Available online at www.sciencedirect.com
ScienceDirect
Phytochemistry 68 (2007) 646–651
PHYTOCHEMISTRY
www.elsevier.com/locate/phytochem

C-methylated and C-prenylated isoflavonoids from root extract of *Desmodium uncinatum*

Salome M. Guchu [a,b], Abiy Yenesew [b,*], Muniru K. Tsanuo [c], Nicholas K. Gikonyo [d], John A. Pickett [e], Antony M. Hooper [e], Ahmed Hassanali [a]

[a] *International Centre of Insect Physiology and Ecology, P.O. Box 30772, Nairobi, Kenya*
[b] *Department of Chemistry, University of Nairobi, P.O. Box 30197, Nairobi, Kenya*
[c] *Department of Chemistry, Jomo Kenyatta University of Agriculture and Technology, P.O. Box 62000, Nairobi, Kenya*
[d] *Department of Pharmacy and complementary/Alternative medicine, Kenyatta University, P.O. Box 43844, Nairobi, Kenya*
[e] *Biological Chemistry Division, Rothamsted Research, Harpenden,Herts A15 2JQ, UK*

Received 12 October 2006; received in revised form 18 November 2006
Available online 17 January 2007

Abstract

A pterocarpan, 1,9-dihydroxy-3-methoxy-2-methylpterocarpan (named uncinacarpan) and two isoflavanones, 5,7-dihydroxy-2′,3′,4′-trimethoxy-6-(3-methylbut-2-enyl)isoflavanone (named uncinanone D) and 5,4′-dihydroxy-7,2′-dimethoxy-6-methylisoflavanone (named uncinanone E), were isolated from the CH_2Cl_2 root extract of *Desmodium uncinatum* (Jacq.) DC and characterised by spectroscopic methods. In addition, a rare pterocarpan edudiol and two known abietane diterpenes, 7-oxo-15-hydroxydehydroabietic acid and 7-hydroxycallitrisic acid were identified. The fraction of the root extract that was analysed induced germination of *Striga hermonthica* seeds, but none of the isolated compounds showed this activity.

Keywords: *Desmodium uncinatum*; Fabaceae; Isoflavonoids; Pterocarpans; Uncinacarpan; Edudiol; Isoflavanones; Uncinanone D; Uncinanone E; *Striga hermonthica*; Germination stimulation

1. Introduction

The genus *Desmodium* (Fabaceae) is used in erosion control, ground cover and wildlife protection in lands cleared of vegetation (Trout, 2004). Many of the species are also highly valued as fodder and in folk medicine. The fodder legumes *Desmodium uncinatum* (silver leaf) and *Desmodium intortum* (green leaf), when deployed as intercrops, have been found to reduce damage to maize by stem borers such as *Busseola fusca* (Noctuidae) and *Chilo partellus* (Pyralidae) (Khan et al., 2000). Volatile repellent emissions from these legumes have been shown to be responsible. When these intercrops are located in areas infested with parasitic witch-weeds such as *Striga hermonthica* (Scrophulariaceae), dramatic reduction in the infestation of maize is observed (Khan et al., 2002, 2006). In addition to effects of increased nitrogen and shading associated with maize-desmodium intercrops, an allelopathic effect is largely responsible for the control of *S. hermonthica*. The root exudate of *D. uncinatum* has been found to stimulate germination of striga seeds and to inhibit radical growth of the resulting seedlings, and this combination represent the allelopathic mechanism associated with striga control (Khan et al., 2002; Tsanuo et al., 2003). It also accounts for the fact that intercropping maize with desmodium over successive years results in a continual and rapid depletion of striga seed bank in the soil (Khan et al., 2002).

In a previous investigation of the aqueous root exudates of *D. uncinatum* (Tsanuo et al., 2003), three isoflavanones

* Corresponding author. Tel.: +254 20 4440044x2170; fax: +254 20 4446138.
E-mail address: ayenesew@uonbi.ac.ke (A. Yenesew).

