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CHEMOTAXONOMY: DISTRIBUTION STUDIES OF SULFUR COMPOUNDS IN *ALLIUM*

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Abstract—Twenty-seven samples of Old World and two New World species of *Allium* have been investigated and the nature and amount of many of the sulfur compounds determined by gas chromatography. Using the sectional classification of L. K. Mann, comparisons were made as to the kind and amounts of these compounds present in species within each section. More often than not, members of each section showed similar characteristic chromatographic patterns for the sulfur compounds, whereas there were distinct differences in pattern at the sectional level.

INTRODUCTION

THERE is a remarkable morphological variation within the genus *Allium*. Systematically, the broad relationships have been based largely upon morphological and cytological characteristics, but many of the sections are poorly defined, and the relationships between the New and Old World species are quite obscure. Of the more than 1000 specific names proposed in the genus, half may prove to be synonyms. Apparently this confusion arises from the fact that the alliums comprise a huge genus of world-wide distribution displaying a great diversity of structure. Additionally, no systematist has had access to adequate material for a comprehensive survey.

Since the writing of Clusius' *Rariorum Plantarum Historia* in 1601, an enormous volume of literature concerning *Allium* systematics has been published.[1,2] In 1827 Don[3] arranged 129 species in eleven "divisions" under seven "sections". Later Regel[4] grouped 262 species under six sections. More recently, Vvedensky[5] has described and classified the alliums of the Soviet Union. Levan's[6-10] extensive cytological investigations have contributed to an increased understanding of relationships between *Allium* species. Working with Old World alliums, Feinbrun[11] pointed out the correlations between chromosome numbers and certain anatomical characteristics of the leaf. Mann[12-13] described the inflorescences and bulb structures of some species of the section *Molium* and used them as indicators of systematic

[1] W. T. STEARN, *Herbertia* **11**, 11 (1944).
[2] H. P. TRAUB, *Plant Life* **24**, 147 (1968).
[3] G. A. DON, *Mem. Wern. Nat. Hist. Soc.* **6**, 1 (1832).
[4] E. REGEL, *Act. Hort. Petrop.* **3**, 1 (1875).
[5] A. I. VVEDENSKY, *Herbertia* **11**, 65 (1944).
[6] A. LEVAN, *Hereditas* **16**, 259 (1932).
[7] A. LEVAN, *Hereditas* **20**, 289 (1935).
[8] A. LEVAN, *Nature* **142**, 118 (1938).
[9] A. LEVAN, *Hereditas* **26**, 353 (1940).
[10] A. LEVAN, *Hereditas* **30**, 468 (1944).
[11] N. FEINBRUN, in *Proc. 9th Internatl. Congr. Genet. Suppl. to Carylologia* (edited by G. MONTALENTI and A. CHIARUGI), Vol. 6, p. 1036 (1954).
[12] L. K. MANN, *Am. J. Botany* **46**, 730 (1959).
[13] L. K. MANN, *Am. J. Botany* **47**, 765 (1960).

relations within the section. In 1959 Hutchinson,[14] using inflorescence type rather than the position of the ovary, moved *Allium* from the Liliaceae to the Amaryllidaceae.

One of the most characteristic properties of *Allium* is its distinctive odor. Very little use had been made of this quality for taxonomic purposes until the advent of GLC. In 1960 Mann and Bernhard[15] proposed examination of the volatile constituents of *Allium* species and isolation of these materials for subsequent chemical and physical analysis. They reasoned that a thorough knowledge of the chemical composition of representative members of this genus should clarify the proposed subgeneric divisions based on morphological and cytological data. Jacobsen *et al.*[16] isolated and identified a number of aliphatic disulfides from various *Allium* species. Later these researchers developed a rapid and sensitive GLC method for the separation and identification of sulfides from *Allium* vapors and surveyed the common food species.[17] Saghir *et al.*[17] noted that, in general, the odor of the various common alliums can be related to the nature of their sulfide content. Further investigations by Saghir *et al.*[18] have indicated that neither the habitat, stage of growth, nor plant part appreciably affects the proportions of alkyl sulfide radicals in the vapor of chopped *Allium* tissue. These studies indicated that the proportions of sulfide radicals do not vary significantly within species and hence can be used in classification. Saghir *et al.*[19] then related the composition of volatiles to the taxonomy of American (New World) alliums.

