

The Chemistry of Some Dalodesmidean Millipedes from Tasmania (Diplopoda, Polydesmida)

Tappey H. Jones,^{*,†} Dylan M. Guthrie,[†] Conor T. Hogan,[†] Donovan J. Robinson,[†] Robert Mesibov,[‡] William A. Shear,[§] Thomas F. Spande,[⊥] and Ralph A. Saporito^{||}

[†]Department of Chemistry, Virginia Military Institute, Lexington, Virginia 24450, United States

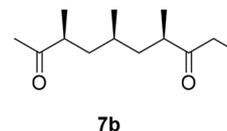
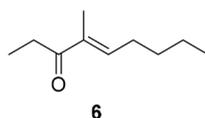
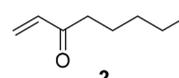
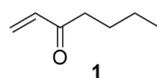
[‡]Retired from Queen Victoria Museum and Art Gallery, living in West Uverstone, Tasmania 7315, Australia

[§]Department of Biology, Hampden-Sydney College, Hampden-Sydney, Virginia 23943, United States

[⊥]Retired from NIDA, NIH, Bethesda, Maryland 20892, United States

^{||}Department of Biology, John Carroll University, University Heights, Ohio 44118, United States

Supporting Information



ABSTRACT: Millipedes (Diplopoda) are well known for their toxic or repellent defensive secretions. As part of a larger investigation, we describe the chemical constituents of 14 species of Tasmanian millipedes in seven genera. Six species in the genus *Gasterogramma* were found to produce acyclic ketones, including the pungent unsaturated ketones **1**, **2**, and **6**, and the novel (*rel*-3*R*,5*S*,7*S*)-3,5,7-trimethyl-2,8-decanedione (**7b**), for which the stereoconfiguration was established by stereoselective syntheses of pairs of isomers. These compounds have not been detected before in millipede defensive secretions. This report is the first on species of the suborder Dalodesmidea (Polydesmida), a dominant component of the soil and litter fauna of the temperate regions of the Southern Hemisphere.

Millipedes (Diplopoda) are an ancient group of terrestrial arthropods, which were among the earliest invaders of land. Most orders of millipedes, harmless detritivores, defend themselves against predators by producing a variety of chemical repellents from paired glands located on either side of their trunk segments. A comprehensive review of over 180 species has recently been published.¹ This method of defense dates back at least 300 million years, since the openings of these glands have been detected in Devonian and Carboniferous fossils. The molecular species produced are remarkably variable from taxon to taxon and include 2-alkylquinazolinone alkaloids (“glomerins”), terpenes, heterocyclic *N*-containing compounds (e.g., polyzonimine and nitropolyzonamine), various alkyl-quinones or -phenols, and cyanogenic compounds that produce HCN with certain enzymes. The order Polydesmida is perhaps the most ubiquitous and diverse taxon of millipedes, including well over 3000 species, and occurs abundantly on all continents except Antarctica. Polydesmidans (e.g., *Pleurolooma flavipes*) were among the earliest millipedes for which the chemical identity of their defenses was established.² For a considerable period following this discovery, it was assumed that polydesmidans

defended themselves with mandelonitrile or benzoyl cyanide, which, in combination with an intrinsic enzyme, degraded to either benzaldehyde or benzoic acid and HCN. However, many polydesmidans produce phenols in addition to the cyanogens, and others rely on phenols alone.³ In many of the defensive secretions, fatty acid esters were also found, often long-chain acetate esters or oleate esters. In some cases, the large proportions of the esters occurring were judged as possibly serving as solvents. Straight-chain aliphatic and aromatic aldehydes and alcohols and occasionally ketones were also seen.¹

