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INFLORESCENCE ODOURS OF *AMORPHOPHALLUS* AND *PSEUDODRACONTIUM* (ARACEAE)

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Key Word Index—*Amorphophallus*; *Pseudodracontium*; Araceae; headspace analysis; inflorescence odour; dimethyl oligosulphides.

Abstract—The inflorescence odours of 18 species of *Amorphophallus* and two species of *Pseudodracontium* were analysed by headspace techniques and compared to the limited data on potential pollinators. The odours of species with 'gaseous' or carrion smells had a simple chemical composition, consisting mainly of dimethyl oligosulphides. The odours of other *Amorphophallus* species having different smells were also generally dominated by one or two compounds: e.g. trimethylamine in *A. brachyphyllus*, isocaproic acid in *A. elatus*, 4-methoxyphenethyl alcohol in *A. albispathus*, and isoamyl acetate with ethyl acetate in *A. haematospadix*. The production of odours containing dimethyl oligosulphides appears to be a common feature of sapromyophilous flowers that attract carrion insects.

INTRODUCTION

The genus *Amorphophallus* Blume ex Decne (Araceae) is estimated to encompass some 170 species distributed mainly in the tropics from West Africa eastward into Polynesia [1]. They are seasonal herbs found mostly in secondary forests or disturbed spots in primary forests and forest margins, and they typically produce one leaf each year from an underground tuber. The inflorescence may replace the leaf in one season or develop alongside it. *Amorphophallus* is well-known for the large size of the inflorescence in some species (e.g. *A. titanum* (Becc.) Becc. ex Arcang.) and for having very strong and obnoxious inflorescence odours [2]. In many species the odour is a nauseating 'gaseous' stench which in some species tends towards the smell of rotting meat. In these carrion-smelling species the olfactory mimicry of decay is often supported visually by the inflorescence being coloured dark brownish or brownish-purple; the gaseous-smelling species generally have pale-coloured inflorescences. Foul floral odours are normally associated with the pollination syndrome of sapromyophily; that is, pollination by insects that breed or feed on dung, decaying matter or fungi [3]. Accordingly, carrion beetles have been identified as the pollinators in two species of *Amorphophallus* [4, 5] and observed in the spathes of others [6–8; Hetterscheid, unpublished observations]. However, not all *Amorphophallus* species are vile-smelling and a diversity of more appealing scents have been noted within the genus [2].

The closely-related genus *Pseudodracontium* N.E. Br. has been revised recently and contains seven species [9]. They all possess an elongate underground tuber but are otherwise similar to *Amorphophallus*, although much less variable. Typically they flower alongside the leaves and have rather inconspicuous green spathes; however, they also produce obnoxious odours. Hetterscheid [1] argues that *Pseudodracontium* is actually part of *Amorphophallus* and may have to be reduced to it.

In this paper we have used headspace techniques to analyse the various odours of 18 species of *Amorphophallus* and two species of *Pseudodracontium* in order to compare the chemical composition of the odour of species showing the sapromyophilous syndrome with other sapromyophilous plants for which odour data is available. We also wished to discover whether there were any chemical similarities between *Amorphophallus* species that were perceived to have diverse inflorescence odours.

RESULTS AND DISCUSSION

Headspace analysis of five *Amorphophallus* species that were perceived to have the nauseating gaseous inflorescence odour (*A. albus* Liu & Wei, *A. bulbifer* Blume, *A. glossophyllus* Hett., *A. prainii* Hook.f. and

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A. sagittarius van Steenis) revealed that this odour consisted almost entirely of dimethyl oligosulphides (Table 1). The major sulphide was dimethyl trisulphide with lesser amounts of dimethyl disulphide; in all, except *A. sagittarius*, dimethyl tetrasulphide could also be detected. Minor components accounted for less than 10% of the volatiles trapped and many were due to atmospheric pollutants as they were also present in control background analyses.

