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Phytochemistry 65 (2004) 915–920
PHYTOCHEMISTRY
www.elsevier.com/locate/phytochem

Constituents of *Pterocarpus marsupium*: an ayurvedic crude drug☆

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Received 15 October 2003; accepted 28 January 2004

Abstract

Five new flavonoid *C*-glucosides, 6-hydroxy-2-(4-hydroxybenzyl)-benzofuran-7-*C*-β-D-glucopyranoside (**1**), 3-(α-methoxy-4-hydroxybenzylidene)-6-hydroxybenzo-2(3H)-furanone-7-*C*-β-D-glucopyranoside (**2**), 2-hydroxy-2-*p*-hydroxybenzyl-3(2H)-6-hydroxy-benzofuranone-7-*C*-β-D-glucopyranoside (**4**), 8-(C-β-D-glucopyranosyl)-7,3′,4′-trihydroxyflavone (**5**) and 1,2-*bis*(2,4-dihydroxy,3-C-glucopyranosyl)-ethanedione (**6**) and two known compounds *C*-β-D-glucopyranosyl-2,6-dihydroxyl benzene (**7**) and sesquiterpene (**8**), were isolated from an aqueous extract of the heartwood of *Pterocarpus marsupium*. The structure has been established using spectroscopic data.

Keywords: *Pterocarpus marsupium* heartwood; Aqueous extract; Flavonoid *C*-glucosides

1. Introduction

The tree *Pterocarpus marsupium* Roxb. (Leguminosae) popularly known as Indian kino or Bija sar, has been used in the treatment of diarrhoea, toothache, fever, urinary tract and skin infections. The wooden glass made up of heartwood of *Pterocarpus marsupium* is being used for drinking water to control blood sugar in Ayurvedic system of medicine (Jain, 1968; Chopra et al., 1958). Our formulation of aqueous extract of heartwood of *P. marsupium* has been tested clinically and found effective in non-insulin dependent diabetes mellitus patients (ICMR, 1998). This prompted us to undertake further investigation of the constituents of aqueous extract. The plant is reported to be rich in polyphenolic compounds (Seshadri, 1972; Maurya et al., 1982; 1984). We have reported the isolation and structure of a novel isoaurone *C*-glucoside, named pterocarposide (**3**) (Handa et al., 2000), from aqueous extract of the heartwood of *Pterocarpus marsupium*. In this paper, we describe the isolation and structure elucidation of five new flavonoid *C*-glucosides, named pteroside (**1**) a benzofuran *C*-glucoside, pteroisoauroside (**2**) an isoaurone *C*-glucoside, a rare natural compound, marsuposide (**4**) a benzofuranone *C*-glucoside and flavon *C*-glucoside (**5**), vijayosin (**6**) and two known compounds *C*-β-D-glucopyranosyl-2,6-dihydroxyl benzene (**7**) and sesquiterpene (**8**), were isolated from an aqueous extract of the heartwood of *Pterocarpus marsupium*.

2. Results and discussion

The NMR data for compounds **1**, **2**, **4**–**6** suggested certain common structural features attributable to one *C*-glucose moiety with the anomeric protons at δ 4.94 (*d*, $J=9.9$ Hz), 5.05 ((*d*, $J=9.8$ Hz), 4.68 (*d*, $J=9.9$ Hz), 5.16 (*d*, $J=9.5$ Hz) and 4.85 (2H, *d*, $J=9.1$Hz) with corresponding carbon signals at δ 75.3, 73.5, 79.7, 74.6 and 74.2 respectively, in the characteristic region of C-1 substituted glucosides. The assignments of carbon signals have been made by analysis of ^{1}H and ^{13}C NMR spectral data and comparison with the reported data (Handa et al., 2000; Zhang et al, 1997; Ohshima et al, 1988; Shirataki et al, 1986) for aromatic *C*-glucosides. The coupling constant of the signals resulting from the anomeric proton of the glucopyranoside indicated the

☆ RRL Communication No. 2316.

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doi:10.1016/j.phytochem.2004.01.021

glucosidic linkage to have β-configuration. Further the position of glucosyl moiety in compounds **1**, **2**, and **4** at C-7 was confirmed by HMBC correlation from anomeric proton to the C-6 and C-7a (Fig. 1).

