

Phenylpropanoids from *Cinnamomum parthenoxylon*

Thitima Rukachaisirikul*, Jukkamong Intaraudom, Suppachai Chawanasak and Apichart Suksamram

Department of Chemistry, Faculty of Science, Ramkhamhaeng University, Bangkok 10240, Thailand.

* Corresponding author, E-mail: thitima@ram1.ru.ac.th

Received 2 Jun 2000

Accepted 28 Jul 2000

ABSTRACT Phenylpropanoids were isolated from the wood of *Cinnamomum parthenoxylon* and their structures were characterized by spectroscopic methods. These compounds include safrole (1), 3,4-methylenedioxybenzaldehyde (2), (+)-3-(3,4-methylenedioxyphenyl)-1,2-propanediol (3), and a mixture of six alkyl *trans*-ferulates bearing alkyl groups of C₂₂ and C₂₄ to C₂₈ (4). This is the first report of the latter two components from *Cinnamomum* species.

KEYWORDS: *Cinnamomum parthenoxylon*, Lauraceae, phenylpropanoids.

INTRODUCTION

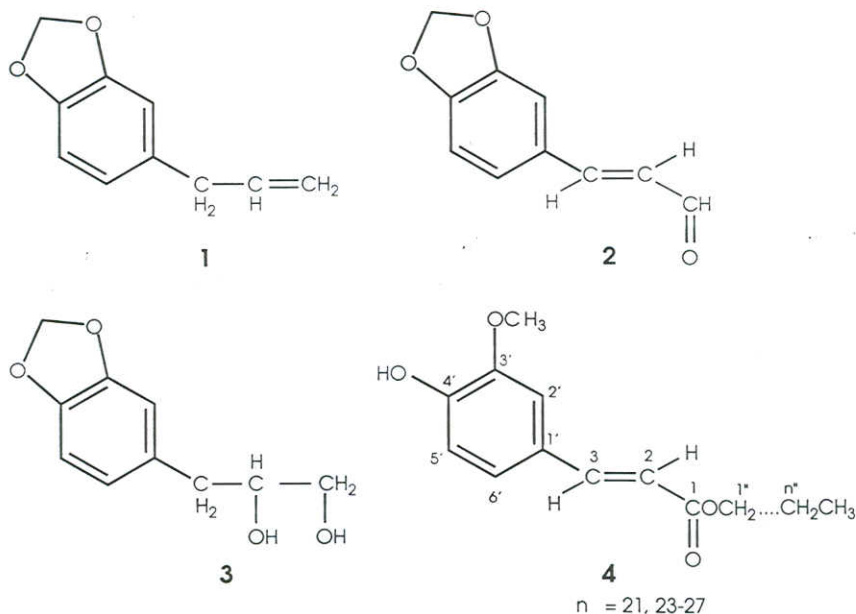
Cinnamomum parthenoxylon Meissn (Lauraceae) is a big tree, with whitish bark, distributed in Malay Peninsula.¹ Its bark is used as a spice in foods and as an excellent tonic, particularly for girls attaining maturity. The oil from the seeds is used for rheumatism.¹ Previous investigations of *C. parthenoxylon* wood oil obtained from China, Malaysia and Vietnam revealed the presence of linalool, methyl eugenol and safrole (1) as major components, respectively.²⁻⁴ We now report the isolation and identification of phenylpropanoids 1-4 from *C. parthenoxylon* wood.

RESULTS AND DISCUSSION

The hexane, dichloromethane and methanol extracts of dried powdered *C. parthenoxylon* wood on repeated column chromatography gave compounds 1-4. Compound 1, a major component, was identified as safrole by comparison of its IR and ¹H NMR spectra with literature data.^{5,6}

Compound 2 was identified as 3,4-methylenedioxybenzaldehyde by its mp, UV⁷, IR and ¹H NMR spectral properties. This compound has previously been isolated from *Cinnamomum micranthum*.⁸

Compound 3 was identified as (+)-3-(3,4-methy-



lenedioxyphenyl)-1,2-propanediol by comparison of its mp, optical rotation, UV, IR and ^1H NMR spectra.⁹ This compound was earlier isolated from sassafras root.⁹ With the aid of DEPTs and HMQC spectra, the assignment for all carbons of 3 is given for the first time (see Experimental).

