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Uncommon 5-Methoxyisoflavans from *Desmodium canum*

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Bioactive minor components of the hexane extract of *Desmodium canum* root have been assigned the new structures **2**–**7** of complex isoflavans. Four of them contain the 6-methyl group typical of the major isoflavanone plant constituents and were named desmodians A–C and 3′-hydroxydesmodian C, the others being 6-desmethyldesmodians A and B. All of the isoflavans except **6** (with a 5-OH group) carry a quite rare 5-OMe substituent.

Introduction

A bioassay-directed fractionation of the root extract of *Desmodium canum* resulted in the isolation of three new antimicrobial isoflavanones from the $CHCl_3$ fraction, such as **1**, with isoprenoid substituents either in ring A or B.[1a] Three further derivatives of 5,7,2′,4′-tetrahydroxy-6-methylisoflavanone, featuring rearranged geranyl substituents in the B ring were isolated from the same fraction.[1b] This paper deals with the isolation, from the bioactive hexane extract, of six new isoflavans **2**–**7** (Figure 1) and the elucidation of their structures.

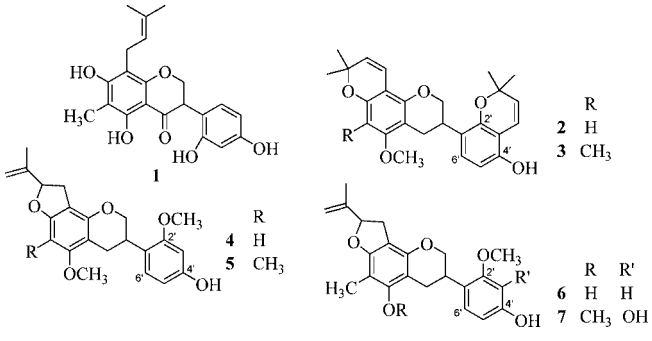

Figure 1. Structures of new compounds isolated from *Desmodium canum*.

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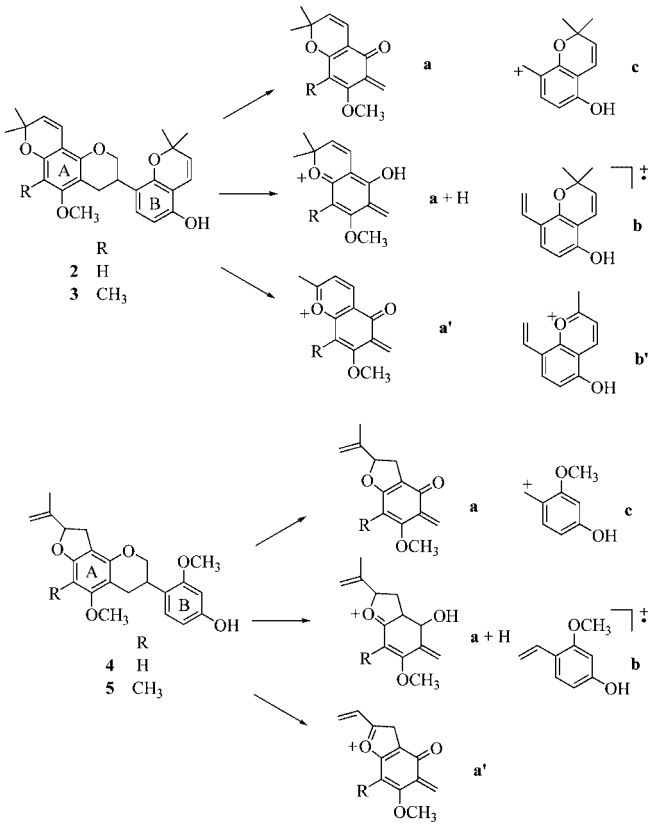
Result and Discussion

