Rabaichromone (**2**). Amorphous, UV λ_{max}^{MeOH} nm: 234, 242, 296, 318; (+NaOH) 243, 252, 295, 375; $[\alpha]_D$ $-132°$ (MeOH; *c* 0.84); ^{1}H NMR: see Table 1; EIMS *m/z* (rel. int.): 392 $[C_{20}H_{24}O_8]^+$ (39), 277 (1), 259 (100), 243 (33), 233 (80), 217 (24), 193 (49), 179 $[C_9H_7O_4]^+$ (1), 163 $[C_9H_7O_3]^+$ (12).

Barbaloin isomers (**3**). Brown, amorphous, UV λ_{max}^{MeOH} nm: 260, 268, 298, 358; (+NaOH) 267, 370, 389, 424, 445; ^{1}H NMR: see Table 2; EIMS *m/z* (rel. int.): 280 $[C_{17}H_{12}O_4]^+$ (79), 262 (31), 256 $[C_{15}H_{12}O_4]^+$ (100), 238 (10).

10-C-*Rhamnosyl aloe-emodin anthrone* (**4**). Amorphous. Found: M^+ 402.1313; $C_{21}H_{20}O_8$ requires 402.1315. UV λ_{max}^{MeOH} nm: 252, 260, 272, 295, 358; (+NaOH) 267, 372, 391, 423, 444; ^{1}H NMR: see Table 2; EIMS *m/z* (rel. int.): 402 $[M]^+$ (18), 298 (16), 280 (44), 262 (54), 256 (100), 238 (14), 227 (18), 210 (25), 147 $[C_6H_{11}O_4]^+$ (4).

11-O-Rhamnosyl aloe emodin (**5**). Amorphous, yellow. Found: M^+ 416.1083; $C_{21}H_{20}O_9$ requires 416.1107. UV λ_{max}^{MeOH} nm: 251, 257, 286, 428; (+NaOH) 234, 244, 250, 256, 261, 280, 508; ^{1}H NMR: see Table 2; EIMS *m/z* (rel. int.): 416 $[M]^+$ (2), 299 (49), 270 (24), 254 $[C_{15}H_{10}O_4]^+$ (100), 241 (22), 225 (25).

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LIGNANS FROM LEAVES OF *CALOCEDRUS FORMOSANA*

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Key Word Index—*Calocedrus formosana*; Cupressaceae; shonanin; 4,4′-dihydroxy-3,3′-dimethoxy-9,9′-epoxylignan; sesamin; yatein.

Abstract—Sesamin, yatein and 4,4′-dihydroxy-3,3′-dimethoxy-9,9′-epoxylignan were isolated from leaves of *Calocedrus formosana*. The structure of the epoxylignan was unambiguously determined by spectroscopic methods and X-ray diffraction.

INTRODUCTION

Calocedrus formosana [1] is an endemic conifer commonly called 'shonan'. Its heartwood is rich in terpenoid acids [2–4]. We have recently reported on the terpenoid constituents of its leaves [5]. In a continuation of this work, we have now isolated (+)-sesamin (**1**) [6], (−)-yatein (**2**) [7] and an epoxylignan (**3**) from the leaves. The lignan components of heartwood, such as hinokinin, hibalactone and calocedrin [8], were not found in leaves.

RESULTS AND DISCUSSION

The epoxylignan (**3**), namely shonanin, was obtained as colourless crystals, mp 136–137°. The structure of this optically inactive compound was determined as 4,4′-dihydroxy-3,3′-dimethoxy-9,9′-epoxylignan from its spectral data. The mass spectrum showed a parent ion at *m/z* 344 corresponding to a molecular formula $C_{20}H_{24}O_5$, while the ^{13}C NMR spectrum displayed only 10 signals, indicating that **3** is a symmetric molecule. The ^{13}C chemical shift values were similar to those of secoisolariciresinol (**4**) [9], except for C-9 (C-9′) appearing at a lower field (Table 1). A single crystal X-ray analysis of shonanin clearly showed the *trans* configuration rather than a *meso* compound.

Crystal data: $C_{20}H_{24}O_5$, orthorhombic, space group *Fdd*2, $a = 21.786(5)$, $b = 16.544(5)$, $c = 9.92(3)$, $Z = 8$; 523 reflections ($I > 2.5\,\sigma$) were measured using MoK_α radiation. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms converged to $R = 0.0623$ and $R_w = 0.0612$. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University

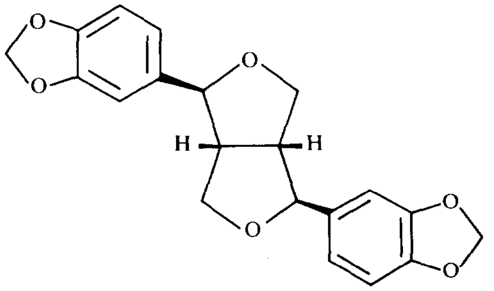
Table 1. ^{13}C NMR data (75 MHz, $CDCl_3$, δ) of compounds **3**, **3a** and **4**

C	**3**	**3a**	**4** [9]
1	132.2 (*s*)	138.1 (*s*)	132.4
2	111.1 (*d*)	112.8 (*d*)	111.7
3	146.4 (*s*)	150.9 (*s*)	146.6
4	143.9 (*s*)	139.2 (*s*)	143.7
5	114.1 (*d*)	122.6 (*d*)	114.3
6	121.2 (*d*)	120.7 (*d*)	121.5
7	39.1 (*t*)	39.4 (*t*)	35.8
8	46.4 (*d*)	46.4 (*d*)	43.7
9	73.2 (*t*)	73.1 (*t*)	60.5
OMe	55.7 (*q*)	55.8 (*q*)	55.7
$MeCO_2$		28.6 (*q*), 169.1 (*s*)	