Compound 4 was obtained as a white solid. Its IR spectrum indicated the presence of a hydroxyl group and a conjugated ester. The UV absorptions (see Experimental) suggested the presence of a phenolic hydroxyl group. The ^1H NMR spectrum of 4 exhibited the characteristics of a feruloyl moiety: a methoxy singlet at δ 3.95, a broad hydroxyl singlet at δ 5.91, two *trans* olefinic protons (δ 6.32 and 7.63, $J = 15.9$ Hz) and three aromatic protons in a 1,3,4-substitution pattern (δ 6.94, 7.06 and 7.10). The presence of an aliphatic alcohol moiety was indicated by a triplet signal at δ 0.90 (terminal methyl), a number of methylene protons at δ 1.27, a quintet signal at δ 1.72 for methylene next to the downfield methylene and the deshielded triplet at δ 4.21 corresponding to a methylene adjacent to an oxycarbonyl functionality. The NOE difference spectrum of 4 revealed that on irradiation of the aromatic methoxy protons at δ 3.95, a significant degree of enhancement was observed for the aromatic proton at δ 7.06. This confirmed the assignment of ferulic acid ester not the isoferulic acid ester. The ^{13}C NMR spectrum also supported the presence of a ferulate ester with resonances attributable to a carbonyl group (δ 167.8), two deshielded oxygen bearing quaternary carbons (δ 146.7 and 148.3), five methine carbons (δ 109.7, 115.1, 116.1, 123.5 and 145.0) and a shielded aromatic quaternary carbon (δ 127.5). The assignment of the ^{13}C NMR chemical shifts of 4 was achieved by the application of DEPTs and HMQC experiments and by comparison with those of reported compounds.¹⁰ The EI mass spectrum showed peaks at m/z 586, 572, 558, 544, 530 and 502 corresponding respectively to ferulate ester molecular ions with the alkyl portions of $\text{C}_{22}\text{H}_{45}$, $\text{C}_{24}\text{H}_{49}$, $\text{C}_{25}\text{H}_{51}$, $\text{C}_{26}\text{H}_{53}$, $\text{C}_{27}\text{H}_{55}$ and $\text{C}_{28}\text{H}_{57}$. The fragments at m/z 194 and 177 corresponded to ferulic acid and feruloyl fragments, respectively. Compound 4 was therefore a mixture of six alkyl *trans*-ferulates bearing alkyl groups of C_{22} and C_{24} to C_{28} . These assignments were based on the same analogy for the characterization of similar alkyl *trans*-ferulates previously isolated from *Pavetta owariensis*¹⁰ and *Abies firma*.¹¹ Previous works had indicated that ferulic acid esters are associated with suberin formation.¹²⁻¹⁴

It should be noted that this is the first report on the occurrence of compounds 3 and 4 in *Cinnamomum* species.

EXPERIMENTAL

General: UV and FT-IR spectra were recorded on a Shimadzu UV-2101 PC and Perkin Elmer Spectrum 2000 spectrophotometers, respectively. NMR spectra were recorded on a Jeol JMN A 500 spectrometer. EI mass spectrum was measured on a Finnigan MAT INCOS 50 spectrometer.

Plant material: The wood of *C. parthenoxylon* was collected from Jana, Songkhla province. A voucher specimen (No. 0024 (RU)) is kept at the Plant Collection Centre, Faculty of Science, Ramkhamhaeng University.

