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Sorgomol, germination stimulant for root parasitic plants, produced by *Sorghum bicolor*

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Abstract

A novel strigolactone sorgomol, germination stimulant for root parasitic plants *Striga* and *Orobanche*, was isolated and structure was elucidated. Sorgomol was more active on *Striga* than on *Orobanche* and may be the immediate precursor of sorgolactone in the biosynthetic pathway of strigolactones.

Keywords: *Sorghum bicolor*; Poaceae; Germination stimulant

Witchweeds (*Striga* spp.) and broomrapes (*Orobanche* and *Phelipanche* spp.) are the two most devastating parasitic plants causing enormous losses of agricultural production.[1] Seeds of these parasites germinate only when they perceive chemical signals, germination stimulants, produced by and released from the roots of plants.[2] Three different classes of plant secondary metabolites, dihydrosorgoleone, sesquiterpene lactones, and strigolactones, are known to induce seed germination of these root parasites.[3] Among them, strigolactones appear to be distributed widely in the plant kingdom. The existence of a novel strigolactone in root exudates of *Sorghum bicolor* has been reported.[4] We describe herein the isolation and structure elucidation of this strigolactone named sorgomol (**2**) (formally named sorghumol).

S. bicolor cv. Hybrid was grown hydroponically and root exudates collected. The root exudates were subjected to solvent partitioning to give a neutral EtOAc soluble fraction (164 mg). This was purified by a silica gel column chromatography eluted with *n*-hexane–EtOAc and two major stimulant activities on *O. minor* seeds were eluted in 40% and 70% EtOAc fractions. The 40% EtOAc fraction was confirmed to contain 5-deoxystrigol (**1**) by ESI–LC/MS and EI–GS/MS analyses. The 70% EtOAc fraction (27.3 mg) was purified by reversed-phase HPLC with an ODS column using CH_3CN/H_2O (30:70 to 100:0 over 40 min, 3 mL/min) as a mobile phase and then with an ODS-CN column using CH_3CN/H_2O (30:70, 1 mL/min) as a mobile phase to afford pure sorgomol (**2**) (1.05 mg).[5]

Compound **2** exhibited a pseudo molecular ion peak, $[M+Na]^+$, in the HR-ESI-TOF-MS spectrum, at *m*/*z* 369.1316 (calcd for $C_{19}H_{22}O_6Na$, 369.1314) corresponding to the molecular formula of $C_{19}H_{22}O_6$. In the EI–GC/MS analysis, it gave an $[M-30]^+$ ion at *m*/*z* 316. A comparison of overall ^1H and ^{13}C NMR data (see Table 1) revealed great similarities between compound **2** and sorgolactone (**3**), which was also isolated from sorghum root exudates.[6]

In fact, ^1H NMR data of **2** and **3** were almost identical except for the absence of the methine proton (δ_H 2.38, m),[7,8] the presence of the hydroxymethylene protons (δ_H

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Table 1
NMR data of sorgomol (**2**)

Position	δ^1H m, Hz	δ^{13}C	DEPT & HMQC
1			
2		170.3	C
3		114.1	C
3a	3.59–3.66, m	36.7	CH
4α	2.74, dd, 17.1, 9.1	42.1	CH_2
4β	2.38, d, 17.1		
4a		137.3	C
5	1.96, m	26.3	CH_2
6	1.70, m	18.9	CH_2
7α	1.27, m	33.1	CH_2
7β	1.70, m		
8		38.2	C
8a		136.2	C
8b	5.51, d, 7.3	88.1	CH
9	7.43, d, 2.5	150.2	CH
10a	3.42, d, 11.7	69.9	CH_2
10b	3.60, d, 11.7		
11	1.04, s	22.2	CH_3
1′			
2′	6.14, t, 1.5	100.4	CH
3′	6.92, t, 1.5	140.8	CH
4′		140.8	C
5′		170.8	C
6′	2.03, t, 1.5	10.7	CH_3

3.42 and 3.60, 2H, AB quartet, $J = 11.7$ Hz), and a slight downfield shift of one of the methylene proton (H-7) in **2**. In addition, compounds **2** and **3** gave almost identical EI-MS. Therefore, compound **2** was deduced to have a hydroxymethylene group at C-8. This was also suggested by detailed interpretation of the NMR spectra, including DEPT, ^{1}H–^{1}H COSY, NOESY, HMQC, and HMBC spectra (Table 1 and Fig. 2), and by the comparison of the NMR data with those of other strigolactones.[7–10] For example, the HMBC correlations were observed between the hydroxymethylene protons (H-10) and C-7, C-8, and C-8a. In addition, the β-orientation of the hydroxymethylene group was assigned since the strong NOE was observed between H-11 and H-8b but not between H-10 and H-8b (Fig. 2).