0031-9422/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.phytochem.2006.11.035

and an isoflavone were isolated and characterized. Of these, 4″,5″-dihydro-5,2′,4′-trihydroxy-5″-isopropenylfurano-(2″,3″;7,6)-isoflavanone (uncinanone B) and 4″,5″-dihydro-2′-methoxy-5,4′-dihydroxy-5″-isopropenylfurano-(2″,3″;7,6)-isoflavanone (uncinanone C) were active, as a moderate striga germination stimulant and as a moderate post-germination radical inhibitor, respectively. The present paper, which reports on the isolation and structure elucidation of three new isoflavonoids from a fraction of CH_2Cl_2 extract of *D. uncinatum* roots, represents part of our current studies to comprehensively examine root chemistry of this plant and to bioassay constituents of different polarity range.

2. Results and discussion

Unlike the aqueous root exudates of *D. uncinatum*, which exhibited both striga germination stimulation and post-germination radicle growth inhibition activities (Tsanuo et al., 2003), the CH_2Cl_2 extract of *D. uncinatum* (fresh roots) only caused germination stimulation of *S. hermonthica* seeds. At 10 μg/ml and 100 μg/ml, the CH_2Cl_2 extract of *D. uncinatum* (roots) stimulated the germination of *S. hermonthica* seeds by $51.5 \pm 2.2\%$ and $61.5 \pm 0.9\%$ respectively. Chromatographic fractionation of the extract on silica gel yielded four fractions with fraction D (eluted with 50% acetone in hexane) giving a potent germination stimulation activity (Table 1). In the same bioassays, GR-24, a synthetic sesquiterpene known to stimulate striga germination (Johnson et al., 1981), caused germination stimulation of $50.2 \pm 4.7\%$ at 5 μg/ml. Isolation and purification of some of the compounds from the fraction of the CH_2Cl_2 extract of *D. uncinatum* (roots) yielded four isoflavonoids (compounds **1**–**4**, Fig. 1), together with two abietane diterpenes. However, none of these compounds exhibited significant striga germination stimulation activities.

The HREIMS of compound **1** gave a molecular ion peak at *m/z* 300.0993 corresponding to the molecular formula of $C_{17}H_{16}O_5$. The ^1H NMR and ^1H,^1H-COSY spectra showed four aliphatic protons in a single spin system at δ 4.22 (*dd*, $J = 4.4$, -10.4 Hz), 3.50 (*dd*, $J = -10.4$, 11.0 Hz), 3.43 (*ddd*, $J = 4.4$, 6.6, 11.0 Hz) and 5.65 (*d*, $J = 6.6$ Hz), attributed to CH_2-6, H-6a and H-11a of a pterocarpan skeleton, respectively (Table 2). The presence of a pterocarpan skeleton was supported by ^{13}C NMR spectrum, which showed the corresponding carbons at δ 66.5 (C-6), 39.5 (C-6a) and δ 76.3 (C-11a). In the ^1H NMR spectrum further signals were observed which showed the presence of a methyl group (δ 2.07, s), a methoxyl group (δ 3.80, s), an aromatic singlet (δ 6.13) and aromatic protons with an ABX spin system (δ 6.33, *d*, $J = 2.2$ Hz; δ 6.36, *dd*, $J = 2.2$, 8.2 Hz and δ 7.12, *d*, $J = 8.2$ Hz). The molecular formula $C_{17}H_{16}O_5$ and the presence of five oxygenated aromatic carbon atoms (δ 155.2, 155.8, 158.8 and 159.8, 160.8) in the ^{13}C NMR spectrum are consistent with two hydroxyl substituents, in addition to the methyl and methoxy groups in the pterocarpan skeleton. Formation of a di-acetate, whose EIMS gave a molecular ion peak at *m/z* 384 confirmed the presence of the two hydroxyl groups in this compound. In the HMBC spectrum (Table 2), correlation of methyl protons (δ 2.07) with the signals at δ 155.8, 105.6 and 159.8 are consistent with a tri-substituted A-ring with the methyl at C-2 and oxygenations at C-1 and C-3. HMBC correlation of the methoxyl protons (δ 3.80) with the signal at δ 159.8 and that of H-11a (δ 5.65) with the signal at δ 155.8 allowed placement of the methoxyl group at C-3 and hydroxyl at C-1. The substitution pattern in A-ring was confirmed by 1D-GOESY experiments, which showed interaction between the methyl protons (δ 2.07) and the methoxyl group (δ 3.80); and between the methoxyl group (δ 3.80) and an aromatic singlet at δ 6.13 (H-4). The ABX spin system corresponds to D-ring protons with the biogenetically expected oxygenation at C-9, and this was confirmed by the HMBC experiments (Table 2). Natural pterocarpans are known to occur in *cis* configuration (Dewick, 1988, 1994). In agreement with this, the coupling constant between H-6a and H-11a ($J = 6.6$ Hz) and the strong NOE between H-11a (δ 5.65) and H-6a (δ 3.43) are consistent with *cis*-geometry at the ring junction (Van Aardt et al., 1999, 2001). This compound showed high negative optical rotation ($[\alpha]_D = -250°$) consistent with 6a*R*:11a*R* absolute configuration (Yenesew et al., 1998). Thus compound **1** was characterized as (6a*R*:11a*R*)-1,9-dihydroxy-3-methoxy-2-methylpterocarpan (**1**) for which the trivial name uncinacarpan is suggested. All the ^1H and ^{13}C NMR spectroscopic signals of **1** (Table 2) were assigned on the basis of ^1H–^1H COSY, GOESY, HMQC and HMBC spectra.

