Phytochemistry, Vol. 28, No. 11, pp. 3242 3243, 1989.
Printed in Great Britain.

0031-9422/89 \$3.00+0.00

TWO PHENYLPROPANOIDS FROM *FLINDERSIA AUSTRALIS* STEM WOOD*

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(*Received in revised form* 6 *April* 1989)

Key Word Index—*Flindersia australis*; Rutaceae; phenylpropanoid; 4′-(3″-methylbut-2″-enyloxy)-3-phenylpropanol; 4′-(3″-methyl-4″-hydroxybutyloxy)-3-phenylpropanol; seselin.

Abstract—Two new phenylpropanoids, 4′-(3″-methylbut-2″-enyloxy)-3-phenylpropanol and 4′-(3″-methyl-4″-hydroxybutyloxy)-3-phenylpropanol were isolated together with the coumarin, seselin from the stem wood of *Flindersia australis*.

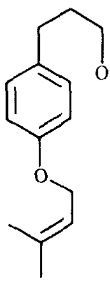
INTRODUCTION

Flindersia australis R. Br (Rutaceae) is a large tree native to Australia. Previous work include the isolation of three flavonoids from its bark [1], seselin and 7-methoxy-8-(3′-methyl-2′-butenyloxy) coumarin from its root bark [2], cycloeucalenol and 24-methylenecycloartanol [3] and the alkaloid, flindersine [4, 5] from its stem wood. We now report the presence of seselin and two new phenyl propanoids in the stem wood extract of *F. australis*.

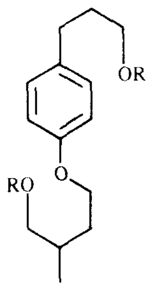
RESULTS AND DISCUSSION

Chromatographic separation of the dichloromethane extract of *F. australis* stem wood gave two phenyl propanoids **1** and **2** together with seselin, previously isolated from its root bark [2]. Our research group was unable to detect any flindersine [6] in the extract although it has been reported to be present in the stem wood [4, 5]. Flindersine has also not been isolated from any other *Flindersia* species [7, 8].

The UV and IR spectra of **1** and **2** indicated them to be aromatic compounds with hydroxyl groups. Their ^{1}H NMR spectra showed AB doublets with $J = 8.5$ Hz in the atomatic region and upfield D_2O exchangeable signals suggesting that a 1,4-disubstituted benzene ring and non-phenolic hydroxyl groups were present. Two CH_2 triplets at $\delta 3.65$ ($J = 6.4$ Hz) and 2.65 ($J = 7.5$ Hz) and a CH_2 triple triplet at 1.87 ($J = 6.4$ and 7.5 Hz) suggested that $-CH_2CH_2CH_2OH$ side-chains were present in both compounds. The compounds were therefore 3-phenylpropanols with side-chains at *para*-position.



1



2 R = H

3 R = $-\overset{\displaystyle O}{\overset{\|}{C}}-Me$

4 R = $-\overset{\displaystyle O}{\overset{\|}{C}}-Ph$

The remaining signals in the ^{1}H NMR spectrum of **1**, $C_{14}H_{20}O_2$ consisted of a triplet, a doublet (δ 4.52) and two methyl singlets suggesting that an O-isopentenyl group was present. A peak at m/z 152 in its mass spectrum for the cleavage of the isopentenyl group and peaks at m/z 134 and 107 for the loss of water and CH_2CH_2OH from the ion thus formed provided further evidence for compound having the 4′-(3″-methylbut-2″-enyloxy)-3-phenylpropanol structure (**1**).

Molecular formula considerations indicated that the $C_5H_{11}O_2$ side chain of the more polar phenyl propanoid **2**, $C_{14}H_{22}O_3$ was saturated. A doublet and a multiplet in the $\delta 3.0$–4.0 region of its ^{1}H NMR spectrum suggested that two $-OCH_2-$groups were present. As compound **2** formed diacetyl and dibenzoyl derivatives and as no more benzyl protons were present, one $-OCH_2-$group must be attached to the benzene ring while the other must be part of a CH_2OH group. A methyl doublet ($\delta 0.98$) and a three proton multiplet at 1.55–1.95 suggested a $-O(CH_2)_2CH(Me)CH_2OH$ side-chain and hence a 4′-(3″-methyl-4″-hydroxybutyloxy)-3-phenylpropanol (**2**) structure for the phenyl propanoid.

