvey14) on the basis of mass spectrometry-mass spectrometry and gas chromatography-mass spectrometry, respectively, but has not previously been isolated.

Compound 4 was isolated as an oily substance with the molecular formula C_{21}H_{26}O_{5}. The 1H-NMR spectrum showed characteristic peaks due to a 4-allyl-2,6-dimethoxyphenoxy group, but no peak ascribable to an α-methylene proton in an acyclic bis-phenylpropanoid. Instead, two double-doublet signals (each one proton) were observed at δ 2.72 (α-Hα; J = 13.4 and 8.3 Hz) and 3.12 (α-Hβ; J = 13.4 and 5.1 Hz). On irradiation at δ 4.33 (β-methene), the two double-doublets at δ 2.72 and 3.12 became two doublets (J = ca. 13 Hz each) and the doublet at δ 1.20 (J = 6.1 Hz, γ-H) became a singlet, suggesting a partial structure of Ph-CH$_2$-CH(R)-CH$_3$ (but with R = 4-allyl-2,6-dimethoxyphenoxyl). The 13C-NMR spectrum showed the presence of a 4-hydroxy-3-methoxyphenyl group (Table I). Based on these findings as well as the mass fragmentation pattern (Table II), the structure of 4 was determined to be 2-(4-allyl-2,6-dimethoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)propane.

Compound 5b was isolated as an oily substance. The MS showed a molecular ion peak at m/z 344 in agreement with a molecular formula of C$_{20}$H$_{24}$O$_{5}$. The 1H-NMR spectrum showed the presence of sec-methyl (δ 1.17, d, J = 6.3 Hz), α- and β-methines (δ 4.82, br s; δ 4.32, m; respectively), an allyl group and six aromatic protons. The 13C-NMR spectrum showed the presence of both 4-hydroxy-3-methoxyphenyl and 4-allyl-2-methoxyphenoxyl groups (Table I), the latter of which was also confirmed by the observation of an intense mass fragment peak at m/z 164 (Table II). On acetylation, 5b yielded a diacetate (1H-NMR, aliphatic and aromatic acetoxyls at δ 2.06 and 2.23, respectively). The small J$_{α,β}$ values of 5b and its acetate (ca. 2—3 Hz and 4.4 Hz, respectively) were indicative of erythro derivatives. Based on these findings, 5b was concluded to be erythro-2-(4-allyl-3-methoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)propan-1-ol.

Compound 6a was isolated as an oily substance, C$_{21}$H$_{26}$O$_{5}$. In contrast to the spectra of the series of acyclic bis-phenylpropanoids mentioned above, the 1H-NMR spectrum showed no signals due to an allyl group but showed characteristic ABX$_3$-type signals at δ 1.88, ca. 6.15 and 6.36 (J$_{AB}$ = 15.8 Hz, J$_{AX}$ = 1.5 Hz and J$_{BX}$ = 6.6 Hz) due to a 1(E)-propenyl group. Further, the spectrum showed signals of one sec-methyl (δ 1.17, d, J = 6.3 Hz), three methoxyls (δ 3.89 and 3.92; 6H and 3H, respectively), two α- and β-methine protons (δ 4.59, d, J = 8.3 Hz; δ ca. 4.09, dq, J = 8.3 and 6.2 Hz) and five aromatic protons. The aromatic proton signal at high field, δ 6.61 (2H, s) and the methoxyl signals at δ 3.89 (6H, s), as well as the 13C-NMR signals (Table I) indicated the presence of a 4-hydroxy-3,5-dimethoxyphenyl group in the molecule. In addition, the 13C-NMR spectrum indicated the presence of a 2-methoxy-4-(1(E)-propenyl)phenoxyl group. These findings and the large J$_{α,β}$ value (8.3 Hz) led to the structure of threo-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-[2-methoxy-4-(1(E)-propenyl)phenoxyl]propan-1-ol for 6a.