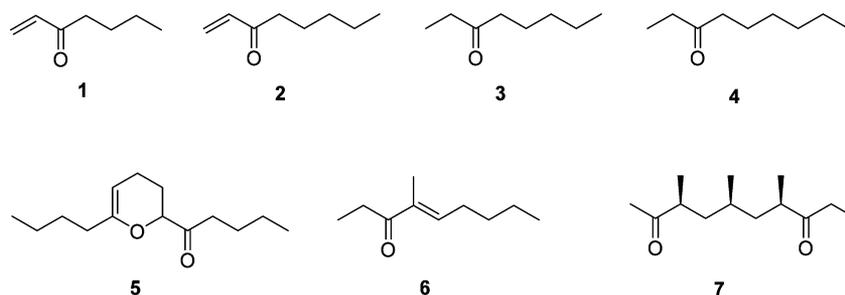
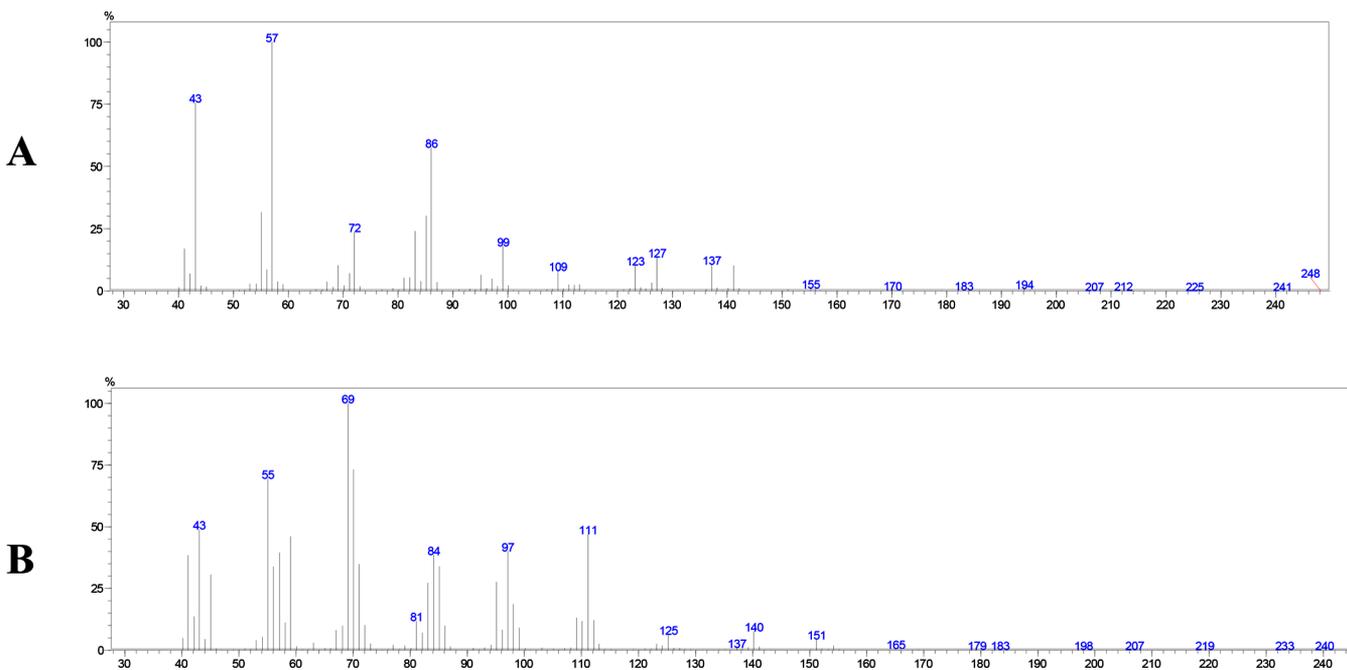
The polydesmidan suborder Dalodesmidea¹ occurs exclusively in the Southern Hemisphere and has been adequately studied taxonomically only for the island state of Tasmania in Australia, where a rich, largely endemic fauna, including 86 described species in the suborder, has been found.⁴ Most are litter-dwelling as adults, but burrowing species with strong-smelling defensive secretions are found in the endemic genera *Atalopharetra*,⁵ *Bromodesmus*,⁶ and *Gasterogramma*.⁷ According to ref 7, the

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Table 1. Aromatic Compounds Detected in Some Tasmanian Millipedes

species	locality	coordinates	date	compounds detected (relative amounts)
<i>Asphalidesmus leae</i> Silvestri, 1910 ²⁴	Keddies Creek, Penguin	−41.1703 146.0539	25 Apr 2015	β -nitrostyrene (90), benzaldehyde (10)
<i>Atalophareta johnsi</i> Mesibov, 2005 ⁵	Butlers Gorge Road	−42.3050 146.3897	12 Apr 2015	<i>p</i> -cresol
<i>Bromodesmus catrionae</i> Mesibov, 2004 ⁶	Weavers Ridge, Nunamara	−41.4178 147.3353	27 Apr 2015	<i>p</i> -cresol (96), phenol (4)
<i>Bromodesmus rufus</i> Mesibov, 2004 ⁶	Lake Highway	−41.7103 146.7278	21 Feb 2015	<i>p</i> -cresol
<i>Dasystigma margaretae</i> Jeekel, 1984 ²⁵	Butlers Gorge Road	−42.3050 146.3897	12 Apr 2015	benzaldehyde
<i>Lissodesmus adrianae</i> Jeekel, 1984 ²⁵	Sideling Range	−41.2669 147.3925	27 Apr 2015	benzaldehyde
<i>Lissodesmus perporosus</i> Jeekel, 1984 ²⁵	Keddies Creek, Penguin	−41.1700 146.0546	27 Nov 2014	<i>o</i> -cresol (98), benzaldehyde (2)
<i>Tasmaniosoma armatum</i> Verhoeff, 1936 ²⁶	Trevallyn Nature Recreation Area, Launceston	−41.1703 146.0539	26 Apr 2015	
		−41.4425 147.0928	27 Apr 2015	benzaldehyde

Figure 1. Compounds detected in *Gasterogramma* species.Figure 2. Compound 7 from *G. rusticum*: (A) EI mass spectrum; (B) EIMS after treatment with LiAlH_4 .

pinkish-purple *Gasterogramma* species have been called “stinky pinkies” by local collectors impressed by the pungency of the secretion. *G. plumleyi* has the strongest smell in the genus and can be detected by treading heavily through its wet forest habitat and sniffing attentively. Prior to this study, no published information has been available on the chemical defenses of dalodesmideans or any millipedes from Tasmania. In this report we document the defensive secretions of 14 Tasmanian dalodesmidean millipedes, including six in the genus *Gasterogramma*. This is the first report of the chemicals of any Tasmanian millipedes.