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*Part 126 in the series 'Natural Product Chemistry'. For Part 125 see Reisch, J. and Gunaherath, G.M.K.B. (1989) *J. Nat. Prod.* **52**, 404.

†Part of the Ph.D. Dissertation, Münster/Peradeniya (Sri Lanka).

A related phenyl propanoid, cuspidiol has been isolated from the bark of *Xanthoxylum cuspidatum* [9] Phenyl propanoids **1** and **2** are respectively 4''-deoxycuspidiol and 2'',3''-dihydrocuspidiol.

EXPERIMENTAL

IR spectra were determined for liquid films on NaCl discs and UV spectra in MeOH solns. ^{1}H NMR spectra were measured at 200 and 300 MHz in $CDCl_3$ solns using TMS as int. standard. MS analyses were carried out at 70 eV. Merck silica gel 60 F_{254} and silica gel 60 grain size 0.063–0.2 mm were used for TLC and CC, respectively. Petrol refers to the fraction of bp 40–60°.

F. australis was collected from a large tree (Q-388) in the Royal Botanic Garden, Peradeniya, Sri Lanka.

Extraction. Dried ground *F. australis* stem wood (1 kg) was extracted at 20° with petrol (5 days) and then with CH_2Cl_2 (3 days). Concn of the latter gave the CH_2Cl_2 extract (12.8 g).

Chromatography of the CH_2Cl_2 *extract.* The CH_2Cl_2 extract (10 g) was chromatographed on silica gel (200 g) using CH_2Cl_2–MeOH mixtures for elution.

Elution with CH_2Cl_2 gave on crystallization from *n*-hexane, seselin, mp 118–119°, (lit. [10] mp 120°), which was identical with an authentic sample (mmp, co-IR).

Elution with CH_2Cl_2–MeOH (99:1) followed by prep. TLC (CH_2Cl_2–MeOH; 49:1) gave 4'-(3''-methylbut-2''-enyloxy)-3-phenylpropanol (**1**) as a colourless oil (220 mg) (HRMS 220.1461 $[M]^+$; Calc. for $C_{14}H_{20}O_2$: 220.1463, 152.0833 $[M-C_5H_8]^+$; calc. for $C_9H_{12}O_2$: 152.0837); UV λ_{max} (log ε) nm: 208 (3.50), 223.5 (3.50), 262 (3.20), 269 (3.19) and 284 (2.94); IR ν_{max} cm^{-1}: 3400, 1620, 1525 and 1250; ^{1}H NMR (300 MHz): δ1.65 (*br s*, 1H, D_2O exchangeable, OH), 1.77 and 1.83 (each *s*, 3H, 3''-Me), 1.88 (*tt*, J = 7.5 and 6.4 Hz, 2H, 2-H), 2.68 (*t*, J = 7.5 Hz, 2H, 3-H), 3.68 (*t*, J = 6.4 Hz, 2H, 1-H), 4.52 (*d*, J = 6.8 Hz, 2H, 1''-H), 5.50 (*t*, J = 6.8 Hz, 1H, 2''-H), 6.86 and 7.17 (each *d*, J = 8.5 Hz, 2H, Ar-H) MS *m/z* (rel. int.): 220 $[M]^+$ (3), 152 (55), 134 (44), 121 (4.5), 107 (100), 94 (12), 77 (18), 75 (26) and 69 (60).

Elution with CH_2Cl_2–MeOH (19:1) followed by prep. TLC (CH_2Cl_2–MeOH; 23:2) gave 4'-(3''-methyl-4''-hydroxybutyloxy)-3-phenylpropanol (**2**) as a colourless oil (285 mg) (HRMS 238.1570 $[M]^+$; Calc. for $C_{14}H_{22}O_3$: 238.1569, 152.0843 $[M-C_5H_{10}O]^+$; Calc. for $C_9H_{12}O_2$: 152.0837); UV λ_{max} (log ε) nm: 223.5 (3.54), 262.5 (3.02), 269 (3.04) and 284 (2.76); IR ν_{max} cm^{-1}: 3380, 1620, 1520, 1255 and 1110; ^{1}H NMR (200 MHz): δ0.98 (*d*, J = 6.7 Hz, 3H, 3''-Me), 1.65 (*m*, $W_{1/2}$ = 6 Hz, 1H, 3''-H), 1.75–1.95 (*m*, $W_{1/2}$ = 16 Hz, 4H, 2 and 2''-H), 2.63 (*t*, J = 7.5 Hz, 2H, 3-H), 3.51 (*d*, J = 5.5 Hz, 4''-H), 3.62 (*t*, J = 6.4 Hz, 2H, 1-H), 4.00 (*m*, $W_{1/2}$ = 14 Hz, 2H, 1''-H), 4.73 (*br s*, 1H, D_2O exchangeable, OH), 6.81 and 7.09 (each *d*, J = 8.6 Hz, 2H, Ar-H); MS *m/z* (rel. int.): 238 $[M]^+$ (14), 152 (68), 134 (89), 107 (100), 77 (30), 75 (30) and 69 (42).

