

SESQUITERPENOIDS FROM *DYSOXYLUM SCHIFFNERI*

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Key Word Index—*Dysoxylum schiffneri*; Meliaceae; sesquiterpenoids; (+)-8-hydroxycalamenene; schiffnerone A; schiffnerone B.

Abstract—The wood of *Dysoxylum schiffneri* (Meliaceae) has yielded the known (+)-8-hydroxycalamenene, the novel sesquiterpenoid, schiffnerone A (1,5-dihydroxy-1,3,5-bisabolatrien-10-one) and the novel trisnorsesquiterpenoid, schiffnerone B (2-hydroxy-11,12,13-trinor-7-calamenone). © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Dysoxylum schiffneri is an Australian member of the Meliaceae family. The genus *Dysoxylum* is noted for the range of classes of compounds produced including diterpenoids, sesquiterpenoids, alkaloids, limonoids and other triterpenoids. The hexane, chloroform and methanol extracts of *D. schiffneri* were examined. All three extracts yielded (+)-8-hydroxycalamenene (**1**) which has been isolated previously from *Dysoxylum acutangulum* [1]. This compound has been shown to exhibit fish toxicity against *Oryzias latipes* at 5 ppm concentration and to have moderate anti-bacterial activity against Gram-positive bacteria at 5–20 ppm. The chloroform extract also yielded the novel sesquiterpenoid, schiffnerone A (**2**) and the trisnorsesquiterpenoid, schiffnerone B (**3**).

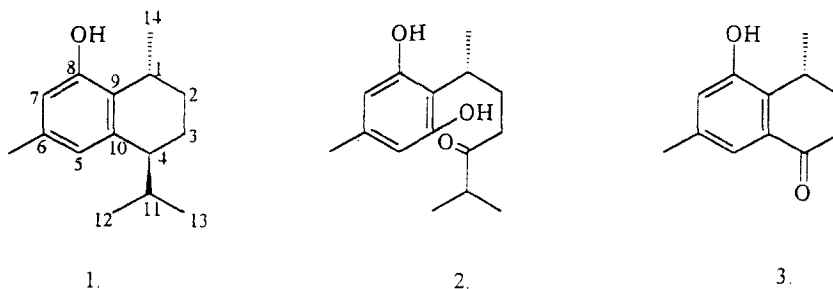
RESULTS AND DISCUSSION

(+)-8-Hydroxycalamenene (**1**) was identified by comparison of NMR, mass spectral and optical rotation data with literature values. High resolution mass spectroscopy of schiffnerone A (**2**), indicated a molecular formula of $C_{15}H_{22}O_3$. A peak at m/z 207 indicated the loss of an isopropyl group. The IR spectrum showed a broad band at 3440 cm^{-1} (OH stretching) and a band at 1705 cm^{-1} (C=O stretching). A singlet at δ 6.18 (2H) was assigned to two equivalent protons in a symmetrically-substituted benzene ring. A broad singlet at δ 5.31 (2H) disappeared on addition of D_2O , indicating two equivalent hydroxy groups on

the benzene ring instead of only one as in compound **1**. Coupling was noted between the aromatic proton signal at δ 6.18 and a three proton singlet at δ 2.16. From this it was deduced that a 2,6-dihydroxy-4-methylbenzene ring was present in the molecule. A six proton doublet at δ 1.01 was seen to be coupled to a multiplet integrating to 1H at δ 2.55. This resonance was not further coupled, thus the keto group was placed here giving a partial structure of $(CH_3)_2CHCO$. A three proton doublet at δ 1.32 was coupled to a multiplet at δ 3.19 (1H). This resonance was coupled to two multiplets at δ 1.70 (1H) and δ 2.26 (1H). These two multiplets were further coupled to a multiplet at δ 2.41 (2H) which was not further coupled. This indicated the partial structure $CH_3CHCH_2CH_2$. Assembling the partial structures gave compound **2**.

Schiffnerone B was isolated in very small amounts. The mass spectrum indicated a molecular formula of $C_{12}H_{14}O_2$ indicating that the molecule had lost three carbon atoms. The IR spectrum also showed OH and C=O stretching (3418 and 1654 cm^{-1} , respectively). The 1H NMR spectrum contained resonances ascribable to two aromatic protons (δ 6.77 and 7.43). These were both coupled to a three proton methyl group singlet at δ 2.29. A sharp singlet at δ 4.87 (1H) disappeared on addition of D_2O indicating a hydroxy group. This was placed at C-8 as in **1** and **2**. A methyl proton doublet at δ 1.31 (H_3-14) was coupled to a multiplet at δ 3.32 (H-1) which was further coupled to a multiplet at δ 2.25 (H-2a). Coupling was observed between this multiplet at δ 2.25 and three one proton multiplets at δ 1.99 (H-2b), 2.55 (H-3a) and 2.80 (H-3b). No resonances ascribable to an isopropyl group were present indicating that this group had been lost. The keto group indicated in the IR spectrum was

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placed at C-4. Thus structure **3** is proposed for schiffnerone **B**. The ^{13}C NMR spectrum was unfortunately too weak to confirm the presence of the keto group.