RESULTS AND DISCUSSION

The methanol extracts of all of the species collected except those in the genus *Gasterogramma* contained aromatic compounds as shown in Table 1. These are phenol, *ortho*- or *para*-cresol, benzaldehyde, and the more unusual β -nitrostyrene, but solely the *E* isomer, not a mixture of *E* and *Z* as previously detected.⁸ These compounds were identified from their published mass spectra and, in the case of the cresols and nitrostyrene, by direct GC/MS comparison with commercial samples. α -Methoxy- β -nitroethylbenzene was also detected in the extract of

Asphalidesmus leae, presumably a Michael-addition product with methanol used for shipment and storage.⁹ An authentic sample was available by treatment of a sample of commercial nitrostyrene with methanol.

The methanol extracts of the *Gasterogramma* species examined were characterized by the presence of acyclic ketones and unsaturated ketones, as shown in Figure 1. The vinyl ketones **1** and **2** had mass spectra matching the published spectra and had mass spectra and GC retention times identical to synthetic samples prepared by pyridinium chlorochromate oxidation of the corresponding commercially available 1-alken-3-ols.¹⁰

The extracts of *G. austrinum*, *G. imber*, and *G. rusticum* contained a component of longer retention time, for which the EIMS was m/z 224 [M^+] (25), 139 (100), 97 (17), 95 (15), 93 (13), 85 (10), 79 (10), 69 (9), 55 (33), 41 (17) and matched that reported for 1-(6-butyl-3,4-dihydro-2H-pyran-2-yl)pentanone (**5**), the hetero Diels–Alder adduct of **1**.¹¹ Traces of this compound were also observed in the preparation of **1**. The previously unreported GC-FTIR spectrum of **5** had significant absorptions at 3040, 1727, 1675, 1072, and 949 cm^{-1} (see Supporting Information).

4-Methyl-4-nonen-3-one, **6**, the major component in the extracts of *G. psi*, had an EIMS of m/z 154 [M^+] (1), 125 (65), and 55 (100) and strong absorptions at 1688 and 1639 cm^{-1} in its GC-FTIR spectrum. Catalytic hydrogenation (PtO_2) of this extract produced a single component with an EIMS of m/z 156 [M^+] (1), 99 (1), 86 (35), 57 (100). A synthetic sample of 4-methyl-4-nonen-3-one (**6**) was prepared by the method of Fales.^{12,13} Upon comparison, the GC retention time, mass spectrum, and GC-FTIR spectrum of the major component in *G. psi* were identical to those of synthetic **6**. Additionally, the GC retention time and mass spectrum of the hydrogenated natural product were identical to those of 4-methyl-3-nonanone prepared by hydrogenation of synthetic **6**.

A new compound, **7**, $\text{C}_{13}\text{H}_{24}\text{O}_2$, was detected in *G. austrinum* and *G. rusticum* for which the EIMS (Figure 2A) had even mass ions at m/z 72 and 86, resulting from McLafferty rearrangements. Its GC-FTIR spectrum indicated only a ketone carbonyl (1724 cm^{-1}). The mass spectrum of the product of lithium aluminum hydride reduction had ions at m/z 45 and 59 (Figure 2B), indicating the presence of a 2-alkanol and a 3-alkanol, respectively. Further microderivitization included treatment of the natural extract with methoxylamine to form a dimethoxime with odd mass ions at m/z 101 and 115, corroborating the McLafferty rearrangements in the original mass spectrum. Also, treatment of the natural diketone with ethanedithiol gave a product with a parent ion at m/z 346, and intense fragment ions at m/z 119 and 133 indicating a methyl dithiolane and an ethyl dithiolane, respectively. Taken together, these data indicated that **7** comprises 3-methyl-2-ketone and 4-methyl-3-ketone moieties with a C_4H_8 unit between them (Figure 3).

Since an unbranched four-carbon connector was assumed initially, the following sketched-out synthetic sequence was undertaken: sequential alkylation of 1,4-dibromobutane with the anion of ethyl 2-methylacetoacetate and then the anion of ethyl 2-methyl-3-oxo-pentanoate, followed by saponification and decarboxylation. This sequence provided a crude sample of a mixture of ketones and esters including the 3,8-dimethyl-2,9-undecanediones having even mass ions at m/z 72 and 86, but for which the EIMS and GC retention times differed from those of natural **7**.

