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The Organosulphur Composition of *Allium* Separated by Different Analytical Methods

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Executive Summary

Various procedures have been examined for the separation of the compound formed in solution *Alliacee* cut plants. To prepare an extract, the product id squeezed through a nylon mesh, saturated in NaCl and shaken twice with dichloromethane, filtering and centrifuging each time. The dichloromethane extracts were combined, dried and concentrated in vacuum at room temperature and then analyzed by HPLC and FT–RMN and/or GC (modified injector).

Supercritical carbon dioxide can also be used as solvent extraction. For the preparation of a distillate at room temperature, the homogenate is subjected to a distillation using an oil bath to keep the container at room temperature. The distillate is colored to –196°C, saturated with NaCl, extracted and analyzed. For a particular plant extracts and distillates obtained at room temperature, they were similar in terms of analytically.

Tion–Sulfines: Primary Products in the Plants Cut *Alliacee*

Besides the lacrymogenic factor, found exclusively in onion but probably formed in other plants from the same species, the primary products detected by HPLC, NMR and GC–MS are tion–sulfines with small amounts of di–and polysulfide and thiosulfate. Along with lacrymogenic factor, the tion–sulfines influence the taste and flavor of *Alliacee* freshly cut and are precursors of all organosulphur compounds formed in the cut plants.

With respect to the thermal instability of *allicin* and other tion–sulfines, surprisingly the vacuum–steam distillation gave a positive result. The distillation at room temperature succeeded due to the stabilizing effect of the water by the hydrogen bonds on the tion–sulfines; slightly acidic conditions (pH 2–4) also seem to stabilize tion–sulfines.

Since tion–sulfines are soluble in water, no any physical law characteristic for insoluble compounds is applied. It is possible that tion–sulfines to form the azeotrope mixture with stirring under the conditions of steam distillation [1].

It requires a few comments on the "good" chromatographic methods for the characterization and quantification tion–sulfineslor trained cutting *Allium* species.

Gas chromatography and tandem heat GC–MS dominated studies of the extract obtained at room temperature, although early works suggest that many components revealed by GC can be "analytical artifacts" [2], and comparable components of Allium species can be achieved using HPLC. Some researchers have shown that some aliphatic tion–sulfines containing up to 8 carbon atoms, survived in the short column GC analysis. Unfortunately, in most studies on volatiles substances of *Alliacee* plants are used long and narrow capillary columns (0.2 mm or 50 m) and/or injection port temperatures up to 280°C. Comparing the results of GC and HPLC of fresh extracts and distillates *Alliacee* plants shows that high temperature gas chromatography injector and column presents a totally inadequate composition of volatile substances and extracts. Thus, the analysis of extract and distilled in vacuum from the *Allium* species, by normal phase of HPLC (polar stationary phase) and by reverse phase HPLC (C–18) indicate tion–sulfines as a dominant component. There was no HPLC argument indicating the presence of polysulfides mentioned in the previous GC–MS studies [3].

Tion–sulfines derivatives are of four types:

completely saturated, the form RS (O) SR '(RR' = Me or Pr);

tion–sulfines mono–or bis–β, γ–unsaturated;

tion–sulfines mono–α, β–unsaturated;

mixes tion–sulfines α, β–and β, γ–unsaturated.

Are omitted from this classification tion–sulfines isomeric bis–α, β–unsaturated Mecha = CHS (O) SCH = CHMe [4].

They are likely to form and rearrange quickly and are a class apart.

General Commentaries on Tion–Sulfines of Each Species of *Alliacee*

One way to classify different *Allium* species, it is by type of tion–sulfines alkyl groups or in a more realistic than the related compounds such as polysulfides.

This type of chemo taxonometric information has been used to determine the relationships between different types of *Allium* [5]. Only the Chinese chives presented a predominance of methyl groups, although all examined *Alliacee* plants containing such groups. Three of the plants examined, garlic, wild garlic clove and garlic with large alkyl allyl group is dominant.

The only plant containing detectable amounts of allyl groups is Chinese chives. Propyl group presents major alkyl in the chives, shallots, leeks and is also present in onions. In disagreement with older publications [6], but according to other researchers observations, propyl group is absent in garlic, wild garlic, garlic chives big Chinese cabbages, being present instead a 1–propenyl. Even if all the plants containing group, 1–propenyl, it is dominant in the onion only. Total percentage of 1–propenyl from tion–sulfines group of onion and bisulfide is misleading since the major part generated as 1–propensulfenic acid, will end as the lacrymogenic factor, which is not included in the calculations because the most part is lost during analysis. However, in an experiment using ether as the extraction solvent in the case of white onion, 0.5 mmol/g of lacrymogenic factor was isolated as compared to 0.2 mmol/g, total amount of thiosulfate. In some extracts were found small amount of bisulfides.