Isolation: The dried, powdered wood (1.93 kg) was extracted successively with hexane, CH_2Cl_2 and MeOH by maceration. Separations and purifications of compounds were carried out on silica gel column chromatography (CC). From the hexane extract, after quick CC eluting by varying proportions of hexane, hexane- CHCl_3 , CHCl_3 -MeOH, 8 fractions were obtained. The first fraction, eluted by hexane to hexane- CHCl_3 (98:2), was rechromatographed using hexane to yield safrole (1) (14.04 g, 0.73 %). The fourth fraction, eluted with a gradient of hexane- CHCl_3 (40:60 to 20:80), was rechromatographed twice using hexane- CHCl_3 (30:70) to yield a mixture of alkyl *trans*-ferulate (4) (112 mg, 0.006 %). The CH_2Cl_2 extract was chromatographed using hexane, hexane- CHCl_3 , CHCl_3 -MeOH in increasing proportions as eluents, and 8 fractions were collected. Rechromatography of the first fraction, eluted by hexane, also afforded safrole (1) (15.58 g, 0.81 %), while the fifth fraction, eluted by hexane- CHCl_3 (20:80), on repeated chromatography twice using hexane- CHCl_3 (50:50) and CHCl_3 -MeOH in increasing proportions as eluents yielded 3,4-methylenedioxcinnamaldehyde (2) (45.8 mg, 0.002 %). The methanol extract was subjected to quick CC with a gradient of hexane, hexane- CHCl_3 , CHCl_3 -MeOH, and 13 fractions were obtained. The seventh fraction, eluted by CHCl_3 , was subjected to two repeated CC, and fractions eluted by MeOH- CHCl_3 (0.5:99.5) afforded (+)-3-(3,4-methylenedioxyphenyl)-1,2-propanediol (3) (133 mg, 0.007 %).

safrole, 1. UV: EtOH λ_{max} 234, 286 nm; IR and ^1H NMR: see ref 5,6.

3,4-methylenedioxcinnamaldehyde, 2. M.p. 81-82°C (lit.⁷ m.p. 84-85°C); UV: see ref 7; IR: $\nu_{\text{max}}^{\text{KBr}}$ 2832, 2768, 2704, 1666, 1620, 1596, 1494, 1448, 1401,

1357, 1259, 1195, 1118, 1037, 961, 927, 860 and 799 cm^{-1} ; ^1H NMR (CDCl_3): δ 5.99 (2H, s, OCH_2O), 6.54 (1H, dd, $J = 15.7, 7.7$ Hz, $\text{CH}=\text{CH}-\text{CO}$), 6.83 (1H, d, $J = 6.8$ Hz, Ar-H-5), 7.04 (1H, d, $J = 1.8$ Hz, Ar-H-2), 7.05 (1H, dd, $J = 6.8, 1.8$ Hz, Ar-H-6), 7.36 (1H, d, $J = 15.7$ Hz, $\text{CH}=\text{CH}-\text{CO}$), 9.63 (1H, d, $J = 7.7$ Hz, CHO).

(+)-3-(3,4-methylenedioxyphenyl)-1,2-propanediol, 3. M.p. 76-77°C (lit.⁹ m.p. 79°C); $[\alpha]_D^{20} +20.7^\circ$ (CHCl_3 , c 0.15) (lit.⁹ $[\alpha]_D^{20} +10^\circ$ (CHCl_3 , c 0.25)); UV, IR, ^1H NMR: see ref 9; ^{13}C NMR (CDCl_3): δ 39.8 (C-3), 66.3 (C-1), 73.5 (C-2), 101.3 (OCH_2O), 108.8 (C-2'), 110.0 (C-5'), 122.6 (C-6'), 131.7 (C-1'), 146.7 (C-4'), 148.2 (C-3').

