Phenylpropanoids from *Cinnamomum parthenoxylon*

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

KEYWORDS: Cinnamomum *parthcnoxylon,* Lauraceae, phenylpropanoids.

INTRODUCTION

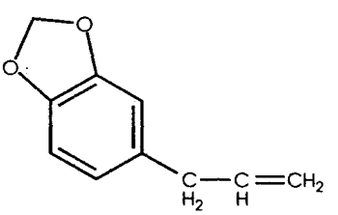
Cinnamomum parthenoxylon Meissn (Lauraceae) is a big tree, with whitish bark, distributed in Malay Peninsula.l Its bark is used as a spice in foods and as an excellent tonic, particularly for girls attaining maturity. The oil from the seeds is used for rheumatism.l Previous investigations *oC* C. *parthenoxylon*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

ReSULTS AND DISCUSSION

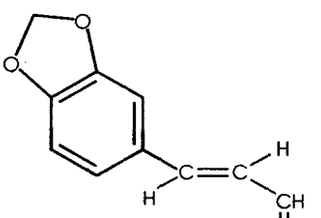
The hexane, dichloromethane and methanol extracts of dried powdered C. *parthenoxylon* wood on .repeated column chromatography gave compounds 1-4. Compound 1, a major component, was identified as safrole by comparison of its IR and lH NMR spectra with literature data.5.6

Compound 2 was ide.ntified as 3,4-methylene-dioxycinnamaldehyde by its mp, UV7, IR and lH NMR spectral properties. This compound has previously been isolated from *Cinnamomum micranthum.8*

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



1



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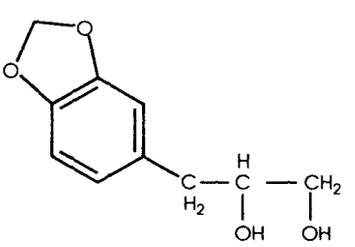

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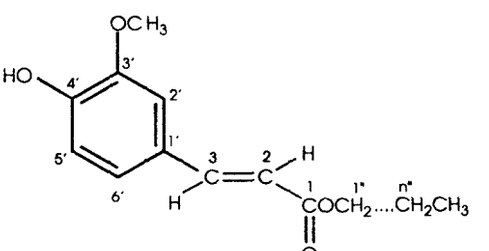

4

n = 21, 23-27

lenedio'"yphen).l}-l ,2-propanediol by compariwn of its.mI', optical rQtation, UV,IR and ^{1}H NMR spectnL[9] This compound W;iSearlier isohned from sassafras root." With the aid of DEPTs and HMQC spectra, the assignment for aU carbons of 3 is given for the first time (see Experimental).

Compound 4 was obtained as a white solid. Its IR spectrum indiCCltedthe presence of a hydroxyl group and a conjugau:d ester. The UV absorptions (see Experimental) suggested the presence of a phenolic hydroxyl group. The IH NMR spectrum of 4 exhibited the characteristics of a feruloyl moiety: a methoxy singlet at 0 3.95, a broad hydroxyl singlet at 0 5.91, two *trans* olefinic protons (06,32 and 7.63,] ,.: 15.9 Hz) and three aromatic protons in a 1,3,4-substitution pattern (0 6.94, 7.06 and 7.10). The presence of an aliphatic alcohol moiety was indicated by a triplet signal at 0 0.90 (terminal methyl), a number of methylene protons at 0 1.27, a quintet signal at 0 1.72 for methylene next to the downfidd methylene and the deshielded triplet at 0 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 0 3.95, a significant degree of enhancement was observed for the aromatic prown at *D* 7.06. This confirmed the assignment of ferulic acid ester not the isoferulic acid ester. The nC NMR spectrum also supported the presence of a ferulate ester with resonances attributable to a carbonyl group (& 167.8), two deshielded oxygen bearing quarternary carbons (0 146.1 and 148.3), five methine carbons (0 109.7, 115.1, 116,1, 123.5 and 145.0) and a shielded aromatic quaternary carbon (0 127.5). The assignmemt of the ^{13}CNMR chemical shifts of 4 was achieved by the application of DEPTs and HMQC experiments and by comparison with those of reported compounds. \0 The El mass specHum showed peaks at mil. 586, 572, 558, 544. 530 and 502 corresponding respectively to ferulate ester molecular ions with the alkyl portions of C22H4,;, C2,H49' Cl,;HSI' Cl6H;3' Cl7H;5 and ClsH;,. The fragments at *mfz* 194 and 177 corresponded to ferulic acid and fernloyI fragments, respectively. Compound 4 waS therefore a mixtUre of six alkyl trans-ferulates bt'aring alkyl groups of *Cll* and C2.;to *Cl*~. These a...<;signmenc'were based on the same analogy for {he characterization of similar alkyl trans-ferulates previously isolated from *Pavetta* owariensislO and *Abies JifmaY* Previous works had indicated that frrulic acid esters are associated with suberin formation. \~.H

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

EXPERIMENTAL

General: UV and FT-IR specna were TecoTrled on a Shimadzu UV-2101 PC and Perkin Elmer Spe~trum 2000 spectrophotomet,~rs, rC5penive]y. NMR spectra were recorded on a Jeol J\1.N A 500 spectrometer. EI mass spectrum waS measured on a Finnigan MAT INCOS 50 spectrometer.