4'-(3''-methyl-4''-acetoxybutyloxy)-3-Phenylpropanylacetate (**3**). Acetylation of **2** (40 mg) with Ac_2O–pyridine (1:1, 0.3 ml) for 6 hr at 20° gave, on purification by prep. TLC (CH_2Cl_2) diacetate **3** as an oil (47 mg) (HRMS 322.1783 $[M]^+$; Calc. for $C_{18}H_{26}O_5$: 322.1780); UV λ_{max} (log ε) nm: 202 (3.82), 225 (4.10), 277 (3.26) and 284 (3.21); IR ν_{max} cm^{-1}: 1720, 1500, 1350, 1215 and 1030; ^{1}H NMR (200 MHz): δ1.02 (*d*, J = 6.6 Hz, 3H, 3''-Me), 1.65 (*m*, $W_{1/2}$ = 6 Hz, 1H, 3''-H), 2.05 (*s*, 6H, OAc), 1.85–2.15 (*m*, $W_{1/2}$ = 18 Hz, 4H, 2 and 2''-H), 2.62 (*t*, J = 7.5 Hz, 2H, 3-H), 3.99 (*t*, J = 6.5 Hz, 2H, 1-H), 3.98 (*d*, J = 6 Hz, 2H, 4''-H), 4.07 (*t*, J = 6.6 Hz, 2H, 1''-H), 6.81 and 7.08 (each *d*, J = 8.5 Hz, 2H, Ar-H); MS *m/z* (rel. int.): 322 $[M]^+$ (8), 262 (4), 189 (9), 182 (6), 134 (75), 107 (35), 105 (44) and 69 (100).

4'-(3''-methyl-4''-benzoylbutyloxy)-3-Phenylpropanyl benzoate (**4**). Benzoylation of **2** (40 mg) with C_6H_5COCl (0.2 ml) in 2 M NaOH (0.5 ml) for 8 hr at 20° gave, on purification by prep. TLC (CH_2Cl_2) dibenzoate **4** as an oil (66 mg) (HRMS 446.2084 $[M]^+$; Calc. for $C_{28}H_{30}O_5$: 446.2093); UV λ_{max} (log ε) nm: 203 (4.08), 227 (4.51), 273 (3.47) and 279 (3.42); IR ν_{max} cm^{-1}: 1710, 1500, 1260, 1235, 1095 and 690; ^{1}H NMR (200 MHz): δ1.13 (*d*, J = 6.5 Hz, 3H, 3''-Me), 1.78 (*m*, $W_{1/2}$ = 6 Hz, 1H, 3''-H), 1.95–2.31 (*m*, $W_{1/2}$ = 18 Hz, 4H, 2 and 2''-H, 2.73 (*t*, J = 7.5 Hz, 2H, 3-H), 4.05 (*dt*, J = 6.4 and 1.4 Hz, 2H, 1''-H), 4.24 (*d*, J = 5.8 Hz, 2H, 4''-H), 4.33 (*t*, J = 6.5 Hz, 2H, 1-H), 6.82 (*d*, J = 8.5 Hz, 2H, 2' and 6'-H), 7.11 (*d*, J = 8.5 Hz, 2H, 3' and 5'-H), 7.4–7.65 and 7.95–8.17 (*m*, 10H, benzoyl H); MS *m/z* (rel. int.): 446 $[M]^+$ (3), 324 (4), 191 (16), 134 (10), 105 (100), 77 (52) and 69 (57).

Acknowledgements—We thank the Deutschen Akademischen Austauschdienst (DAAD) and the Deutschen Forschungsgemeinschaft for financial assistance. We also thank Mr B. Sumithraarachchi of the Royal Botanic Garden, Peradeniya, Sri Lanka, for the plant material.

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