In order to prepare diketones with branched C_4H_8 units between the carbonyl groups, a diastereomeric mixture of 2-

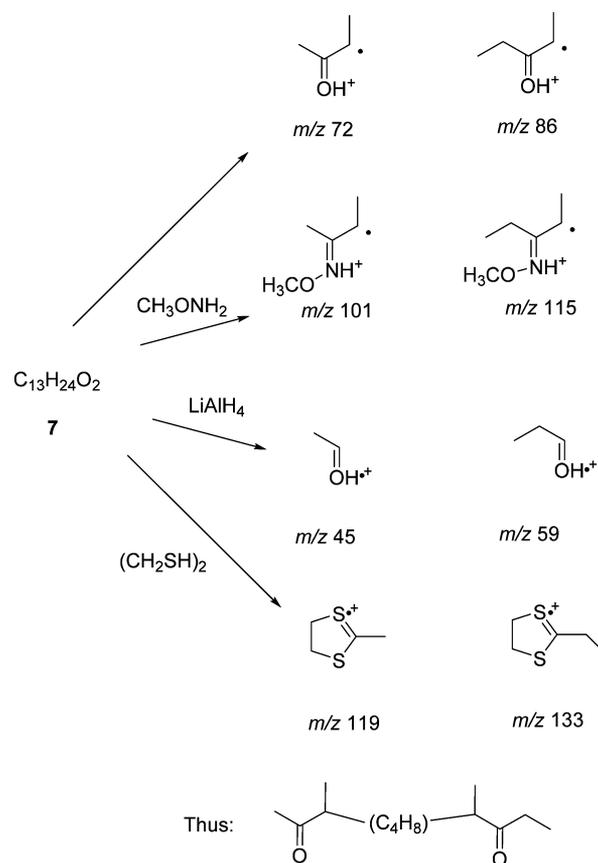
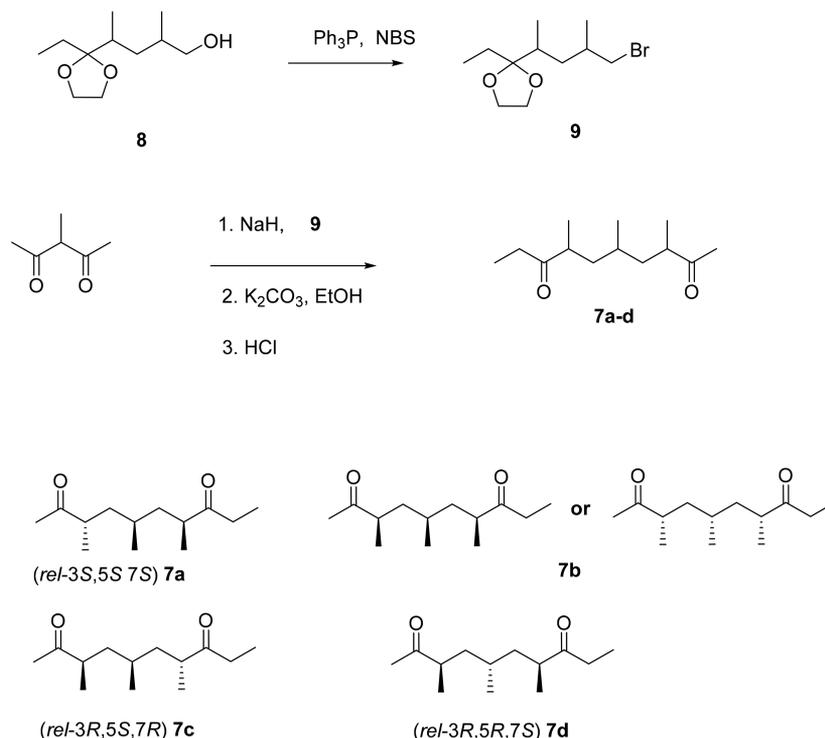


Figure 3. Mass spectrometric fragmentations from the derivatives of natural **7**.

ethyl-2-(1,3-dimethyl-4-hydroxybutyl)-1,3-dioxolanes (**8**)¹⁴ prepared from a diastereomeric mixture of 2,4-dimethylglutaric anhydrides was brominated,¹⁵ to provide 2-ethyl-2-(1,3-dimethyl-4-bromobutyl)-1,3-dioxolane (**9**) in good yield. This compound was condensed with 3-methyl-2,4-pentanedione, so that the subsequent deacylation would avoid mixtures, as we experienced, resulting from competitive deacylation and decarboxylation. The resulting diketone was deacetylated,¹⁶ then hydrolyzed to provide an equimolar mixture of the four diastereomers of 3,5,7-trimethyl-2,8-decanedione (**7a–d**) (labeled in order of their GC elution times), with nearly identical mass spectra. The retention time and mass spectrum of the diketone from *G. rusticum* matched those of the second eluting isomer, **7b** (Scheme 1, Figure 4).

To establish the relative configurations of the isomers of **7**, parallel syntheses of pairs of isomers were carried out starting from *meso*-2,4-dimethylglutaric anhydride.¹⁷ 2-Ethyl-2-(*rel*-1*S*,3*R*-dimethyl-4-hydroxybutyl)-1,3-dioxolane (**10**)¹⁴ and 2-methyl-2-(*rel*-1*S*,3*R*-dimethyl-4-hydroxybutyl)-1,3-dioxolane (**12**),¹⁸ both prepared from *meso*-2,4-dimethylglutaric anhydride,¹⁷ were carefully brominated to provide the bromoketals **11** and **13**, respectively (Scheme 2). Bromoketals **11** and **13** were condensed with the anions of 3-methyl-2,4-pentanedione and 4-methyl-3,5-heptanedione, respectively. After deacetylation, the synthesis starting with **10** produced isomers **7a** and **7b**, while **7b** and **7c** were formed from **13** (Scheme 2). Since neither precursor could be expected to provide **7d**, it was concluded that the relative configuration of the natural 3,5,7-trimethyl-2,8-decanedione was the “all-*syn*” (*rel*-3*R*,5*S*,7*S*) diastereomer. Throughout this work care had to be taken to avoid isomerization during the

Scheme 1. 3,5,7-Trimethyl-2,8-decanedione Diastereomers



bromination step and during the removal of the ethylene ketal group. It should be noted that samples of natural **7b** stored for a few months at $-15\text{ }^\circ\text{C}$ began to epimerize via enolization.

