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2,5-DIARYL-3,4-DIMETHYLTETRAHYDROFURAN LIGNANS FROM *TALAUMA HODGSONII*

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Key Word Index—*Talauma hodgsonii*; Magnoliaceae; lignans.

Abstract—One new and two known 2,5-diaryl-3,4-dimethyltetrahydrofuran lignans were isolated from the bark of *Talauma hodgsonii*.

INTRODUCTION

Previous work on *Talauma* species, generally on the bark, has led to isolation of relatively common aporphine alkaloids and lignans of the 2,6-diaryl-3,7-dioxabicyclo[3,3,0]-octane type [1–4]; in one instance the root bark of *T. obovata* yielded the sesquiterpene lactones costunolide and parthenolide [5]. We have now examined the stem bark of *T. hodgsonii* Hook. f. and Thoms. from Thailand. Isolated were the known 2,5-diaryl-3,4-dimethyltetrahydrofuran type lignans (−) galbacin (**1a**) [6], (−) **1b** [7] and the new analogue (−) **1c** which we have named talaumidin. Earlier workers [8] have reported the aporphine alkaloids lanuginosine and liriodenine from the bark and the lignans (+)-sesamin, (+)-fargesin and (+) pinoresinol dimethyl ether from the leaves of Indian *T. hodgsonii*.

RESULTS AND DISCUSSION

The ^{1}H NMR spectrum of the 3,4-dimethyl-2,5-diaryltetrahydrofuran moiety of the new lignan **1c** was very similar to the spectra of **1a** and **1b**, the signals of H-2 and H-5 being superimposed at δ 4.63 (J = 9.2 Hz) as were those of H-3 and H-4 at δ 1.78, while the chemical shifts of the two methyls at C-3 and C-4 at δ 1.06 and 1.04 (both *d*s, J = 5.8 Hz) differed only slightly. Consequently all four substitutents on the tetrahydrofuran ring were in a *trans* relationship, like those in **1a** and **1b**. One of the aryl substituents was a 3,4-methylenedioxyphenyl group (two proton singlet at δ 5.96, doublets at δ 6.95, J = 1.8 Hz, H-2″ and 6.79, J = 8 Hz, H-5″ and a *dd* at δ 6.86 J = 8, 1.8 Hz, H-6″). The second aryl substituent was an anisyl group (doublets at δ 6.96 J = 1.8 Hz, H-2′ and 6.91, J = 8, H-5′, *dd* at 6.87, J = 8, 1.8 Hz, H-6′, and a methoxyl singlet at δ 3.93) corroborated by a positive $FeCl_3$ test, a bathochromic shift in the UV spectrum on addition of base and the formation of a monoacetate whose ^{1}H NMR spectrum exhibited the expected shifts in the signals of the anisyl portion. The negative rotation of talaumidin indicated that the absolute configuration was the same as that of (−) galbicin, i.e. 2*S*,3*S*,4*S*,5*S*.

The ^{13}C NMR spectrum of talaumidin is listed in Table 1 and compared with the previously unreported ^{13}C NMR spectra of **1a** and **1b**. Assignments of C-2′,5′,6′ and C-2″, C-5″ and C-6″ were confirmed by HETCOR. Selective INEPT experiments led to the assignment of the other frequencies. Thus in the case of **1c** irradiation at the frequency of H-2, H-5 enhanced the carbon doublets at δ 106.6 *d*, 1.085 *d* (C-2′ and C-2″), 119.7 *d*, 119.4 *d* (C-6′ and C-6″), as well as those at 50.9 *d* and 51.2 *d* (C-3 and C-4) and the signal at δ 13.8 (two methyls). Irradiation at the frequency of OMe at δ 3.93 enhanced the singlet at δ 146.6 which could therefore be assigned to C-3, while irradiation at the frequency of —OCH_2O— enhanced carbon singlets at δ 146.9 and 147.8, i.e. C-4″ and C-4′, respectively.