Compound 7b had the molecular formula C$_{22}$H$_{28}$O$_{7}$. The 1H-NMR spectrum showed characteristic signals indicative of a bis-phenylpropanoid derivative; one sec-methyl (δ 1.12, d, J = 6.4 Hz), four methoxyls (δ 3.89), α- and β-methines (δ 4.75, br s; δ 4.35, dq, J = 2.8 and 6.4 Hz), an allyl group and four aromatic protons. A 4-allyl-2,6-dimethoxyphenoxyl group was apparent from the 1H-NMR, 13C-NMR (Table I) and mass (Table II) spectra, but common substituents such as 4-hydroxy-3,5-dimethoxyphenyl and 4-hydroxy-3-methoxyphenyl groups were absent in the molecule. The coupling constants (J = ca. 1.4 Hz) of the signals at δ 6.42 and 6.58 suggested that these aromatic protons were located in the meta position with respect to each other. Further, the two methoxy signals at δ 55.9 and lower field, 60.8, in the 13C-NMR spectrum suggested the presence of a 3-hydroxy-4,5-dimethoxyphenyl group.15) The 13C-NMR signals assignable to this group were in good agreement with those reported.15)
These findings and the small \( J_{\alpha,\beta} \) value (2.7 Hz) led to the structure of \textit{erythro}-2-(4-allyl-2,6-dimethoxyphenoxy)-1-(3-hydroxy-4,5-dimethoxyphenyl)propan-1-ol for 7b.

A \( ^1\)H-NMR technique provided a convenient way to assign \textit{threo} and \textit{erythro} diastereomers of acyclic bis-phenylpropanoids, \( J_{\alpha,\beta} \) values being in the range of 8.0—8.6 Hz\(^{15}\) for the \textit{threo} derivatives and 2.7—4.4 Hz for the \textit{erythro} derivatives.\(^{5a,b,c,e,9,15}\) However, the diagnostic \( \alpha \)-methine proton did not show a simple doublet for such compounds as 2a, 5b and 7b, due to overlapping with a \( \beta \)-proton signal or spin–spin coupling with an \( \alpha \)-hydroxyl proton. The difficulty in determining \( J_{\alpha,\beta} \) values could be overcome in general by using CD\(_3\)COOD instead of CDCl\(_3\) as a solvent. On the other hand, the diastereomers were quite simply assignable on the basis of a diagnostic methyl signal in the \(^{13}\)C-NMR spectrum, this signal appearing at \( \delta 16.5—17.4 \) for the \textit{threo} derivatives and at 12.6—13.9 for the \textit{erythro} derivatives.\(^{9,15}\)

The acyclic bis-phenylpropanoids, Ph—CH(OH)—CH(O—Ph)—CH\(_3\), have been isolated exclusively from plants in the family of Myristicaceae.\(^{16}\) Among them, all of the compounds isolated so far from \textit{Virola surinamensis} (ROL.) WARD. belong to the \textit{threo} series carrying a 2-methoxy-4-(1(E)-propenyl)phenoxy group, while those from \textit{Myristica fragrans} belong to the \textit{erythro} series carrying a 4-allyl-2,6-dimethoxyphenoxy group.\(^{15}\) However, we have isolated \textit{threo} and \textit{erythro} acyclic derivatives with a 4-allyl-2,6-dimethoxyphenoxy (1a and 1b; 2a and 2b; 3b; 7b), a 4-allyl-2-methoxyphenoxy (5b) or a 2-methoxy-4-(1(E)-propenyl)phenoxy group (6a) from the aril of \textit{Myristica fragrans}. In addition, we have isolated a new derivative (7b) possessing a 3-hydroxy-4,5-dimethoxyphenyl group as well as \( \alpha \)-methoxy (2a and 2b) and \( \alpha \)-dihydro (4) derivatives.

In conclusion, seven acyclic bis-phenylpropanoids have been isolated as new natural products from the aril of \textit{Myristica fragrans}. This is the first report of the co-existence of both \textit{threo} and \textit{erythro} diastereomers of acyclic bis-phenylpropanoids in the same plant.

**Experimental**

**Apparatus**—All melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. \( ^1\)H-NMR and \( ^{13}\)C-NMR spectra were measured with JEOL GX-270 (\( ^1\)H, 270 MHz) and JEOL FX-90Q (\( ^{13}\)C, 22.5 MHz) spectrometers with tetramethylsilane as an internal standard. MS were measured with a JMS-DX 300 mass spectrometer (JEOL) at an ionization voltage of 70 eV. Ultraviolet (UV) spectra were measured with a Shimadzu UV-210 digital double beam spectrophotometer. Infrared (IR) spectra were taken on a Hitachi 260-10 infrared spectrometer.

**Plant Material**—The arils of \textit{Myristica fragrans} (mace) were purchased from W. Wilbert and Co. (Colombo, Sri Lanka) in 1983, and were ground before extraction.