Because the soil-burrowing genera *Atalopharetra*, *Bromodesmus*, and *Gasterogramma* secrete defensive chemicals unlike those of log- and litter-dwelling genera (see Table 1), it is possible that such differences reflect different predators. Since a phylogenetic classification of the suborder Dalodesmidea is lacking, and *Asphalidesmus* has yet to be assigned to a family,^{19,20} we cannot yet confidently assign secretion differences to phylogenetics or ecology. It could be that differences between defensive secretions and millipede environment may have developed independently and any correlations are coincidental. The secretion, mainly of *o*-cresol, by *Lissidesmus perporosus* placed in a log- and litter-dwelling genus otherwise producing only benzaldehyde, suggests this might be the case.

It has been noted¹ that some compounds produced by millipedes are effective repellents of vertebrates but have no effect on ants, and vice versa, suggesting that the evolution of defensive secretion compounds may depend, in some cases, on the predators faced by them. Still, with the exception of the extraordinary diversity found among the Polydesmida, the general class of secretion compounds (e.g., quinones, alkaloids, terpenes) appears uniform among several of the other orders. For example, every species of the order Callipodida that has been examined produced *p*-cresol. After mapping the compounds produced on a phylogenetic tree of orders, it was concluded that in the subclass Helminthomorpha, which includes the order Polydesmida, the ancestral form of defensive secretion was phenol.¹

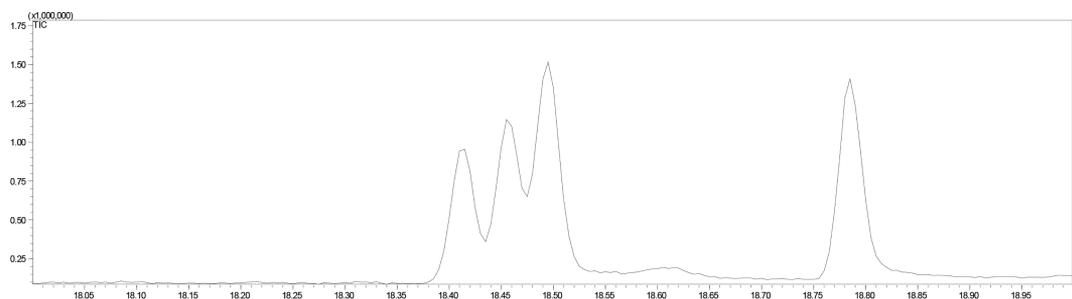
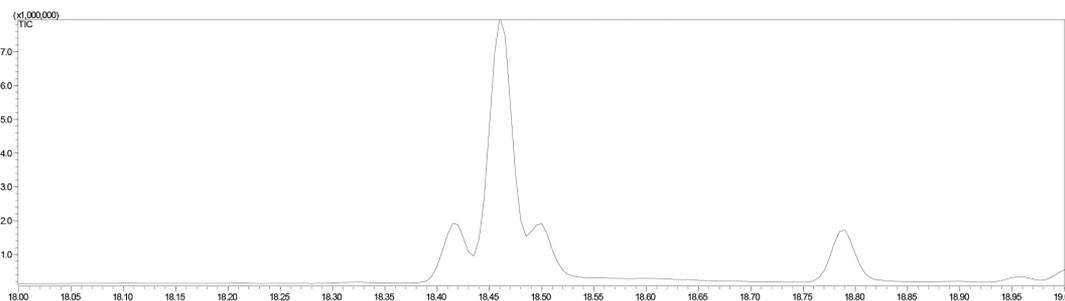
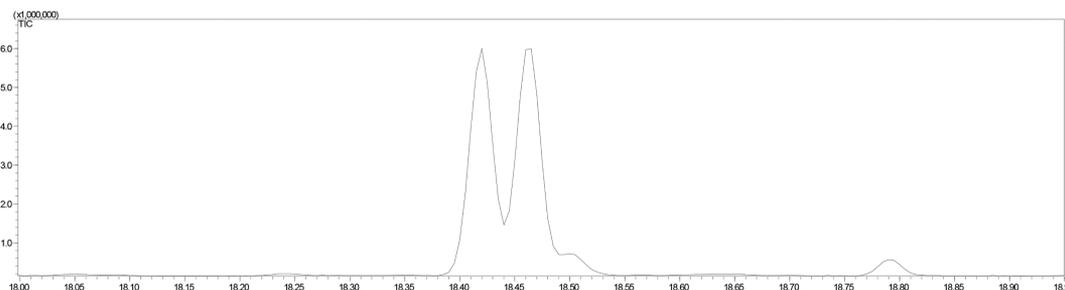
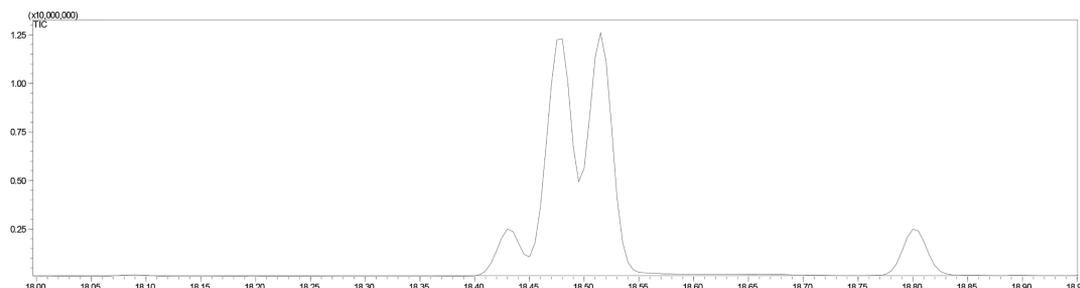
Most noteworthy in this investigation are the acyclic ketones present in *Gasterogramma* species, which are quite different from the usual array of aromatic compounds, *N*-containing heterocycles, and quinones commonly reported from millipedes. Rather, they are more reminiscent of the exocrine chemistry of