Two examples of species perceived as having a rotting meat odour, *A. konjac* K. Koch and *A. maximus* (Engl.) N.E. Br., also produced mainly dimethyl oligosulphides; however, in these species the dimethyl disulphide predominated. In *A. paeoniifolius* (Dennst.) Nicolson, which was perceived to have a mixture of gaseous and rotting meat odours, dimethyl disulphide and dimethyl trisulphide were present in approximately equal amounts. Dimethyl oligosulphides were also produced by the inflorescences of four other species having different odours: *A. titanum* (Becc.) Becc. ex Arcang. in which the gaseous-type odour was perceived to be mixed with that of urine; *A. cicatricifer* Hett. which had additional fruity aromas; *A. arnautovii* Hett. which smelt spicy; and *A. eichleri* (Engl.) N.E. Br. in which a rotting meat odour was mixed with that of dung. No additional compounds could be detected by headspace analysis which might account for the urine or spicy odours of *A. titanum* and *A. arnautovii*, but in *A. eichleri* the faecal odour was possibly due to the presence of 2-heptanone and indole modifying the smell of the sulphides, and in *A. cicatricifer* the major acetophenone component together with the aromatic ester, 1-phenylethyl acetate, probably gave the fruity smells. Both *Pseudodracontium fallax* Serebr. and *P. lacourii* (Lind. & André) N.E. Br. had gaseous odours, but in the latter an anise-like component could be perceived. Again, chemical analysis showed that the odour consisted mainly of dimethyl oligosulphides with the trisulphide predominating, but both species also produced an aromatic alcohol, 4-methoxyphenethyl alcohol.

In the *Amorphophallus* species in which the inflorescence odour was perceived to be quite distinct from the typical gaseous or rotting meat smell, the chemical composition was generally entirely different. The strong fried fish odour of *A. brachyphyllus* Hett. (sp. ined.) was predominantly due to trimethylamine, while isocaproic acid (4-methyl pentanoic acid) was the only compound detectable in the strong cheesy odour of *A. elatus* Hook. f. (isocaproic acid has the odour of pungent cheese). The unusual banana odour of *A. haematospadix* Hook. f. was found to be due to isoamyl acetate ('banana oil') although there was also a major ethyl acetate component. Ethyl acetate was also the major component in the odour of *A. annulifer* Hett. in which a perceived rotting meat component to the odour was probably due to small amounts of dimethyl disulphide. The strong anise-like odour produced by *A. albispathus* Hett. was found to be composed of almost pure 4-methoxyphenethyl alcohol, the same compound present in the odour of the two *Pseudodracontium* species examined. Finally, the monoterpenoid ocimene (*cis* or *trans*) dominated the odour of *A. margaritifer* (Roxb.) Kunth. (several other monoterpenoids were also present as minor constituents); this species lacks an appendix and so presumably the odour emanated from the flowers or staminodes.

In consisting mainly of dimethyl oligosulphides, the inflorescence odours of many *Amorphophallus* species and the two *Pseudodracontium* species show similarities to the odour of another foul-smelling aroid, *Sauromatum venosum* (Ait.) Kunth (reported as *S. guttatum* Schott) [10]. This species was found to produce dimethyl mono-, di-, tri- and tetrasulphies with the trisulphide predominating, but the odour also contained indole, as in *A. eichleri*, and skatole. The odour of another carrion-smelling sapromyophilous plant *Hydnora africana* Thunb. (Hydnoraceae) has also been reported to consist of dimethyl di- and trisulphides together with long chain organic acids [11]. Thus carrion-odour mimicry appears to be associated with sulphides and contrasts with the dung-odour mimicry reported for *Arum maculatum* L. in which sulphides were not detected and the major components were identified as indole, *p*-cresol and 2-heptanone together with numerous terpenoids [12]. However, high levels of sulphides have also been found in two presumed bat-pollinated flowers, *Crescentia cujete* L. (Bignoniaceae) and *Pilosocereus tweedyanus* (Britton & Rose) Byles & Rowley (Cactaceae) [13] and so these compounds are not exclusive to the odours of sapromyophilous plants.

