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THE COMPOSITION OF VOLATILES FROM DIFFERENT PARTS OF *ALLIUM TUBEROSUM* PLANTS

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Key Word Index—*Allium tuberosum*; Liliaceae; Chinese chives; chemotaxonomy; volatiles; disulphides.

Abstract—The percentage of methyl and 2-propenyl (allyl) radicals present in the volatile disulphides liberated from chopped *Allium tuberosum* tissue was monitored. Quantitative differences were detected when different parts of the same plants were analysed. The significance of this finding to previous chemotaxonomic work using volatiles from *Alliums* as characters is discussed.

INTRODUCTION

Several workers have suggested that the volatile sulphur components liberated on damage to *Allium* species can be used as characters for their classification [1–3]. These volatile sulphur compounds arise by enzymic breakdown of flavour precursors which are alkyl and alkenyl substituted cysteine sulphoxides. Either, *S*-1-propenyl-L-cysteine sulphoxide, or the 2-propenyl, 1 propyl, or methyl-L-cysteine sulphoxides, or various combinations of these are present in the different members of the genus [3]. The relative proportions of the alkyl and alkenyl radicals can be determined by GLC [1], and quantitative and qualitative comparisons made between different species. Quantitatively, the amounts of volatile sulphur components and precursors obtainable from *Allium* species change during their growth [5, 6] and with the part of the plant taken [6, 7], but previous work with some American *Allium* species has suggested that the proportions of the various radicals present do not vary significantly within each species. Neither habitat, nor stage of growth, nor plant part analysed, were found to appreciably affect the proportions of the various radicals in the sulphide containing vapours from the chopped tissues of the species tested [5]. Hence, it was suggested that these ratios could be used as characters for the classification of species in the *Allium* genus [2].

Some species of *Allium* have been analysed in different laboratories with broadly similar results, whilst in others such as *A. tuberosum* and *A. chinense* markedly different values have been found [3]. Saghir *et al.* found *A. tuberosum* to be a "high methyl" containing species, the percentage of methyl to propyl to 2-propenyl radicals being 91 : < 1 :9 [4], whereas Freeman and Whenham [3] found the same ratio to be 39 :1 :60 and classified this species with those containing *S*-2-propenyl-L-cysteine sulphoxide as a major flavour precursor. Some of this variation can be accounted for by differences in the headspace and GLC methods used [3]. In this paper the composition of the volatiles and the proportions of the different radicals liberated from *Allium tuberosum* have been re-examined in relation to the different parts of the plant used in the analyses.

RESULTS AND DISCUSSION

Plants were divided into: leaf laminae, leaf bases, rhizome and roots and samples of volatiles collected. GLC showed three major disulphide peaks to be present in all chromatograms, corresponding to dimethyl disulphide, methyl-2-propenyl disulphide, and di-2-propenyl disulphide [4]. Using these three peaks, the proportions of the alkyl and alkenyl radicals present in the volatiles from each region of the plants tested were determined (Table 1). Small amounts of propyl radicals were found in some samples but accounted for less than 1% of the total peak area so have not been included.

The results show that there are marked differences between the proportions of methyl to 2-propenyl radicals in the volatiles obtained from different parts of the plant. The methyl radicals predominate in volatiles from leaves and roots, whereas in the rhizome the situation is reversed with 2-propenyl radicals predominating. The results confirm those of Freeman and Whenham [3] who used rhizomes for their analyses, and also those of Saghir *et al.* who used leaf tissue, and suggest that the differences obtained between the two groups could have been partly due to the different parts of the plants used.

Table 1. GLC headspace analyses of *Allium tuberosum* plants. Relative proportions of radicals in headspace vapours from various parts of the plant

	Leaf laminae		Leaf bases		Roots		Rhizome	
Plant no.	methyl	2-propenyl	methyl	2-propenyl	methyl	2-propenyl	methyl	2-propenyl
1	62	38	60	40	57	43	27	73
2	66	34	63	37	43	57	23	77
3	55	45	64	36	56	44	19	81
4	57	43	59	41	51	49	30	70
5	73	27	63	37	60	40	42	58
6	82	18	82	18	54	46	34	66
7	77	23	—	—	59	41	30	70
8	80	20	73	27	58	42	46	54
9	72	28	—	—	64	36	60	40
10	84	16	70	30	57	43	44	56
11	71	29	50	50	51	49	38	62
Average	71	29	65	35	55	45	36	64

In chemotaxonomic. analyses, therefore, it is clearly necessary to examine the same plant part when surveying different species.