Compound **2** was assigned a molecular formula of $C_{21}H_{22}O_5$ (*m/z* 354.1467) from HREIMS. The ^1H and ^{13}C NMR spectra (Table 2) showed this compound to be a pterocarpan derivative with a 3-methylbut-2-enyl, a methoxyl and two hydroxyl substituents. Comparison of the NMR data of compound **2** with those of compound **1** (Table 2) showed that **2** differs from **1** by the presence of a 3-methylbut-2-enyl group in place of a methyl group

Table 1
Germination response of *Striga hermonthica* seeds to fractions of CH_2Cl_2 extract of *Desmodium uncinatum* roots

Test solution	Percentage mean germination (±SE), $n = 10$			
	100 ppm	10 ppm	5 ppm	1 ppm
CH_2Cl_2 extract	61.5 (1.0)^{a,b}	51.5 (2.2)^{b,c,d}		36.8 (2.1)^{e,f}
Fraction A	0.6 (0.6)^{g}	0.4 (0.4)^{g}		0.0 (0.0)^{g}
Fraction B	46.2 (1.9)^{c,d,e}	42.6 (1.2)^{d,e}		29.4 (2.4)^{f}
Fraction C	57.6 (3.9)a,b,c	50.2 (2.8)^{b,c,d}		35.8 (0.7)^{e,f}
Fraction D	67.8 (3.6)^{a}	53.8 (4.3)^{b,c,d}		41.4 (3.1)^{d,e,f}
GR-24 (Johnson et al., 1981)			50.2 (4.7)^{b,c,d}	

Means with the same letter are not significantly different ($P < 0.05$) by Tukey's studentized range test.