Pteroside (**1**) was assigned the molecular formula, $C_{21}H_{22}O_8$ (FAB-MS, *m*/*z* 403 $[M+H]^+$). This conclusion was supported by the ^1H and ^{13}C NMR spectra. The presence of hydroxyl groups and the phenyl nucleus was indicated by the IR absorptions (ν_{max} 3300, 1600, 1584 and 1512 cm^{-1}). The UV spectrum of the compound showed absorption maxima in MeOH (λ_{max} 220, 242, 253 and 284 nm). The ^1H and ^{13}C NMR spectra (Table 1) indicated the presence of an isolated methylene group δ 3.95 (2H, *s*), δ_C 33.9, one proton at δ 6.20 (1H, *s*, H-3), δ_C 102.5, along with two *ortho* coupled aromatic protons at δ 7.20 (1H, *d*, $J=8.4$ Hz), δ_C 120.3 and 6.72 (1H, *d*, $J=8.4$ Hz), δ_C 112.3, assigned to H-4 and H-5 indicating that only these two protons belong to the A-ring and that C-6 and C-7 are occupied by a hydroxyl and glucosyl groups respectively. One A_2B_2 aromatic system at δ 7.13 (2H, *d*, $J=8.4$ Hz, H-2′, 6′), δ_C 130.0 and 6.74 (2H, *d*, $J=8.4$ Hz, H-3′, 5′), δ_C 115.4 was found. The consideration of spectral data enabled us to construct pteroside as 6-hydroxy-2-(4-hydroxybenzyl)-benzofuran-7-*C*-β-D-glucopyranoside. Treatment of pteroside with acetic anhydride and pyridine afforded pteroside hexaacetate, $C_{33}H_{34}O_{14}$ (**1a**) (FAB-MS, *m*/*z* 655 $[M+H]^+$). The NMR spectra (Table 1) confirmed the diphenolic character of pteroside. There was a downfield shift of aromatic protons from δ 6.72 to δ 7.46 (H-5) and from δ 6.74 to δ 7.36 (H-3′, 5′) in hexaacetyl pteroside confirming the assignment of phenolic hydroxyl groups at C-6 and C-4′. Hence pteroside characterized as 6-hydroxy-2-(4-hydroxybenzyl)-benzofuran-7-*C*-β-D-glucopyranoside (**1**) is a new naturally occurring compound (Fig. 1).

Pteroisoauroside (**2**) was assigned the molecular formula, $C_{22}H_{22}O_{10}$ (FAB-MS, *m*/*z* 447 $[M+H]^+$). This conclusion was supported by the ^1H and ^{13}C NMR spectra. The investigations of ^1H and ^{13}C NMR (Table 2) spectra of pteroisoauroside (**2**) and pteroisoauroside hexaacetate (**2a**) indicated that compound **2** was based on the same parent system of pterocarposide (**3**) (Handa et al., 2000) isolated previously from the *P. marsupium*, differed only in absence of an isolated olefin proton at δ 7.57 and appearance of one methoxy signal at δ 3.91 (3H, s), δ_C 49.9. The absence of olefinic proton defines the position of methoxy group. Further

