(350 mg), 50% EtOAc in C_6H_6 gave L-epicatechin (400 mg) and pure EtOAc afforded β-sitosteryl-β-glucoside (100 mg).

Prinsepiol. Crystallized from EtOAc–petrol, mp 191–192°; $[\alpha]_D^{EtOAc}$ −18.41°. (Found: C, 61.2; H, 6.1. $C_{20}H_{22}O_8$ requires: C, 61.5; H, 5.7%.) UV λ_{max}^{MeOH} nm: 234, 280. IR ν_{max}^{KBr} cm^{-1}. 3200, 1600, 1505, 1450, 1422, 1360, 1340, 1245, 1200, 1150, 1118, 1080, 1022, 985, 955, 935, 905, 870, 835. ^{1}H NMR (δ, $CDCl_3$/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 × OMe). MS (*m/z*, rel. int.): 390 (M^+, 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_2O–pyridine, crystallized from EtOAc–petrol, mp 130–131°, $[\alpha]_D^{EtOAc}$ −11.76°. λ_{max}^{MeOH} nm: 280. (Found: C, 59.8; H, 5.8. $C_{28}H_{30}O_{12}$ requires: C, 60.2; H, 5.4%). ν_{max}^{KBr} cm^{-1}: 1755, 1730, 1610, 1585, 1500, 1480, 1435, 1260, 1200, 1115, 1085, 1040, 890. ^{1}H NMR (δ, $CDCl_3$): 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 × OMe), 2.32 (*s*, 6H, two phenolic OAc), 1.80 (*s*, 6H, two aliphatic acetoxyls).

Dimethylprinsepiol. Prepared from CH_2N_2–Et_2O, crystallized from Et_2O, mp 168–170°. $[\alpha]_D^{EtOAc}$ −53.73° (Found: C, 63.4; H, 5.4. $C_{22}H_{26}O_8$ requires C, 63.1; H, 5.2%.) λ_{max}^{MeOH} nm: 234; 280. ^{1}H NMR ($CDCl_3$, δ): 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. ^{1}H NMR ($CDCl_3$, δ): 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 × OMe), 2.40 (*s*, 6H, 2 × 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*-α-L-arabinopyranosyl-8-*C*-β-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*-α-L-arabinopyranosyl-8-*C*-β-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*-glycosylflavones, 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-

tivated plants. **1**, **2** and **4** showed the same UV spectrum and diagnostic shifts as luteolin and **3**, **5** and **6** the same UV spectrum as apigenin. Their chromatographic properties were those of *C*-glycosides and no sugar was obtained on acid hydrolysis. Permethylation and mass spectrometry of PM ethers showed **1** to be a 6-*C*-arabinosyl-8-*C*-hexosylluteolin (M^+ 734, M-131 > M-175, M-131 > M-119 > M-145) [3], **2** to be a 6-*C*-hexosyl-8-*C*-pentosylluteolin (M^+ 734, M-175 > M-131), **3** to be a 6 - *C* - arabinosyl - 8 - *C* - hexosylapigenin (M^+ 704, M-131 > M-175, M-131 > M-119 > M-145), **4** to be a 6 - *C* - hexosyl - 8 - *C* - pentosylluteolin (M^+ 734, M-175 > M-131), **5** to be a 6 - *C* - hexosyl - 8 - *C* - pentosylapigenin (M^+ 704, M-175 > M-131) and **6** to be a 6 - *C* - hexosyl - 8 - *C* - pentosylapigenin (M^+ 704, M-175 > M-131). From cochromatography (PC and TLC) of the free and permethylated compounds **3** was found to be identical with isoschaftoside (6 - *C* - *α* - L - arabinopyranosyl - 8 - *C* - *β* - D - glucopyranosylapigenin) [4] and different from corymboside (6 - *C* - *α* - L - arabinopyranosyl - 8 - *C* - *β* - D - galactopyranosylapigenin) [5], **5** was shown to be identical with schaftoside (6 - *C* - *β* - D - glucopyranosyl - 8 - *C* - *α* - L - arabinopyranosylapigenin) [6] and different from isocorymboside (6 - *C* - *β* - D - galactopyranosyl - 8 - *C* - *α* - L - arabinopyranosylapigenin) [7] or vicenin - 3 (6 - *C* - *β* - D - glucopyranosyl - 8 - *C* - *β* - D - xylopyranosylapigenin) [8] and **6** was found to be identical with neoschaftoside [9] [6 - *C* - *β* - D - glucopyranosyl - 8 - *C* - *β* - L - arabinopyranosylapigenin (E. Besson and J. Chopin, unpublished results)] and different from isocorymboside or vicenin-3. Similarly, **2** was shown to be identical with carlinoside, a natural 6 - *C* - hexosyl - 8 - *C* - pentosylluteolin (MS of PM ether) from *Carlina vulgaris*, assumed to be 6 - *C* - glucosyl - 8 - *C* - arabinosylluteolin [10] and different from lucenin-3 (6 - *C* - *β* - D - glucopyranosyl - 8 - *C* - *β* - D - xylopyranosylluteolin) [11] and **4** to be identical with neocarlinoside (6 - *C* - *β* - D - glucopyranosyl - 8 - *C* - *β* - L - arabinopyranosylluteolin), a natural 6 - *C* - hexosyl - 8 - *C* - pentosylluteolin co-occurring with carlinoside, schaftoside and neoschaftoside in rice plant (H. Fukami and E. Besson, unpublished results). This compound was named neocarlinoside because of the similarity of the sugar signals in the ^1H NMR spectrum of its perdeuteriomethyl ether with those of PDM neoschaftoside (E. Besson and J. Chopin, unpublished results). The coexistence of **1** with carlinoside and neocarlinoside, their MS and chromatographic properties strongly suggested **1** to be 6 - *C* - *α* - L - arabinopyranosyl - 8 - *C* - *β* - D - glucopyranosylluteolin and **2** (carlinoside) to be the corresponding Wessely–Moser isomer 6 - *C* - *β* - D - glucopyranosyl - 8 - *C* - *α* - L - arabinopyranosylluteolin. This was confirmed by acid isomerization of **1**, carlinoside and neocarlinoside which all gave rise to the same mixture of three products, chromatographically identical with **1**, **2** and **4**. Therefore the name isocarlinoside is proposed for the new natural di-*C*-glycosylflavone **1**, which may be identical with a luteolin *C*-pentoside-*C*-hexoside coexisting with schaftoside and isoschaftoside in *Takakia lepidozioides* [12].