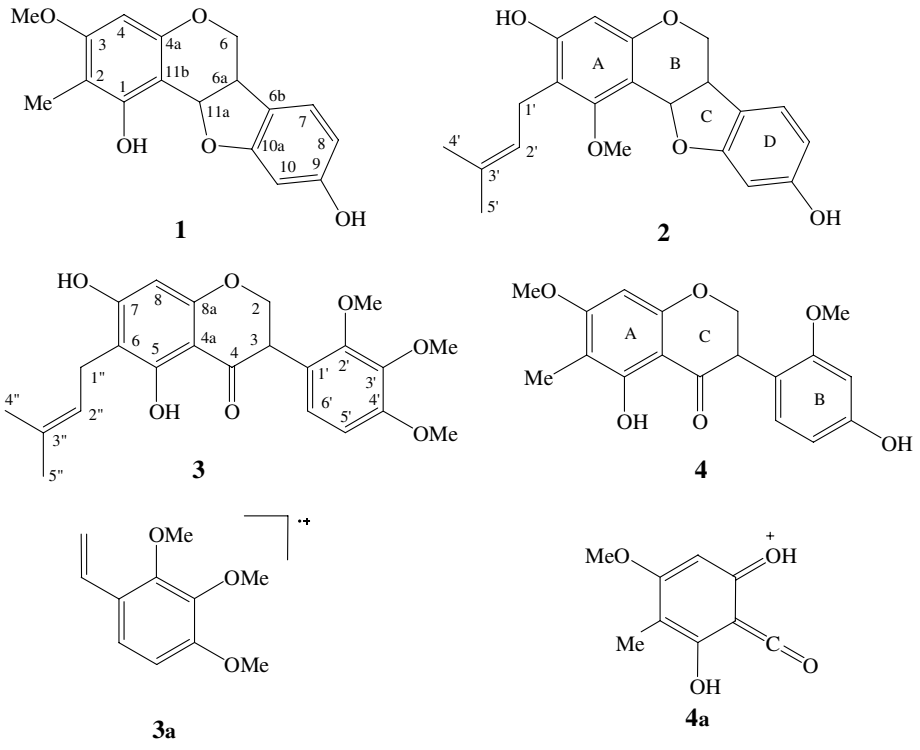

Fig. 1. Structures of isoflavonoids isolated from the roots of *Desmodium uncinatum*.

at C-2. The placement of the 3-methylbut-2-enyl group at the C-2 position was confirmed by the HMBC spectrum showing correlations between the methylene protons at C-1′ (δ 3.39, *d*, $J = 6.3$ Hz) with C-1 (δ 159.9), C-2 (δ 114.3) and C-3 (δ 157.8). The ^{13}C chemical shift position of the methoxyl group in **2** (δ 63.5) is substantially downfield compared to what has been observed in **1** (δ 54.9) suggesting that it is di-*ortho* substituted consistent with its

Table 2
^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectral data along with HMBC correlations of **1** and **2**

Position	**1** (MeOH-d_4)		HMBC	**2** ($CDCl_3$)		HMBC
	δ_C	δ_H(J in Hz)		δ_C	δ_H (J in Hz)	
1	155.8			159.9		
2	105.6			114.3		
3	159.8			157.8		
4	91.6	6.13 *s*	C-2, 3, 4a, 11b	100.9	6.26 *s*	C-2, 3, 4a, 11b
4a	155.2			155.8		
6	66.5	3.50 *dd* (−10.4, 11.0)	C-4a, 6a, 6b, 11a	66.7	3.59 *t* (−11.0, 11.4)	C-4a, 6b, 11a
		4.22 *dd* (4.4, −10.4)	C-4a, 6a, 6b, 11a		4.16 *dd* (−11.0, 5.0)	C-4a, 6a, 6b, 11a
6a	39.5	3.43 *ddd* (4.4, 6.6, 11.0)	C-6, 6b, 10a	39.3	3.38 *ddd* (5.0, 6.6, 11.4)	C-6, 6b, 10a
6b	118.4			119.9		
7	124.9	7.12 *d* (8.2)	C-9, 6a, 10a	125.2	7.07 *d* (8.0)	C-9, 6a, 10a
8	107.6	6.36 *dd* (8.2, 2.2)	C-9, 10, 6b	107.8	6.35 *dd* (8.1, 2.1)	C-10, 6b
9	158.8			157.2		
10	97.9	6.33 *d* (2.2)	C-8, 9, 6b, 10a	98.9	6.38 *d* (2.0)	C-8, 6b
10a	160.8			161.3		
11a	76.3	5.65 *d* (6.6)	C-1, 6, 6a, 11b	76.3	5.63 *d* (6.6)	C-1, 6, 6a, 11b, 4a
11b	101.8			107.3		
1′				23.4	3.39 *d* (6.3)	C-1, 2, 3, 2′, 3′
2′				122.4	5.24 *br t* (6.8)	C-2, 4′, 5′
3′				135.9		
4′				18.4	1.83 *s*	C-2′, 3′, 5′
5′				26.2	1.76 *s*	C-2′, 3′, 4′
1-OCH_3				63.5	3.91 *s*	C-1
2-CH_3	7.2	2.07 *s*	C-1, 2, 3			
3-OCH_3	54.9	3.80 *s*	C-3			

location at C-1 (Panichpol and Waterman, 1978). This was confirmed from HMBC correlation between the methoxyl protons with C-1 and from NOE (in a GOESY experiment) interaction of the methoxyl protons with H-11a (δ 5.63) and with methylene protons (δ 3.39) at C-1′ of the 3-methylbut-2-enyl group at C-2. Thus compound **2** was characterized as 3,9-dihydroxy-1-methoxy-2-(3-methylbut-2-enyl)pterocarpan. This compound (trivial name edudiol) was previously isolated from *Neorautanenia edulis* and its structure proposed on the basis of chemical inter-conversion and comparison with other pterocarpans (Brink et al., 1977). Here the first detailed NMR evidence for the structure of this compound is provided.