Following our examination of the root components of *Desmodium canum* we investigated the bioactive hexane extract: together with the previously described isoflavanones[1a] and common triterpenes, six new isoflavans were isolated. All of the compounds featured a fully reduced heterocyclic ring (UV: λ_{max} = 280 nm) without carbonyl groups (IR: absence of a ν_{CO} absorption) as in a flavan or isoflavan skeleton. The typical resonances for the heterocyclic ring[2] and the signals for the prenyl substituents in the ^{1}H- and ^{13}C NMR spectra (Tables S1, S2 and S3, see Supporting Information) indicate that the metabolites are complex isoflavans. As for other isoflavonoids, the mass spectra of these compounds were characterized (Scheme 1) by fragments (**a**, **a** + H, **b**) that were produced by a retro-Diels–Alder reaction and tropylium-like ions (**c**).[3] These ions include either the A or B rings and are highly diagnostic for the substitution pattern of the compounds. Moreover, the prenyl substituent in complex isoflavonoids is responsible for a parallel fragmentation, which originates in most cases by the loss of a methyl group (15 mu) from the molecular ion.[1a,4] The intensity of the $[M - Me]^+$ ion and consequently the intensities of the retro-Diels–Alder fragments (**a′**, **b′**) depends on the nature of the prenyl substituent. For instance, the loss of Me from a chromene ring, as in **2** and **3**, gives a more intense ion than $[M]^+$,[5] whereas the same loss from an isopropenylfuran ring yields a less intense fragment. The EIMS spectra of isoflavans from *Desmodium canum* are summarized in Table 1. The unambiguous identification of the fragments by high-resolution mass spectroscopy allowed the confirmation of the substitution pattern of the A and B rings and to assign the correct structures.

The ^{1}H- and ^{13}C NMR spectra of **2** and **3** (Table S1) revealed the presence of two 2,2-dimethyl-2*H*-dihydropyran rings, one methoxy and one phenoxy group. The two ^{1}H NMR spectra differ from one another by the presence of



Scheme 1. Main fragments in the mass spectra of complex isoflavans isolated from *Desmodiun canum*.

the signal for an aromatic methyl group in **3** instead of the resonance for an aromatic proton in **2**. Accordingly, the resonance at δ = 92 ppm for the aromatic CH in the ^{13}C NMR spectrum of **2** was shifted to δ = 106 ppm in the ^{13}C NMR spectrum of **3** and attributed to a quaternary aromatic carbon. The methoxy group, as well as one of the dihydropyran rings, must be located on ring A, as suggested by the mass fragmentation (vide supra); in particular, the different values of the chemical shifts in the ^{13}C NMR spectra clearly indicate that the OMe group in **3** is *ortho* to the new methyl group. Therefore, the substitution pattern of ring A in **3** requires the methoxy group at C-5, the methyl group at C-6 and the pyran ring fused at 7-O and C-8. The second dihydropyran ring and the phenolic group belong to ring B, again assigned from the mass fragmentation pattern. The presence of signals for the two *ortho* protons in both ^{1}H NMR spectra and the resonances of the oxygenated aromatic carbons in the ^{13}C NMR spectra are in accordance with a 2′,4′-dioxy substitution of ring B, with the dihydropyran ring fused at C-3′. The free hydroxy group can be located at either the 2-′ or 4′-position, the latter being suggested by a negative Gibbs test.[6] In the carbon spectrum of the methyl derivatives of **2** and **3**, the new OMe resonance appeared at highfield (at δ = 55 ppm) and confirmed the original 4′-OH substitution. The two isoflavans were thus assigned structures **2** and **3**. On consideration of the isoflavanones previously isolated from *Desmodium canum* (desmodianones A–F), all of which contain a 6-methyl substituent, **3** and **2** were named desmodian A and 6-desmethyldesmodian A, respectively.

The A rings of isoflavans **4** and **5** both have a 5-methoxy group and an isopropenyl dihydrofuran ring as substituents, but they differ in the presence, or lack thereof, of the 6-methyl group, as it was demonstrated for **2** and **3**. The mass fragmentation pattern (**b**, **c** and related ions) and the ^{1}H- and ^{13}C NMR spectroscopic data (Table S2) of **4** and **5** reveal that the substitution pattern of the B rings is the same as those of **2** and **3** and involves a methoxy and a phenolic hydroxy group located in the 2′- and 4′-positions, respectively. The relative positions (2′-OMe and 4′-OH) were assigned on the basis of the following considerations: (1) a negative Gibbs test: the position *para* to the hydroxy group is not free,[6] (2) the H-3′ signal appears in a highfield

Table 1. Mass spectroscopic data[a] [*m*/*z* (%)] for isoflavans isolated from *Desmodium canum*.