The present paper explores the variations in volatile constituents in a number of Old World alliums and their utilization in clarifying the systematics of these species.

RESULTS AND DISCUSSION

The chemical constituents of greatest interest are those volatiles which give alliums their characteristic odors and flavors, mostly derivatives of free sulfur-containing amino acids. These have been studied in some detail in garlic (*Allium sativum* L.), the common onion (*A. cepa* L.), and a few other species.[20-26] These substances are known to vary from species to species, but no one has yet attempted to survey representative members of the whole genus.

In this study seven principal components of *Allium* vapors have been isolated and identified. These appear to be the most common constituents of the species examined (Table 3 and Fig. 1). They are dimethyl disulfide (peak 1), diallyl sulfide (peak 4), methyl-*n*-propyl disulfide (peak 7), methyl allyl disulfide (peak 9), di-*n*-propyl disulfide (peak 14), *n*-propyl allyl disulfide (peak 17), and diallyl disulfide (peak 20). In order to improve the sensitivity of the analytical procedures, dual channel GLC, a technique using a single column attached to hydrogen flame and electron capture detectors was employed.[27]

[14] J. HUTCHINSON, *The Families of Flowering Plants*, Vol. II, 792 pp., *Monocotyledons*, 2nd edition, Oxford University Press (1959).
[15] L. K. MANN and R. A. BERNHARD, Private communications.
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[17] A. R. SAGHIR, L. K. MANN, R. A. BERNHARD and J. V. JACOBSEN, *Proc. Am. Soc. Hort. Sci.* **84**, 386 (1964).
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[24] J. F. CARSON and F. F. WONG, *J. Agri. Food Chem.* **9**, 140 (1961).
[25] A. I. VIRTANEN, *Angew. Chem. Intern. Ed.* **1**, 299 (1962).
[26] A. I. VIRTANEN and E. J. MATIKKALA, *Acta Chem. Scand.* **13**, 1898 (1959).
[27] D. M. OAKS, H. HARTMANN and K. P. DIMICK, *Anal. Chem.* **36**, 1560 (1964).

TABLE 1. MANN'S PROVISIONAL SECTIONS FOR GENUS *Allium* IN THE OLD WORLD*

1. *Anguinum* G. Don ex Koch (1837)
   type species, *A. victorialis*
2. *Alliotypus* Dumortier (1827)
   t. spp., *A. sativum* or *A. ampeloprasum*
3. *Briseis* (Salisb.) Stearn (1946)
   t. spp., *A. triquetrum*
4. *Cepa* (Moench) Prokhanov (1931)
   t. spp., *A. cepa*
5. *Chamaeprason* F. Hermann (1939)
   t. spp., *A. chamaemoly*
6. *Codonoprasum* (Rchb.) Endl. (1836)
   t. spp., *A. oleraceum*
7. *Haemoprason* F. Hermann (1939)
   t. spp., *A. melanantherum*
8. *Melanocrommyum* Webb et Berth. (1848)
   t. spp., *A. nigrum*
9. *Microscordum* Maxim. (1887)
   t. spp., *A. monanthum*
10. *Molium* G. Don ex Koch (1937)†
    t. spp., *A. neapolitanum* or *A. roseum*
11. *Nectaroscordum* (Lindley) Grenier et Godron (1855)
    t. spp., *A. siculum*
12. *Ophioscorodon* (Wallr.) Endl. (1836)
    t. spp., *A. ursinum*
13. *Petroprason* F. Hermann (1939)
    t. spp., *A. obliquum*
14. *Phyllodolon* (Salisb.) Prokhanov (1931)
    t. spp., *A. fistulosum*
15. *Rhizirideum* G. Don ex Koch (1837)
    t. spp., *A. senescens*
16. *Schoenoprasum*‡
17. *Xanthoprason* F. Hermann (1939)
    t. spp., *A. moly*

* From unpublished notes of the late L. K. Mann and based upon the work of Stearn.[1]

† Stearn[1] lists *Molium* as a synonym of *Moly* Endl. (1836).

