Pergamon

PII: S0031-9422(97)00876-5

Phytochemistry, Vol. 48, No. 8, pp. 1457–1459, 1998

Printed in Great Britain
0031-9422/98/$—see front matter

BARBACARPAN, A PTEROCARPAN FROM *CROTALARIA BARBATA*‡

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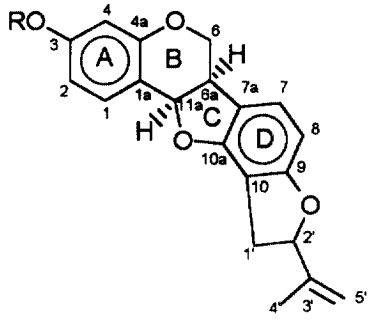
(*Received in revised form* 15 *September* 1997)

Key Word Index—*Crotalaria barbata*; Leguminosae; pterocarpan; barbacarpan.

Abstract—A new pterocarpan, barbacarpan, has been isolated from the chloroform soluble fraction of an alcoholic extract of the dried aerial parts of *Crotalaria barbata*. The structure was established as 1,2 dihydro-2-isopropenyl-3-hydroxyfurano [2,3-*l*] pterocarpan from spectroscopic evidence.

INTRODUCTION

Pterocarpans are found widely in both temperate and tropical genera of the subfamily Papilionoideae of the Leguminosae [1]. Many pterocarpans, including several isolated from the fungus inoculated parts of *Glycine max*, have been shown to possess antifungal activity [2, 3]. As part of a phytochemical study on Indian medicinal plants, *Crotalaria barbata*, a shrub that grows in Nilgiris and Mathura hills of India, was subjected to chemical investigation to afford a new pterocarpanoid, barbacarpan (**1**).



1 R = H
2 R = Ac

RESULTS AND DISCUSSION

The chloroform soluble fraction from the alcoholic extract of the dried aerial parts of *C. barbata* was subjected to column chromatography over silica gel, followed by flash chromatography to yield barbacarpan (**1**) as colourless needles. The IR spectrum showed absorption bands at 3373, 1024 cm^{-1} (hydroxy); 2927 and 1604 cm^{-1} (aromatic). The UV absorption maximum at 285 nm suggested the aromatic nature of **1**. The EIMS of **1** displayed a molecular ion peak at *m/z* 332 consistent with the molecular formula $C_{20}H_{18}O_4$ (supported by ^{13}C NMR). The ^1H NMR spectrum (Table 1) exhibited a sharp singlet at δ 1.80 (3H) for a methyl group and two broad singlets at δ 4.90 (1H) and 5.10 (1H) for an exomethylene group, suggesting the presence of isopropenyl side chain. The presence of two double doublets at δ 3.01 (1H) and 3.28 (1H), and a triplet at δ 5.18 (1H) for a methine proton were characteristic of a dihydrofuran ring [4, 5] substituted at position 2′. The above data confirmed the presence of a 2′-isopropenyl dihydrofuran ring system in **1**.

The ^1H NMR spectrum of **1** also showed five aromatic protons resonating at δ 6.38 (*d*), 6.45 (*d*), 6.55 (*dd*), 7.02 (*d*) and 7.54 (*d*), three carbinol proton signals at δ 3.62 (*t*), 4.28 (*dd*) and 5.51 (*d*), and a multiplet at δ 3.55 characteristic of a pterocarpan skeleton [6]. The ^{13}C NMR spectrum of **1** displayed carbon signals for 20 carbons. The signal assignments were made on the basis of DEPT spectra revealing the presence of eight quaternary carbons, eight methine carbons, three methylene carbons and one methyl group. The carbon resonances appeared at δ 39.64 (CH), 66.72 (CH_2), 78.90 (CH), 101.50 (CH), 103.75 (CH), 108.45 (C), 109.76 (CH), 112.68 (CH), 119.47 (C), 123.63 (CH), 132.31 (CH), 155.70 (C), 156.80 (C), 157.17 (C), 162.14 (C), confirming the presence of a pterocarpan

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‡ CDRI Communication No. 5640.

Table 1. ^{1}H NMR spectral data of barbacarpan **1** and its monoacetate **2** in $CDCl_3$

	1	**2**
Position	^{1}H (J = Hz)	^{1}H (J = Hz)
1	6.38 *d* (8.1)	6.38 *d* (8.1)
2	6.55 *dd* (8.1, 2.1)	6.81 *dd* (8.1, 2.1)
4	6.45 *d* (2.1)	6.71 *d* (2.1)
6	3.62 *t* (10.2)	3.62 *t* (10.2)
	4.28 *dd* (10.5, 4.8)	4.28 *dd* (10.5, 4.8)
6a	3.55 *dt* (9.2, 4.5)	3.55 *dt* (9.2, 4.5)
7	7.02 *d* (7.8)	7.02 *d* (7.8)
8	7.54 *d* (7.8)	7.02 *d* (7.8)
11a	5.51 *d* (6.6)	5.51 *d* (6.6)
1′	3.01 *dd* (8.1, 12.6)	3.01 *dd* (12.6, 8.1)
	3.28 *dd* (8.5, 12.6)	3.28 *dd* (8.5, 12.6)
2′	4.90 *brs*	4.92 *brs*
	5.18 *brs*	5.09 *brs*
5′	1.80 *s*	1.79 *s*
OH	5.00 *brs*	—
OAc	—	2.30 *s*

