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DIALLYL DI-, TRI- AND TETRASULPHIDE FROM *ADENOCALYMMA ALLIACEAE*

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Key Word Index—*Adenocalymma alliaceae*; Bignoniaceae; diallyl disulphide; diallyl trisulphide; diallyl tetrasulphide; 1-octen-3-ol.

Abstract—The essential oil from flowers and leaves of *Adenocalymma alliaceae* (Bignoniaceae) consists almost entirely of diallyl di-, tri-and tetra-sulphide, a mixture formerly encountered within the *Allium* genus but never before convincingly recognized within the class of dicotyledonous angiosperms.

INTRODUCTION

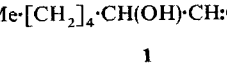
In 1911, Peckolt [1] drew attention to the garlic odour of the leaves of the Brazilian species *Adenocalymma sagotii* Bur. et K. Sch. ('Cipó d'alko'), Bignoniaceae, used by the native population in combating infections. We now report the results of a study by GC–MS of the odoriferous principles in fresh leaves and flowers of *A. alliaceae* Mart.

RESULTS AND DISCUSSION

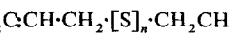
When concentrated ethereal extracts of steam distillates of fresh leaves of *A. alliaceae* were subjected to GLC, a remarkably simple pattern appeared, essentially consisting of four peaks, numbered 1–4 in the order of increasing retention time; the relative peak heights were *ca* 1:5:5:1. In the flower distillate, only peaks nos. 2–4, in an unchanged ratio, were prominent.

The MS characteristics of the compounds, represented by peaks nos. 1–4, are summarized in Table 1. From these data their structures can be unequivocally established as 1-octen-3-ol (**1**), diallyl disulphide (**2**), diallyl trisulphide (**3**), and diallyl tetrasulphide (**4**). The eight most prominent peaks in the MS of fraction no. 1 (Table 1) are identical with those reported for 1-octen-3-ol [3], a widespread alcohol within the plant kingdom. More interest is associated with the sulphur constituents (**2**)–(**4**). About 85 years ago, Semmler [4] established the presence of **2**, **3**, and, tentatively, **4** in garlic oil (*Allium sativum*). The finding of **2** and **3** in garlic has been repeatedly confirmed and extended to other species of the genus *Allium* [5, 6]. The unambiguous recognition of diallyl di-, tri-, and tetra-sulphide (**2**)–(**4**) in volatiles from a dicotyledon, however, appears to be without precedent. The alleged occurrence of **2** in asafoetida, an oleoresin from *Ferula* species [7], we consider doubtful in view of the detailed studies recently performed on asafoetida volatiles in the Danish laboratory and elsewhere [8, and refs. therein]. Again, the suggested presence of **2** in volatiles from *Descurainia sophia* (Cruciferae) [9] rests on unconvincing evidence.

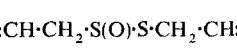
In *Allium* sp., **2** and **3** derive from allicin (**5**) which, in its turn, results from enzymic fission of alliin (**6**) [6, and refs. therein]. It would be of considerable interest to know whether an identical chemical apparatus is operating within dicotyledonous taxa. Studies towards this goal are in progress.



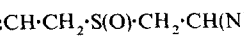
1



2, $n = 2$
3, $n = 3$
4, $n = 4$



5



6

Table 1. The eight most prominent peaks in the MS of the major volatiles from leaves of *Adenocalymma alliaceae*, arranged in the order of increasing retention times

Peak no. in GLC	*m/e* (% relative intensity)							
1*	57 (100)	29 (17)	43 (15)	72 (14)	41 (11)	27 (9)	55 (7)	85 (6)
2†	41 (100)	39 (25)	81 (12)	45 (12)	146‡ (7)	73 (5)	105 (5)	113 (2)
3§	41 (100)	73 (86)	45 (44)	39 (41)	113 (38)	29 (10)	72 (8)	47 (8)
4‖	41 (100)	39 (35)	73 (29)	105 (18)	45 (17)	146 (16)	64 (15)	29 (11)

* Not observable in flower distillates

† A published MS of diallyl disulphide [2], containing noticeable peaks at *m/e* 114, 67, and 54 in addition to those here reported, was obviously recorded on a non-homogeneous specimen.

‡ Molecular ion.

§ Molecular ion observable, *m/e* 178 (2.3%).

‖ Molecular ion observable, *m/e* 210 (2.9%).

EXPERIMENTAL

Leaves and flowers were collected from specimens of *A. alliaceae* grown as ornamentals in the Botanical Garden of Andhra University, Waltair, India. The fresh materials were cut into small pieces and subjected to steam distillation. The distillates were saturated with NaCl and extracted with several portions of Et_2O. The dried extracts were carefully concentrated to small vols before being subjected to GC–MS.

These were performed on a VG MM 70-70 instrument, interfaced to a glass column (1.5 m × 2 mm i.d.), packed with 5% OV-101, through a glass jet separator. The operating conditions were: column temp. 70–250° at 8°/min; injector 250°; transfer lines and separator 250°; carrier gas He 20 ml/min; ionization energy 70 eV; ion source temp. 240°.

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COMPOSES HALOGENES D'UNE ALGUE ROUGE, *FALKENBERGIA RUFOLANOSA* TETRASPOROPHYTE D'*ASPARAGOPSIS ARMATA*

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Key Word Index—*Asparagopsis armata*; gametophyte; *Falkenbergia rufolanosa*; tetrasporophyte; red alga; Rhodophyceae; halomethanes; haloacetones.

Abstract—Water extraction of fresh *Falkenbergia rufolanosa* followed by water–ether partition, yielded halomethanes, polyhalo ethyl and methyl acetates and especially polyhalo acetones. It is the first example of polyhalo compounds extracted from a tetrasporophyte in the Bonnemaisoniaceae.

INTRODUCTION

La plupart des algues rouges appartenant à la famille des Bonnemaisoniaceae possèdent des cellules sécrétrices spéciales qui jouent probablement un rôle important dans le métabolisme des halogènes et dont la présence semble en relation avec certaines propriétés antibactériennes [1, 2]. Deux espèces particulières, *Asparagopsis taxiformis* et *A. armata*, ont donné lieu ces toutes dernières années à des inventaires chimiques détaillés [1–7]. Nous avons nous-mêmes rendu compte récemment [8] de propriétés d'autoconservation exceptionnelles d'*A. armata* à l'état broyé dans l'eau de mer. Les premiers résultats d'une étude de la composition chimique du broyat de l'algue en milieu aqueux nous ont permis de constater des analogies de composition entre