‡ There is a section *Schoenoprasum* (Kunth) Endl. (1836). It is a synonym of section *Alliotypus* Dumortier (1827), but it does not include *A. schoenoprasum*. Mann believed *Schoenoprasum* should be a separate section and include *A. schoenoprasum*. Proper usage indicates a new name for this proposed section is necessary.

When the various alliums were examined using the above system, all the familiar sulfur compounds were detected on both channels, but, interestingly enough, a number of new sulfur compounds became evident. However, Virtanen and coworkers[28] have demonstrated that the compound S-(1-propenyl)cysteine sulfoxide is present in onions and the seed of chive (*A. schoenoprasum* L.) and this substituted amino acid, an analog of alliin,[17] could give rise to 1-propenyl sulfides. Thus, the number of disulfides possible in *Allium* increases by an additional nine, since dipropenyl disulfide can occur as three isomers, *cis–cis*, *trans–trans*, *cis–trans*, and methyl-1-propenyl, *n*-propyl-1-propenyl, and allyl-1-propenyl disulfides can each occur as two isomers, *cis* and *trans*. Additionally, of course, one may propose a similar scheme for the monosulfides since diallyl monosulfide has been found in various alliums. Thus some thirty mono- and disulfides could be present in alliums. Whether all of the possible isomers are actually present in these plants is not known. Recently Wijers *et al.*[29] identified methyl-1-propenyl disulfide in an oil derived from *A. cepa* and *n*-propyl-*cis*-1-propenyl disulfide and *n*-propyl-*trans*-1-propenyl disulfide from *A. schoenoprasum*. In another investigation, Brodnitz *et al.*[30] reported the presence of methyl-*cis*-1-propenyl disulfide, methyl-*trans*-1-propenyl disulfide, *n*-propyl-*cis*-1-propenyl disulfide, *n*-propyl-*trans*-1-propenyl disulfide, two methyl propyl trisulfides, two propyl propenyl trisulfides and 3,4-dimethylthiophene in an onion oil.

In addition to the mono- and disulfides present among the volatiles, numerous authors have indicated the presence of mercaptans, trisulfides, and higher polysulfides.[24,31] Interestingly enough, none of the common alliums examined showed any evidence for the

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[29] H. E. WIJERS, L. BRANDSMA, H. BOELENS and A. V. D. GEN, *Rec. Trav. Chim.* **88**, 519 (1969).
[30] M. H. BRODNITZ, C. L. POLLOCK and P. P. VALLON, *J. Agri. Food Chem.* **17**, 760 (1969).
[31] O. WAHLROOS and A. I. VIRTANEN, *Acta Chem. Scand.* **19**, 1327 (1965).

presence of sulfur compounds containing ethyl radicals. Our investigations, as yet unpublished, have indicated that sulfur compounds containing ethyl radicals may appear in certain American wild onions.

