

## PRINSEPIOL, A LIGNAN FROM STEMS OF *PRINSEPIA UTILIS*

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**Key Word Index**—*Prinsepia utilis*; Rosaceae; prinsepiol; L-epicatechin;  $\beta$ -sitosteryl- $\beta$ -glucoside; lignan.

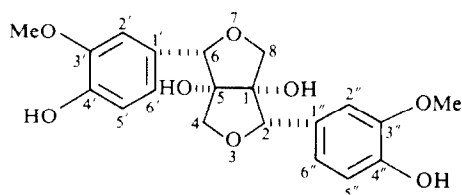
**Abstract**—Chemical investigation of *Prinsepia utilis* yielded a new lignan designated prinsepiol, in addition to L-epicatechin and  $\beta$ -sitosteryl- $\beta$ -glucoside. Prinsepiol was shown to be 1,5 - dihydroxy - 2,6 - di(4' - hydroxy - 3' - methoxyphenyl) - 3,7 - dioxabicyclo[3,3,0]octane, on the basis of spectral and other evidence.

### INTRODUCTION

The oil of *Prinsepia utilis*, a shrub, is used externally in the treatment of rheumatism [1]. The present chemical examination of its stems has shown the presence of L-epicatechin,  $\beta$ -sitosteryl- $\beta$ -glucoside and a new compound. Elemental analysis and mass spectrometry ( $M^+$  390) indicated a molecular formula of  $C_{20}H_{22}O_8$ . UV and IR data suggested its aromatic nature. It formed a tetra-acetate whose NMR spectrum showed the presence of two alcoholic acetoxyls ( $\delta$ 1.80), two phenolic acetoxyls ( $\delta$ 2.32) and two methoxyls ( $\delta$ 3.88). These accounted for six of the eight oxygen atoms of the parent compound. The remaining two oxygen atoms were inferred to be present as ether links in view of the absence of carbonyl absorption in the IR spectrum. Coupled with the fact that the carbon skeleton is derived from 18 carbons (accounting for two methoxyls), the new compound could be a lignan.

anisotropy of the aryl rings in the *cis* stereo relationship. The coincidence of the signals due to H-2 and H-6 and those due to H-4 and H-8 suggests the stereochemistry at C-2 and C-6 in prinsepiol is identical. The presence of peaks in the mass spectrum of prinsepiol at  $m/z$  238 ( $M^+$  - ArCHO), 179 (Ar-CH=C(OH)CH<sub>2</sub>), 164 (Ar-CH=C=O) and 151 (Ar-C≡O) is also consistent with structure 1. Prinsepiol is thus 1,5 - dihydroxy - 2,6 - di(4' - hydroxy - 3' - methoxyphenyl) - 3,7 - dioxabicyclo[3,3,0]octane. <sup>13</sup>C NMR shifts also led to the same conclusion and the assignments supported by off resonance decoupling are shown in Table 1.

A survey of the literature shows that there is one previously reported lignan, wodeshiol [2], having a ditertiary glycoyl system with aryl rings carrying methylenedioxy groups. Prinsepiol is thus the second member of the series. Comparison of the optical properties suggests that wodeshiol and prinsepiol have the same absolute configuration.



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A complete analysis of the NMR of the compound and its acetate fully corroborates the above conclusion and leads to the symmetrical structure 1. The methylene and methine proton signals were at  $\delta$ 4.32(s) and  $\delta$ 5.24(s) in the parent compound and at  $\delta$ 4.52(s) and  $\delta$ 5.30(s) in the acetate. Apart from these, there were no signals attributable to any protons  $\alpha$  to acetoxyl groups; hence the hydroxyls are tertiary in the parent compound. The chemical shift of the two acetoxyls at  $\delta$ 1.80 is *ca* 0.2 ppm upfield from the normal position expected for an alcoholic acetoxyl group and is consistent with the expected shielding due to diamagnetic

### EXPERIMENTAL

Stems (2 kg) of *P. utilis* Royle from Solan, Himachal Pradesh, India, chopped into small pieces, were extracted with hot EtOH and CC carried out on the extracts (Si gel). Elution with 25% EtOAc in  $C_6H_6$  afforded prinsepiol

Table 1. <sup>13</sup>C NMR of prinsepiol (DMSO-*d*<sub>6</sub>)

Values	Carbon No.	Off resonance
55.54	Methoxyl carbon	<i>q</i>
74.56	4,8	<i>t</i>
86.91	2,6	<i>d</i>
87.49	1,5	<i>s</i>
112.20	2',2''	<i>d</i>
114.49	5',5''	<i>d</i>
120.09	6',6''	<i>d</i>
128.39	1',1''	<i>s</i>
145.84	3',3''	<i>s</i>
146.82	4',4''	<i>s</i>

(350 mg), 50% EtOAc in C<sub>6</sub>H<sub>6</sub> gave L-epicatechin (400 mg) and pure EtOAc afforded  $\beta$ -sitosteryl- $\beta$ -glucoside (100 mg).