Compound **3** was assigned a molecular formula of $C_{23}H_{26}O_7$ (*m*/*z* 414.1678) from HREIMS. A set of aliphatic proton signals (δ 4.40, *dd*, $J = 5.4$, -10.8 Hz; δ 4.51, *dd*, $J = -10.8$, 11.0 Hz and δ 4.23, *dd*, $J = 5.5$, 11.0 Hz) and carbon signals (δ 70.8, δ 47.8 and δ 197.9) in the ^{1}H and ^{13}C NMR spectra (Table 3) are consistent with compound **3** being an isoflavanone derivative (Tsanuo et al., 2003). The ^{1}H and ^{13}C NMR (Table 3) revealed the presence of a 3-methylbut-2-enyl, three methoxyl and two hydroxyl substituents on the isoflavanone skeleton. The presence of an aromatic singlet (δ 5.97) and two *ortho*-coupled aromatic protons (δ 6.91, *d*, $J = 8.6$ Hz and δ 6.78, *d*, $J = 8.6$ Hz) was also evident from ^{1}H NMR spectrum. In the MS the fragment ion at *m*/*z* 194 (**3a**) resulting from *retro*-Diels Alder (RDA) cleavage of C-ring indicated the placement of the three methoxyl groups in B-ring and the two hydroxyl and the 3-methylbut-2-enyl groups in A-ring. With the biogenetically expected oxygenations at C-5 and C-7, the 3-methylbut-2-enyl group could either be at C-6 or C-8. In the HMBC spectrum, the singlet at δ 5.97 and the methylene protons (δ 4.40, *dd*, $J = 5.4$, -10.8 Hz and δ 4.51, *dd*, $J = -10.8$, 11.0 Hz) at C-2 showed correlation with C-8a (δ 161.8) allowing the assignment of the singlet at δ 5.97 to H-8; consequently the 3-methylbut-2-enyl group could only be placed at C-6. This was confirmed by the HMBC experiment, showing the correlations between the methylene protons at C-1″ (δ 3.25, *d* 7.1 Hz) with C-5 (δ 161.8), C-6 (δ 108.7) and C-7 (δ 164.9). In the B-ring, the two *ortho*-coupled doublets at δ 6.78 and 6.91 ($J = 8.6$ Hz) can be assigned to H-5′ and H-6′ with the three methoxyl groups being at C-2′, C-3′ and C-4′. The ^{13}C NMR chemical shift positions for B-ring carbon atoms and the methoxyl groups are consistent with the placement of the methoxyl groups at C-2′, C-3′ and C-4′. Hence compound **3** was characterized as 5,7-dihydroxy-2′,3′,4′-trimethoxy-6-(3-methylbut-2-enyl) isoflavanone (**3**) for which the trivial name uncinanone D is suggested.

Compound **4**, $C_{18}H_{18}O_6$ (*m*/*z* 330.1103) is also an isoflavanone derivative having two methoxyl, two hydroxyl and a methyl substituents (Table 3). In the EIMS the fragment ion at *m*/*z* 181 (**4a**) resulting from RDA cleav-

Table 3
^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectral data along with HMBC correlations of **3** and **4**