alkyl *trans*-ferulate mixture, 4. M.p. 68-71°C; UV: $\lambda_{\text{max}}^{\text{EtOH}}$ 216, 236, 326 nm; (NaOH) 214, 382 nm; IR: $\nu_{\text{max}}^{\text{KBr}}$ 3450, 1713, 1632, 1599, 1518, 1269, 1177, 1028, 980, 840, 821, 718 cm^{-1} ; ^1H NMR (CDCl_3): δ 0.90 (3H, t, $J = 6.8$ Hz, CH_2-Me), 1.27 (br s, CH_2), 1.72 (2H, quint, $J = 6.9$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_2$), 3.95 (3H, s, OMe), 4.21 (2H, t, $J = 6.9$ Hz, CO_2CH_2), 5.91 (1H, br s, OH), 6.32 (1H, d, $J = 15.9$ Hz, $\text{CH}=\text{CH}-\text{CO}$), 6.94 (1H, d, $J = 8.2$ Hz, Ar-H-5), 7.06 (1H, d, $J = 1.7$ Hz, Ar-H-2), 7.10 (1H, dd, $J = 8.2, 1.7$ Hz, Ar-H-6), 7.63 (1H, d, $J = 15.9$ Hz, $\text{CH}=\text{CH}-\text{CO}$); ^{13}C NMR (CDCl_3): δ 14.5 (Me), 23.1 (C-n"), 26.4 (C-3"), 29.2 (C-2"), 29.7-30.1 (C-4" to (n-2)"), 32.3 (C-(n-1)"), 56.3 (OMe), 65.0 (C-1"), 109.7 (C-2'), 115.1 (C-5'), 116.1 (C-2), 123.5 (C-6'), 127.5 (C-1'), 145.0 (C-3), 147.1 (C-4'), 148.3 (C-3'), 167.8 (C-1); EIMS m/z (rel. int.): 586 (6), 572 (1), 558 (89), 544 (4), 530 (100), 502 (1) (each $[\text{M}]^+$), 194 (74), 177 (58), 150 (17), 137 (21).

ACKNOWLEDGEMENTS

This work was supported by the Thailand Research Fund (TRF). We are indebted to Mrs. Wanna Sririnnuth and Miss Wanwimon Thabdee, Scientific and Technological Research Centre, Chulalongkorn University, for recording the NMR spectra, and to Miss Amporn Srisutthipruth, Faculty of Science, Mahidol University, for recording the mass spectrum.

REFERENCES

- Burkill I H (1966) *A Dictionary of the Economic Products of the Malay Peninsula*. Ministry of Agriculture and Co-operatives, Kuala Lumpur, Vol 1, p 561-2.
- Tao G, Lu A, Jiang Z, Chen H, Zhang X, Sun H, Ding J, Ding L and Wu Y (1987) New resource plants of natural camphor and linalool. *Zhiwu Xuebao* 29, 541-8. CA 108: 72155a (1988).
- Yaacob KB, Zakaria Z and Ramli Z (1990) Major constituents of *Cinnamomum parthenoxylon* wood oil. *J Essent Oil Res* 2, 51.
- Dung NX, Moi LD, Hung ND and Leclercq PA (1995) Constituents of the essential oils of *Cinnamomum parthenoxylon* (Jack) Nees from Vietnam. *J Essent Oil Res* 7, 53-6.
- Pouchert CJ (1985) *The Aldrich Library of FT-IR Spectra*. Aldrich Chemical Company, Inc, Wisconsin, Vol 1, p 1054C.
- Pouchert C J and Behnke J (1993) *The Aldrich Library of ^{13}C and ^1H FT NMR Spectra*, 3rd ed. Aldrich Chemical Company, Inc., Wisconsin, Vol 2, p 232B.
- Dallacker F and Schubert J (1975) Derivatives of methylenedioxybenzene: on polyenecarboxylic imides of methylenedioxybenzene. *Chem Ber* 108, 95-108.
- Clifford MN and Hole M (1977) The naturally occurring cinnamaldehydes. *Process Biochem* 12, 5-9.
- Hoke M and Haensel R (1972) New investigation of sassafras root. *Arch Pharm (weinheim)* 305, 33-9 (Ger). CA 76: 13818k (1972).
- Balde AM, Claeys M, Pieters LA, Wray V and Vlietinck AJ (1991) Ferulic acid esters from stem bark of *Pavetta owariensis*. *Phytochemistry* 30, 1024-6.
- Tanaka R, Inosiri A, Yoneda M, Ishida T, Namada A and Matsunaga S (1990) A tetracyclic triterpene lactone and other constituents from the bark of *Abies firma*. *Phytochemistry* 29, 3263-5.
- Laver ML and Fang HHL (1989) Ferulic acid esters from the bark of *Pseudotsuga menziesii*. *J Agric Food Chem* 37, 114-6.
- Kolattukudy PE and Dean BB (1974) Structure, gas chromatographic measurement, and function of suberin synthesized by potato tuber tissue slices. *Plant Physiol* 54, 116-21.
- Riley RG and Kolattukudy PE (1975) Evidence for covalently attached p-coumaric acid and ferulic acid in cutins and suberins. *Plant Physiol* 56, 650-4.