**Chromatography**—Silica gel, Wako gel C-200, was used for column chromatography. Merck Kieselgel 60 F\(_{254}\) plates were used for thin layer chromatography (TLC) and Merck PSC-60 F\(_{254}\) plates for preparative TLC. Solvent systems used were as follows: A, CHCl\(_3\)—MeOH (9:1, v/v); B, benzene—EtOAc (9:1, v/v); C, benzene—acetone (9:1, v/v). Spots on the plate were detected under ultraviolet light.

**Isolation of Components of Mace**—Crude powder of mace (936 g) was extracted with MeOH at room temperature as described in a previous paper.\(^9\) The extract (290 g) was partitioned between 95% MeOH and n-hexane. A portion of the 95% MeOH soluble (84.5 g) was separated into acidic, phenolic and neutral fractions. The phenolic fraction (31.5 g) was chromatographed on silica gel with benzene containing increasing amounts of ethyl acetate, and the new compounds 1a, 2b, 3b, 4, 5b, 6a and 7b were obtained in yields of 110, 120, 240, 50, 30, 110 and 30 mg, respectively, along with the known constituents.\(^9\)

\textit{threo}-2-(4-Allyl-2,6-dimethoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)propan-1-ol (1a)—High-resolution MS, Caled for C\(_{22}\)H\(_{26}\)O\(_{6}\), \( m/z: 374.1730 \) (M \(^+\)). Found, \( m/z: 374.1746 \). IR (KBr) cm\(^{-1}\): 3475 (OH), 1615, 1540, 1525 (aromatic). \( ^1\)H-NMR (CDCl\(_3\)) \( \delta: 1.18 \) (3H, d, \( J=6.3 \) Hz, \( \alpha \)-H \~3), 3.35 (2H, d, \( J=6.6 \) Hz, \( \alpha' \)-H \~2), 3.87 (9H, s, -OMe \~3), ca. 3.85—3.95 (\( \beta \)-H, overlapped with the peaks of methoxy groups), 4.60 (1H, d, \( J=6.6 \) Hz, \( \beta \)-H), 5.06—5.15 (2H, m, \( \alpha' \)-H \~2), 5.85—6.01 (1H, m, \( \alpha \)-H \~3), 6.44 (2H, s, 3′-H and 5′-H), 6.84—6.87 (3H, 2-H, 5-H and 6-H). \( ^1\)H-NMR (CD\(_3\)COOD) \( \delta: 1.16 \) (3H, d, \( J=6.3 \) Hz, \( \gamma \)-H \~3), 3.35 (2H, d, \( J=6.7 \) Hz, \( \gamma' \)-H \~2), 3.83 (3H, s, 3-OMe), 3.86 (6H, s, 2′-OMe and 5′-OMe), 4.02 (1H, br d, \( J=6.3, 8.4 \) Hz, \( \beta \)-H), 4.66 (1H, d, \( J=8.4 \) Hz, \( \alpha \)-H), 5.06—5.15 (2H, m, \( \gamma' \)-H \~2), 5.80—6.03 (1H, m, \( \beta' \)-H), 6.50 (2H, s, 3′-H and 5′-H), 6.82—6.93 (3H, aromatic H).
erythro-2-(4-Allyl-2,6-dimethoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)-1-methoxypropane (2b) —— High-resolution MS, Calcd for C_{23}H_{26}O_{7}, m/z: 388.1886 (M^+). Found, m/z: 388.1896. 1H-NMR (CDCl_{3}) δ: 1.25 (3H, d, J = 6.6 Hz, -CH2-CH3), 3.33 (2H, d, J = 6.8 Hz, -CH2-O), 3.59 (6H, -OMe), 3.79 (6H, -OMe), 3.87 (3H, -OMe), 4.16 (1H, dd, J = 3.4, 6.6 Hz, J = 6.6 Hz, -CH2-O, -ArH). 4.40 (1H, d, J = 3.4 Hz, -ArH), 5.06—5.14 (2H, m, γ'-H ÷ 2), 5.55 (1H, s, -OH), 5.89—6.07 (1H, m, β'-H), 6.38 (2H, s, 3'-H and 5'-H), 6.72—6.93 (3H, m, 2-H, 5-H and 6-H).

erythro-2-(4-Allyl-2,6-dimethoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)propan-1-ol (3b) —— High-resolution MS, Calcd for C_{24}H_{28}O_{7}, m/z: 404.1835 (M^+). Found, m/z: 404.1800. 1H-NMR (CDCl_{3}) δ: 1.11 (3H, d, J = 6.4, γ-H ÷ 3), 3.37 (2H, d, J = 6.8 Hz, -CH2-O), 3.80 (6H, -OMe ÷ 2), 3.87 (3H, -OMe), 4.31 (1H, dq, J = 2.8, 6.4 Hz, J = 6.4 Hz, -CH2-O, -ArH), 4.78 (1H, brd, J = ca. 2.8 Hz, -ArH), 5.10—5.17 (2H, m, γ'-H ÷ 2), 5.44 (1H, s, -OH), 5.9—6.1 (1H, m, β'-H), 6.46 (2H, s, 3'-H and 5'-H), 6.55 (2H, s, 2-H and 6-H).