Position	**3** (MeOH-d_4)		HMBC	**4** ($CDCl_3$)		HMBC
	δ_C	δ_H(*J* in Hz)		δ_C	δ_H (*J* in Hz)	
2	70.8	4.40 *dd* (5.4, −10.8) 4.51 *dd* (−10.8, 11.0)	C-4, 8a, 1′ C-4, 8a	71.0	4.45 *dd* (−10.9, 5.5) 4.55 *dd* (−10.9, 11.0)	C-3, 4, 8a, 1′ C-3, 4, 8a
3	47.8	4.23 *dd* (11.0, 5.5)	C-2, 4, 1′, 2′, 6′	47.1	4.31 *dd* (11.0, 5.5)	C-2, 4, 1′, 2′, 6′
4	197.9			197.9		
4a	102.4			103.6		
5	161.8			161.1		
6	108.7			106.2		
7	164.9			165.8		
8	94.2	5.97 *s*	C-4a, 6, 7, 8a	90.8	6.05 *s*	C-6, 7, 8a, 4a
8a	161.8			161.9		
1′	121.6			115.7		
2′	152.2			158.9		
3′	142.5			100.0	6.47 *d* (2.1)	C-1′, 2′, 4′, 5′
4′	154.1			157.0		
5′	107.7	6.78 *d* (8.6)	C-1′, 3′, 4′	107.7	6.41 *dd* (8.1, 2.1)	C-1′, 3′, 4′
6′	125.1	6.91 *d* (8.6)	C-3, 2′, 4′	131.3	6.97 *d* (8.1)	C-3, 2′, 4′
1″	20.9	3.25 *d* (7.1)	C-5, 6, 7, 2″, 3″		2.04 *s*	C-5, 6, 7
2″	122.9	5.24 *br t* (7.3)				
3″	130.6					
4″	24.9	1.79 *s*	C-2″, 3″, 4″			
5″	16.8	1.70 *s*	C-2″, 3″, 5″			
5-OH					12.33 *s*	C-4a, 5, 6
7-OCH_3				56.2	3.89 *s*	C-7
2′-OCH_3	60.3	3.87 *s*	C-2′	56.0	3.80 *s*	C-2′
3′-OCH_3	60.0	3.85 *s*	C-3′			
4′-OCH_3	55.5	3.88 *s*	C-4′			
6-CH_3				7.2	2.04, *s*	C-5, 6, 7

age of C-ring is consistent with the placement of one hydroxyl (δ 12.33 for 5-OH), methoxyl (at C-7) and methyl (at C-6 or C-8) in A-ring. HMBC correlation of the methyl protons (δ 2.04) with C-5 (δ 161.1), C-6 (δ 106.2) and C-7 (δ 165.8), and correlation of the aromatic singlet (δ 6.05) with C-8a (δ 161.9) and C-4a (δ 103.6) allow the assignment of the singlet to H-8 and location of the methyl at C-6. The placement of latter was confirmed by a GOESY experiment, which showed NOE interaction between the methyl protons (δ 2.04) with both 5-OH (δ 12.33) and 7-OMe (δ 3.89). An AXY spin system at δ 6.97 (*d*, $J = 8.1$ Hz), δ 6.41 (*dd*, $J = 2.1$,8.1 Hz) and δ 6.47, (*d*, $J = 2.1$ Hz) can be assigned to H-6′, H-5′ and H-3′ respectively of B-ring, with the remaining methoxyl and hydroxyl groups being at C-2′ and C-4′. A GOESY experiment showed interaction of the methoxyl group (δ 3.80) with H-3′ (δ 6.47), CH_2-2 (δ 4.45 and δ 4.55) and H-3 (δ 4.31) consistent with the placement of the methoxyl group at C-2′. This was confirmed from the HMBC spectrum which showed correlations between the methoxyl protons (δ 3.80) and C-2′ (Table 3). Thus the new compound is 5,4′-dihydroxy-7,2′-dimethoxy-6-methylisoflavanone (**4**) for which the trivial name uncinanone E is assigned.

The known abietane diterpenes, 7-oxo-15-hydroxydehydroabietic acid (Ayer and Macaulay, 1987) and 7-hydroxycallitrisic acid (Lee et al., 1994) were identified by comparison of their spectroscopic and physical data with those reported in the literature.

3. Experimental

3.1. General

UV spectra were recorded on a 168-diode array detector module attached to a Beckman System gold 126 HPLC system on a reverse phase C-18 silica. Mass spectra were obtained using a VG Autospec spectrometer at 70 eV. NMR data were acquired using Bruker Avance 500 spectrometer. Column chromatography was performed using silica gel 60 Merck (70–230 mesh).

3.2. Plant material

The seeds of *D. uncinatum* (Jacq.) DC were purchased from Western Seed Company, Kitale, Kenya, and planted in June, 2004 at Mbita Point Field Station (MPFS) of the International Centre of Insect Physiology and Ecology (ICIPE), Mbita, Kenya. The plants were uprooted after four months. The seeds of *S. hermonthica* were collected from *Striga* plants parasitizing maize at MPFS.

3.3. Germination assay

Preparation (surface sterilization and pre-conditioning) of *S. hermonthica* seeds was done according to Thuring et al. (1997). Germination tests were carried out in accordance with Tsanuo et al. (2003) and data subjected to Tukey's Studentised Range Test (SAS Statistical package, version 8.0).