Unfortunately, few published observations exist on potential pollinators of *Amorphophallus* and these often pertain to insects seen trapped in the spathe rather than actually pollinating the flowers. However, carrion beetles do appear to be the insects most often observed in spathes, and in *A. johnsonii* N.E. Br. and *A. hohenackeri* (Schott) Engl. & Gehrm. the carrion beetles *Phaeochrous ampulus* and *Haptoncurina motschulshii*, respectively, have been shown to be effective pollinators [4, 5]. We have not been able to analyse the inflorescence odours of these two species, but the carrion beetle *Diamesus osculans* and a scarab beetle (*Ardoretus* sp.) have been reported in the spathes of *A. titanum* and *A. paeoniifolius*, both of which produce dimethyl oligosulphides (Table 1). Dimethyl oligosulphides are likely to be effective odour cues for carrion beetles as they are present in the odour of meat [14]. Also, these sulphides have been shown to be attractants for various carrion flies, such as several blowflies (*Calliphora*, *Lucilia*, *Sarcophaga* and *Phormia* species) [10, 15], as well as *Musca domestica* [16]. Furthermore, dimethyl disulphide is a component of the commercial screwworm fly bait 'Swormlure' [17] and is used for host location by the sheep blowflies *Lucilia sericata* and *L. cuprina* [18]. The odour of the stinkhorn fungus *Phallus impudicus* Pers., which consists mainly of dimethyl oligosulphides [10], also attracts

Table 1. Levels (%) of compounds identified in the inflorescence odours of *Amorphophallus* and *Pseudodracontium* species

			Compound name (identification criteria*)																	
Date of odour collection	Odour collection time	Species	Dimethyl disulphide (a)	Dimethyl trisulphide (b)	Dimethyl tetrasulphide (b)	4-Methoxyphenethyl alcohol (a)	Trimethylamine (a)	Isoamyl acetate (a)	Isocaproic acid (a)	Ethyl acetate (a)	Ocimene (*cis* or *trans*) (b)	2-Heptanone (a)	Indole (a)	Acetic acid (a)	Limonene (a)	Acetophenone (b)	1-Phenylethyl acetate (b)	1,2-Dimethoxybenzene (b)	Phenylethyl alcohol (a)	Odour
4.5.95	17.30–19.30	*A. konjac*	76	17																Rotting meat
27.4.95	13.00–16.00	*A. maximum*	69	21											4					Rotting meat
21.5.95	17.30–19.30	*A. paeoniifolius*	47	41	4															Gaseous + rotting meat
7.7.96	08.00 09.00	*A. albus*	23	59	9															Gaseous
16.4.95	07.30–10.30	*A. bulbifer*	2	96	1															Gaseous
11.4.95	07.30–08.30	*A. glossophyllus*	20	71	2															Gaseous
9.4.95	09.30–11.30	*A. prainii*	30	65	1															Gaseous
28.5.95	07.00–10.00	*A. sagittarius*	28	64																Gaseous
30.7.95	18.00 20.00	*A. titanum*	75	10																Gaseous + urine
28.3.95	06.05–07.05	*A. arnautovii*	74	16											1					Spicy
28.4.95	17.30–19.30	*A. eichleri*	62	15	1							7	2						1	Rotting meat + dung
18.8.96	18.05–18.40	*A. cicatricifer*	24	30												39	6			Gaseous + fruity
22.5.95	06.45–08.45	*P. fallax*	17	62	15	3														Gaseous
3.5.95	07.30–10.10	*P. lacourii*	28	43	6	15														Gaseous + anise-like
21.5.95	07.00 09.00	*A. albispathus*				99														Anise-like
7.4.95	17.00–18.00	*A. brachyphyllus*					85													Fried fish
13.7.96	08.00–11.30	*A. haematospadix*						25		65										Bananas
3.6.95	08.00–10.00	*A. elatus*							100											Strong cheese
31.7.96	20.15–21.15	*A. annulifer*	8					7		60		2		5						Strong cheese + rotting meat
1.7.95	16.30–19.30	*A. margaritifer*									76							7		Weak cheese

* Compound identified by comparing RR_t and/or MS with (a) authentic standard or (b) published data.

many saprophageous flies [19], including the black blowfly, *Phormia regina* [20].