EXPERIMENTAL

Plant material

Bark of *Talauma hodgsonii* Hook. f. and Thoms. was collected in Chiang Mai, Thailand, in October 1992. A voucher specimen is on deposit in the Her-

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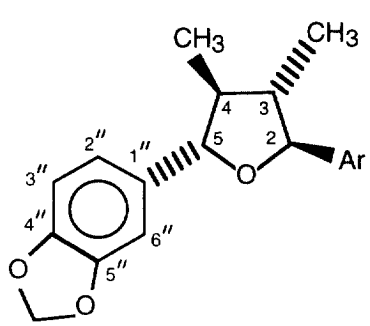
Table 1. ^{13}C NMR spectra of **1a–c** and **1c**-acetate (75 MHz, $CDCl_3$)

C	1a	1b	1c	1c-Ac
2	88.1 *d*	88.2 *d*	88.4 *d*	88.4 *d*
3	50.9 *d*	51.1 *d*	50.9 *d*	51.2 *d*
4	50.9 *d*	50.8 *d*	51.2 *d*	50.9 *d*
5	88.1 *d*	88.3 *d*	88.2 *d*	87.9 *d*
1′	136.2 *s*	134.7 *s*	134.1 *s*	139.0 *s*
2′	107.8 *d*	109.1 *d*	108.5 *d*	109.9 *d*
3′	147.6 *s*	148.9 *s*	146.6 *s*	141.4 *s*
4′	146.8 *s*	148.4 *s*	145.1 *s*	151.0 *s*
5′	106.4 *d*	110.7 *d*	114.0 *d*	122.4 *s*
6′	119.6 *d*	118.6 *d*	119.7 *d*	118.3 *d*
1″	136.2 *s*	138.5 *s*	136.5 *s*	136.2 *s*
2″	107.8 *d*	106.9 *d*	106.6 *d*	106.5 *d*
3″	147.6 *s*	147.4 *s*	147.8 *s*	147.0 *s*
4″	146.8 *s*	146.9 *s*	146.9 *s*	147.0 *s*
5″	106.4 *d*	107.9 *d*	107.9 *d*	107.9 *d*
6″	119.9 *d*	119.7 *d*	119.4 *d*	119.7 *d*
Me(2)	13.6 *q*	13.8 *q*	13.8 *q*	14.0 *q*, 13.7 *q*
OCH_2O	100.8 *t*	100.9 *t*	100.9 *t*	100.9 *t*
OMe		55.9 *q*, 55.8 *q*	55.9 *q*	55.9 *q*
Ac				169.2 *s*, 20.7 *q*

barium of the Royal Forestry Department, Bangkok, Thailand.

Extraction and isolation

Dried and powdered bark of *Talauma hodgsonii* (2 kg) was percolated with MeOH at room temp. to exhaustion. Evapn of the soln at red pres gave 142 g of crude extract which was dissolved in $CHCl_3$ at 40°, filtered and evaporated again at red press to give 16.51 g of a gum which was chromatographed over silica gel (200 g) and eluted with petrol–$CHCl_3$, $CHCl_3$–Me_2CO and MeOH, 500 ml fractions being collected as follows: frs 1–42 (petrol–$CHCl_3$, 7:3), frs 43–110 (petrol–$CHCl_3$, 1:1), frs 111–159 (petrol–$CHCl_3$, 3:7), frs 160–170 (petrol–$CHCl_3$, 1:9), frs 171–176 ($CHCl_3$–Me_2CO, 9:1) and fr 177 (MeOH).



1a Ar = Piperonyl
b Veratryl
c Anisyl

Frs 1–13 contained nonpolar material which was not studied further. Frs 14–24 (1.2 g) were combined. Recrystallization from MeOH afforded β-sitosterol (344 mg); purification of the mother liquor on PTLC (silica gel, petrol–EtOAc–Me_2CO–HCO_2H, 85:13:2:1) gave two subfrs. The less polar subfr. (242 mg) after PTLC (silica gel, petrol–EtOAc, 9:1) furnished 173 mg of (−) galbacin (**1a**); the more polar subfr. (38 mg) gave after PTLC (silica gel, petrol–EtOAc–Me_2CO, 17:1:3) 17 mg of (−) **1b**. Frs 25–42 were also combined and purified by PTLC (silica gel, toluene–EtOAc–Me_2CO–HCO_2H, 92:7:1:1) to give a further 13 mg of (−) **1b**. Combination of frs 43–47 and purification (PTLC, silica gel, toluene–EtOAc–Me_2CO–HCO_2H, 75:20:5:1 eluted twice) furnished 32 mg of (−) **1c**.