Plant material: The wood of C. *partltC1loxylon* was collected from lana, $ongkhla province. A \'oucher specimen (No. 0024 (RU)) is kept at the Plant Collection Centre, Faculty of Science. Ramkham-haeng University.

Isohltion: The dried, powdered wood (1.93 kg) was extracted successively with hexane, CH2Cl2<lnd MeOH by marceration. Separations and purifications of compounds were cained out on silica gel column chromatography (CC). From the hexane extract, after quick CC eluting by vaT)ing proportions of hexane, hexane-CHC1), CHCl)-MeOH , 8 fr(lctiQus were obtained. The first fraction, eluted by hexane to hexane-CHCI) (98:2), was rechromatographed using hexane to yield safrole (1) (14.04 g, 0.73 %). The fourth fraction, eluted with a gradient of hexane-CHCI) (40:60 to 20:80), was rechromatographed twice using hexane-CHCi) 00:70) to yield a mixtUTc of alkyl trans-fcrulate (4) (112 mg, 0.006 %). The CH2Cl2extract waS chromatographed using hexane, hexane-ClICl), CHCI)-MeOH in increasing pro-portions as eluents, and 8 fractions were collected. RechromatOgraphy of the first fntction. eluted by hexane, also afforded safrole (1) (15.58 g, 0.81 %), while the fifth fraction, eluted by hexane-CHCl) (20:80), on repeated chromatography tWice u$ing hexane-CHCl) (50:50) (lnd CHCI3-\teOH in increasing proportions as eluents yidded 3,4~ methyltnedioxycinnamaldehyde (2) (45.8 mg. 0.002 %). The methanol extnlct waS subjected to quick CC with a gradient of hexane, htxane-CHCl}. CHCl3~ MeOH, and 13 fractions were obtained. The seventh fraction, eluted by CHCl), was subjecred to two repeated e.C, and fractions eluted b)' MeOH-CHG, (0.5:995) afforded (+)3-0,4-methylendio~"yphenyl)-1,2-propanediol (3) (~3 trig, 0.007 %).

saJrole, 1. UV: EtOH A".., 234, 286 nm; 1R and IH NMR: see ref 5,6.

3,4-methylenedioxycinnamaldeltydc. 2. M.p. 81-*B2°C* (lit,7m.p. 84-85°C); UV: see ref 7; IR:V~~'2832, 2768,2704, 1666, 1620, 1596, 1494-, 1448, 14tH,

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, CH=C<u>H</u>-CO), 6.83 (1H, *d*, J = 6.8 Hz, Ar-<u>H</u>-5), 7.04 (1H, *d*, J = 1.8 Hz, Ar-<u>H</u>-2), 7.05 (1H, *dd*, J = 6.8, 1.8 Hz, Ar-<u>H</u>-6), 7.36 (1H, *d*, J = 15.7 Hz, C<u>H</u>=CH-CO), 9.63 (1H, *d*, J = 7.7 Hz, C<u>H</u>O).

(+)-3-(3,4-methylenedioxyphenyl)-1,2-propanediol, 3. M.p. 76-77°C (lit.[9] m.p. 79°C); $[\lambda]_D^{31}$+20.7° (*CHCl*$_3$, *c* 0.15) (lit.[9] $[\alpha]_D^{20}$ +10° ($CHCl_3$, *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: λ_{max}^{EtOH} 216, 236, 326 nm; (*NaOH*) 214, 382 nm; IR: ν_{max}^{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-<u>Me</u>), 1.27 (*br* s, CH_2), 1.72 (2H, *quint*, J = 6.9 Hz, $CO_2CH_2C\underline{H}_2$), 3.95 (3H, *s*, OMe), 4.21 (2H, *t*, J = 6.9 Hz, $CO_2C\underline{H}_2$), 5.91 (1H, *br* s, OH), 6.32 (1H, *d*, J = 15.9 Hz, CH=C<u>H</u>-CO), 6.94 (1H, *d*, J = 8.2 Hz, Ar-<u>H</u>-5), 7.06 (1H, *d*, J = 1.7 Hz, Ar-<u>H</u>-2), 7.10 (1H, *dd*, J = 8.2, 1.7 Hz, Ar-<u>H</u>-6), 7.63 (1H, *d*, J = 15.9 Hz, *C<u>H</u>=CH-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 $[M]^+$), 194 (74), 177 (58), 150 (17), 137 (21).

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