Since the homogenates of the plants were kept 24 hours in menthol prior to extraction and analyzed by chromatographic methods, were isolated other organo–sulfur compounds. *Allium* homogenates prepared from peeled bulbs (garlic, wild garlic, large cabbages, onions, shallots) or from clean plants such as leeks, chives, Chinese chives, roots and the ends were removed, were stored at room temperature for 30 minutes, then analyzed by rapid extraction and concentration. Analytical results were not changed after increasing the time between homogenization and extraction in 6 hours [7].

When homogenates were kept overnight at room temperature, the only significant change was the disappearance of MeCH=CHS(O)SR type of tion–sulfines. In terms of quantitative analysis, there is some variation between the different extraction methods.

Organoleptic assessment of distillates by steam distillation of onions at room temperature shows that intensifies the taste and smell compared to smell freshly cut plants. From the point of view of plant specimens, the situation is ambiguous. The relative percentage of the various alkyl groups may vary depending on the, depending on the variety of plant, depending on the stage of development and on the growth and storage conditions. Regarding plant samples, they exhibit variations in percentages of the methyl group.

Tion–sulfines mono–and bis–β–γ–unsaturated derivatives

First tion–sulfines found was allicin, so it will be considered first chemistry of this compound. Is a colorless, unstable antibacterial and characteristic smell of garlic? While allicin was first described as optically inactive, more recent works suggests that in fact is naturally optically active, as determined by HPLC detector qualitative chiral quantitative polarimeter.

The allicin has a specific rotation of –3.90°, since optical purity is unknown.

Tion–sulfines such as methyl–2–methyl–2–propantiosulfinat were prepared in optically active form [8]. In the absence of the tert–butyl group or other bulky, they tend to become unstable optically. If the optical activity of the allicin is real, the question is what is its origin?

According to the above proposed mechanisms for the formation of the tion–sulfines, if allicin naturally derived from 2–propensulfenic free achiral or its anion, then it must be achiral. On the other hand, if sulfenic acid remains bound through the alliinase hydrogen bond where it is attacked by a second free sulfenic acid, it is possible induction asymmetry results in allicin optically active. Further research is needed to clarify these possibilities. Decomposition of native allicin result in sulfur dioxide, allyl alcohol, dymetiltrisulfur, diallyl mono–, di–and trisulfides and allyl–methyl–di–and trisulfides, while passing by gas chromatography provides a mixture in a ratio of 2.4:1 3–vinyl–3,4–dihydro–1,2–ditiin 3–vinyl–3,6–dihydro–1,2–ditiin. Tion–sulfines (RSO2SR') with disulfide produced by disproportionation most tion–sulfines, no formation of allicin. Compounds of the 3–vinyl–3,4–dihydro–1,2–ditiin 3–vinyl–3,6–dihydro–1,2–ditiin were considered to be products of dehydrogenation allicin formed according to the equation formation –propyl–1–propenyl disulfide of propil propantiosulfinates. The studies made of other persons on the mechanism of decomposition of allicin were induced by a collaborative study with other researchers on identifying several antithrombotic substances isolated from extracts of garlic. Chromatographic separation of the minced garlic solution resulted menthol allicin, diallyl di–, tri–and tetrasulphides, ally–metiltrisulfura, 2–vinyl–2,4–dihydro–1,3–ditiin, 3–vinyl–3,4–dihydro–ditiin –1,2–isomers with two polar compounds, showing the largest antithrombotic activity [9].

Substances were called (E)–and (Z)–ajoene (origin from the Spanish word for garlic origin "ajo", pronounced "ho"), characterized by spectroscopy and synthetic methods as (E)–and (Z)–4,5,9–tritiadodeca–1,6,11–trien–9 oxide.

Final Remarks

What could be more familiar and enjoyable than the fresh minced garlic, chopped or boiled onion, steaming leek, chives finely cut, immature or delicate tales? Adjectives associated with these herbs are: spicy, imposing, and distinct. Even Latin name *Allium* derives from the Celtic word "*all*" which means harsh, betrays the presence of flavors and smells, all with one common element: sulfur. Most of this sulfur–containing *alil* compounds originates from *Allium*. The presence of these organosulphur compounds defines the character of this species.

The great American poet Carl Sanburg said: "*Life itself is like an onion: it has a stunning number of layers. Removed one by one and sometimes starts cry*". "Number of layers" of the onion correlates with the structure of the alliaceous plants, representing microcosms in the field of chemistry [10]. More specifically, the composition of the alliaceous plants provide example of sulfur compounds with physiological activity such as:

organosulphur mediator/agent which has unusual links due to the stereo chemical features related to the presence of sulfur;

unusual organosulphur heterocycles with important spectroscopic properties;

reactions redox involving sulfur compounds;

pericycles reactions involved in synthetic organic chemistry.

As to the extracts and the potions of the garlic and onion were used in folk medicine, commercial products derived from these plants are widely in use in many countries.

Moreover, according to epidemiological evidence, reduced risk of cancer is associated with a high consumption of alliaceous plants. From this reason health organizations recommend the use of garlic and onions as feedstock for diets designed to prevent cell malignancy. For all these reasons, a detailed research of the organosulphur chemistry of the genus *Allium* seems justified.

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