TABLE 2. SOURCE OF MATERIAL OF OLD WORLD ALLIUMS*

Allium species	Source and date of acquisition
A. longicuspis Regel.	Main Botanical Gardens, Academy of Science, Moscow, U.S.S.R., 1958 (2)
A. rotundum L.	Botanical Gardens, Lund, Sweden, 1953 (2)
A. sativum L.	William Seyman, San Jose, Calif., U.S.A. 1952 (2)
A. triquetrum L.	Royal Botanical Gardens, Kew, Surrey, 1956 (2)
A. cepa L., "Southport White Globe"	Basic Vegetable Products, Inc., Vacaville, Calif., U.S.A. 1967 (2)
A. cepa L., "Ever-ready"	Ken Smith, San Joaquin Valley, Calif., U.S.A. 1954 (1) (2)
A. galanthum Kar. & Kir.	Botanical Gardens, Alma Ata, Kazakhstan, U.S.S.R., 1958 (1) (2)
A. pskemense B. Fedtsch. (Moscow)	Main Botanical Gardens, Academy of Science, Moscow, U.S.S.R., 1958 (1) (2)
A. pskemense B. Fedtsch. (Alma Ata)	Botanical Gardens, Alma Ata, Kazakhstan, U.S.S.R., 1958 (1) (2)
A. pskemense B. Fedtsch. (Taschkent)	Botanical Gardens, Copenhagen, Denmark (original source Taschkent, U.S.S.R.), 1966 (2).
A. roylei Stearn	V. B. Sharma, Ku College, India, 1957 (1) (2)
A. oleraceum L.	Royal Botanical Gardens, Kew, Surrey, 1956 (2)
A. christophii Trautv.	Botanical Gardens, Copenhagen, Denmark, 1951 (1) (2)
A. monophyllum Vved.	Oxford Botanical Gardens, Oxford, 1956 (2)
A. ursinum L.	Royal Botanical Gardens, Kew, Surrey, 1956 (2)
A. globosum Marsch.-Bieb.	Prof. Marion Ownbey, Washington State Univ., Pullman, Wash., U.S.A., 1957 (1) (2)
A. platyspathum Schrenk.	Botanical Gardens, Alma Ata, Kazakhstan, U.S.S.R., 1958 (2)
A. altaicum Pall. (Alma Ata)	Botanical Gardens, Alma Ata, Kazakhstan, U.S.S.R., 1958 (2)
A. altaicum Pall. (Murmansk)	Botanical Gardens, Murmansk, U.S.S.R., 1958 (2)
A. fistulosum L.	Botanical Gardens, Copenhagen, Denmark, 1956 (2)
A. nutans L.	J. M. Aubert, Champex, Switzerland, 1951 (2)
A. ramosum L.	Royal Botanical Gardens, Kew, Surrey, 1952 (2)
A. tuberosum Rott. ex Spreng.	Rex Pearce Nursery, Mooretown, N.J., 1940 (2)
A. scabriscapum Boiss. et. Kotschy	Botanical Gardens, Alma Ata, Kazakhstan, U.S.S.R., 1958 (2)
A. senescens L.	J. M. Aubert, Champex, Switzerland, 1951 (2)
A. caesium Schrenk.	Komarov Institute of the Academy of Sciences of the U.S.S.R., Leningrad, U.S.S.R., 1958 (2)
A. schoenoprasum L.	James A. Perry, San Gabriel, Calif., U.S.A. 1957 (2)
A. canadense L.	Prof. Marion Ownbey, Washington State Univ., Pullman, Wash., U.S.A., 1965 (1) (2)
A. plummerae S. Wats.	F. W. Gould, Ramsey Canyon, Huachuca Mts., Cochise Co., Arizona, U.S.A., 1964 (1) (2)

* Meaning of designations: (1) Herbarium specimen preserved at the Department of Vegetable Crops, University of California, Davis, Calif., U.S.A. (2) Sample from plants cultivated at Davis, Yolo Co., Calif., U.S.A.

Examination of the gas chromatograms of the *Allium* volatiles revealed a marked response from the electron capture detector and little or no response from the coincident flame signal during the later portions of the chromatograms. Oaks *et al.*[27] have demonstrated that the ratio of electron capture response to flame response becomes an important value for component identification. This response ratio, ϕ, is low for mercaptans (0·13–0·48) and monosulfides (0·01–0·04), but increases for saturated disulfides (0·77–3·3) and becomes large for unsaturated disulfides (8·4–20). Trisulfides yield remarkably high values of 180–350. These

data tend to support the view that many of the later chromatographic peaks could be unsaturated disulfides and even low-molecular-weight trisulfides.

The results of the analyses of the various species are presented here arranged according to the sections recognized by Mann (Table 1 and Fig. 1).