EXPERIMENTAL

Plant material. Cultivated *Lespedeza capitata* Michaux was collected in Beaulieu (Loiret), France.

Extraction. Dried powdered leaves (2.5 kg) were successively extracted with petrol and boiling 80% EtOH (2 × 20.1., 45 min). The EtOH extract was concd under red. pres., the residue dissolved in boiling H_2O (1 l.) and filtered. The filtrate was successively extracted with Et_2O (3 l.), EtOAc (10 l.) and *n*-BuOH (10 l.). The BuOH extract was fractionated first on a polyamide column with a H_2O–MeOH gradient (0–50% MeOH), then on cellulose TLC in BAW (4:1:5) and 15% HOAc.

1 (*isocarlinoside*). TLC (cellulose) R_f 0.22 (15% HOAc), 0.22 (BAW); (polyamide) 0.62 (H_2O–EtOH–MeCOEt–$MeCOCH_2COMe$, 13:3:3:1). UV λ_{max}^{MeOH} nm: 258, 272, 349; + NaOMe 267, 280sh, 340sh, 404; + $AlCl_3$ 276, 290, 330sh, 424; $AlCl_3$ + HCl 262sh, 278, 290sh, 360, 384sh; +NaOAc 272sh, 280, 334sh, 404; +NaOAc + H_3BO_3 266, 380, 420sh. Permethylation and TLC [7]. MS of the PM ether: EMIS 70 eV, *m/z* (rel. int.) 734 M^+(10), 719 M-15 (24), 703 M-31 (100), 615 M-119 (34), 603 M-131 (38), 589 M-145 (27), 571 M-163 (13), 559 M-175 (20).

2 (*carlinoside*). TLC (cellulose) R_f 0.30 (15% HOAc), 0.25 (BAW); (polyamide) 0.65 (H_2O–EtOH–MeCOEt–$MeCOCH_2COMe$, 13:3:3:1). UV λ_{max}^{MeOH} nm: 259, 270, 350; + NaOMe 267, 280sh, 340sh, 404; + $AlCl_3$ 276, 290, 330sh, 424; +$AlCl_3$ + HCl 264sh, 280, 290sh, 360, 384; +NaOAc 274sh, 282, 404; +NaOAc + H_3BO_3 268, 380, 420sh. MS of the PM ether: EIMS 70 eV, *m/z* (rel. int.) 734 M^+ (21), 719 M-15 (35), 703 M-31 (100), 631 M-103 (17), 615 M-119 (8), 603 M-131 (12), 589 M-145 (6), 571 M-163 (34), 559 M-175 (41), 545 M-189 (21).

3 (*isoschaftoside*). TLC (cellulose) R_f 0.30 (15% HOAc), 0.35 (BAW); (Si gel) 0.25 (EtOAc–pyridine–H_2O–MeOH 80:12:10:5); (polyamide) 0.70 (H_2O–EtOH–MeCOEt–$MeCOCH_2COMe$, 13:3:3:1). UV λ_{max}^{MeOH} nm: 271, 332; +NaOMe 282, 334, 398; +$AlCl_3$ 278, 304, 344, 380; +$AlCl_3$ + HCl 278, 304, 342, 378sh; +NaOAc 281 300sh, 384; +NaOAc + H_3BO_3 272, 332, 380sh. MS of the PM ether: EIMS 70 eV, *m/z* (rel. int.) 704 M^+ (12), 689 M-15 (32), 673 M-31 (100), 585 M-119 (50), 573 M-131 (62), 559 M-145 (36), 541 M-163 (26), 529 M-175 (38).