skeleton [7]. The presence of carbon signals at δ 86.40 (C-2′), 31.76 (C-1′), 143.89 (C-3′), 111.98 (C-4′) and 17.18 (C-5′) provided further support for a dihydrofuran ring substituted at the C-2′ position. Acetylation of **1** afforded the monoacetate **2** as a semi solid. A molecular ion peak at m/z 364 (M^+) confirmed the presence of one free hydroxyl group. The ^{1}H NMR spectrum of **2** showed a sharp singlet at δ 2.30 (*s*, 3H) due to one acetoxy methyl group. It further showed two downfield shifted (+0.26 ppm) aromatic protons at δ 6.71 (*d*) and 6.81 (*dd*) but the rest of the spectrum was very similar to that of **1**.

The presence of four *ortho*-coupled aromatic protons at δ 7.54 (*d*, J = 7.8 Hz); 7.02 (*d*, J = 7.8 Hz), 6.55 (*dd*, J = 8.1, 2.1 Hz) and 6.38 (*d*, J = 8.1 Hz), and one *meta*-coupled proton at δ 6.45 (*d*, J = 2.1 Hz) revealed that the hydroxyl group and the isopropenyl-dihydrofuran side chain must be substituted in different phenyl rings. A careful comparison of the ^{13}C NMR data of **1** with literature data reported for 3-hydroxy pterocarpanoids [7] allowed the hydroxyl group to be placed at C-3. The down field shift of the aromatic proton signals of H-4 at δ 6.71 (+0.26 ppm) and H-2 at δ 6.81 (+0.26 ppm) in the ^{1}H NMR spectrum of **2**, further supported the presence of hydroxylation at C-3 in ring A of **1**. The ^{13}C NMR chemical shifts at 162.14 (C-10a), 108.45 (C-10) and 155.70 (C-9), and two *ortho*-coupled aromatic protons at δ 7.54 (*d*) and 7.02 (*d*) revealed that the isopropenyl-dihydrofuran side structure attached at the C-9 and C-10 positions as in the case of crotmarine reported from *Crotalaria madurenses* [8].

The above spectroscopic data thus unambiguously led to the identification of barbacarpan as 1,2 dihydro-2-isopropenyl-3-hydroxyfurano [2,3-*l*] pterocarpan (**1**). The absolute sterochemistry at C-6a and C-11a was taken as R, R based on the negative optical rotation [9] and ^{1}H NMR signals [6] reported for the R, R configuration of naturally occurring pterocarpanoids. This is the first report of a pterocarpanoid in the genus *Crotalaria*.

EXPERIMENTAL

Mps: Uncorr. TLC: Silica gel G (SISCO) Spots were visualized by spraying with IM H_2SO_4 and heating to 100°. Column chromatography: Silica gel (60–120 mesh); Flash column chromatography: EF-10 (EYELA) A.S.C. Silica gel (230–400 mesh). ^{1}H and ^{13}C NMR spectra were run using TMS as the internal reference.

Extraction and isolation

The plant material was collected from Udhagamandalum, in the Nilgiris Hills of India in 1991. The shade dried aerial parts (11 kg) were extracted with distilled alcohol (3 × 2.5 l), and the combined extracts were concentrated to yield a crude alcoholic extract. The crude extract was fractionated into *n*-hexane, chloroform, *n*-butanol and aq. fractions

A part of the chloroform soluble fraction (5 g) was subjected to column chromatography over silica gel with a gradient elution of chloroform: methanol (1–20%), and 30 frs of 100 ml each were collected. Similar fractions were combined after monitoring by TLC to give four subfractions a–d. Subfractions b–d afforded fatty esters, sterols and β-sitosterol-β-D-glucoside respectively. The chloroform–methanol (5%) eluted subfraction a (100 mg) was further purified by flash chromatography over silica gel eluting with a stepwise gradient of *n*-hexane–chloroform, and 50 frs of 2 ml each were collected. Fractions 20–32 afforded **1** (30 mg) as colourless needles, m.p. 75°, $[\alpha]_D^{27}$ −154° (c = 0.01, $CHCl_3$), EIMS (70 eV); m/z 322 (M^+), 307 $(M-15)^+$, 305, 279, 264, 160, 147, 77; ^{1}H and ^{13}C NMR data in Tables 1 and 2 respectively.

Table 2. ^{13}C NMR spectral data of **1** in $CDCl_3$

Carbon no.	$^\delta$C	DEPT	Carbon no.	$^\delta$C	DEPT
1a	112.68	C	8	101.50	CH
1	132.31	CH	9	155.70	C
2	109.76	CH	10	108.45	C
3	157.17	C	10a	162.14	C
4	103.75	CH	11a	78.90	CH
4a	156.80	C	1′	31.76	CH_2
6	66.72	CH_2	2′	86.40	CH
6a	39.64	CH	3′	143.89	C
7a	119.47	C	4′	111.98	CH_2
7	123.63	CH	5′	17.18	CH_3

Acknowledgements—Financial assistance to one of us (U.V.B.) from CSIR, New Delhi in the form of Senior Research Fellowship is gratefully acknowledged. Thanks are due to the Director and Dr D. K. Kulshrestha CDRI for encouragement and RSIC staff for spectral data.

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