2 $C_{26}H_{28}O_5$	**3** $C_{27}H_{30}O_5$	**4** $C_{22}H_{24}O_5$	**5** $C_{23}H_{26}O_5$	**6** $C_{22}H_{24}O_5$	**7** $C_{23}H_{26}O_6$	Ion
420 (18)	434 (31)	368 (50)	382 (62)	368 (56)	398 (88)	$[M]^+$
405 (69)	419 (100)	353 (19)	367 (36)	353 (38)	383 (31)	$[M - Me]^+$
219 (12)	233 (24)	219 (100)	233 (100)	219 (100)	233 (100)	$[\mathbf{a} + H]^+$
218 (12)	232 (17)	218	232	218	218	$[\mathbf{a}]^+$
217 (40)	231 (30)	–	–	–	–	$[\mathbf{a} - H]^+$
203 (100)	217 (75)	203 (32)	217 (58)	203 (60)	217 (32)	$[\mathbf{a}']^+$
195 (30)[b]	202 (52)[b]	–	–	–	–	$[M - 2Me/2]^{+2}$
190 (10)	204 (3)	190	204	190	204 (9)	$[\mathbf{a} - CO]^+$
175 (16)	189 (13)	175 (24)	189 (36)	–	189 (20)	$[\mathbf{a}' - CO]^+$
202 (8)	202 (52)[b]	150 (27)	150 (25)	150 (92)	166 (31)	$[\mathbf{b}]^+$
189 (17)	189 (13)	137 (22)	137 (32)	137 (100)	153 (28)	$[\mathbf{c}]^+$
187 (39)	187 (39)	–	–	–	–	$[\mathbf{b}']^+$
–	–	135 (27)	135 (35)	135 (73)	151 (10)	$[\mathbf{b} - Me]^+$
–	–	121 (11)	121 (35)	–	–	$[\mathbf{b} - CHO]^+$
–	–	–	–	–	133 (26)	$[\mathbf{b} - Me - H_2O]^+$
–	–	107 (29)	107 (53)	107 (86)	123 (27)	$[\mathbf{c} - OCH_2]^+$

[a] The structures of all the ions were confirmed by HRMS. [b] In the spectra of **2** and **3**, quite intense doubly charged ions are present at *m*/*z* (%) = 195(30) and 202 (52, overlapped with **b** ion)[4] corresponding to the loss of one methyl group from each chromene moiety $[M - 2Me/2]^{+2}$.

environment in the ^{1}H NMR spectrum relative to the H-5′ signal as in 2′-OMe, 4′-OMe[7] and 2′-OMe, 4′-OH[8] substituted isoflavonoid B rings; the opposite is true for 2′-OH, 4′-OH[7] and 2′-OH, 4′-OMe[9,10] substitutions, (3) comparable shifts (+0.40 versus +0.38 ppm) were obtained in the ^{1}H NMR spectra in C_5D_5N for the H-3′ and H-5′ signals; the values are both typical of protons *ortho* to a free phenolic group,[11] (4) the C-3′ resonance (at δ = 99 ppm) is in agreement with a 2′-OMe, 4′-OH substitution, whereas a 2′-OH, 4′-OMe substitution would require a value of 103 ppm.[8] Analogously C-1′ appears at δ = 116 ppm (2′-OH) instead of 120 ppm (2′-OMe). The two metabolites were assigned structures **4** and **5**, named 6-desmethyldesmodian B and desmodian B, respectively.