EXPERIMENTAL

Dysoxylum schiffneri was collected and identified in Australia by Prof D. A. H. Taylor and Dr Tony Irvine. Voucher specimens are retained in the Forest Herbarium, Oxford (DAHT 329).

Dried, milled wood (200 g) was extracted successively with hexane, CHCl_3 , and MeOH. The extracts were separated using CC over silica gel (Merck 9385) using $\text{MeCl}_2/\text{EtOAc}$ in varying proportions. All three extracts yielded 8-hydroxycalamenene (**1**). Compounds **2** and **3** were isolated from the CHCl_3 extract. NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer and NMR data is given in Tables 1 and 2.

8-Hydroxycalamenene (**1**). 1,2,3,4-tetrahydro-4-isopropyl-1,6-dimethylnaphthalene, (2.9 g), HRMS m/z

Table 1. ^1H NMR data for compounds **1–3** (300 MHz, CDCl_3)

	1	2	3
H-1	3.07 <i>m</i>	3.19 <i>m</i>	3.32 <i>m</i>
H-2			
a	1.51 <i>m</i>	1.70 <i>m</i>	2.25 <i>m</i>
b	1.81 <i>m</i>	2.26 <i>m</i>	1.99 <i>m</i>
H-3			
a	1.78 <i>m</i>	2.41 <i>m</i>	2.55 <i>m</i>
b			2.80 <i>m</i>
H-4	2.46 <i>m</i>	—	—
H-5	6.57 <i>bs</i>	6.18 <i>bs</i>	7.43 <i>bs</i>
H-7	6.39 <i>bs</i>	6.18 <i>bs</i>	6.77 <i>bs</i>
H-11	1.98 <i>dd</i>	2.55 <i>m</i>	—
H-12	0.81 <i>d</i> (7.0)	1.01 <i>d</i> (7.0)	—
H-13	0.97 <i>d</i> (7.0)	1.01 <i>d</i> (7.0)	—
H-14	1.20 <i>d</i> (7.0)	1.32 <i>d</i> (7.0)	1.31 <i>d</i> (6.8)
3H-15	2.21 <i>s</i>	2.16 <i>s</i>	2.29 <i>s</i>
8-OH	5.30 <i>bs</i>	5.31 <i>bs</i>	4.87 <i>bs</i>
10-OH	—	5.31 <i>bs</i>	—

Table 2. ^{13}C NMR data for compounds **1–3** (75 MHz, CDCl_3)

Carbon atom	1	2	3
1	26.8 <i>d</i>	29.0 <i>d</i>	26.1 <i>d</i>
2	27.3 <i>t</i>	29.2 <i>t</i>	29.1 <i>t</i>
3	19.3 <i>t</i>	38.5 <i>t</i>	33.8 <i>t</i>
4	43.3 <i>d</i>	217.5 <i>s</i>	*
5	123.1 <i>d</i>	155.2 <i>s</i>	120.1 <i>d</i> [†]
6	135.1 <i>s</i>	115.1 <i>s</i>	*
7	113.6 <i>d</i>	109.8 <i>d</i>	121.0 <i>d</i> [†]
8	153.1 <i>s</i>	155.2 <i>s</i>	151.1 <i>s</i>
9	126.4 <i>s</i>	137.3 <i>s</i>	*
10	141.3 <i>s</i>	109.8 <i>s</i>	*
11	33.4 <i>d</i>	40.1 <i>d</i>	—
12	19.8 <i>q</i> [†]	18.3 <i>q</i> [†]	—
13	21.2 <i>q</i> [†]	18.1 <i>q</i> [†]	—
14	22.3 <i>q</i>	19.1 <i>q</i>	14.0 <i>q</i>
15	21.4 <i>q</i>	20.9 <i>q</i>	18.4 <i>q</i>

* Sample too weak for detection of these resonances.

[†] Values in the same column may be interchanged.

218.1652 ($\text{C}_{15}\text{H}_{22}\text{O}$ req. 218.1670), $[\alpha]_{\text{D}}^{25} = +36.5^\circ$ (*c*, 0.050 in CHCl_3) (lit. +38° [1]).

Schiffnerone **A** (**2**). 1,5-dihydroxy-1,3,5-bisabolatrien-10-one (47 mg), mp 128–130°, $[\alpha]_{\text{D}}^{25} = +80^\circ$ (CHCl_3 ; *c* 0.060). HRMS m/z 250.1579 ($\text{C}_{12}\text{H}_{22}\text{O}_3$ req. 250.1659). IR: $\gamma_{\text{max}}^{\text{NaCl}}$ cm^{-1} : 3439, 2968, 2926, 2877, 1705, 1628, 1467, 1425, 1361, 1263. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 228 ($\xi = 13925$), 264 ($\xi = 7485$).

Schiffnerone **B** (**3**). 2-hydroxy-11,12,13-trinor-7-calamenone (2.9 mg). HRMS m/z 190.1066 ($\text{C}_{12}\text{H}_{14}\text{O}_2$ requires 190.0994). IR $\gamma_{\text{max}}^{\text{NaCl}}$ cm^{-1} : 3418, 2930, 2895, 2098, 1653, 1579, 1470. UV $\lambda_{\text{max}}^{\text{EtOH}}$: 229 ($\xi = 8527$), 265 ($\xi = 5284$), 315 ($\xi = 1855$).

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