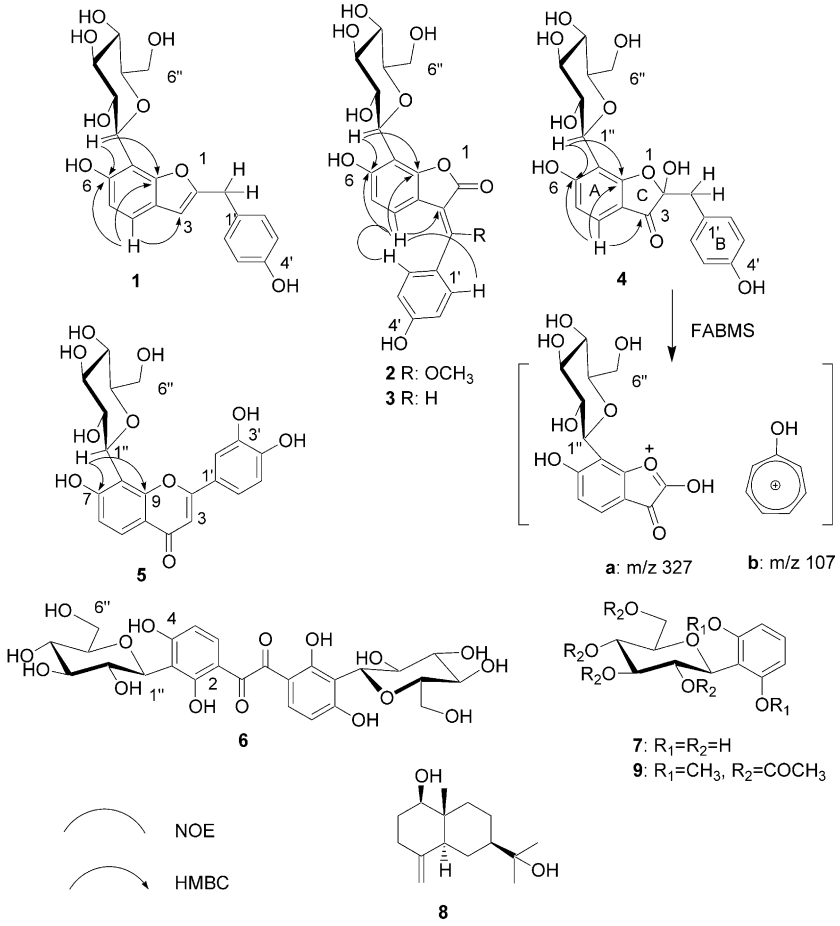

Fig. 1.

Table 1
^{1}H and ^{13}C NMR spectral data of pteroside (**1**) (CD_3OD) and pteroside hexaacetate (**1a**) ($CDCl_3$)

Position	**1** δ_H (J in Hz)	**1** δ_C	**1a** δ_H (J in Hz)	**1a** δ_C
2	–	153.2	–	149.6[a]
3	6.20 (*s*)	102.5	6.38 (*s*)	103.4
3a	–	122.2	–	117.4
4	7.20 (*d*, 8.4)	120.3	6.92 (*d*, 8.4)	121.1
5	6.72 (*d*, 8.4)	112.3	7.46 (*d*, 8.4)	121.8
6	–	157.7	–	153.2[a]
7	–	108.8	–	112.0
7a	–	154.8	–	145.7[a]
CH_2	3.95 (*s*)	33.9	4.16 (*s*)	34.4
1′	–	128.8	–	134.5
2′,6′	7.13 (*d*, 8.4)	130.0	7.10 (*d*, 8.3)	129.9
3′,5′	6.74 (*d*, 8.4)	115.4	7.36 (*d*, 8.3)	121.8
4′	–	156.1	–	158.6[a]
1″	4.94 (*d*, 9.9)	75.3	5.02 (*d*, 9.9)	74.5
2″	4.19 (*m*)	72.3	5.28 (*t*, 9.4)	70.5
3″	3.50 (*m*)	79.0	5.73 (*t*, 9.3)	73.3
4″	3.50 (*m*)	70.9	5.42 (*t*, 9.2)	68.5
5″	3.50 (*m*)	81.4	3.85 (*m*)	76.5
6″a	3.88 (*dd*, 1.8, 11.7)	62.1	4.10 (*dd*, 2.6, 12.7)	62.3
6″b	3.72 (*dd*, 4.9, 11.7)	–	4.41 (*dd*, 4.2, 12.7)	–
OCOMe	–	–	2.42 (*s*)	21.1
	–	–	2.35 (*s*)	21.1
	–	–	2.16 (*s*)	20.7
	–	–	2.09 (*s*)	20.7
	–	–	2.08 (*s*)	20.6
	–	–	1.58 (*s*)	20.1
OCOMe	–	–	–	170.6
	–	–	–	170.4
	–	–	–	169.6
	–	–	–	169.6
	–	–	–	169.4
	–	–	–	169.1

[a] Values may be interchanged within the column.

