CLVII. THE LIBERATION OF METHYL SULPHIDE BY SEAWEED.

By PAUL HAAS.

From the Botanical Department of University College, London.

(Received April 12th, 1935.)

THE smell given off from seaweed is of two kinds—that associated with decomposing weed and that evolved by the weed in its natural condition. It is the smell of decomposing weed which is usually the more noticeable by the seaside, being characterised as a rule by a more or less distinct odour of hydrogen sulphide which arises in part, presumably, from the putrefactive reduction of the organically combined sulphates which form a marked characteristic of so many marine algae [Haas, 1921; Haas and Russell-Wells, 1923]. There do not appear to be any recorded observations on the nature of volatile odoriferous principles given off by undecomposed seaweed, and it is with this aspect of the question that the present communication deals. The immediate incentive for this investigation was the peculiarly penetrating, somewhat sickly odour, suggestive of a volatile phosphorus compound, given off from *Polysiphonia fastigiata* on drying.

The persistent occurrence of this smell, no matter from what locality or at what season of the year the material had been collected, suggested that the smell was due to some change inherent in the weed, associated either with the drying process or with injury due to cutting, and not to accidental contamination or to bacterial action; the latter suggestion was moreover rendered improbable by the short interval elapsing between the time of collection of the weed and the appearance of the smell. The fact that material which had been killed by immersion in boiling water no longer gave the smell suggested that the production of the smell was in some way connected with a disturbance of the normal metabolism of the plant. The investigation of this matter is reserved for a future occasion.

EXPERIMENTAL.

With a view to identify the odoriferous principle concerned a five-litre flask was filled as rapidly as possible with freshly gathered cut up weed. The flask, fitted with a cork through which passed a long tube reaching to the bottom and a short delivery tube, was placed in a large water-bath kept at 30°. By means of a filter-pump a current of air charged with the evolved gas was then drawn through a series of different solvents such as water, alcohol or acetone; in each of these the gas was soluble, imparting a strong smell to the solution. On passing the gas previously dried by quicklime and calcium chloride into concentrated sulphuric acid it was likewise absorbed, but the resulting solution was odourless, though on dilution with water the odour at once reappeared. This circumstance rendered possible the collection of a reserve of gas for subsequent examination; it was found, in fact, that the gas could be recovered unchanged from this solution after six months by dropping it carefully into ice-cold water.

On passing the dried gas into a dilute solution of bromine in carbon tetrachloride the colour of the bromine was rapidly discharged with the simultaneous

formation of clusters of lemon-yellow glistening crystals. Pressed on a porous porcelain tile these crystals were found to be both volatile and deliquescent, and even when placed in a desiccator over phosphorus pentoxide they tended to disappear in the course of a short time. This substance was readily soluble in water, alcohol, ether and chloroform, but could be recrystallised from hot carbon tetrachloride, though not without some loss due to volatilisation, and melted with evolution of gas at 93–94°.

A small quantity of this substance, heated in a Carius tube for six hours to 300° with pure concentrated nitric acid, free from sulphuric acid, yielded a considerable quantity of sulphuric acid but not a trace of phosphoric acid, thus showing that it contained sulphur. A search in the literature for a bromine derivative of an alkyl sulphide having the melting-point above quoted proved unavailing, and being unfamiliar with the smell of alkyl sulphides I consulted Prof. Challenger who suggested that the smell of an aqueous solution of the gas evolved from the weed resembled that of methyl sulphide. I therefore procured from Messrs British Drug Houses an authentic sample of methyl sulphide and dissolved a little of it in water; on drawing air through the solution, drying the issuing gas with calcium chloride and passing it into a dilute solution of bromine in carbon tetrachloride as before, the same lemon-yellow crystals appeared; these crystals likewise melted at 93–94°, and when mixed with some of the crystals obtained from the natural source still melted at the same temperature, thus establishing the identity of the material prepared from the two sources. This circumstance could leave no doubt that the gas given off from *Polysiphonia* was in fact methyl sulphide.

On referring to the literature it was found that Cahours [1875] had obtained by the action of bromine on methyl sulphide in the presence of water a solution which on evaporation over sulphuric acid deposited amber-yellow transparent glistening octahedral crystals; he stated that the crystals were deliquescent but did not mention that they were volatile or that they had a melting-point. On repeating this preparation according to his description it was found that his crystals were in fact identical with these produced in carbon tetrachloride, in the absence of water, and had the same melting-point, 93–94°, which was not depressed by admixture with some of the crystals prepared from the *Polysiphonia* gas. It seems desirable therefore to put these facts on record and so amplify the data furnished by Cahours concerning this compound which he was the first to prepare.

With a view still further to confirm the identity of the substance evolved from *Polysiphonia fastigiata* the dried gas was passed into a saturated alcoholic solution of mercuric chloride and into an aqueous solution of potassium chloroplatinite. The precipitates obtained in each case were proved by their appearance and by their melting-points and mixed melting-points to be identical with the corresponding compounds prepared under identical conditions from the authentic sample of methyl sulphide.

DISCUSSION.

So far as I have been able to ascertain this is the first recorded case of the evolution of methyl sulphide in appreciable quantity from a plant. Traces of this substance have been found in the first runnings of the distillation of certain essential oils, such as American peppermint oil and the oils distilled from species of *Pelargonium* of African origin and from *Brassica juncea* seeds. In all these examples however the methyl sulphide occurs only in very small quantity and is not the sole or even the major constituent of the essential oil, and certainly

cannot be detected in the smell of the original plant, as in the case of *Polysiphonia*.

It is worthy of note that the only other natural source of methyl sulphide recorded is a petroleum oil from Ohio described by Mabery and Smith [1891]. While the occurrence of the same substance in two such widely different materials as seaweed and mineral oil may be no more than a coincidence, it may at least be said that the finding of detectable quantities of methyl sulphide in a seaweed is not inconsistent with the theory of algal origin which has been suggested for some oil fields.

SUMMARY.

1. Methyl sulphide has been identified as the odoriferous principle evolved from *Polysiphonia fastigiata*.
2. The melting-point of the bromine derivative of methyl sulphide, originally prepared by Cahours, is recorded for the first time.
3. Attention is drawn to the other recorded natural occurrences of methyl sulphide.

I should like to express my acknowledgment for help both in collecting material and in some of the preliminary experimental work which was given by Mr W. K. H. Karstens during his tenure here of a grant from the Vollenhoven foundation of Leyden University.

REFERENCES.

- Cahours (1875). *Compt. Rend. Acad. Sci.* **60**, 650.
Haas (1921). *Biochem. J.* **15**, 469.
— and Russell-Wells (1923). *Biochem. J.* **17**, 696.
Mabery and Smith (1891). *Amer. Chem. J.* **13**, 237.

Note added May 23rd, 1935. Since writing the above I have been able to examine two other samples of *Polysiphonia nigrescens* and have found that they likewise gave off methyl sulphide.