The ^{1}H- and ^{13}C NMR (Table S3) and MS (Table 1) spectroscopic data require that compound **6** has the same B ring as **4** and **5**, the same 6-methyl in the A ring as **3** and **5**, but a 5′-hydroxy instead of the 5′-methoxyl group. This substitution pattern was confirmed by methylation of **6** with CH_2N_2, which gave the same final product of **5** in the reaction. Therefore, the compound was thus assigned structure **6** and the name desmodian C.

Conversely, compound **7** has the same A ring (the same **a** and **a**′ ions) and an extra hydroxy group in ring B (**b** and **c** ions shifted by 16 mu) as compared with isoflavan **5**. The presence in the ^{1}H NMR spectrum of signals for two *ortho* coupled protons (H-5′ and H-6′) and in the ^{13}C NMR spectrum of two resonances at ca. 60 ppm for two *ortho* disubstituted methoxy groups require only two possible arrangements of ring B: the 3′,4′-dihydroxy-2′-methoxy-substitution pattern, suggested from the co-occurrence of **4**–**6** instead of the 2′,4′-dihydroxy-3′-methoxy arrangement and was confirmed by acetylation of **7**. The downfield shift of H-6′ (δ =0.25 ppm) in the diacetyl derivative revealed that the second free hydroxy group was at the C-3′ position. In conclusion, the last metabolite was assigned structure **7**, that is, 3′-hydroxydesmodian B.

Available CD and ORD data of isoflavans (reviewed by D. Slade et al.[12]) connect the signs of Cotton effects (CE) in the regions 260–320 nm and 220–260 nm with the absolute configuration. The heterocyclic ring of isoflavans **2** and **3** was assigned the (3*S*) configuration because of the presence of a positive band at ca. 248 nm and a negative band at ca. 293 nm. Compounds **4**–**7**, also with the (3*S*) configuration, showed an additional curve, which was attributed to the presence of a second undefined chiral centre.[13]

While compounds **3** and **5**–**7** exhibit the rare 6-methyl group, typical of the isoflavonoids that are isolated from *Desmodium canum*, isoflavans **2**–**5** and **7** are the first to be isolated with a 5-OCH_3 substituent.

Experimental Section

General Experimental Procedures: Melting points were determined with a Kofler apparatus and are uncorrected. ^{1}H- and ^{13}C NMR spectra were determined with a Varian Gemini instrument and referenced to tetramethylsilane as an internal standard in the reported solvents. IR spectra were determined with a Perkin–Elmer 237 spectrophotometer. Electron impact and fast atom bombardment mass spectra were determined with a VG 7070EQ spectrometer. Optical rotations were measured with a Perkin- Elmer 243 polarimeter at 21 °C. CD spectra were recorded at room temperature with a JASCO J-715 spectropolarimeter.

Plant and Extraction: Collection and identification of *Desmodium canum* (Gmel.) Shintz et Tellung (Leguminosae) have been reported in our previous papers, as well as extraction, partition of the extract, isolation and structure assignment of the main[1a] and minor[1b] isoflavanone components of the ethyl acetate extract.

Isolation of Isoflavans: Extended chromatography on silica gel columns (hexane/EtOAc mixtures) and preparative thin layers (with $CHCl_3$) of the residue of the hexane washings (4 g from 1.3 Kg of roots) afforded, besides the reported major isoflavanones,[1a] compounds **2** (40 mg), **3** (80 mg), **4** (50 mg), **5** (120 mg), **6** (21 mg) and **7** (5 mg). Friedelanol, lupeol, *epi*-friedelanol and *β*-sitosterol were also isolated and identified by comparison to authentic specimens. Further quantities of **6** (45 mg) and **7** (20 mg) were obtained during the purification of desmodianone A from the CH_2Cl_2 extract.[1a] The isoflavans were mostly vitreous solids and their methyl and acetyl derivatives oily products, unless otherwise reported.