EXPERIMENTAL

Plants were grown from seed obtained from the National Vegetable Research Station, Wellesbourne; in a greenhouse under 16 hr day 8 hr night conditions at approximately 20°. Plants to be used were taken at intervals throughout a year and were analysed individually. The plants were divided into leaf laminae (green), leaf bases (white), roots, and rhizomes which were taken to be those parts covered with dried leaf bases [8]. Equal quantities of tissue were taken for analysis from each part of the plant. The amounts varied from plant to plant from 2 g to 5 g. The material was finely chopped up and placed in a 500 ml flask at 40° for 30 min. 500 ml headspace vapour was collected by the method of Freeman and Whenham [3] by a cold trap and introduced into a gas chromatograph. Dual 2 m × 3 mm ID glass columns of Carbowax 1540, 8% on DMDS-treated Chromosorb W were used. The injection temperature was held at 150°, and the column temperature at 50° for 10 min then programmed to rise at 2° per min to 130° where it was held for 15 min. N_2 carrier gas was used at a flow rate of 8 ml/minute. A dual F.I.D. system was used and peaks were integrated electronically. Major peaks were identified by their coincidence with marker compounds and by relative retention indices. Proportions of radicals present in the three major disulphides were determined by the method of Saghir *et al.* [4].

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(−)-(*S,S*)-12-HYDROXY-13-OCTADEC-*cis*-9-ENOLIDE, A 14-MEMBERED LACTONE FROM *CREPIS CONYZAEFOLIA* SEED OIL

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Key Word Index—*Crepis conyzaefolia*; Compositae; large-ring lactone; 12,13-dihydroxyoleic acid; GC–MS, ORD.

Abstract—*Crepis conyzaefolia* (Gouan) Dalle Torre seed oil contains about 3% of (−)-(*S,S*)-12-hydroxy-13-octadec-*cis*-9-enolide (**1**), a lactone of (−)-*threo*-12,13-dihydroxyoleic acid. The absolute configuration of the acid has been established as D-12, L-13 (12-*S*, 13-*S*) and the lactone has the same absolute configuration.

INTRODUCTION

An earlier investigation of *Crepis conyzaefolia* seed oil disclosed the presence of four epoxy fatty acids—vernolic [(+)-12,13-epoxyoctadec-*cis*-9-enoic], 12,13-epoxystearic, (+)-12,13-epoxyoctadec-*trans*-6-*cis*-9-dienoic and 12,13-epoxy-octadec-*cis*-6-*cis*-9-dienoic [1]. During the isolation of these compounds, a fifth unusual component was collected. It was neither an epoxy acid nor a homolog or isomer of any of the aliphatic acids usually found in seed oils and was not included in the previous fatty acid composition [1]. Its GLC and MS characteristics indicated that it had at least one free hydroxyl group, and the IR spectrum was similar to that of a hydroxy methyl ester (methyl ricinoleate). Its PMR spectrum showed no evidence of methyl ester absorption but otherwise resembled fatty acid spectra. The compound has now been identified as (−)-(*S,S*)-12-hydroxy-13-octadec-*cis*-9-enolide (**1**), a lactone of (−)-*threo*-12,13-dihydroxyoleic acid. It becomes the third large-ring lactone to have been isolated from seed oils [2].

RESULTS

When basic hydrolysis of **1** yielded 12,13-dihydroxyoleic acid (**2a**), a lactone structure was immediately suspected. The lactone obviously contained a free hydroxyl group as indicated by its IR spectrum and MS of its silylation product. Structural proof for the dihydroxyoleic acid was derived from its melting point and ORD values, from its TLC migration and from the