4 (*neocarlinoside*). TLC (cellulose) R_f 0.32 (15% HOAc), 0.38 (BAW); (polyamide) 0.60 (H_2O–EtOH–MeCOEt–$MeCOCH_2COMe$, 13:3:3:1). UV λ_{max}^{MeOH} nm: 256, 272, 350; +NaOMe 268, 404; +$AlCl_3$ 278, 300sh, 340sh, 424; +$AlCl_3$ + HCl 264 sh, 278, 298sh, 358, 384sh; +NaOAc 280, 330sh, 392; + NaOAc + H_3BO_3 264, 376, 420sh. MS of the PM ether: EIMS 70 eV, *m/z* (rel. int.) 734 M^+ (8), 719 M-15 (30), 703 M-31 (100), 631 M-103 (18), 615 M-119 (6), 603 M-131 (14), 589 M-145 (6), 571 M-163 (41), 559 M-175 (54), 545 M-189 (20).

5 (*schaftoside*). TLC (cellulose) R_f 0.42 (15% HOAc), 0.40 (BAW); (Si gel) 0.25 (EtOAc–pyridine–H_2O–MeOH, 80:12:10:5); (polyamide) 0.70 (H_2O–EtOH–MeCOEt–MeCOMeCOMe, 13:3:3:1). UV λ_{max}^{MeOH} nm: 272, 332; +NaOMe 280, 332, 396; +$AlCl_3$ 280, 305, 340, 380; +$AlCl_3$ + HCl 280, 305, 340, 380sh; +NaOAc 282, 386; +NaOAc + H_3BO_3 280, 318, 336. MS of the PM ether: EIMS 70 eV, *m/z* (rel. int.) 704 M^+ (7), 689 M-15 (26), 673 M-31 (100), 601 M-103 (3), 585 M-119 (4), 573 M-131 (8), 559 M-145 (4), 541 M-163 (35), 529 M-175 (43), 515 M-189 (8).

6 (*neoschaftoside*). TLC (cellulose) 0.45 (15% HOAc), 0.44 (BAW); (Si gel) 0.36 (EtOAc–pyridine–H_2O–MeOH, 80:12:10:5); (polyamide) 0.65 (H_2O–EtOH–MeCOEt–$MeCOCH_2COMe$, 13:3:3:1). UV λ_{max}^{MeOH} nm: 272, 334;

+NaOMe 280, 332, 390; +$AlCl_3$ 280, 306, 348, 380; +$AlCl_3$+HCl 278, 304, 346, 380sh; +NaOAc 280, 306sh, 380; +NaOAc + H_3BO_3 274, 316, 340, 400sh. MS of the PM ether: EIMS 70 eV, *m/z* (rel. int.) 704 M^+ (10), 689 M-15 (32), 673 M-31 (100), 601 M-103 (18), 573 M-131 (18), 541 M-163 (41), 529 M-175 (45), 515 M-189 (23).

Acid isomerization. The sample (1 mg) was dissolved in MeOH–4 N HCl (1:1) (2 ml) and heated for 6 hr in a sealed tube under N_2 at 100°. After repeated evaporations, the residue was taken up in H_2O and extracted with *n*-BuOH. The products were identified by TLC (cellulose) in BAW.

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O-GLYCOSYLATED *C*-GLYCOSYLFLAVONES FROM *PASSIFLORA PLATYLOBA*

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Key Word Index—*Passiflora platyloba*; Passifloraceae; *C*-glycosylflavonoids; isovitexin 7-rhamnoglucoside; isomollupentin (6-*C*-arabinosylapigenin); isomollupentin 7-rhamnoglucoside; isovitexin; vitexin; esculetin.

Abstract—Five *C*-glycosylflavonoids including two new compounds, isovitexin 7-rhamnosylglucoside and isomollupentin 7-rhamnosylglucoside, were obtained from the leaves of *Passiflora platyloba*. The known flavonoids were isovitexin, vitexin and isomollupentin (6-*C*-arabinosylapigenin). In addition, the coumarin esculetin was isolated.

As part of a broad biochemical systematic investigation of the mostly New World genus *Passiflora* (Passifloraceae), we report here the flavonoid chemistry of *P. platyloba* Killip, a species which like other *Passiflora* taxa we have recently investigated [1–3], is rich in *C*-glycosylflavonoids. It is hoped that these chemical studies will ultimately provide some insight into the chemical basis for the choice of different *Passiflora* species as larval food plants by different species of neotropical butterflies of the genus *Heliconius*.

In the present investigation, the leaves of *P. platyloba* afforded isovitexin as the major compound along with vitexin, esculetin, isomollupentin (6-*C*-arabinosylapigenin) [4] and two new *C*-glycosylflavonoids, isovitexin 7-rhamnosylglucoside and isomollupentin 7-rhamnosylglucoside.