3.4. Extraction and isolation

Fresh roots (7.8 kg) of *D. uncinatum* were extracted in CH_2Cl_2 and dried in vacuo at 40 °C to give 12.3 g of extract. A part of the extract (9 g) was subjected to vacuum liquid chromatography on silica gel eluting with *n*-hexane containing increasing amounts of acetone. This afforded four major fractions each ca.500 ml (A–D): A (eluted with *n*-hexane, 1.5 g), B (eluted with 5% acetone in hexane, 3 g), C (20% acetone in hexane, 490 mg) and D (eluted with 50% acetone, 4.5 g). Fraction D was loaded onto a silica gel column and eluted with hexane containing increasing amounts (5%, 20%, 50%, 75%, 100%) of EtOAc to give five sub-fractions each ca. 200 ml. The sub-fractions that was eluted with 20–75% EtOAc-hexane were combined and part of this was further purified on a semi-prep HPLC (Ultrasphere C-18 column, 10 mm × 250 mm, 5 μm, gradient elution with MeCN and H_2O mxtures: 50% MeCN in H_2O (4 min), gradual increase to 90% MeCN (19 min), gradual decrease to 50% MeCN (4 min) and maintained at this level (3 min) before the next cycle of injection. The flow rate was 3 ml/min and elution of the compounds was monitored at 215 nm). This yielded four isoflavonoids, **1** (4.7 mg, $R_t = 7.7$ min), **2** (0.7 mg, $R_t = 10.9$ min), **3** (1.9 mg, $R_t = 16.2$ min) and **4** (0.9 mg, $R_t = 12.3$ min) and two abietane diterpenes, 7-oxo-15-hydroxydehydroabietic acid (17.8 mg, $R_t = 4.8$ min) and 7-hydroxycallitrisic acid (10.5 mg, $R_t = 14.5$ min).

3.5. Uncinacarpan (*1*)

White paste. $[\alpha]_D^{25} = -250^{\circ}$ (*c* 0.001, MeOH). UV λ_{max}-(MeOH) nm: 283, 234. IR ν_{max} (NaCl)cm^{-1}: 3580, 2827, 1624, 1608, 1593, 1498, 1456. ^{1}H NMR (Table 2). ^{13}C NMR (Table 2). EIMS *m*/*z* (rel. int.): 300 $[M]^+$ (100), 299 (40), 285 (10), 191 (8), 178 (10), 167 (10), 150 (8). HREIMS *m*/*z* 300.0993 $[M]^+$ (Calc. for $C_{17}H_{16}O_5$: 300. 0998). Compound **1** was acetylated in the usual way to give uncinacarpan diacetate as colourless paste. EIMS *m*/*z* (rel. int.): 384 ($[M]^+$, 5), 383 (15), 341 (10), 299 (25), 191 (5), 178 (5), 167 (15), 149 (33), 43 (100).

3.6. Edudiol (*2*)

Amorphous powder. UV λ_{max}(MeOH) nm: 286, 234. IR ν_{max} (NaCl)cm^{-1}: 3585, 3054, 2927, 1621, 1591, 1495, 1455. ^{1}H NMR (Table 2). ^{13}C NMR (Table 2). EIMS *m*/*z* (rel. int.): 354 $[M]^+$ (100), 299 (46), 283 (22), 147 (8), 123 (8). HREIMS *m*/*z* 354.1467 $[M]^+$ (Calc. for $C_{21}H_{22}O_5$: 354.1467).

3.7. Uncinanone D (3)

Amorphous powder. UV λ_{max}(MeOH) nm: 295, 235. IR ν_{max} (NaCl)cm^{-1}: 3661, 2926, 1637, 1605, 1496, 1468. ^{1}H NMR (Table 3). ^{13}C NMR (Table 3). EIMS *m/z* (rel. int.): 414 [M$^+$] (30), 359 [M–C_4H_7]$^+$ (30), 194 [$C_{11}H_{14}O_3$]$^+$ (100), 181 (85), 179 (30), 165 (10), 151 (10). HREIMS *m/z* 414.1678 [M$^+$] (Calc. for $C_{23}H_{26}O_7$: 414.1679).