I. *Section* Alliotypus. *A. longicuspis* and *A. sativum* are similar in having a preponderance of constituents containing the allyl radical. Both show high levels of methyl allyl disulfide

TABLE 3. RELATIVE RETENTION VOLUMES OF SOME SULFIDE CONSTITUENTS OF *Allium* VAPORS

Peak number and compound	V_R/V_R Replicates	V_R/V_R Known $\bar{X} \pm 2S$*	V_R/V_R Replicates	V_R/V_R From *Allium* $\bar{X} \pm 2S$*
1. Dimethyl disulfide	17	0·216 ± 0·007	49	0·212 ± 0·008
2. di-*n*-Propyl sulfide	2	0·236	—	—
3. Unknown	—	—	19	0·263 ± 0·008
4. Diallyl sulfide	21	0·313 ± 0·008	34	0·313 ± 0·009
5. Unknown	—	—	37	0·351 ± 0·010
6. Unknown	—	—	5	0·424 ± 0·008
7. Methyl-*n*-propyl disulfide	19	0·458 ± 0·007	52	0·455 ± 0·009
8. Unknown	—	—	27	0·525 ± 0·008
9. Methyl allyl disulfide	19	0·569 ± 0·007	32	0·569 ± 0·009
10. Unknown	—	—	30	0·593 ± 0·004
11. Unknown	—	—	16	0·645 ± 0·018
12. Unknown	—	—	12	0·920 ± 0·007
13. Unknown	—	—	5	0·931 ± 0·010
14. di-*n*-Propyl disulfide	23	1·000	49	1·000
15. Unknown	—	—	8	1·132 ± 0·008
16. Unknown	—	—	24	1·162 ± 0·006
17. *n*-Propyl allyl disulfide	5	1·254 ± 0·008	26	1·256 ± 0·016
18. Unknown	—	—	32	1·304 ± 0·009
19. Unknown	—	—	10	1·471 ± 0·018
20. Diallyl disulfide	18	1·582 ± 0·013	13	1·585 ± 0·019
21. Unknown	—	—	7	1·641 ± 0·014
22. Unknown	—	—	3	1·723 ± 0·008
23. Unknown	—	—	4	1·906 ± 0·006
24. Unknown	—	—	11	1·984 ± 0·011
25. Unknown	—	—	2	2·010 ± 0·005
26. Unknown	—	—	3	2·038 ± 0·002
27. Unknown	—	—	2	2·558 ± 0·006
28. Unknown	—	—	8	2·635 ± 0·006
29. Unknown	—	—	2	2·766 ± 0·004

* $X \pm S$ = arithmetic mean ± 2X standard deviation.
(Stationary Phase: Carbowax 20 M. di-*n*-propyl disulfide = 1·000.)

and very high levels of diallyl disulfide. Methyl disulfide is present in low concentration, and di-*n*-propyl disulfide is absent. There are small quantities of diallyl sulfide, methyl-*n*-propyl disulfide, and *n*-propyl allyl disulfide present. This pattern appears to be consistent with the findings of Saghir *et al.*[17] and is typical of garlic-like alliums.

The diagram of *A. rotundum* is distinctly different from the above two species and is characterized by a small level of *n*-propyl allyl disulfide, a moderate level of dimethyl disufide and relatively high levels of methyl-*n*-propyl disulfide and di-*n*-propyl disulfide. Diallyl sulfide and methyl allyl, and diallyl disulfides are absent. This is typical of the onion-like alliums.[17]

Thus the volatile pattern of *A. rotundum* appears to be more like members of section *Cepa* than section *Alliotypus*.

II. *Section* Briseis. *A. triquetrum* contains a large proportion of dimethy disulfide and moderate proportions of methyl-*n*-propyl and methyl allyl disulfides. There are small amounts of some fourteen other volatiles. It should be noted that no large amounts of di-*n*-propyl, *n*-propyl allyl, or diallyl disulfides are indicated on the diagram.

III. *Section* Cepa. Members of this section are characterized by the presence of very large amounts of di-*n-propyl* disulfide, moderate amounts of methyl *n*-propyl disulfide, small