Table 2
^{1}H and ^{13}C NMR spectral data of pteroisoauroside (**2**) (CD_3OD) and pteroisoauroside hexaacetate (**2a**) ($CDCl_3$)

Position	**2** δ_H (J in Hz)	**2** δ_C	**2a** δ_H (J in Hz)	**2a** δ_C
2	–	168.00	–	169.42
3	–	118.29	–	120.31
3a	–	107.45	–	112.87
4	7.73 (*d*, 8.5)	120.68	7.10 (*d*, 8.6)	124.07
5	6.89 (*d*, 8.5)	112.75	8.05 (*d*, 8.6)	121.98
6	–	160.93	–	161.06[a]
7	–	104.57	–	109.17
7a	–	154.31	–	152.75[a]
1′	–	118.29	–	127.19
2′,6′	7.91 (*dd*, 2.5, 8.7)	129.49	7.31 (*d*, 8.7)	131.26
3′,5′	6.84 (*dd*, 2.5, 8.7)	114.51	8.16 (*d*, 8.7)	121.98
4′	–	164.23	–	164.29[a]
=C(OMe)	–	152.03	–	152.30[a]
OMe	3.91 (*s*)	49.92	3.96 (*s*)	52.18
1″	5.05 (*d*, 9.8)	73.52	5.05 (*d*, 9.9)	74.71
2″	4.78 (*m*)	72.99	5.77 (*t*, 9.5)	70.83
3″	3.60 (*m*)	76.94	5.31 (*t*, 9.6)	73.23
4″	3.60 (*m*)	69.54	5.44 (*t*, 9.4)	68.77
5″	3.60 (*m*)	79.93	3.90 (*m*)	76.96
6″a	4.30 (*br dd*, 1.5, 11.0)	61.81	4.40 (*dd*, 3.7, 12.5)	62.43
6″b	3.75 (*br dd*, 4.0, 11.0)	–	4.12 (*br d*, 12.5)	–
OCOMe	–	–	2.45 (*s*)	21.57
	–	–	2.39 (*s*)	21.42
	–	–	2.20 (*s*)	21.07
	–	–	2.10 (*s*)	21.05
	–	–	2.07 (*s*)	21.05
	–	–	1.69 (*s*)	20.59
OCOMe	–	–	–	171.03
	–	–	–	171.81
	–	–	–	169.88
	–	–	–	169.70
	–	–	–	169.47
	–	–	–	169.42

[a] Values may be interchanged within the column.

the stereochemistry about the alkene bond in the compound pteroisoauroside was defined by the observation of nuclear Overhauser effect between the methoxy group and the protons at C-2′ and 6′, and absence of nOe between the methoxy and H-4 (Fig. 1). Hence pteroisoauroside characterized as 3-(α-methoxy-4-hydroxybenzylidene)-6-hydroxybenzo-2(3H)-furanone-7-*C*-β-D-glucopyranoside is a novel member of isoaurone class. Naturally occurring 2(3H)-benzofuranones are extremely rare and the only compound reported (Pelter et al., 1976) so far has been characterized on the basis of ^{13}C data and confirmed by synthesis (Gray et al., 1979). A few papers describing synthesis, reactions and oxidations of isoaurones are available (Burke et al, 1997; Gadre et al., 1988; Moriarty et al., 1984) However, no literature report about the occurrence of 2(3H)-benzofuranone glycosides (either C–C or C–O) is available. Pteroisoauroside (**2**) is a new naturally occurring isoaurone glycoside.

Marsuposide (**4**) assigned the molecular formula $C_{21}H_{22}O_{10}$ on the basis of strong peak at m/z 435 $[M+H]^+$ in the FAB mass spectrum, together with the support of spectroscopic data. The compound displayed diagnostic IR absorption (ν_{max} 3300, 1680, 1608, 1510, 1444 cm^{-1}) for hydroxyls, carbonyl group and aromatic ring. UV spectrum showed absorption in MeOH maxima (λ_{max} 211, 240, 282, 333 nm) with a bathochromic shift on addition of NaOAc to ((λ_{max} 211, 261, 283, 344 nm). The ^{1}H and ^{13}C NMR spectra (Table 3) indicated the presence of one benzylic methylene group at δ 2.90 (1H, *d*, $J=13.7$ Hz) and 3.11 (1H, *d*, $J=13.7$ Hz), two *ortho*-coupled aromatic protons at δ 6.61 (1H, *d*, $J=8.5$ Hz) and 7.03 (1H, *d*, $J=8.5$ Hz) and one A_2B_2 aromatic system at δ 6.61 (2H, *d*, $J=8.5$ Hz) and 7.13 (2H, *d*, $J=8.5$ Hz). A consideration of the spectral data suggested that **4** was benzofuranone derivative containing phenolic hydroxyl group and glucose moiety in ring-A and one alcoholic hydroxyl group in ring-B and one phenolic hydroxyl group in ring-C. Treatment of marsuposide with acetic anhydride and pyridine afforded marsuposide heptaacetate, $C_{35}H_{36}O_{17}$, FAB-MS, m/z

