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NEOLIGNANS FROM *CARYODAPHNOPSIS BAVIENSIS*

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Key Word Index—*Caryodaphnopsis baviensis*; Lauraceae; fruits; leaves and twigs; bark; neolignans.

Abstract—Besides the eupomatenoids 1, 3, 5 and 6, 5-(*erythro*-1,2-dihydroxypropyl)-2-(4-hydroxyphenyl)-3-methylbenzo[*b*]furan, 5-(*erythro*-1,2-dihydroxypropyl)-2-(4-hydroxy-3-methoxyphenyl)-3-methylbenzo[*b*]furan, (2*R*,3*R*)-2,3-dihydro-2-(4-hydroxyphenyl)-3-methyl-5-[(*E*)-1-propenyl]benzo[*b*]furan, *erythro*-1-(3,4-methylenedioxyphenyl)-2-{4-[(*E*)-1-propenyl]phenoxy}propan-1-ol, (+)-sesamin, isolinderanolide and icariside D_1, two new neolignans have been isolated from *Caryodaphnopsis baviensis*. Their structures were elucidated as 3-methyl-2-(3,4-methylenedioxyphenyl)-5-[(*E*)-3-oxo-1-propenyl]benzo[*b*]furan and 4-hydroxy-α-{4-[(*E*)-1-propenyl]phenoxy}propiophenone. © 1997 Elsevier Science Ltd

INTRODUCTION

Recently we reported a series of eupomatenoids [1,2] and other constituents [3] from *Caryodaphnopsis tonkinensis* endemic to Vietnam. In continuation of our phytochemical studies, we have now examined the constituents of *C. baviensis*, a further endemic Lauraceae species growing as shrub in this country and which has not been investigated previously. Isolation was performed by a series of column chromatographic separations and preparative TLC.

RESULTS AND DISCUSSION

From different parts of *C. baviensis*, the neolignans, eupomatenoid 1 (**1**) [4] (yield 0.01% from fruits, 0.0015% from leaves and twigs), eupomatenoid 3 (**2**) [5] (yield 0.41% from fruits, 0.09% from leaves and twigs, 0.02% from bark), eupomatenoid 5 (**3**) [5] (yield 0.14% from fruits, 0.03% from leaves and twigs, 0.01% from bark), eupomatenoid 6 (**4**) [5] (yield 0.05% from fruits, 0.06% from leaves and twigs, 0.01% from bark), two polar eupomatenoids [**5**: 5-(*erythro*-1,2-dihydroxypropyl)-2-(4-hydroxyphenyl)-3-methylbenzo[*b*]furan [2], yield 0.005% from fruits; **6**: 5-(*erythro*-1,2-dihydroxypropyl)-2-(4-hydroxy-3-methoxyphenyl)-3-methylbenzo[*b*]furan [2], yield 0.004% from fruits], the dihydrobenzofuran **7** [(2*R*,3*R*)-2,3-dihydro-2-(4-hydroxyphenyl)-3-methyl-5-[(*E*)-1-propenyl]benzo[*b*]furan [[6], yield 0.02% from fruits], the neolignan **8** [*erythro*-1-(3,4-methylenedioxyphenyl)-2-{4-[(*E*)-1-propenyl]phenoxy} propan-1-ol [[3], yield 0.02% from fruits], the lignan (+)-sesamin (**9**) [7] (yield 0.22% from fruits), the γ-lactone isolinderanolide (**10**) [8] (yield 0.006% from fruits), the β-phenylethanoic glycoside icariside D_1 (**11**) [9] (yield 0.003% from fruits) and two new neolignans have been isolated. The new structures have been elucidated as 3-methyl-2-(3,4-methylenedioxyphenyl)-5-[(*E*)-3-oxo-1-propenyl]benzo[*b*]furan (**13**) (yield 0.005% from fruits) and 4-hydroxy-α-{4-[(*E*)-1-propenyl]phenoxy}propiophenone (**14**) (yield 0.006% from fruits), as outlined below.

The elemental composition of compound **13** was $C_{19}H_{14}O_4$ according to high-resolution mass spectrometry. Comparison of the NMR spectra (Table 1) with those of eupomatenoids [1, 3] indicated a benzo[*b*]furan ring system and the nature as well as the positions of the substituents.