opilionids.¹¹ The extracts of the *Gasterogramma* species are all characterized by a series of aliphatic ketones (Figure 1, Table 2). The 3-ketones **3**, **4**, and **6** are common or well-described compounds. The pungent aroma of these millipedes is due mainly to the vinyl ketones **1** and **2**, which are present in all the species except *G. psi* and *G. wynyardense*, where their odors are due to the unsaturated ketone **6**. The noxious, volatile, and chemically reactive nature of these vinyl ketones suggests a defensive role. It is noteworthy that 1-hepten-3-one (**1**) is also accompanied by its hetero Diels–Alder dimer **5**, as it is in an opilionid.¹¹ On the other hand, the role of (*rel*-3*R*,5*S*,7*S*)-3,5,7-trimethyl-2,8-decanedione (**7b**) in *G. rusticum* and *G. austrinum* is uncertain.

The all-*syn* skipped methyl structure of **7b** is likely derived from a propionate pathway, as summarized for various pheromones by Francke and Dettner.²¹ In arthropods, notable examples of compounds containing the “all *syn*” stereochemistry that we have observed with the millipede diketone **7b** are lardolure, the pheromone of the mite *Lardoglyphus koni*, and vittalactone, an aggregation pheromone of the cucumber beetle, *Acalymma vittatum*.^{22,23} On the other hand, the “all-*syn*” skipped methyl moiety of **7b** has been established recently as part of the structure of the baulamycins, raising the possibility of an antimicrobial role for this compound given the damp conditions of these millipedes’ environment.³⁰

EXPERIMENTAL SECTION

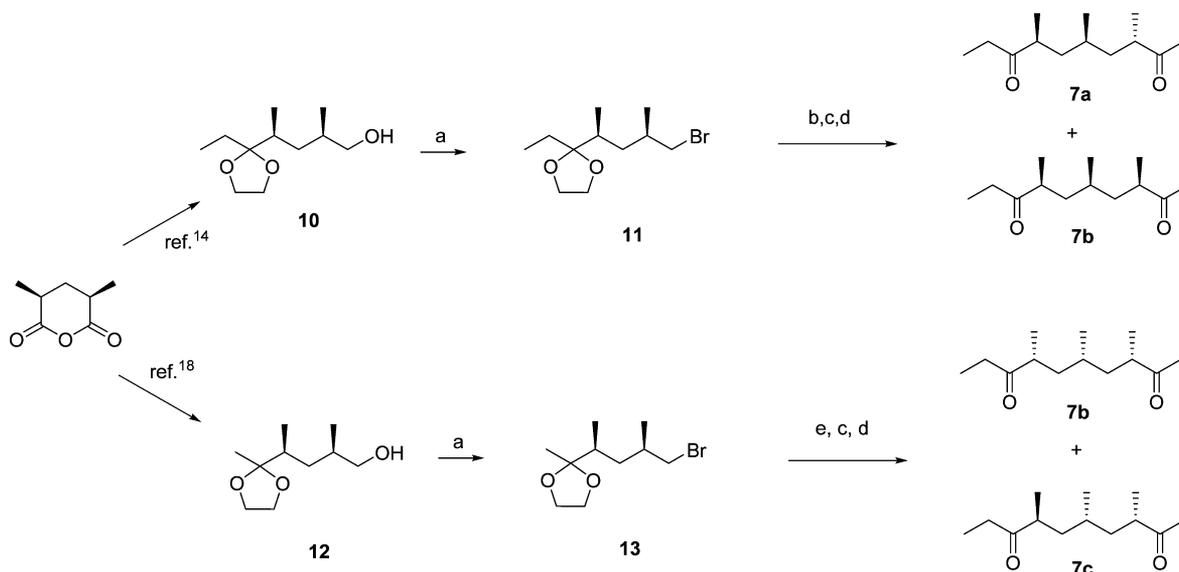
General Experimental Procedures. The millipedes sampled in this study ranged from 7 to 20 mm in length and were found in soil or rotting logs. One or two specimens of each species were individually picked up with soft forceps, gently whisked with tissue to remove soil debris, and placed directly into ca. 1 mL of methanol in 3 mL glass vials with Teflon-lined caps. Vials were sealed in plastic before shipping from R.M. in Australia to T.J. in the United States. Voucher specimens (see Supporting Information) are deposited at the Virginia Museum of Natural History, Martinsville, VA, USA.