Frs 48–52 were also combined and subjected to CC over silica gel, 100 ml subfractions being collected as follows: subfrs 1–47 (petrol–$CHCl_3$, 4:1), subfrs 48–63 (petrol–$CHCl_3$, 3:2), subfrs 64–75 (petrol–$CHCl_3$, 2:3), subfrs 76–85 (petrol–$CHCl_3$, 1:4), subfrs 86–100 ($CHCl_3$), subfrs 101–105 ($CHCl_3$–Me_2CO, 9:1), subfrs 106–107 ($CHCl_3$–Me_2CO, 1:1) subfr. 108 (Me_2CO) and subfr. 109 (MeOH). Combination of subfrs 7–17 followed by PTLC (silica gel, petrol–EtOAc–Me_2CO–HCO_2H, 75:24:5:1) gave 10 mg of (−) **1b** and 11 mg of (−) **1c**.

(−) Galbacin (**1a**) [6, 9] and lignan **1b** [7] were identified by MS, rotation and ^1H NMR. The rotation of **1b**. $[\alpha]_D^{20}$ −83.0 (*c* 0.003, $CHCl_3$), was somewhat greater than the value of −41.7 reported in the literature [7].

Talaumidin ([2S,3S,4S,5S]-3,4-*dimethyl*-2-[3-*methoxy*-4-*hydroxyphenyl*]-5[3,4-*methylenedioxyphenyl*]-*tetrahydrofuran* (**1c**). Viscous gum; MS-EI *m/z* (rel. int.): 342 $[M]^+$ (65), 285 (5), 257 (7), 221 (8), 206 (18), 190 (100), 175 (52), 145 (70), 131 (38), 117 (48), 91 (48); UV (MeOH) λ_{max} (log ε): 283.0 (37), 233 (4.0); UV (MeOH + NaOH); λ_{max} (log ε) 289.6 (3.9), 248 (4.1); $[\alpha]_D^{20}$ −90.2 (*c* −0.01, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 6.96 (*d*, *J* = 1.8 Hz, H-2′), 6.95 (*d*, *J* = 1.8 Hz, H-2″), 6.91 (*d*, *J* = 8 Hz, H-5′), 6.87 (*dd*, *J* = 8.0, 1.8 Hz, H-6′), 6.86 (*dd*, *J* = 8.0, 1.8 Hz, H-6″), 6.79 (*d*, *J* = 8.0 Hz, H-5″), 5.96 (*s*, 2p, —OCH_2O—), 4.63 (*d*, *J* = 9.2 Hz, 2p, H-2, 5), 3.93 (*s*, 3p, —OMe), 1.78 (*m*, 2p, H-3,4), 1.06 and 1.04 (both *d*, *J* = 5.8 Hz and 3p, two methyls); ^{13}C NMR: Table 1.

Acetylation of **1c** (20 mg with Ac_2O–Py followed by the usual work-up) afforded 17 mg of the monoacetate as a viscous gum; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.04 (*d*, *J* = 1.6 Hz, H-2″), 7.01 *d*, *J* = 8 Hz, H-5′), 6.93 (*dd*, *J* = 8 Hz, H-6′), 6.93 (*d*, *J* = 1.5 Hz, H-2′), 6.85 (*dd*, *J* = 8, 1.5 Hz, H-6′), 6.79 (*d*, *J* = 8 Hz, H-5′), 5.96 (*s*, 2p, —OCH_2—), 4.68 (*d*, *J* = 9 Hz, H-5), 4.63 (*d*, *J* = 9.1 Hz, H-2), 2.86 (*s*, 3p, OMe), 2.32 (*s*, 3p, OAc), 1.78 (*m*, 2p, H-3,4), 1.08 and 1.04

(both *d* and 3p, $J = 5.8$ Hz, two methyls); ^{13}C NMR: Table 1.

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