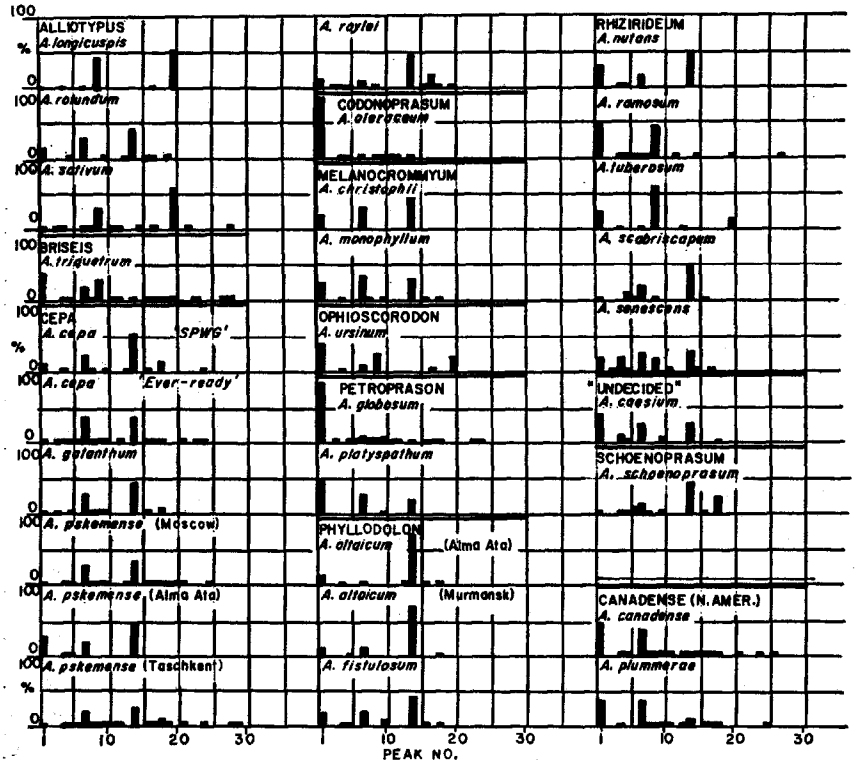

FIG. 1. PROPORTIONS, BASED ON INTEGRATION OF PEAK AREAS, OF TWENTY-NINE COMPONENTS PRESENT IN THE VAPORS OF CHOPPED ALLIUMS.

The total concentration of the twenty-nine constituents for each allium equals 100 per cent. Identification of peak numbers is presented in Table 3. Names in bold face type indicate sections; those in italics indicate species.

amounts of a large number of the other volatiles and by the virtual absence of diallyl disulfide. A sample of one member of this section, *A. pskemense* from Alma Ata, shows a rather high level of dimethyl disulfide, a trace of diallyl disulfide and an absence of many of the minor peaks; but the general pattern is close to that of other members of the section. *A. roylei* exhibits a smaller methyl-*n*-propyl disulfide peak and a slightly larger *n*-propyl allyl disulfide peak, but the general features of the pattern are again consistent with its assignment to this section.

IV. *Section* Codonoprasum. The significant features of the *A. oleraceum* figure are preponderant dimethyl disulfide peak and small amounts of eight other volatiles including

diallyl sulfide, and methyl-*n*-propyl, methyl allyl, and di-*n*-propyl disulfides. There are no *n*-propyl allyl or diallyl disulfides. This pattern bears considerable resemblance to that of *A. globosum*.

V. *Section* Melanocrommyum. The two members of this section examined, *A. christophii* and *A. monophyllum*, show the presence of large amounts of dimethyl disulfide, methyl-*n*-propyl disulfide and di-*n*-propyl disulfide. The pattern of volatiles from these two species bears a close resemblance to those of members of the section *Cepa* with the exceptions that both contain a greater proportion of dimethyl disulfide and less of the minor constituents than do members of section *Cepa*.

VI. *Section* Ophioscorodon. *A. ursinum* exhibits a large dimethyl disulfide peak, moderate amounts of methyl allyl disulfide and diallyl disulfide, a significant quantity of methyl-*n*-propyl disulfide, and traces of diallyl sulfide and *n*-propyl allyl disulfide. There is no di-*n*-propyl disulfide present. Thus on the basis of volatile patterns, this species resembles members of the section *Alliotypus* except that it lacks a strong dimethyl disulfide peak.