2-(4-Allyl-2,6-dimethoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)propan-1-ol (4b) —— High-resolution MS, Calcd for C_{22}H_{24}O_{6}, m/z: 374.1730 (M^+). Found, m/z: 374.1765. 1H-NMR (CDCl_{3}) δ: 1.17 (3H, d, J = 6.3 Hz, -CH2-CH3), 3.36 (2H, d, J = 6.8 Hz, -CH2-O), 3.89 (6H, -OMe), 4.32 (1H, m, β-H), 4.82 (1H, br s, -ArH), 5.13—5.07 (2H, m, γ'-H ÷ 2), 5.57 (-OH), 6.2—5.9 (1H, m, β'-H), 6.7—7.0 (6H, aromatic H). On acetylation, 5b yielded a diacetate, erythro-1-acetoxy-1-(4-acetoxy-3-methoxyphenyl)-2-(4-allyl-2,6-dimethoxyphenoxy)propane. High-resolution MS, Calcd for C_{24}H_{28}O_{7}, m/z: 428.1834 (M^+). Found, m/z: 428.1789. 1H-NMR (CDCl_{3}) δ: 1.20 (3H, d, J = 6.1 Hz, γ-H ÷ 3), 2.72 (1H, dd, J = 13.4, 8.3 Hz, -CH2-O), 3.12 (1H, dd, J = 13.4, 5.1 Hz, -CH2-O), 3.34 (2H, d, J = 6.8 Hz, -CH2-O), 3.80 (6H, -OMe ÷ 5-OMe), 3.82 (3H, s, -OMe), 4.33 (1H, m, -ArH), 5.07—5.15 (2H, m, γ'-H ÷ 2), 5.48 (1H, s, -OH), 5.92—6.02 (1H, m, β'-H), 6.40 (2H, s, 2'-H and 6'-H), 6.70 (1H, dd, J = 8.1, 1.7 Hz, 6-H), 6.77 (1H, d, J = 1.7 Hz, 2-H), 6.82 (1H, d, J = 8.1 Hz, 5-H).

erythro-2-(4-Allyl-2-methoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)propan-1-ol (5b) —— MS m/z: 344 (M^+). 1H-NMR (CDCl_{3}) δ: 1.17 (3H, d, J = 6.3 Hz, -CH2-CH3), 1.23 (3H, d, J = 6.3 Hz, -CH2-CH3), 2.06 (3H, s, -OAc), 2.23 (3H, s, -OAc), 2.35 (2H, d, J = 6.6 Hz, -CH2-O), 3.71 (3H, s, -OMe), 3.76 (3H, s, -OMe), 4.45 (1H, m, -ArH), 4.97—5.03 (2H, m, γ'-H ÷ 2), 5.86 (1H, d, J = 4.4 Hz, -ArH), 5.8—6.0 (1H, m, β'-H), 6.6—7.0 (6H, aromatic H). Assignments of α- and β- H were confirmed by double resonance experiments.


10) 1H-NMR spectral data for 1b in CD3COOD were as follows: δ: 1.11 (3H, d, J = 6.4 Hz, γ-H × 3), 3.36 (2H, d, J = 6.6 Hz, α'-H × 2), 3.85 (3H, s, 3-OMe), 3.86 (6H, s, 2'-OMe and 6'-OMe), 4.32 (1H, m, γ'-H), 4.84 (1H, d, J = 2.9 Hz, γ'-H), 5.06—5.15 (2H, m, γ'-H), 5.98—6.05 (1H, m, β'-H), 6.52 (2H, s, 3'-H and 5'-H), 6.68—6.98 (3H, m, 2-H, 5-H and 6-H).

11) In a preceding paper, we reported the first isolation of threo-2-(4-allyl-2,5-dimethoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)-1-methoxypropane from mace (see ref. 9).