Table 3
^{1}H and ^{13}C NMR spectral data of marsuposide (**4**) (CD_3OD) and marsuposide heptaacetate (**4a**) ($CDCl_3$)

Position	**4** δ_H (J in Hz)	**4** δ_C	**4a** δ_H (J in Hz)	**4a** δ_C
2	–	106.5	–	103.6
3	–	171.8	–	171.2
3a	–	110.1	–	110.5
4	7.03 (*d*, 8.5)	125.0	6.86 (*d*, 8.3)	132.1
5	6.61 (*d*, 8.5)	112.5	7.63 (*d*, 8.3)	121.6
6	–	166.5	–	168.1[a]
7	–	110.5	–	113.3
7a	–	166.8	–	150.6[a]
1′	–	125.5	–	125.9
2′,6′	7.13 (*d*, 8.5)	132.9	7.06 (*d*, 8.3)	132.4
3′,5′	6.61 (*d*, 8.5)	115.7	7.31 (*d*, 8.3)	121.7
4′	–	156.6	–	168.3[a]
CH_{2a}	3.11(*d*, 13.7)	42.2	3.23 (*d*, 14.3)	40.2
CH_{2b}	2.90 (*d*, 13.7)		3.07 (*d*, 14.3)	
1″	4.68 (*d*, 9.9)	79.7	4.76 (*d*, 10.0)	74.6
2″	4.20 (*m*)	73.8	5.14 (*t*, 9.3)	70.0
3″	3.72 (*m*)	79.9	5.66 (*t*, 9.4)	71.9
4″	4.20 (*m*)	71.4	5.26 (*t*, 9.3)	68.7
5″	3.50 (*m*)	82.5	3.81 (*m*)	75.4
6″a	3.92 (*dd*, 6.1, 11.5)	62.8	4.43 (*dd*, 4.4, 12.5)	62.4
6″b	3.75 (*dd*, 2.1, 11.5)	–	4.14 (*dd*, 2.6, 12.5)	–
OCOMe	–	–	2.41 (*s*)	21.6
	–	–	2.30 (*s*)	21.5
	–	–	2.14 (*s*)	21.4
	–	–	2.09 (*s*)	21.2
	–	–	2.06 (*s*)	21.1
	–	–	2.02 (*s*)	21.0
			1.74 (*s*)	20.6
OCOMe	–	–	–	171.1
	–	–	–	170.9
	–	–	–	170.8
	–	–	–	170.7
				170.0
	–	–	–	169.9
	–	–	–	169.8

[a] Values may be interchanged within the column.

729$[M+H]^+$, 751 $[M+Na]^+$. The NMR spectra of marsuposide heptaacetate (Table 3) confirmed the diphenolic character of marsuposide. The FAB mass spectrum of **4** showed $[M+H]^+$ at m/z 435 for $C_{21}H_{22}O_{10}$ with other significant fragment ion at m/z 457 $[M+Na]^+$, 418, 327, 299, 107 93. A consideration of the mass spectral fragment ion at m/z 327(**a**) 299(**a**-CO) and 107(**b**) further supported the hypothesis. On the basis of the above evidence the structure of **4** was established as 2-hydroxy-2-*p*-hydroxybenzyl-3(2H)-6-hydroxybenzofuranone-7-*C*-β-D-glucopyranoside. This is the first reported isolation from the plant source.