6-Desmethyldesmodian A (2): $[\alpha]_D^{21}$ = –24 (*c* 1.4, $CHCl_3$). UV (MeOH): λ_{max} (logε) = 228 (4.30), 280 (3.80) nm. IR ($CHCl_3$): $\tilde{\nu}$ = 3600, 3340, 1610, 1595, 1588, 1124 cm^{-1}. CD (MeOH, 4.5 10^{-5}): $\Delta\varepsilon$ = 312 (0), 293 (–2.14), 270 (0), 259 (–0.9), 253 (0), 243 (+2.51), 236 (0), 233 (–2.15), 229 (0), 218 (+8.3). ^{1}H- and ^{13}C NMR spectra are given in Table S1. EIMS is given in Table 1. HRMS: calcd. for $C_{26}H_{28}O_5$ 420.1937; found 420.1956. *Monoacetyl derivative*: partial ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.29 (s, 3 H, OCOMe) ppm. *Monomethyl derivative*: partial ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.81 (s, 3 H, OMe), 3.70 (s, 3 H, OMe) ppm. Partial ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 55.8, 55.5 (2 × OMe) ppm.

Desmodian A (3): $[\alpha]_D^{21}$ = –23 (*c* 0.8, $CHCl_3$). UV (MeOH): λ_{max} (logε) = 228 (4.30), 280 (3.80) nm. IR ($CHCl_3$): $\tilde{\nu}$ = 3600, 3340, 1605, 1595, 1588, 1125 cm^{-1}. CD (MeOH, 4.35 10^{-5}): $\Delta\varepsilon$ = 310 (0), 294 (–1.46), 268 (0), 259 (–0.9), 253 (0), 245 (+2.21), 237 (0), 233 (–2.15), 229 (0). ^{1}H- and ^{13}C NMR spectra are given in Table S1. EIMS is given in Table 1. HRMS: calcd. for $C_{27}H_{30}O_5$ 434.2093; found 434.2103. *Monoacetyl derivative*: partial ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.29 (s, 3 H, OCOMe) ppm. *Monomethyl derivative*: partial ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.76, 3.65 (s, 3 H each, 2 × OMe) ppm. Partial ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 60.1 (5-OMe), 55.7 (4′-OMe) ppm.

6-Desmethylesmodian B (4): $[\alpha]_D^{21}$ = +6 (*c* 0.9, $CHCl_3$). UV (MeOH): λ_{max} (logε) = 232 (4.12), 280 (3.62) nm. IR ($CHCl_3$): $\tilde{\nu}$ = 3600, 3360, 1614, 1590, 1503, 1150 1120, 1095, 956 cm^{-1}. CD (MeOH, 3.6 10^{-5}): $\Delta\varepsilon$ = 290 (0), 281 (–1.22), 264 (0), 248 (+1.85), 244 (0), 238 (–3.33). ^{1}H- and ^{13}C NMR spectra are given in Table S2. EIMS is given in Table 1. HRMS: calcd. for $C_{22}H_{24}O_5$ 368.1623; found 368.1601.

Desmodian B (5): $[\alpha]_D^{21}$ = +8 (*c* 1.2, $CHCl_3$). UV (MeOH): λ_{max} (logε) = 280 (3.80) nm. IR ($CHCl_3$): $\tilde{\nu}$ = 3590, 3360, 1612, 1592, 1505, 1155, 1120, 1095, 956 cm^{-1}. CD (MeOH, 2.8 10^{-5}): $\Delta\varepsilon$ = 305 (0), 293 (–2.14), 270 (0), 261 (–0.6), 251 (0), 243 (+2.85), 236 (0), 233 (–2.15), 229 (0), 218 (+8.3). ^{1}H- and ^{13}C NMR spectra are given in Table S2. EIMS is given in Table 1. HRMS: calcd. for $C_{22}H_{24}O_5$ 382.1781; found 382.1779. *4′-O-Methyldesmodian B* (with CH_2N_2 in Et_2O): IR ($CHCl_3$): $\tilde{\nu}$ = 1610, 1582, 1500, 1153,

1120, 1092 cm^{-1}. Partial ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.75 (s, 6 H, 2 × OMe), 3.66 (s, 3 H, OMe) ppm. Partial ^{13}C NMR (75 MHz, C_2D_6CO, 25 °C): δ = 60.1 (5-OMe), 55.7, 55.9 (2′-OMe, 4′-OMe) ppm. EIMS: *m*/*z* (%) = 396 (42) $[M]^+$, 381 (18) $[M - Me]^+$, 233 (8) [**a** + H]$^+$, 232 (40) [**a**]$^+$, 217 (31) [**a**′]$^+$, 164 (100) [**b**]$^+$, 149 (41) [**b** – Me]$^+$, 151 (35) [**c**]$^+$, 135 (6) [**b** – CHO]$^+$, 121 (27) [**c** – OCH_2]$^+$.

