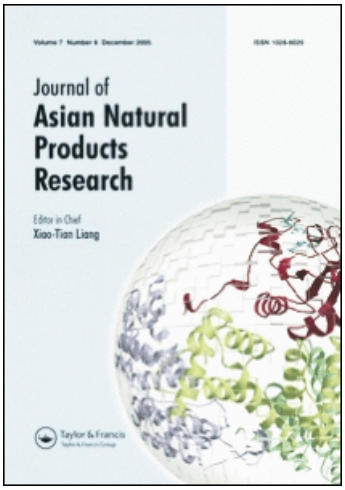

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A NEW ISOFLAVONE GLUCOSIDE FROM *PTEROCARPUS SANTALINUS*

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A new isoflavone glucoside (**1**) together with the known santal has been isolated from the heartwood of *Pterocarpus santalinus*. Based on spectral methods, the structure of the new compound was elucidated as 4′,5-dihydroxy 7-O-methyl isoflavone 3′-O-β-D-glucoside.

Keywords: *Pterocarpus santalinus*; Fabaceae; Heartwood; Isoflavonoids

INTRODUCTION

Pterocarpus santalinus L. (Fabaceae) popularly known as Red Sanders and one of the most important trees of commercial value, is endemic to Seshachalam hill range of Palakonda region and forests of North Arcot [1]. The paste of the wood has been used as a cooling external application for inflammations and headache, as antipyretic, anthelmintic, aphrodisiac, alexeteric, and in biliousness, mental aberrations and ulcers. An infusion of the wood was used in the control of diabetes [2]. A red dye, santalin (besides terpenoids, flavonoids and sterols) was also isolated from the wood. In a continuation of our phytochemical investigations on *P. santalinus* earlier we reported a new triterpene [3] and a new isoflavone [4] and in the present communication we describe the isolation and characterization of a new isoflavone glucoside from *P. santalinus*.

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RESULTS AND DISCUSSION

Compound **1** was obtained as light yellow amorphous powder and exhibited a green colour with $FeCl_3$ reagent and positive Molisch test, which indicated its glycosidic nature. The FABMS of **1** showed negative molecular ion peak at *m/z* 461 [M-H]$^-$ and the elemental analysis showed C 57.11%, H 4.81%, which corresponds to the molecular formula $C_{22}H_{22}O_{11}$. The IR spectrum showed the presence of free hydroxyl group at 3445 cm^{-1}, ketone group at 1658 cm^{-1}, C–O–C band at 1059 cm^{-1} and other bands at 1545 and 1470 cm^{-1}, assignable to an aromatic ring. The UV spectrum of **1** exhibited absorptions at 271 nm and 326 (sh) nm, indicative of its isoflavone nature [5,6]. This was supported by ^{1}H and ^{13}C NMR spectra, which showed resonances at δ 8.12 for H-2 and at 151.90 ppm for C-2 (Table I), characteristic of isoflavone skeleton [5,7]. A bathochromic shift observed by adding $AlCl_3$ and HCl suggested the presence of a free hydroxyl group at C-5, which is chelated with carbonyl function at C-4 [8]. This hypothesis was then confirmed by its ^{1}H NMR spectrum (Table I) which showed a singlet at δ 12.30, exchangeable with D_2O.

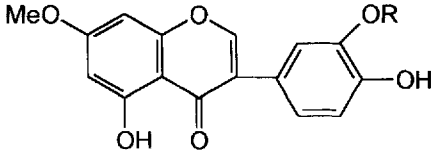
TABLE I ^{1}H- and ^{13}C-NMR spectral data of **1** ($CDCl_3$)

Position	δ *H, J* (Hz)	δ *C*	*DEPT*
2	8.12	151.9	CH
3		123.2	C
4		177.53	C
5		157.34	C
6	6.34 d (2.0)	98.1	CH
7		164.77	C
8	6.56 d (2.0)	95.70	CH
9		160.3	C
10		112.7	C
1′		126.63	C
2′	6.98 d (2.0)	115.4	CH
3′		152.4	C
4′		140.4	C
5′	6.75 d (8.0)	116.45	CH
6′	7.12 dd (8.0 & 2.0)	128.92	CH
1″	5.02 d (6.98)	102.4	CH
2″		75.22	CH
3″	3.35–3.82 m	77.45*	CH
4″		71.29	CH
5″		77.28*	CH
6″		62.28	CH_2
OMe	3.76 s	57.44	CH_3
OH	12.30 s		

*Assignments are interchangeable.