High-resolution mass spectrometry indicated the elemental composition of compound **14** to be $C_{18}H_{18}O_3$. Important fragments were observed by splitting of the molecule between carbonyl and C-α as expected for structure **14**. The NMR spectra (Table 2) were compared with those of *erythro*-1-(3,4-methylenedioxyphenyl)-2-{4-[(*E*)-1-propenyl]phenoxy} propan-1-ol (**8**) [3] and were in agreement with structure **14**. The absolute configuration was not established.

Icariside D_1 (**11**) [9] was identified by combined use of one- and two-dimensional NMR experiments including direct and long-range ^1H,^{13}C correlation spectra. Because of severe signal overlapping of most

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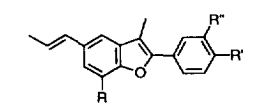
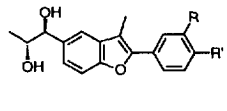
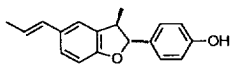


1 R = OMe, R' + R'' = OCH_2O
2 R = H, R' + R'' = OCH_2O
3 R = H, R' = OH, R'' = OMe
4 R = H, R' = OH, R'' = H



5 R = H, R' = OH
6 R = OMe, R' = OH



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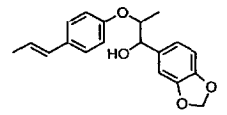

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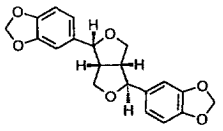

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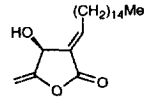

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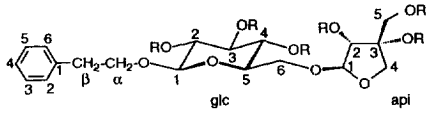
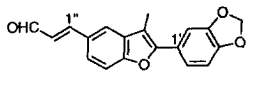


11 R = H
12 R = Ac



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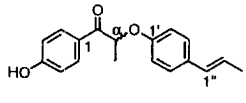

14

hexose proton signals, the vicinal coupling constants could not be determined. Therefore, the hexaacetate **12** was prepared and investigated by NMR methods. The coupling constants observed clearly showed the presence of β-glucopyranose. ^1H,^{13}C long-range shift correlation experiments yielded complete and unambiguous assignments of the ^1H and ^{13}C signals of **11** and **12** (Table 3). The chemical shifts of the apiose moiety ^{13}C-atoms agreed with those of a β-D-apio-D-furanosyl residue [10]. Therefore, the configuration of apiose given in formula **11** was assumed.

EXPERIMENTAL

Plant material. Fruits, leaves, twigs and bark of *C. baviensis* (Lec.) A.-Shaw were collected in Bavi, Hanoi, in November 1992. The species was identified by Dr Tran Dinh Dai, Hanoi. A voucher specimen is deposited in the Herbarium of the Institute of Ecology and Natural Resources of the National Centre for Scientific Research, Hanoi.

3-*Methyl*-2-(3,4-*methylenedioxyphenyl*)-5-[(E)-3-*oxo*-1-*propenyl*]*benzo*[b]*furan* (**13**). Fruits were dried at 40°, ground and extracted with 95% MeOH at room temp. This soln was then extracted with petrol. After evapn of petrol *in vacuo*, the residue was purified by flash CC over silica gel with *n*-hexane–EtOAc (1:1). Amorphous, yield 0.005%. R_f 0.47 (silica gel, *n*-hexane–EtOAc, 7:3). EI-MS (70 eV) *m/z* (rel. int.): 306.0894 $[M]^+$ ($C_{19}H_{14}O_4$, calcd 306.0892) (100), 278.0937 $[M-CO]^+$ ($C_{18}H_{14}O_3$, calcd 278.0943) (55).

4-*Hydroxy*-α-{4-[(E)-1-*propenyl*]*phenoxy*}*propiophenone* (**14**). After extraction of the MeOH soln with petrol (see isolation of **13**), the organic solvent was evapd *in vacuo* and the aqueous soln extracted with EtOAc. EtOAc was removed *in vacuo* and the residue purified by flash CC over silica gel with *n*-hexane–EtOAc (3:2). Oil, yield 0.006%. R_f 0.29 (silica gel, *n*-hexane–EtOAc, 7:3). $[\alpha]_D^{22}$ +26.7° ($CHCl_3$; *c* 1.00), CD: $\Delta\varepsilon_{333}$ +0.60 (MeOH). EI-MS (70 eV) *m/z* (rel. int.): 282.1257 $[M]^+$ ($C_{18}H_{18}O_3$, calcd 282.1256) (53), 161.0977 $[M-HOC_6H_4CO]^+$ ($C_{11}H_{13}O$, calcd 161.0966) (85), 121.0320 $[HOC_6H_4CO]^+$ ($C_7H_5O_2$, calcd 121.0290) (100).