VII. *Section* Petroprason. The two species examined displayed very dissimilar chromatograms. *A. globosum* shows a preponderance of dimethyl disulfide in its vapors, with small amounts of some fifteen other components. Its chromatogram bears a strong resemblance to that of *A. oleraceum* in section *Codonoprasum*. *A. globosum* apparently contains many more trace volatiles than does *A. oleraceum*. *A. platyspathum* shows large amounts of dimethyl disulfide, methyl-*n*-propyl disulfide, and di-*n*-propyl disulfide. There is a small amount of peak 10 present. This pattern is similar to that of the members of section *Melanocrommyum* examined except that the proportions of the major components are reversed.

VIII. *Section* Phyllodolon. The two samples of *A. altaicum* examined present similar chromatograms. These are characterized by a large percentage of di-*n*-propyl disulfide, together with small amounts of dimethyl disulfide and methyl-*n*-propyl disulfide. No methyl allyl, *n*-propyl allyl, or diallyl disulfides is present. There are minor differences in the trace peaks. *A. fistulosum* also displays a large di-*n*-propyl disulfide peak and approximately equal amounts of dimethyl disulfide and methyl-*n*-propyl disulfide. Although its volatile pattern somewhat resembles those of members of section *Cepa*, it lacks the higher number trace volatiles characteristic of *Cepa*.

IX. *Section* Rhizirideum. Five representative species were examined and the analyses indicate that members of this section fall into three distinct groups. *A. nutans* and *A. scabriscapum* present similar patterns exhibiting large amounts of di-*n*-propyl disulfide, moderate quantities of methyl-*n*-propyl disulfide, and small to moderate amounts of dimethyl disulfide. No *n*-propyl allyl or diallyl disulfides are present. This pattern is somewhat similar to those shown by members of section *Cepa*, but the quantity of methyl-*n*-propyl disulfide is generally lower in the *Rhizirideum* species examined, and there are fewer trace peaks than among *Cepa* members.

The diagrams for *A. ramosum* and *A. tuberosum* show these species fall into a second pattern characterized by large methyl allyl and dimethyl disulfide components. Both species show small to moderate amounts of diallyl disulfide. This pattern bears some similarity to *A. ursinum* in section *Ophioscorodon*, but differs in that the methyl allyl disulfide component appears to be larger in both *A. ramosum* and *A. tuberosum*, and that *n*-propyl allyl disulfide is absent.

A. senescens exhibits a third and unique pattern showing virtually equal amounts of dimethyl disulfide, diallyl sulfide, methyl-*n*-propyl, methyl allyl, and di-*n*-propyl disulfides. There is a small amount of *n*-propyl allyl disulfide present, but no diallyl disulfide. This

pattern resembles no other species examined in this study. Since *A. senescens*, the type species of this section, is the only species which is permanently and irrevocably associated with the sectional name, it appears that this pattern may well be the "typical" pattern for *Rhizirideum* members.

X. *Unassigned species.* Mann could not classify some seventy-seven species, including those which form part of Vvedensky's[5] section *Haplostemon*, because there was insufficient taxonomic information available on them. Of these, *A. caesium* shows a strong dimethyl disulfide component and moderate amounts of methyl-*n*-propyl and di-*n*-propyl disulfides. There is a small amount of diallyl sulfide and an absence of methyl allyl, and diallyl disulfides. Thus *A. caesium* resembles the *A. monophyllum* component pattern, but the proportions of dimethyl and methyl-*n*-propyl disulfides are reversed, and the diallyl sulfide component is greater in the former.

XI. *Section* Schoenoprasum. The chive is the most widely distributed member of the alliums,[1] and its chromatographic pattern is unique too. The chromatogram is dominated by a large di-*n*-propyl disulfide peak and a rather substantial peak 18. There is a moderate amount of methyl-*n*-propyl disulfide and small amounts of dimethyl disulfide, and diallyl sulfide. Methyl allyl, *n*-propyl allyl, and diallyl disulfides are absent.

XII. Allium canadense *alliance*. The American alliums, including the "canadense alliance" informally used by Ownbey,[19] have recently been classified as section *Amerallium* by Traub.[32] The type species is *A. canadense*. Two species from this North American alliance are included for the purpose of comparison. The chromatograms of both *A. canadense* and *A. plummerae* show large amounts of dimethyl and methyl-*n*-propyl disulfides. There are traces of numerous other components with no evidence of diallyl disulfide in either species. These patterns are quite distinctive and do not resemble any of those of the Old World alliums examined in this study.

