

Molecules of Interest

Sorgoleone

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ABSTRACT

Sorgoleone, a major component of the hydrophobic root exudate of sorghum [*Sorghum bicolor* (L.) Moench], is one of the most studied allelochemicals. The exudate also contains an equivalent amount of a lipid resorcinol analog as well as a number of minor sorgoleone congeners. Synthesis of sorgoleone is constitutive and compartmentalized within root hairs, which can accumulate up to 20 µg of exudate/mg root dry weight. The biosynthesis pathway involves unique fatty acid desaturases which produce an atypical 16:3 fatty acyl-CoA starter unit for an alkylresorcinol synthase that catalyzes the formation of a pentadecatrienylresorcinol intermediate. This intermediate is then methylated by SAM-dependent O-methyltransferases and dihydroxylated by cytochrome P450 monooxygenases. An EST data set derived from a *S. bicolor* root hair-specific cDNA library contained all the candidate sequences potentially encoding enzymes involved in the sorgoleone biosynthetic pathway. Sorgoleone interferes with several molecular target sites, including inhibition of photosynthesis in germinating seedlings. Sorgoleone is not translocated acropetally in older plants, but can be absorbed through the hypocotyl and cotyledonary tissues. Therefore, the mode of action of sorgoleone may be the result of inhibition of photosynthesis in young seedlings in concert with inhibition of its other molecular target sites in older plants. Due to its hydrophobic nature, sorgoleone is strongly sorbed in soil which increases its persistence, but experiments show that it is mineralized by microorganisms over time.

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1. Introduction

1.1. Nomenclature consideration

Sorgoleone normally refers to **1** (2-hydroxy-5-methoxy-3-[(8Z,11Z)-8',11',14'-pentadecatriene]-p-benzoquinone [CAS 105018-76-6]), one of the major components of the oily substance exuding from the roots of sorghum (*Sorghum bicolor* (L.) Moench) (Fig. 1). However, the nomenclature surrounding sorgoleone requires some clarifications because this term can also include the reduced form of **1** and a number of structurally related lipophilic p-benzoquinones present in small amounts in the oily exudate (see Section 2) (Chang et al., 1986; Netzly et al., 1988). This latter use of the term sorgoleone should be avoided because the exudate also contains an equivalent amount of non-quinoid lipid resorcinols (Dayan et al., 2009; Erickson et al., 2001; Fate and Lynn, 1996). Adding further confusion, **1** has mistakenly been called xenognosin (Fate and Lynn, 1996) although the name xenognosin was already associated with a modified chalcone isolated from tragacanth (*Astragalus* spp.)

gum extracts (El-Fery and Hufford, 1982). In this review, the term sorgoleone will refer exclusively to **1**, unless specifically indicated otherwise.

1.2. Sorgoleone discovery and allelopathy

Sorgoleone was first discovered by investigators searching for secondary metabolites involved in triggering the germination of the obligate parasitic plant *Striga asiatica* (witchweed) (Chang et al., 1986; Netzly et al., 1988). It was later demonstrated that **1** was not a chemical cue involved in the complex chemical communication between parasitic weeds and their host plants (Chang et al., 1986; Fate and Lynn, 1996; Hauck et al., 1992; Hess et al., 1992). However, germination of *Striga hermontica* seed was directly related to the concentration of the dihydrosorgoleone (**2**), the reduced form of **1**. Other scientists suggested that **1** may be involved in allelopathic potential of sorghum. Indeed, sorghum has been known to cause 'soil sickness' and affect the growth of other crops in rotation systems (Breazeale, 1924; Einhellig and Rasmussen, 1989; Forney et al., 1985; Putnam et al., 1983). Early studies reported that several classes of water-soluble compounds, such as the phenolics, may be responsible for these allelopathic properties,