Vijayoside (**5**) was assigned the molecular formula $C_{21}H_{20}O_{10}$ (FAB-MS, m/z 433 $[M+H]^+$). This conclusion was supported by ^{13}C NMR and DEPT spectra. The compound was proved to be phenol from its positive phosphomolybedic acid test (Seher and Seifen, 1959), ferric chloride test (Fink and Fink, 1949). It was recognized to be flavone as it responded to Shinoda test

Table 4
^{1}H and ^{13}C NMR spectral data of vijayoside (**5**) in DMSO-d_6

Position	**5** δ_H (J in Hz)	**5** δ_C
2	–	159.4
3	6.98 (*s*)	104.4
4	–	173.9
5	8.28 (*d*, 8.3)	130.9
6	6.95 (*d*, 8.3)	115.3
7	–	161.7
8	–	112.0
9	–	159.4
10	–	113.2
1′	–	123.2
2′	7.84 (*br d*, 2.1)	115.3
3′	–	147.7
4′	–	159.4
5′	6.99 (*br d*, 8.7)	115.3
6′	7.97 (*br dd*, 2.1, 8.7)	126.1
1″	5.16 (*d*, 9.5)	74.6
2′	4.25 (*t*, 9.1)	71.9
3′	3.51–3.80 (*m*)	79.3
4′	3.51–3.80 (*m*)	71.4
5′	3.51–3.80 (*m*)	82.1
6′a	4.04 (*br d*, 11.9)	62.3
6′b	3.85 (*br dd*, 4.6, 12.0)	–

(Grayer, 1989). The presence of hydroxyl, carbonyl, and phenyl nucleus was indicated by the IR absorption at (ν_{max} 3228, 1615, 1554, 1448, 1422 cm^{-1}). The UV spectrum of the compound showed absorption maxima (λ_{max} 219, 238, 260, 320, 358 nm) which underwent bathochromic shift on addition of NaOAc ((λ_{max} 219, 238, 267, 320, 367 nm) indicating the presence of a free hydroxyl group located at C-7 and C-4′. The ^{1}H NMR spectrum (Table 4) displayed broadening of signals in the aromatic regions presumably because of the steric crowding of the glucosyl and B-ring (Bezuidenhoudt et al., 1987). The inspection of spectrum revealed singlet signal at δ 6.98 (1H) characteristic of proton at C-3 of flavone. A doublet proton signal at δ 8.28 (1H, *d*, $J=8.3$ Hz) which is lowfield shifted due to the effect of neighbouring C=O, is *ortho*-coupled with the doublet signal at δ 6.95 (1H, *d*, $J=8.3$ Hz), this *ortho* coupling system is assigned to the proton at C-5 and C-6 indicating that only these two protons belong to the A-ring and that C-7 and C-8 are occupied by a hydroxyl and glucosyl groups respectively. Further the position of glucosyl moiety at C-8 was confirmed by HMBC correlation from anomeric proton to the C-7 and C-9 (Fig. 1). The proton signals at δ 7.84 (1H, *br d*, $J=2.1$ Hz), 7.97 (1H, *br dd*, $J=2.1$, 8.7 Hz) and 6.99 (1H, *d*, $J=8.7$ Hz) are assigned to the protons of the B-ring. Thus, the above analysis led to the structure 8-(C-β-D-glucopyranosyl)-7,3′,4′-trihydroxyflavone (**5**), reported for the first time from plant source.

Vijayosin (**6**) has the molecular formula $C_{26}H_{30}O_{16}$, confirmed by EIMS at m/z 598 $[M]^+$ and a fragment ion at m/z 299 and ^{1}H and ^{13}C NMR analysis. The IR

spectrum showed bands (ν_{max} 3450, 1710, 1608, 1460, 1302 cm^{-1}) for hydroxyl, carbonyl, and aromatic ring. The UV spectrum of the compound showed absorption maxima at (λ_{max} 221, 268, 274 nm). The ^1H and ^{13}C NMR spectra (experimental) revealed two *ortho* coupled aromatic protons at δ 6.98 (*d*, $J=9.1$ Hz), δ_C 113.0, and 8.90 (*d*, $J=9.1$ Hz), δ_C 128.3 and chelated hydroxyl groups at δ 11.90 (s) suggesting presence of two 2,3,4-trisubstituted aromatic rings connected with ethanedione moiety. Presence of *C*-glucosyl unit at C-3 and hydroxyl groups at C-2 and C-4 were in accordance with ^{13}C NMR spectra (experimental). Consideration of the ^1H NMR spectra and typical MS fragmentation pattern of benzils (Kricka et al., 1973) established the structure for vijayosin as 1,2-*bis*(2,4-dihydroxy,3-C-glucopyranosyl)-ethanedione. Naturally occurring benzils are rare and the only compound 2,4,2-trihydroxy-4′-methoxybenzil has been reported (Ferrari et al., 1984). However no literature report about the occurrence of benzyl *C*-glycoside is available. Thus, compound **6** is the first naturally occurring benzil *C*-glycoside.