3.8. Uncinanone E (4)

Amorphous powder. UV λ_{max}(MeOH) nm: 291, 236. ν_{max} (NaCl)cm^{-1}: 2924, 1639, 1618, 1581, 1509. ^{1}H NMR (Table 3). ^{13}C NMR (Table 3). EIMS *m/z* (rel. int.): 330 [M$^+$] (30), 181 [$C_9H_9O_4$]$^+$ (100), 150 (14), 135 (10), 107 (10). HREIMS *m/z* 330.1103 [M$^+$] (Calc. for $C_{18}H_{18}O_6$: 330.1103).

Acknowledgements

We acknowledge the support from Rockefeller foundation, research Grant No. 2004 FS 022, and the German Academic Exchange Service (DAAD) for a Ph.D. scholarship to SMG.

References

Ayer, W.A., Macaulay, J.B., 1987. Metabolites of the honey mushroom, *Armillaria mellea*. Can. J. Chem. 65, 7–14.

Brink, A.J., Rall, G.J.H., Breytenbach, J.C., 1977. Pterocarpans of *Neorautanenia edulis* and *N. amboensis*. Phytochemistry 16, 273–276.

Dewick, P.M., 1988. Isoflavonoids. In: Harborne, J.B. (Ed.), The Flavonoids: Advances in Research Since 1980. Chapman and Hall Ltd., London, pp. 125–210.

Dewick, P.M., 1994. Isoflavonoids. In: Harborne, J.B. (Ed.), The Flavonoids: Advances in Research Since 1986. Chapman and Hall Ltd., London, pp. 117–238.

Johnson, A.W., Gowda, G., Hassanali, A., Knox, J., Monaco, S., Razawi, Z., 1981. The preparation of synthetic analogues of strigol. J. Chem. Soc. Perkin Trans. I 6, 1734–1743.

Khan, Z.R., Pickett, J.A., van den Berg, J., Wadhams, L.J., Woodcock, C.M., 2000. Exploiting chemical ecology and species diversity: stem borer and *Striga* control for maize and sorghum in Africa. Pest Manag. Sci. 56, 957–962.

Khan, Z.R., Hassanali, A., Overholt, W., Khamis, T.M., Hooper, T., Pickett, J.A., Wadhams, L.J., Woodcock, C.M., 2002. Control of witchweed *Striga hermonthica* by intercropping with *Desmodium* spp., and the mechanism defined as allelopathic. J. Chem. Ecol. 28, 1871–1885.

Khan, Z.R., Pickett, J.A., Wadhams, L.J., Hassanali, A., Midega, C.A.O., 2006. Combined control of *Striga hermonthica* and stemborers by maize-*Desmodium* spp. intercrops. Crop Protect. 25, 989–995.

Lee, C., Fang, J., Cheng, Y., 1994. Abietanes from leaves of *Juniperus chinensis*. Phytochemistry 35, 983–986.

Panichpol, K., Waterman, P.G., 1978. Novel flavonoids from the stem of *Popowia cauliflora*. Phytochemistry 17, 1363–1367.

Thuring, J.J.F., Nefkens, G.H.L., Zwanenburg, B., 1997. Synthesis and biological evaluation of strigol analogue Carba-GR 24. J. Agric. Food Chem. 45, 1409–1414.

Trout, K., 2004. Trout's Notes on the Genus Desmodium (Chemistry, Ethnomedicine, Pharmacology, Synonyms and Miscellany). <http://trout.yage.net/sc/D2_2004_Trout.pdf>.

Tsanuo, M.K., Hassanali, A., Hooper, A.M., Khan, Z., Kaberia, F., Pickett, J.A., Wadhams, L.J., 2003. Isoflavanones from the allelopathic aqueous root exudates of *Desmodium uncinatum*. Phytochemistry 64, 265–273.

Van Aardt, T.G., Van Rensburg, H., Ferreira, D., 1999. Direct synthesis of pterocarpans via aldol condensation of phenylacetates with benzaldehydes. Tetrahedron 55, 11773–11786.

Van Aardt, T.G., Van Rensburg, H., Ferreira, D., 2001. Synthesis of isoflavonoids. Enantiopure *cis*- and *trans*-6a-hydroxypterocarpans and a racemic *trans*-pterocarpan. Tetrahedron 57, 7113–7126.

Yenesew, A., Midiwo, J.O., Miessner, M., Heydenreich, M., Peter, M.G., 1998. Two prenylated flavanones from stem bark of *Erythrina burttii*. Phytochemistry 48, 1439–1443.