Synthetic mixture of **7a – 7d**Coinjection of *G. rusticum* extract with **7a – 7d**Mixture of **7a-7d** prepared from bromoketal **11**Mixture of **7a-7d** prepared from bromoketal **13****Figure 4.** Gas chromatographic comparisons of the natural and synthetic stereoisomers of 3,5,7-trimethyl-2,8-decanedione (**7**).

Chemical Analyses. GC-MS was carried out in the EI mode using a Shimadzu QP-2010 GC-MS equipped with an RTX-5, 30 m × 0.25 mm i.d. column. The instrument was programmed from 60 to 250 °C at 10°/min. Vapor phase FT-IR spectra were obtained using a Hewlett-Packard model 5965B detector interfaced with a Hewlett-Packard 5890 gas chromatograph fitted with a 30 m × 0.25 mm RTX-5 amine column. NMR spectra were determined in CDCl₃ using a Varian Mercury 400

NMR spectrometer. HRMS were obtained by the Mass Spectrometry Laboratory of the School of Chemical Sciences at the University of Illinois–Urbana using a Waters GCT Premier time-of-flight mass spectrometer or a Waters Micromass VG 70-VSE mass spectrometer.

Microchemical Techniques. In *G. rusticum*, and to a lesser extent in *G. austrinum*, compound **7** was detected, for which the GC-FTIR spectrum (see [Supporting Information](#)) showed a strong absorption at

Scheme 2. Synthetic Routes to Diastereomers of 7^a

^aConditions: (a) Ph_3P , NBS. (b) 3-Methyl-2,4-pentanedione, NaH/DMF. (c) K_2CO_3 , EtOH reflux. (d) PPTS. (e) 4-Methyl-3,5-heptanedione, NaH/DMF.

Table 2. Defensive Chemistry of Some *Gasterogramma* Species^a

species	locality	coordinates	date	compound (relative amount)							
				1	2	3	4	5	6	7	8
<i>G. austrinum</i> Mesibov 2003 ²⁷	Van Moreys Road, Margate	−43.0641 147.1871	19 Feb 2015	78	6			10		2	4
<i>G. imber</i> Mesibov, 2003 ²⁷	Butlers Gorge Road	−42.3050 146.3897	12 Apr 2015	92				8			
<i>G. plomleyi</i> Mesibov, 2003 ²⁷	Sideling Range	−41.2667 147.3986	27 Apr 2015		93	7					
<i>G. psi</i> Jeekel, 1982 ²⁸	Keddies Creek, Penguin	−41.1700 146.0546	27 Nov 2014				15		85		
		−41.1703 146.0539	26 Apr 2015								
<i>G. rusticum</i> Mesibov, 2003 ²⁷	Stoodley	−41.3828 146.3836	16 May 2015	69	3			13		15	
		−41.3828 146.3836	11 Jun 2015								
		−41.3858 146.4006	8 Aug 2015								
		−41.3975 146.3868	4 May 2016								
<i>G. wynyardense</i> Mesibov, 2003 ²⁷	Oldina Road	−41.0208 145.6767	17 May 2015						100		

^a8 = benzaldehyde.

1724 cm^{-1} , with its mass spectrum (A) shown in Figure 2. The HRMS of 7 follows: m/z 212.1772 (calcd for $\text{C}_{13}\text{H}_{24}\text{O}_2$, 212.1776). Removal of the solvent in vacuo from the extracts provided a sample containing only 5 and 7. A portion of this mixture was dissolved in diethyl ether and treated with lithium aluminum hydride to provide a compound with the mass spectrum B shown in Figure 2. Treatment of a portion of 7 with methoxylamine gave a dimethyl oxime, having a mass spectrum with important ions at m/z 239 (10), 170 (30), 156 (55), 115 (100), and 101 (85). Another portion of this mixture was treated with ethanedithiol to provide a bis-ethyl dithiolane, for which the mass spectrum had important ions at m/z 364, ($[\text{M}]^+$, 1), 133 (100), and 119 (70) (Figure 3).