The presence of sugar moiety in **1** was confirmed by the ^{1}H NMR signals at δ 3.82–3.35 and signals below 70 ppm in the ^{13}C NMR spectrum. A loss of 162 mass units from the molecular ion, in the FABMS and a signal at 62.28 ppm shown by DEPT to represent a CH_2 group, suggested that the sugar moiety is either glucose or galactose. The carbohydrate moiety was confirmed as glucose by acid hydrolysis and subsequent sugar analysis. The glucose ^{13}C spectral data were in agreement with the literature [9–11]. The anomeric glucose proton appeared at δ 5.02 as a doublet with a coupling constant of $J = 6.98$ Hz, indicating β-linkage of the glucose unit to the aglycon [6]. Except for the signals of glucose, the ^{13}C NMR and DEPT spectra of compound **1** showed the presence of 16 carbon signals in the aglycon moiety: nine quaternary carbons amongst which were one carbonyl carbon (δ 177.53), six CH carbons, and one methyl carbon.

The signals at δ 6.56 (d, $J = 2.0$ Hz), 6.34 (d, $J = 2.0$ Hz) in ^{1}H NMR spectrum suggested that A ring was functionalized at C-5, C-7 and the fragment at *m/z* 166 formed after retro-Diels Alder cleavage further supported that **1** has methoxy and hydroxy group in ring A. The three-proton singlet at δ 3.76, indicated an aromatic methoxy group, was assigned to the 7-position and confirmed by the fact that there were no bathochromic shift in the UV absorption maximum with NaOAc, thereby eliminated the presence of sugar moiety in ring A. Furthermore, the signals at δ 6.98 (d, $J = 2.0$ Hz), 6.75 (d, $J = 8.0$ Hz) and 7.12 (dd, $J = 8.0$ and 2.0 Hz) established the presence of three aromatic protons in ring B. The fragment ion at *m/z* 134 due to cleavage of ring C indicated that the ring B possessed two hydroxyl groups. On the other hand, it was assumed on biogenetic grounds that one of the two hydroxyl groups in ring B should occupy the C-4′ position [12] and further confirmed by bathochromic shift in the UV spectrum in the presence of NaOMe. The attachment of sugar moiety to the 3′-position was confirmed by the pronounced downfield shift of C-3′ [7]. Thus compound **1** was characterized as 4′,5-dihydroxy 7-O-methoxy isoflavone 3′-O-β-D-glucose. To our knowledge compound **1** has not been reported previously from any plant source.



R = Glc

Simultaneous occurrence of isoflavonoid aglycons and their O-glycosides have, however, been reported previously from several plant species [13–15].

EXPERIMENTAL SECTION

General Experimental Procedures

M.p.'s are uncorrected. UV spectra were taken in MeOH on Beckman 25 spectrophotometer. IR spectra were run in KBr. EIMS was recorded on a VG micromass 7070 H mass spectrometer at 70 eV. FABMS was obtained in negative ion mode using a glycerol matrix on VG Micro Mass Zab-HF mass spectrometer. ^{1}H and ^{13}C NMR spectra were determined on a Bruker AM 200 and 50 MHz, respectively. Samples were run in $CDCl_3$ or DMSO-*d*6 with TMS as internal Standard.

Plant Material

The heartwood of *P. santalinus* was collected from the Tirumala Hills, Tirupati and a voucher specimen has been deposited in the Herbarium of the Botany Department, Sri Venkateswara University, Tirupati.