Synthesis of 1,2-*bis*(2,4-dihydroxy, 3-glucopyranosyl)-ethanedione and 1,2-*bis*(2-hydroxy,4-methoxy,3-glucopyranosyl tetraacetate)-ethanedione were attempted. First heating resorcinol with oxalic acid in trifluoroacetic acid (Woods et al., 1964) afforded 2,2′,4,4′-tetrahydroxybenzil (FABMS; *m/z* 275 $[M+H]^+$), whereas under the same reaction conditions compound **7** failed to produce compound **6**. Compound **7** on methylation with diazomethane followed by acetylation (Ac_2O/pyridine) gave β-D-glucopyranosyl-2,6-dimethoxy benzene tetraacetate (**9**), the ^1H NMR of which was identical with that of synthetic product (Eade et al., 1975). Reaction of β-D-glucopyranosyl-2,6-dimethoxy benzene tetraacetate (**9**) with oxalyl chloride in presence of anhydrous aluminium chloride was unsuccessful. Different reaction conditions were tried in all the cases starting material was recovered. However, reaction of resorcinol methylether under same reaction conditions gave 2,2′-dihydroxy,4,4′-dimethoxybenzil (FABMS; *m/z* 303 $[M+H]^+$) (Ferrari et al., 1984).

Two known compounds, *C*-β-D-glucopyranosyl-2,6-dihydroxyl benzene (**7**) (Eade, et al., 1975) and sesquiterpene alcohol (**8**) (Adinarayana, et al., 1982) were isolated and characterized by comparison of the spectral data reported.

3. Experimental

3.1. General procedures

Melting points were recorded on a Complab melting point apparatus and are uncorrected. ^1H NMR (200 MHz) and ^{13}C NMR (50.32 MHz) spectra were recorded on Bruker DPX-200 MHz, FAB-MS on JOEL SX 102/DA-600 mass spectrometer, IR on Hitachi 270-30 IR spectrophotometer, UV on Perkin–Elmer-15 UV spectrophotometer, and optical rotation on Perkin–Elmer model 241 digital polarimeter. Flash chromatography was performed using flash silica gel (230–400 mesh) and TLC on precoated silica gel plates.

3.2. Plant material

The tree was collected from the forest of Madhya Pradesh, India during November 1992 and its identity as *Pterocarpus marsupium* was confirmed by Dr. B.N. Mehrotra, Botany Division, Central Drug Research Institute, Lucknow, India, where a voucher specimen (No. 5645) of the plant has been deposited in the Herbarium. The wooden logs were cut longitudinally to separate the inner heartwood.

3.3. Extraction and isolation

The powdered heartwood (5 kg) of *Pterocarpus marsupium* was exhaustively extracted with hot water (4×16 l). The concd. extract (500 g) was suspended in H_2O (2.0 l) and successively partitioned with EtOAc and *n*-BuOH. Afforded EtOAc soluble fraction (70 g) and *n*-BuOH soluble fraction (170 g). A part of (65 g) *n*-BuOH fraction, on repeated flash chromatography over silica gel using $CHCl_3$–MeOH (19:1) as solvent, afforded pteroside (**1**, 100 mg), $CHCl_3$–MeOH (9:1) pteroisoauroside (**2**, 28 mg), marsuposide (**4**, 50 mg), $CHCl_3$–MeOH (4:1) vijayoside (**5**, 60 mg), (**7**, 82 mg) and $CHCl_3$–MeOH (7:3) vijayosin (**6**, 10 mg). EtOAc soluble fraction (50 g), on repeated flash chromatography over silica gel using EtOAc as solvent, afforded sesquiterpene alcohol (**8**, 4.10 g).