3,5,7-Trimethyl-2,8-decanedione (7a–d). Solid *N*-bromosuccinimide, 55 mg (3.2 mmol), was added in small portions to a solution containing 0.32 g (1.68 mmol) of hydroxyketal 8 and 0.85 g of triphenylphosphine in 7 mL of dimethylformamide (DMF). The mixture was warmed to 50 °C for 15 min and worked up following a published procedure⁶ to provide 0.36 g of 2-ethyl-2-(1,3-dimethyl-4-bromobutyl)-1,3-dioxolane (9) as a pair of diastereomers. MS: m/z 237 (10), 235 (10) ($[\text{M} - 29]^+$), 101 (100). In a separate flask, 65 mg of NaH in 10 mL of DMF was treated with 0.3 g of 3-methyl-2,4-pentanedione under an argon atmosphere. The mixture was stirred for 5 min, 1 mL of DMF containing 0.36 g of 9 was added, and stirring was continued for 4 days. The mixture was diluted with water and extracted with ether (3 × 50 mL). The combined ether extracts were dried over

anhydrous MgSO_4 . After filtration, the solvent was removed under reduced pressure, and the residue was dissolved in 30 mL of EtOH, treated with 0.5 g of K_2CO_3 , and refluxed for 48 h. The reaction was worked up following a known procedure¹⁷ to provide 0.16 g of a mixture of the four diastereomers of 7 with GC retention times of 7a, 18.43 min; 7b, 18.47 min; 7c, 18.51 min, and 7d, 18.80 min, with all having nearly identical mass spectra. The GC-mass spectrum and -retention time of 7 from *G. rusticum* matched those of 7b, as confirmed by co-injection with natural 7 (Figure 4).

2-Ethyl-2-(rac-1S,3R-dimethyl-4-bromobutyl)-1,3-dioxolane (11). A 0.40 g sample of 2-ethyl-2-(*rel*-1S,3R-dimethyl-4-hydroxybutyl)-1,3-dioxolane (10)¹⁴ was brominated in a similar manner except that pyridinium tosylate²⁹ was used for the final ketal removal to give 0.48 g of 2-ethyl-2-(*rel*-1S,3R-dimethyl-4-bromobutyl)-1,3-dioxolane (11): ¹H NMR (CDCl_3 , 400 MHz) δ_{H} , 3.94 (4H, m), 3.42 (1H, dd, $J = 10.0, 3.8$ Hz), 3.29 (1H, dd, $J = 10.0, 6.1$ Hz), 1.89 (1H, m), 1.79 (1H, m), 1.67–1.58 (4H, m), 1.03 (3H, d, $J = 6.3$ Hz), 0.91 (3H, d, $J = 6.9$ Hz), 0.87 (3H, t, $J = 7.3$ Hz); ¹³C NMR (CDCl_3 , 101 MHz) δ_{C} 113.9, 65.32, 65.27, 40.84, 36.89, 36.67, 32.62, 26.45, 20.23, 14.63, 7.42; HRCIMS m/z 265.0792 (calcd for $\text{C}_{11}\text{H}_{22}\text{O}_2$ ⁷⁹Br, 265.0803). This sample of 11 was carried through the above sequence except that pyridinium tosylate (PPTS)²⁹ was used for the final ketal removal to provide a mixture mainly of 7a and 7b (7a–d ratio, 1.0:1.0:0.07:0.07) (Scheme 2).

2-Methyl-2-(rac-1S,3R-dimethyl-4-bromobutyl)-1,3-dioxolane (13). A 0.23 g sample of 2-methyl-2-(*rel*-1S,3R-dimethyl-4-

hydroxybutyl)-1,3-dioxolane (**12**)¹⁸ was brominated in a similar manner to give 0.27 g of 2-methyl-2-(*rel*-1*S*,3*R*-dimethyl-4-bromobutyl)-1,3-dioxolane (**13**), for which the NMR data follows: ¹H NMR (CDCl₃, 400 MHz) δ_H 3.93 (4H, m), 3.42 (1H, dd, *J* = 10.0, 3.9 Hz), 3.29 (1H, dd, *J* = 10.0, 6.0 Hz), 1.91 (1H, m), 1.74–1.62 (3H, m), 1.24 (3H, s), 1.04 (3H, d, *J* = 6.5 Hz), 0.95 (3H, d, *J* = 6.8 Hz); ¹³C NMR (CDCl₃, 101 MHz) δ_C 112.19, 64.62, 64.52, 40.89, 38.60, 37.16, 32.70, 20.18, 20.14, 15.16; HRCIMS *m/z* 251.0647 (calcd for C₁₀H₂₀O₂⁷⁹Br, 251.0647). This sample of **13** was carried through the above sequence using 4-methyl-3,5-heptanedione instead of 3-methyl-2,4-pentanedione and using pyridinium tosylate for the final ketal removal to provide a mixture mainly of **7b** and **7c** (**7a–d** ratio, 0.2:1.0:1.0:0.2) (Scheme 2).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jnatprod.7b00806.

Voucher numbers for specimens at the Virginia Museum of Natural History, Martinsville, VA; GC-FTIR spectrum of natural **5**; GC-FTIR spectrum of natural **7**; EI mass spectrum of the dimethoxime of natural **7**; EI mass spectrum of the diethylenethioketal of natural **7**; ¹H and ¹³C NMR spectra of compound **11**; ¹H and ¹³C NMR spectra of compound **13** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail (T. H. Jones): jonesth@vmi.edu. Phone: 540-464-7422. Fax: 540-464-7261.

ORCID

Tappey H. Jones: 0000-0001-8807-3017

Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published ASAP on December 15, 2017, with errors in the names of the soil-burrowing genera on the fourth page in the text. The corrected version was reposted on December 20, 2017.