1357, 1259, 1195, 1118, 1037, 961, 927, 860 and 799 cm^{-1} ; ^1H NMR (CDCl_3): δ 5.99 (2H, s, OCH_2O), 6.54 (1H, dd, $J = 15.7, 7.7$ Hz, $\text{CH}=\text{CH}-\text{CO}$), 6.83 (1H, d, $J = 6.8$ Hz, Ar-H-5), 7.04 (1H, d, $J = 1.8$ Hz, Ar-H-2), 7.05 (1H, dd, $J = 6.8, 1.8$ Hz, Ar-H-6), 7.36 (1H, d, $J = 15.7$ Hz, $\text{CH}=\text{CH}-\text{CO}$), 9.63 (1H, d, $J = 7.7$ Hz, CHO).

(+)-3-(3,4-methylenedioxyphenyl)-1,2-propanediol, 3. M.p. 76–77°C (lit.⁹ m.p. 79°C); $[\lambda]_D^{20} +20.7^\circ$ (CHCl_3 , c 0.15) (lit.⁹ $[\alpha]_D^{20} +10^\circ$ (CHCl_3 , c 0.25)); UV, IR. ^1H NMR: see ref 9; ^{13}C NMR (CDCl_3): δ 39.8 (C-3), 66.3 (C-1), 73.5 (C-2), 101.3 (OCH_2O), 108.8 (C-2'), 110.0 (C-5'), 122.6 (C-6'), 131.7 (C-1'), 146.7 (C-4'), 148.2 (C-3').

alkyl *trans*-ferulate mixture, 4. M.p. 68–71°C; UV: $\lambda_{\text{max}}^{\text{EtOH}}$ 216, 236, 326 nm; (NaOH) 214, 382 nm; IR: $\nu_{\text{max}}^{\text{kBr}}$ 3450, 1713, 1632, 1599, 1518, 1269, 1177, 1028, 980, 840, 821, 718 cm^{-1} ; ^1H NMR (CDCl_3): δ 0.90 (3H, t, $J = 6.8$ Hz, CH_2-Me), 1.27 (br s, CH_2), 1.72 (2H, quint, $J = 6.9$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_2$), 3.95 (3H, s, OMe), 4.21 (2H, t, $J = 6.9$ Hz, CO_2CH_2), 5.91 (1H, br s, OH), 6.32 (1H, d, $J = 15.9$ Hz, $\text{CH}=\text{CH}-\text{CO}$), 6.94 (1H, d, $J = 8.2$ Hz, Ar-H-5), 7.06 (1H, d, $J = 1.7$ Hz, Ar-H-2), 7.10 (1H, dd, $J = 8.2, 1.7$ Hz, Ar-H-6), 7.63 (1H, d, $J = 15.9$ Hz, $\text{CH}=\text{CH}-\text{CO}$); ^{13}C NMR (CDCl_3): δ 14.5 (Me), 23.1 (C-n"), 26.4 (C-3"), 29.2 (C-2"), 29.7–30.1 (C-4" to (n-2)"), 32.3 (C-(n-1)"), 56.3 (OMe), 65.0 (C-1"), 109.7 (C-2'), 115.1 (C-5'), 116.1 (C-2), 123.5 (C-6'), 127.5 (C-1'), 145.0 (C-3), 147.1 (C-4'), 148.3 (C-3'), 167.8 (C-1); EIMS m/z (rel. int.): 586 (6), 572 (1), 558 (89), 544 (4), 530 (100), 502 (1) (each $[\text{M}]^+$), 194 (74), 177 (58), 150 (17), 137 (21).