Regrettably, selection of samples used in this study was limited to those cultures available to the author. Thus, only one species each for five sections could be examined, obviously an inadequate sampling. Among the seven sections for which there is data for two or more species, the included species were similar in four sections and dissimilar in three others. These were the non-conformity of the volatile pattern of *A. rotundum* with the other *Alliotypus* species examined, the apparent similarity of *A. globosum* with *A. oleraceum*, and the five species in section *Rhizirideum*. This section traditionally has comprised those species which lack distinctive features which might be used to group them into more natural and meaningful aggregations. Thus in a sense it might be described as a "catch all" section. In view of this, it is not surprising that their volatile patterns are also diverse.

Excluding the exceptions noted above, the volatile patterns examined in this study do show notable differences between sections. Because of the limited sample it is not possible to make any firm generalization. There is, however, the suggestion that species which are clearly related otherwise tend to resemble each other chemically, and that each species has a specific sulfide pattern. Obviously, there is now a need for additional investigation and, above all, a greater sampling of diverse species.

EXPERIMENTAL

The assignment of species to sections (Table 1) is based on extensive study of morphological, cytological, ecological and distributional characteristics of the Old World representatives of *Allium* by the late Professor

[32] H. P. TRAUB, *Plant Life* 23, 89 (1967).

L. K. Mann.[33] The species used for chromatographic analysis in this study and their sources are indicated in Table 2. These species are representative of eleven of the sixteen proposed sections. In addition, two species of North American alliums are included for comparison. All determinations were verified by the late Professor Mann.

The composition of the volatiles was made by a rapid, sensitive GLC procedure.[17] The method of sample preparation has been described previously.[17] A major innovation employed in this study was the use of dual channel GLC.[27] The identity, number of replicates, and relative retention volumes of the components examined are presented in Table 3. Details of the identification of chromatographic peaks are presented elsewhere.[16-17,34] The operating conditions of the gas chromatograph are presented in Table 4.

TABLE 4. OPERATING CONDITIONS FOR AEROGRAPH MODULINE MODEL 1520B* GAS CHROMATOGRAPH FOR GLC OF SULFIDES FROM *Allium*

Stationary liquid phase	5% (w/w) Carbowax 20 M†
Solid support	Firebrick (acid washed) 100/120 mesh‡
Column length	10ft (stainless steel)
Column diameter	0·125 in. O.D.; 0·0787 in. I.D.
Column temperature	90°
Injection block temperature	120°
Detector oven temperature	180°
Detectors	Hydrogen flame and electron capture
Hydrogen flow rate	25 ml/min
Air flow rate	350 ml/min
Nitrogen flow rates	25 ml/min; 25 ml/min
Recorder ranges (each channel)	1 mV
Chart speed	20 in./hr
Electrometer range (flame)	2×10^{-12} amp full scale
Electrometer range (E.C.)	2×10^{-10} amp full scale

* Varian Aerograph, Walnut Creek, California, U.S.A.
† Analytical Engineering Laboratories, Inc., Hamden, Connecticut, U.S.A.
‡ U.S. Standard Screen.

It was previously determined, that within the limits of experimental error, the proportions of the various sulfides were the same in vapors from different parts of the same plant, from plants collected at different geographic locations, and from plants sampled at different stages of growth.[18] In the present study a minimum of two or more separate samples using fresh bulbs was analyzed for each species examined. An exception was the case of *A. schoenoprasum* where only foliage leaves were used since this species produces no well-defined bulbs. Any variation in the composition of the volatiles of any two species which had a magnitude greater than that allowed for variability due to sampling technique, was considered to be significant in determining relationships within the genus.

An Aerograph model 471 digital integrator system with automatic printer was used to obtain peak areas and provide the quantitative data for constituent distribution.

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[33] L. K. MANN, unpublished notes and observations.
[34] R. A. BERNHARD, A. R. SAGHIR, J. V. JACOBSEN and L. K. MANN, *Arch. Biochem. Biophys.* **107**, 137 (1964).