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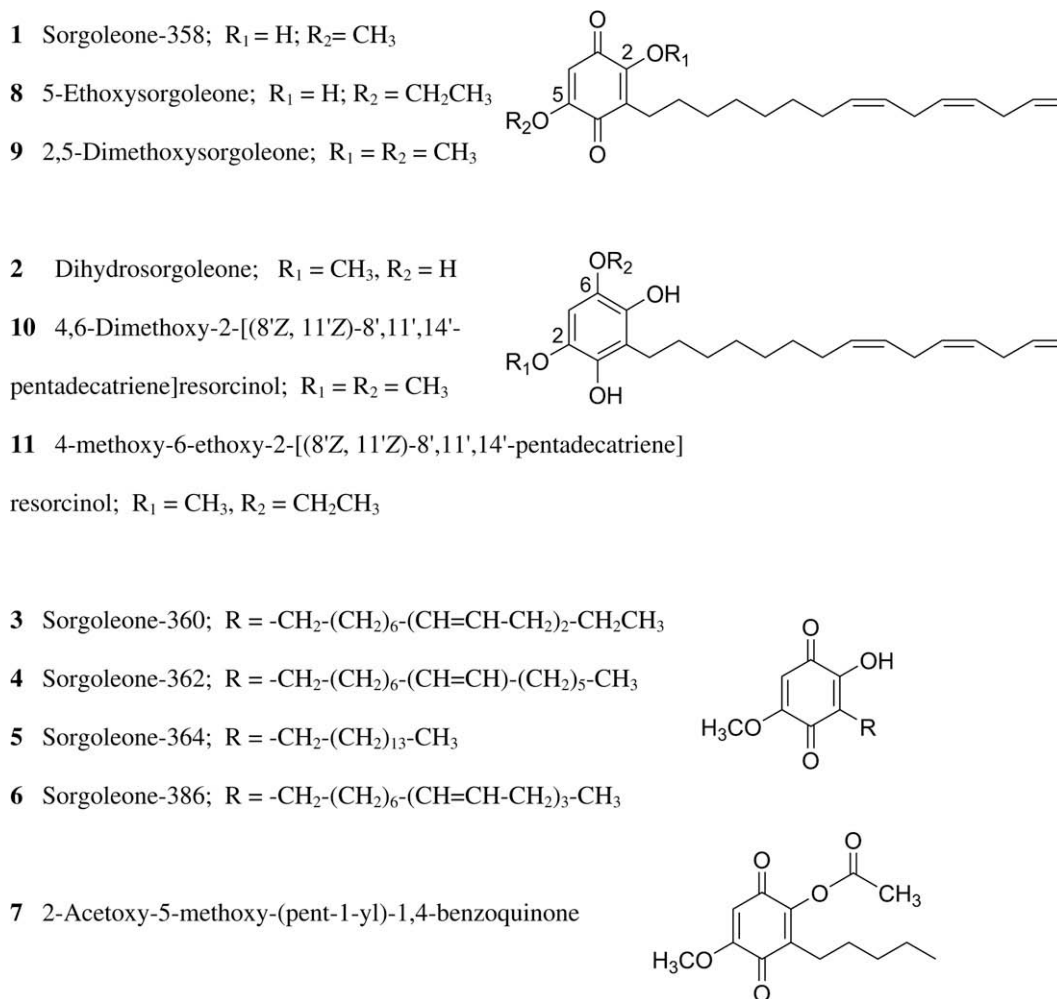


Fig. 1. Structure of sorgoleone and related quinoid and resorcinolic lipids present in the sorghum root hair exudate.

but these compounds are ubiquitous in plants and are not likely to be involved in the unique activity observed in sorghum (Alsaadawi et al., 1986; Lehle and Putnam, 1983; Panasiuk et al., 1986). On the other hand, **1** is an uncommon lipid benzoquinone with herbicidal activity produced exclusively by sorghum species (Netzly and Butler, 1986). It suppresses the growth of a large number of plant species, but it is most active on small-seeded plants (Barbosa et al., 2001; de Souza et al., 1999; Einhellig and Souza, 1992; Forney et al., 1985; Netzly and Butler, 1986; Panasiuk et al., 1986). Sorghum is sometimes used in integrated pest management systems as a green manure or as a cover crop to suppress weed populations (Weston, 1996) or as a crop residue in no-tillage farming (Alsaadawi and Dayan, 2009) (see Section 5).

2. Structure elucidation and analogs

As mentioned above, **1** is a major constituent of the root extract of *S. bicolor*. Sorgoleone and dihydrosorgoleone (**2**) were identified and distinguished from each other in the ^1H NMR spectrum of the whole extract. The quinone form (**1**) accounts for approximately half of the exudate (Czarnota et al., 2003b; Netzly et al., 1988). GC–MS analysis of individual droplets collected with PDMS probes (Fig. 2) indicated that the remainder of exudate consists of the resorcinol **10** (Dayan et al., 2009; Erickson et al., 2001). The extract also contains several congeners of **1**, but in much lower quantities (Kagan et al., 2003) (Fig. 1).

The major and three minor benzoquinone constituents of the exudate were isolated by HPLC, identified by electron impact mass spectrometry, and were referred to as sorgoleone-358 (**1**), sorgoleone-360, sorgoleone-362, and sorgoleone-386, respectively, based on the observed molecular ions (Netzly et al., 1988). The identification of these phytotoxins as benzoquinones was also supported by ^1H NMR, reportedly showing the signal at δ 5.9 (s, 1H) ppm, which is characteristic for the quinoid proton; cf. δ 6.3 (s, 1H) ppm for the hydroquinone proton.

Successful isolation of sorgoleone analogs with varying number carbons and double bonds in the aliphatic side chain was achieved by argentation chromatography (Kagan et al., 2003). Sorgoleone-360 (**3**), sorgoleone-362 (**4**), sorgoleone-364 (**5**), and sorgoleone-386 (**6**) were purified and full structural characterization was performed by 1- and 2-dimensional NMR spectroscopy, revealing the number and positions of the double bonds in the lipid chain. Sorgoleone-364 has a fully saturated aliphatic 15-carbon chain. Interestingly, sorgoleone-360, sorgoleone-362, and sorgoleone-386 did not have the terminal double bond that is a characteristic feature of sorgoleone-358 (**1**). These four “sorgoleones” inhibited PSII similarly in an assay using spinach thylakoid membranes, suggesting that the aliphatic side chain is not essential for activity. Barbosa et al. (2001), in their investigation of the phytotoxic activity of **1**, **5** and a synthetic analog (2-acetoxy-5-methoxy-3-(pent-1-yl)-1,4-benzoquinone (**7**) likewise concluded that the activity resides in the quinone moiety. In support

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