Desmodian C (6): M.p. 178–9 °C, $[\alpha]_D^{21}$ = +6 (*c* 0.8, $CHCl_3$). UV (MeOH): λ_{max} (logε) = 229 (4.18), 284 (3.71) nm. IR ($CHCl_3$): $\tilde{\nu}$ = 3590, 3340, 1612, 1590, 1500, 1155, 1125, 1095, 957 cm^{-1}. CD (MeOH, 3.5 10^{-5}): $\Delta\varepsilon$ = 365 (0), 345 (–1.21), 330 (0), 310 (+2.66), 275 (0), 247 (+5.50), 219 (0), 211 (–11.0). ^1H- and ^{13}C NMR spectra are given in Table S3. EIMS is given in Table 1. HRMS: calcd for $C_{22}H_{24}O_5$ 368.1624; found 368.1595. To desmodian C (40 mg) in $CHCl_3$ (2 mL) and MeOH (few drops), a saturated solution of CH_2N_2 in Et_2O (2 mL) was added. After 2 h the reaction mixture was dried and passed through a silica gel column with CH_2Cl_2/hexane (3:2) as the eluent to give 4′-*O*-methyldesmodian B (16 mg, coincident with the previous product) and 4′-*O*-methyldesmodian C (26 mg). M.p. 152–154 °C. Partial ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.80 (s, 6 H, 2 × OMe) ppm. Partial ^{13}C NMR (75 MHz, C_2D_6CO, 25 °C): δ = 55.6, 55.9 (2′-OMe, 4′-OMe) ppm. EIMS: *m*/*z* (%) = 382 (77) $[M]^+$, 367 (24) $[M - Me]^+$, 219 (7) [**a** + H]$^+$, 218 (43) [**a**]$^+$, 203 (30) [**a**′]$^+$, 164 (100) [**b**]$^+$, 149 (30) [**b** – Me]$^+$, 151 (37) [**c**]$^+$, 135 (5) [**b** – CHO]$^+$, 121 (32) [**c** – OCH_2]$^+$.

3′-Hydroxydesmodian B (7): M.p.143–144 °C. $[\alpha]_D^{21}$ = +9 (*c* 0.7, $CHCl_3$). UV (MeOH): λ_{max} (logε) = 229 (4.18), 284 (3.71) nm. IR ($CHCl_3$): $\tilde{\nu}$ = 3540, 3340, 1616, 1595, 1500, 1155, 1128, 1098, 950 cm^{-1}. CD (MeOH, 2.5 10^{-5}): $\Delta\varepsilon$ = 302 (0), 297 (–0.3), 291 (0), 283 (+2.50), 278 (0), 271 (–7.50), 257 (0), 248 (+8.20). ^1H- and ^{13}C NMR spectra are given in Table S3. EIMS is given in Table 1. HRMS: calcd. for $C_{23}H_{26}O_6$ 398.1781; found 398.1778. *Diacetyl derivative* (pyr/Ac_2O): oil. Partial ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.00 (d, *J* = 8.0 Hz, 1 H, 6′ H, +0.25), 6.96 (d, *J* = 8.0 Hz, 1 H, 5′ H, +0.5), 2.31 (s, 6 H, 2 × $OCOCH_3$) ppm

Supporting Information (see footnote on the first page of this article): ^1H- and ^{13}C NMR spectroscopic data for isoflavans **2** and **3** (Table S1), **4** and **5** (Table S2) and **6** and **7** (Table S3).

Acknowledgments

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