3.4. Pteroside (*1*)

Light brown crystals from (H_2O–MeOH: 19:1), mp 117–18 °C, $[\alpha]_D^{29}$ +9.15° ($c=0.295$, MeOH). IR (KBr) ν_{max} cm^{-1}: 3300, 1600, 1584 1512. UV (MeOH) λ_{max} nm: 220, 242, 253 284. Positive FAB-MS *m/z*: 403 $[M+H]^+$. ^1H and ^{13}C NMR: Table 1. Pteroside hexaacetate (**1a**) recrystalized from hexane–EtOAc, m.p. 80–81 °C, $[\alpha]_D^{29}$ −85.4° ($c=0.185$, $CHCl_3$). IR (KBr) ν_{max} cm^{-1}: 1724, 1702, 1605, 1385, 1200. UV ($CHCl_3$) λ_{max} nm: 248, 252, 278, 286. Positive FAB-MS *m/z*: 655 $[M+H]^+$. ^1H and ^{13}C NMR: Table 1.

3.5. Pteroisoauroside (*2*)

Light yellow crystals, mp 197–199 °C, $[\alpha]_D^{29}$ +11.4° ($c=0.07$, MeOH). IR (KBr) ν_{max} cm^{-1}: 3230, 1735, 1618, 1585, 1440. UV (MeOH) λ_{max} nm: 207, 232, 331. Positive FAB-MS *m/z*: 447 $[M+H]^+$. ^1H and ^{13}C NMR: Table 2. Pteroisoauroside hexaacetate (**2a**)

recrystallized from MeOH, mp 88–89 °C, $[\alpha]_D^{29}$ −80.0° ($c = 0.30$, $CHCl_3$). Positive FAB-MS m/z: 721 $[M + Na]^+$. ^1H and ^{13}C NMR: Table 2.

3.6. Marsuposide (4)

Light yellow crystals, mp 156–158 °C, $[\alpha]_D^{26}$ +8.4° ($c = 0.225$, MeOH). IR (KBr) ν_{max} cm^{-1}: 3300, 1680, 1608, 1510, 1444. UV (MeOH) λ_{max} nm: 211, 240, 282, 333; (+NaOAc) nm: 211, 261, 283, 344. Positive FAB-MS m/z: 435 $[M + H]^+$, 457 $[M + Na]^+$, 418, 327, 299, 107. ^1H and ^{13}C NMR: Table 3. Marsuposide heptaacetate (**4a**), crystallized from mixture of *n*-hexane and EtOAc, mp 108–109 °C, $[\alpha]_D^{29}$ −29.0° ($c = 0.25$, $CHCl_3$). Positive FAB-MS m/z: 729 $[M + H]^+$, 751 $[M + Na]^+$. ^1H and ^{13}C NMR: Table 3.

3.7. Vijayoside (5)

Yellow needles from mixture of H_2O–MeOH (19:1), mp 202–204 °C, $[\alpha]_D^{19}$ +25.6^0 (c = 0.5, MeOH). UV (MeOH) λ_{max} nm: 219, 238, 260, 320, 358; (+NaOAc) nm: 219, 238, 267, 320, 367. IR (KBr) ν_{max} cm^{-1}: 3228, 1617, 1554, 1448, 1422. Positive FAB-MS m/z: 433 $[M + H]^+$. ^1H and ^{13}C NMR: Table 4.

3.8. Vijayosine (6)

Pale yellow amorphous powder, mp 296–198 °C, $[\alpha]_D^{29}$ +32.14 ($c = 0.056$, DMSO). IR (KBr) ν_{max}: 3450, 1710, 1608, 1460, 1302 cm^{-1}). UV (DMSO) λ_{max} nm: 221, 268, 274 nm. EIMS m/z 598 $[M]^+$, 299. ^1H NMR (200 MHz, DMSO-d_6) δ: 11.90 (2H, *s*, OH), 8.90 (2H, *d*, $J = 9.1$ Hz, H-6), 8.26 (2H, *s*, OH), 6.98 (2H, *d*, $J = 9.1$ Hz, H-5), 4.85 (2H, *d*, $J = 9.1$Hz, H-1″), 3.10–4.40 (sugar protons). ^{13}C NMR (50.32 MHz, DMSO-d_6) δ: 192.0 (2×CO), 160.5 (2×C-4), 158.8 (2×C-2), 128.3 (2×C-6), 123.4 (2×C-1), 113.0 (2×C-5), 108.9 (2×C-3), 82.6 (2×C-5″), 79.9 (2×C-3″), 79.5 (2×C-2″), 74.2 (2×C-1″), 71.5 (2×C-4″), 62.3 (2×C-6″).

Acknowledgements

We thank ICMR, New Delhi for financial support of this work.

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