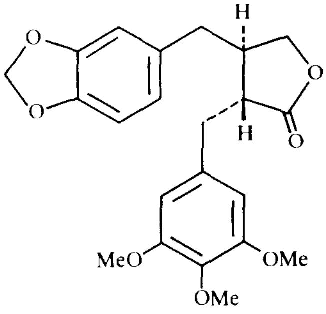
Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

It is noted that a component of fir wood [10], namely 3,4-divanillyltetrahydrofuran, has the structure **3**. However, the crystalline 3,4-divanillyltetrahydrofuran, mp 116–117°, has been reported to be an optically active compound, $[\alpha]_D^{25} -52.2°$ (tetrahydrofuran; *c* 1.4). The physical properties of this compound and shonanin are obviously different, but the lack of spectral data for the former precludes further comparison.

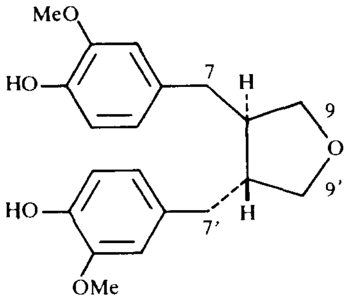
The occurrence of 9,9′-epoxylignan (**3**) is significant as the naturally occurring epoxylignans usually have 7,7′- and 7,9′-linkages. Besides **3**, the known lignans with 9,9′-linkage occur as higher oxidative derivatives of lactones and hemiacetals [6, 11–13]. While other lignan compon-



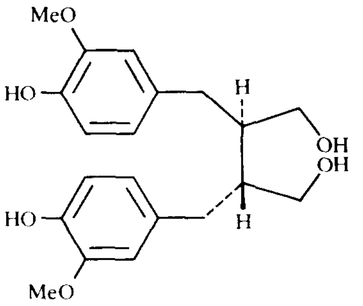
1



2

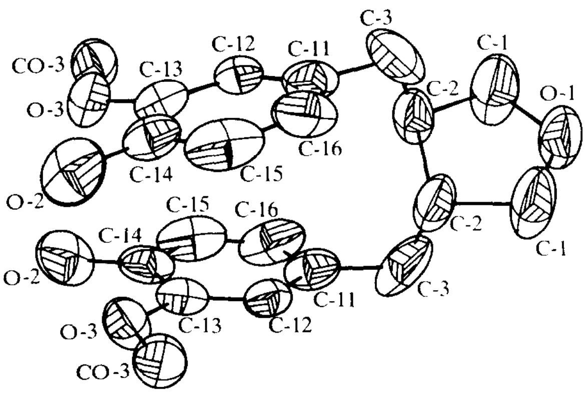


3



4

ORTEP drawing of **3**



ents of *C. formosana* contain methylenedioxyphenyl subunits, shonanin has 3-methoxyphenol moieties.

EXPERIMENTAL

Calocedrus formosana (Florin) Florin was collected in the Taichung county [8]. Leaves were air-dried and exhaustively extracted with Me_2CO. After removal of solvent, the residue was extracted several times with hexane, followed by with EtOAc. The concentrated EtOAc extractive was chromatographed on a silica gel column with elution by hexane–EtOAc gradients, and purified on a HPLC μ-Porasil column to give shonanin (**3**). Colourless needle crystals, mp 136–137° (hexane–EtOAc 3:7). $[\alpha]_D^{25}$ 0° ($CHCl_3$; c 0.73). UV $\lambda_{max}^{CHCl_3}$ nm ($\log \varepsilon$): 237 (3.47), 277 (3.72); IR ν_{max}^{KBr} cm^{-1}: 3339 (OH), 1604, 1512, 1267, 1242, 1154; EIMS m/z (rel. int.): 344 (48), 189 (20), 139 (39), 138 (100), 137 (92), 123 (30), 122 (23), 107 (25), 106 (40); ^1H NMR ($CDCl_3$, 300 MHz): δ2.15 (2H, *m*, H-8, 8′), 2.53 (4H, *m*), 3.52 (2H, *dd*, $J = 8.7$, 5.7 Hz), 3.80 (6H, *s*, 2 × OMe), 3.90 (2H, *dd*, $J = 8.7$, 6.6 Hz), 5.61 (2H, *s*, 2 × OH), 6.48 (2H, *d*, $J = 1.7$ Hz, H-2, 2′), 6.56 (2H, *dd*, $J = 8.0$, 1.7 Hz, H-6, 6′), 6.78 (2H, *d*, $J = 8.0$ Hz). Treatment of shonanin with Ac_2O in pyridine gave a diacetate (**3a**) as colourless needles, mp 146–147°. IR ν_{max}^{KBr} cm^{-1}: 1756, 1604, 1508; EIMS m/z (rel. int.): 428 (18), 387 (30), 386 (92), 345 (46), 344 (100), 137 (54), 136 (28); ^1H NMR ($CDCl_3$): δ2.21 (2H, *m*), 2.28 (6H, *s*, 2 × $MeCO_2$), 2.57 (2H, *dd*, $J = 13.5$, 6.0 Hz), 2.66 (2H, *dd*, $J = 13.5$, 8.3 Hz), 3.53 (2H, *dd*, $J = 8.7$, 5.7 Hz), 3.77 (6H, *s*, 2 × OMe), 3.92 (2H, *dd*, $J = 8.7$, 6.5 Hz), 6.64 (2H, *br d*, $J = 8.5$ Hz), 6.65 (2H, *br s*), 6.90 (2H, *br d*, $J = 8.5$ Hz).

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