The pollinators of *Amorphophallus* species having inflorescence odours different from the typical gaseous or rotten meat stenches are unknown. However, indications as to the type of potential pollinator may come from plants which produce similar floral odours. 4-Methoxybenzyl alcohol, the lower homologue of 4-methoxyphenethyl alcohol produced by *A. albispathus*, occurs in the inflorescence odour of another 'sweet'-smelling aroid, *Spathiphyllum cannifolium* Schott, together with other methoxbenzenoids [21]. These benzenoid compounds have been shown to be attractive to tephritid fruitflies [22]. Similarly, isovaleric acid, the lower homologue of isocaproic acid produced by *A. elatus*, has been reported in the odours of several foul-smelling flowers such as some *Masdevallia* species (Orchidaceae) [23], *Deherainia smaragdina* (Planch. ex Linden) Decne., *Theophrasta americana* L. (Theophrastaceae) [24], *Leontopodium alpinum* Cass. [25] and *Senecio articulatus* Sch. Bip. (Asteraceae) [26]. In all of these species, flies have been implicated in pollination, although this has only been shown conclusively for *L. alpinum* [25]. Trimethylamine, produced by *A. brachyphyllus*, has also been reported in the condensates from cut appendices of *Sauromatum venosum* and *Dracunculus vulgaris* Schott (Araceae) [27], but was not detected in headspace analysis of the former species [10]. This compound is an indicator of decay in fish [28] and it has been shown to be an attractant for houseflies (*Fannia* spp.) [29], thus carrion insects are again likely pollinators.

The inflorescence odours of *Amorphophallus* may have taxonomic significance. Species producing dimethyl oligosulphides are thought to form two related groups and the anise-scented *A. albispathus* is thought to be closely related to two species, *A. longituberosus* (Engl.) Engl. and Gehrm. and *A. coudercii* (Bogner) Bogner, which are also perceived to have anise-like odours (Hetterscheid, unpublished data). Furthermore, species of *Pseudodracontium* are possibly most closely related to these anise-like scented *Amorphophallus* species (Hetterscheid, unpublished data), a hypothesis supported by the presence of 4-methoxyphenethyl alcohol in the odours of *A. albispathus*, *P. fallax* and *P. lacourii*.

Several other interesting and unusual inflorescence odours in *Amorphophallus* have been noted by one of us (WLAH) but as yet we have either not had the opportunity to analyse these or the analyses have been unsuccessful. For example, *A. odoratus* Hett. has an odour of carrots, *A. manta* Hett. smells strongly of chocolate, whilst *A. yuloensis* H. Li has a lemon odour. Thus, the genus *Amorphophallus* offers the opportunity to study how floral odours can evolve in response to the selective forces on cross-pollination success. However, in order to correlate the various inflorescence odours with insect attraction, field observations on the pollinators of *Amorphophallus* species are required.

EXPERIMENTAL

Odour collection. Plants were cultivated at Leiden Botanic Garden or at Aalsmeer, The Netherland (the one exception was *A. titanum* which flowered at the Royal Botanic Gardens, Kew). The odour was collected from an inflorescence soon after the spathe unfurled; i.e. during the female phase. The inflorescence was left attached to the plant and a trap (100 mm long × 3 mm diameter; SGE) packed with 100 mg of Tenax GR 35/60 (Alltech) was positioned near to the appendix. Air was then drawn through the trap at a rate of 50 ml min^{-1}, by means of a portable pump, for the periods given in Table 1. For smaller inflorescences the appendix was covered by a clear nylon bag. Only one inflorescence of each species was sampled.

GS-MS analysis. The trapped odour was analysed by direct thermal desorption-GC-MS (thermal desorption injector, SGE; GC, Perkin-Elmer Model 8500; MS, Finnigan-MAT Ion Trap Detector 800 Series). The trap was desorbed for 4 min in a flow of helium carrier gas at 250° onto a 25 m × 0.22 mm i.d. × 0.25 μm BPX5 capillary column (SGE) held at 40°. Following desorption, chromatography proceeded using a temperature programme of 40–260° at 5° min^{-1}. The effluent from the column was split between a FID and the MS (scan rate 1 s^{-1}; m/z range 38–400; AGC m/z 38) and peaks were identified by comparing their relative retention times and mass spectra with published data [29, 30] or, where possible, with purchased standards.

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