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Table 1. ^{13}C and ^1H NMR data of compound **13** [126/500 MHz, $CDCl_3$, ^1H,^1H coupling constants (Hz) in parentheses]

Pos.	^{13}C	^1H	Pos.	^{13}C	^1H
2	152.2	—	3′	148.0	—
3	110.1	—	4′	147.8	—
3a	132.1	—	5′	108.7	6.94 *d* (7.9)
4	119.9	7.71 *d* (1.6)	6′	121.2	7.29 *dd* (5.2/1.6)
5	132.4	—	1″	153.8	7.60 *d* (15.9)
6	124.8	7.52 *dd* (8.5/1.8)	2″	127.4	6.76 *dd* (15.9/7.5)
7	111.6	7.49 *d* (8.3)	3″	193.7	9.72 *d* (7.9)
7a	155.3	—	3-Me	9.4	2.46 *s*
1′	128.8	—	OCH_2O	101.4	6.04 *s*
2′	107.2	7.31 *d* (2.0)			

Table 2. ^{13}C and ^{1}H NMR data of compound **14** [126/500 MHz, $CDCl_3$, $^{1}H,^{1}H$ coupling constants (Hz) in parentheses]

Pos.	^{13}C	^{1}H	Pos.	^{13}C	^{1}H
1	127.1	—	1″	130.1	6.28 *dq* (15.6/1.7)
2/6	131.6	8.02 *d* (8.7)	2″	123.9	6.05 *dq* (15.6/6.7)
3/5	115.1	6.78 *d* (8.7)	3″	18.4	1.82 *dd* (6.7/1.4)
4	160.6	—	α	87.2	5.40 *q* (7.0)
1′	156.4	—	β	19.0	1.69 *d* (6.7)
2′/6′	115.6	6.86 *d* (9.0)	C=O	197.8	—
3′/5′	127.0	7.18 *d* (8.7)	OH	—	6.20 *br s*
4′	131.5	—			

Table 3. ^{13}C and ^{1}H NMR data of compounds **11** and **12** [126/500 MHz, $CDCl_3$–CD_3OD (19:1) (**11**), $CDCl_3$ (**12**), ^{1}H, ^{1}H coupling constants (Hz) in parentheses]

Pos.	**11** ^{13}C	**11** ^{1}H	**12** ^{13}C	**12** ^{1}H
1	139.1	—	138.1	—
2/6	128.9	7.29 *m*	128.9	7.19 *m*
3/5	129.5	7.24 *m*	128.3	7.26 *m*
4	126.8	7.21 *m*	126.3	7.19 *m*
β	36.7	2.97 *m*	35.8	2.88 *m*
		2.95 *m*		
α	71.3	4.11 *ddd* (9.5/8.0/7.0)	70.4	4.11 *m*
		3.76 *ddd* (9.6/7.7/7.7)		3.66 *m*
glc-1	103.7	4.28 *d* (7.7)	100.5	4.47 *d* (7.9)
glc-2	74.3	3.27 *dd* (8.4/8.1)	71.2	4.95 *dd* (9.6/8.1)
glc-3	77.3	3.40 *m*	72.8	5.16 *dd* (9.5/9.5)
glc-4	70.9	3.39 *m*	69.1	4.92 *dd* (9.6/9.6)
glc-5	76.0	3.39 *m*	73.2	3.64 *m*
glc-6	68.0	3.98 *m*	66.5	3.70 *dd* (11.3/1.8)
		3.67 *dd* (11.2/4.9)		3.60 *dd* (11.3/6.6)
api-1	110.2	5.01 *d* (2.0)	106.0	5.03 *br s*
api-2	77.4	3.93 *br s*	76.1	5.33 *br s*
api-3	79.9	—	84.0	—
api-4	74.6	3.98 *m*	72.4	4.22 *d* (10.6)
		3.83 *d* (9.9)		4.14 *d* (10.6)
api-5	65.4	3.63 *d* (11.7)	63.0	4.74 *d* (12.4)
		3.60 *d* (11.7)		4.57 *d* (12.4)

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