Extraction and Isolation

The air-dried and powdered heartwood (600 g) of *P. santalinus* was defatted and exhaustively extracted with methanol at room temperature. The MeOH extract was concentrated under reduced pressure and the resulting residue was suspended in water and extracted with EtOAc. The EtOAc soluble portion was subjected to column chromatography over silica gel and eluted with a solvent gradiant ranging from 100% $CHCl_3$ to 50% MeOH in $CHCl_3$ (v/v). A total of 76 fractions of 75 ml each were collected. Fractions obtained from $CHCl_3$ upon removal of solvent followed by recrystallization yielded a solid (15 mg), identified as santal. Fractions obtained from 30% MeOH, on concentration gave a yellow solid (0.12 g) which on crystallization from MeOH furnished light yellow amorphous powder (35 mg) of compound **1**.

4′,5-Dihydroxy-7-O-methoxyisoflavone 3′-O-β-D-glucoside (**1**) Compound **1** was obtained as light yellow coloured amorphous powder from MeOH, m.p. 123–125°C, UV (MeOH): λ_{max} (log ε) 271 (4.42), 326 (3.76); +$AlCl_3$ 303; +HCl 307; +NaOAc 273; NaOMe 378 nm; IR (KBr) ν_{max}

3445, 3300, 1658, 1545, 1470, 1100, 1059, 1020, 984, 928 cm $^{-1}$; ^{1}H-NMR and ^{13}C-NMR data: see Table I; FABMS *m/z* [M + H]$^{+}$ 461, 300 [M − 162].

Acid Hydrolysis of **1** Compound **1** (12 mg) on acid hydrolysis with 7% aqueous alcoholic H_2SO_4 at 100°C for 3 h and after usual work-up gave aglycone (santal) and sugar (glucose).

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References

[1] A. Ramakrishna, *Indian Forester*, 1962, **21**, 202–206.
[2] K.R. Kirtikar and B.D. Basu, *Indian Medicinal Plants*, Periodical Experts, New Delhi, India, 1981, Vol. 1, p. 826.
[3] K.S. Krishnaveni and J.V. Srinivasa Rao, *Fitoterapia*, 1999 (in press).
[4] K.S. Krishnaveni and J.V. Srinivasa Rao, *Phytochemistry*, 1999 (in press).
[5] K.R. Markham, *Techniques of Flavonoid Identification*, Academic Press, New York, 1982, pp. 39, 88.
[6] P.M. Dewick, In *The Flavonoids: Advances in Research*; J.B. Harborne and T.J. Mabry, Eds., Chapman and Hall, London, 1982.
[7] P.K. Agarwal, *Carbon 13-NMR of Flavonoids*, Elsevier Science, Amsterdam, 1989.
[8] T.J. Mabry, K.R. Markham and M.B. Thomas, *The Systematic Identification of Flavonoids*, Springer, Berlin, 1970.
[9] I. Merfort and D. Wendisch, *Planta Med.*, 1987, **53**, 434–437.
[10] P.K. Agarwal, *Phytochemistry*, 1992, **31**, 3307–3330.
[11] K. Bock and C. Pedersen, *Adv. Carbohydr. Chem. Biochem.*, 1983, **41**, 27–66.
[12] E. Ebel and K. Halhbrock, In *The Flavonoids: Advances in Research*, J.B. Harborne and T.J. Mabry, Eds., Chapman and Hall, London, 1982.
[13] W. Dement and T.J. Mabry, *Phytochemistry*, 1972, **11**, 1089–1093.
[14] S. Ahnut, H.Z. Dietmar, R. Mues, W. Barz, K. Mackenbrock, J. Koster and K.R. Markham, *Phytochemistry*, 1984, **23**, 1073–1075.
[15] J. Koster, D. Strack and W. Barz, *Planta Med.*, 1983, **48**, 131–135.