**Prinsepiol.** Crystallized from EtOAc-petrol, mp 191–192°;  $[\alpha]_D^{EtOAc}$  –18.41°. (Found: C, 61.2; H, 6.1. C<sub>20</sub>H<sub>22</sub>O<sub>8</sub> requires: C, 61.5; H, 5.7%.) UV  $\lambda_{max}^{MeOH}$  nm: 234, 280. IR  $\nu_{max}^{KBr}$  cm<sup>–1</sup>: 3200, 1600, 1505, 1450, 1422, 1360, 1340, 1245, 1200, 1150, 1118, 1080, 1022, 985, 955, 935, 905, 870, 835. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>/TFA): 6.97 (*br s*, 6H, aromatic protons), 5.24 (*s*, 2H, H-2, H-6), 4.32 (*s*, 4H, H-4, H-8), 3.95 (*s*, 6H, 2  $\times$  OMe). MS (*m/z*, rel. int.): 390 (M<sup>+</sup>, 20), 238 (3.8), 179 (2.5), 164 (3.1), 153 (98.7), 152 (80), 151 (100), 137 (98.7).

**Prinsepiol tetra-acetate.** Prepared from Ac<sub>2</sub>O-pyridine, crystallized from EtOAc-petrol, mp 130–131°,  $[\alpha]_D^{EtOAc}$  –11.76°.  $\lambda_{max}^{MeOH}$  nm: 280. (Found: C, 59.8; H, 5.8. C<sub>28</sub>H<sub>30</sub>O<sub>12</sub> requires: C, 60.2; H, 5.4%.)  $\nu_{max}^{KBr}$  cm<sup>–1</sup>: 1755, 1730, 1610, 1585, 1500, 1480, 1435, 1260, 1200, 1115, 1085, 1040, 890. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 7.0 (*br s*, 6H, aromatic protons), 5.30 (*s*, 2H, H-2, H-6), 4.52 (*s*, 4H, H-4, H-8), 3.88 (*s*, 6H, 2  $\times$  OMe), 2.32 (*s*, 6H, two phenolic OAc), 1.80 (*s*, 6H, two aliphatic acetoxylys).

**Dimethylprinsepiol.** Prepared from CH<sub>2</sub>N<sub>2</sub>-Et<sub>2</sub>O, crystallized from Et<sub>2</sub>O, mp 168–170°.  $[\alpha]_D^{EtOAc}$  –53.73° (Found: C,

63.4; H, 5.4. C<sub>22</sub>H<sub>26</sub>O<sub>8</sub> requires C, 63.1; H, 5.2%.)  $\lambda_{max}^{MeOH}$  nm: 234; 280. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 6.89 (*br s*, 6H, aromatic protons), 5.04 (*s*, 2H, H-2, H-6), 4.20 (*s*, 4H, H-4, H-8), 3.92 (*s*, 12H, four aromatic OMe).

**Prinsepiol ditosylate.** Prepared from TsCl-pyridine. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.70 (*d*, 4H, *J* = 9 Hz), 7.25 (*d*, 4H, *J* = 9 Hz), 6.88 (*s*, 6H, aromatic protons of lignan), 4.94 (*s*, 2H, H-2, H-6), 4.08 (*s*, 4H, H-4, H-8), 3.50 (*s*, 6H, 2  $\times$  OMe), 2.40 (*s*, 6H, 2  $\times$  Me).

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## ISOCARLINOSIDE, A DI-C-GLYCOSYLFLAVONE FROM *LESPEDEZA CAPITATA*

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**Key Word Index**—*Lespedeza capitata*; Leguminosae; di-C-glycosylflavones; schaftoside; neoschaftoside; isoschaftoside; carlinoside; neocarlinoside; isocarlinoside; 6-C- $\alpha$ -L-arabinopyranosyl-8-C- $\beta$ -D-glucopyranosylluteolin.

**Abstract**—Six di-C-glycosylflavones isolated from *Lespedeza capitata* leaves were identified as schaftoside, neoschaftoside, isoschaftoside, carlinoside, neocarlinoside and a new natural compound: isocarlinoside (6-C- $\alpha$ -L-arabinopyranosyl-8-C- $\beta$ -D-glucopyranosylluteolin).

## INTRODUCTION

*Lespedeza capitata* Michx. is known as a rich source of iso-orientin. Other C-glycosylflavones: vitexin, isovitexin, orientin and three 3-O-glycosylflavonols: isorhamnetin, quercetin and kaempferol 3-O-rutinosides have also been reported from this plant [1]. More recently, a thorough study of the minor constituents of the aerial parts disclosed the existence of other O-glycosylflavones and seven di-C-gly-

cosylflavones, three of which derived from luteolin and four from apigenin [2]. We now report the identification of six of them, one being a new natural compound.

## RESULTS AND DISCUSSION

Compounds 1–6 were isolated from the butanol-soluble fraction of an ethanolic extract of dry powdered leaves collected before flowering from cul-