ACKNOWLEDGEMENTS

This work was supported by the Thailand Research Fund (TRF). We are indebted to Mrs. Wanna Sririnnuth and Miss Wanwimon Thabdee, Scientific and Technological Research Centre, Chulalongkorn University, for recording the NMR spectra, and to Miss Amporn Srisutthipruth, Faculty of Science, Mahidol University, for recording the mass spectrum.

REFERENCES

- Burkill I H (1966) *A Dictionary of the Economic Products of the Malay Peninsula*. Ministry of Agriculture and Co-operatives, Kuala Lumpur, Vol 1, p 561–2.
- Tao G, Lu A, Jiang Z, Chen H, Zhang X, Sun H, Ding J, Ding L and Wu Y (1987) New resource plants of natural camphor and linalool. *Zhiwu Xuebao* 29, 541–8. CA 108: 72155a (1988).
- Yaacob KB, Zakaria Z and Ramli Z (1990) Major constituents of *Cinnamomum parthenoxylon* wood oil. *J Essent Oil Res* 2, 51.
- Dung NX, Moi LD, Hung ND and Leclercq PA (1995) Constituents of the essential oils of *Cinnamomum parthenoxylon* (Jack) Nees from Vietnam. *J Essent Oil Res* 7, 53–6.
- Pouchert CJ (1985) *The Aldrich Library of FT-IR Spectra*. Aldrich Chemical Company, Inc. Wisconsin, Vol 1, p 1054C.
- Pouchert C J and Behnke J (1995) *The Aldrich Library of ^{13}C and ^1H FT NMR Spectra*, 3rd ed. Aldrich Chemical Company, Inc., Wisconsin, Vol 2, p 232B.
- Dallacker F and Schubert J (1975) Derivatives of methylenedioxybenzene: on polyenecarboxylic imides of methylenedioxybenzene. *Chem Ber* 108, 95–108.
- Clifford MN and Hole M (1977) The naturally occurring cinnamaldehydes. *Process Biochem* 12, 5–9.
- Hoke M and Haensel R (1972) New investigation of sassafras root. *Arch Pharm (weinheim)* 305, 33–9 (Ger). CA 76: 13818k (1972).
- Balde AM, Claeys M, Pieters LA, Wray V and Vlietinck AJ (1991) Ferulic acid esters from stem bark of *Pavetta owariensis*. *Phytochemistry* 30, 1024–6.
- Tanaka R, Inosiri A, Yoneda M, Ishida T, Namada A and Matsunaga S (1990) A tetracyclic triterpene lactone and other constituents from the bark of *Abies firma*. *Phytochemistry* 29, 3263–5.
- Laver ML and Fang HHL (1989) Ferulic acid esters from the bark of *Pseudotsuga menziesii*. *J Agric Food Chem* 37, 114–6.
- Kolattukudy PE and Dean BB (1974) Structure, gas chromatographic measurement, and function of suberin synthesized by potato tuber tissue slices. *Plant Physiol* 54, 116–21.
- Riley RG and Kolattukudy PE (1975) Evidence for covalently attached p-coumaric acid and ferulic acid in cutins and suberins. *Plant Physiol* 56, 650–4.