The C-2′ configuration of **2** was estimated to be an *R* from its CD spectrum; the sign of the CD changed from

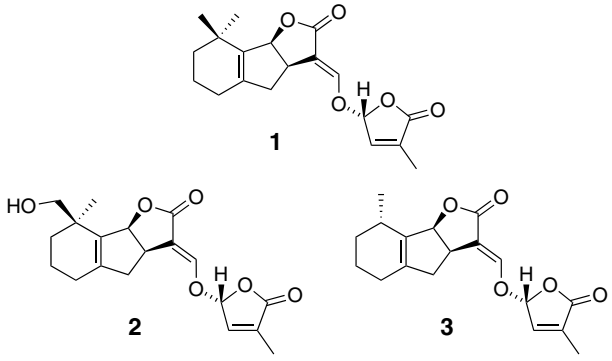

Fig. 1. Structures of 5-deoxystrigol (**1**), sorgomol (**2**), and sorgolactone (**3**).

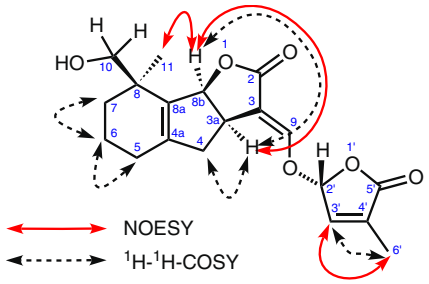

Fig. 2. Key NOESY and COSY correlations for sorgomol (**2**).

negative to positive around 270 nm.[11] Consequently, the chemical structure of the novel strigolactone sorgomol (**2**) was determined as shown in Figure 1.[12]

Sorgomol (**2**) showed potent germination stimulation activity on the seeds of root parasitic weeds and was ca. 1000-fold more active on *S. hermonthica* than on *O. minor* in our germination assays. For example, **2** at 2 pM elicited 50% germination of *S. hermonthica* seeds but 2 nM was needed to achieve 50% germination of *O. minor* seeds.

According to the biosynthetic pathway of strigolactones proposed recently,[13,14] sorgolactone (**3**) is derived from 5-deoxystrigol (**1**) which is generated by oxidative cleavage of carotenoids. It is likely that a P450 oxidizes 5-deoxystrigol (**1**) to sorgomol (**2**), and further oxidation and decarboxylation of **2** affords sorgolactone (**3**).

The ratio of 5-deoxystrigol to sorgomol in the root exudates of this sorghum cultivar grown hydroponically was 1 to 5–10 depending on the growth stages and the growth conditions.

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Supplementary data

Supplementary data associated with this article (^{1}H NMR, GC–MS and CD spectra) can be found, in the online version, at doi:10.1016/j.tetlet. 2008.01.131.

References and notes

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5. One of the referees pointed out how we could obtain such an amount of pure compound. Our response to this comment is as follows. The

production of strigolactones varies with plant species, their growth stages, and growth conditions. The 20-day-old seedlings of sorghum cv. Hybrid produces ca. 4 ng of sorgomol per plant per day when they are grown hydroponically under phosphate starvation. When we collected root exudates for structure elucidation, we used charcoal cartridges to absorb strigolactones released into the growth media. Under these conditions, the seedlings seemed to produce more strigolactones. We normally use large containers as in Ref. 4, and each container (containing 10 L of growth media) support ca. 2000 seedlings. Therefore, we could collect ca. 10–20 μg of sorgomol per container per day. Therefore, it was not so difficult to collect 1 mg of pure sorgomol.

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12. Sorgomol (**2**): EIMS *m*/*z* (rel. int.) 316 $[M-30]^+$ (10), 219 (21), 201 (100), 173 (12), 97 (48). UV λ_{max} (CH_3CN) 239.1 nm. CD (CH_3CN; *c* 0.00006) λ_{max} ($\Delta\varepsilon$) 190.5 (+6.59), 210.0 (−6.29), 237.5 (+4.48) nm. For ^1H and ^{13}C NMR spectroscopic data, see Table 1.
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