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TWO SULFUR CONSTITUENTS FROM *ALLIUM SCHOENOPRASUM*

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Key Word Index—*Allium schoenoprasum*, Alliaceae, steam volatile oil, methyl pentyl disulfide, pentyl hydrodisulfide

Abstract—Two kinds of disulfide has been isolated from *Allium schoenoprasum* and their structures established as methyl pentyl disulfide and pentyl hydrodisulfide by spectroscopic and synthetic methods These compounds, which smell like sweet onions, are important aroma constituents

INTRODUCTION

The flavor constituents of *Allium* have been widely studied [1–4], especially those of the onion, *A cepa* [5–8] In our previous paper [9], the new sulfur cyclic compounds, *cis*- and *trans*-3,5-diethyl-1,2,4-trithiolane, were reported in the volatile oil of the flowers of *A cepa*

The volatile flavor constituents of *A schoenoprasum* have been reported by Wahlroos and Virtanen [10], but methyl pentyl disulfide (**1**) and pentyl hydrodisulfide (**2**) have not been described before In this paper we report their isolation and synthesis

RESULTS AND DISCUSSION

A volatile oil was obtained by steam distillation of the green leaves of *A schoenoprasum* L The oil was placed on a column of Si gel and divided into three fractions by elution with hexane, hexane–ether (19 1), (9 1), (4 1) and ether Compounds **1** and **2** were isolated from the fraction eluted with hexane and purified by prep GC **1** and **2** were present in amounts of *ca* 1 6% and 2 5% of the steam volatile oil

1 exhibited IR absorptions at 1430, 1415, 1305, 1270 and 1250 cm^{-1} attributed to $-S-CH_2-$, $-S-Me$, $-SS-CH_2$ and $-SS-Me$ The mass spectrum ($[M+2]^+$ ion at *m/z* 152, $[M]^+$ ion at *m/z* 150) showed a base peak at *m/z* 43 due to expulsion of $C_3H_7^+$, and other extremely characteristic fragments appeared at *m/z* 122, 108, 94 and 80 Its ^1H NMR spectrum showed signals assignable to two methyls at δ1 02 (*t*, $J = 8$ Hz) and 2 56 (*s*), methylenes at 1 54 (*s*), 1 78 (*m*, $J = 8$ Hz) and 2 87 (*t*, $J = 8$ Hz) From these data, the only possible structure for this compound is methyl pentyl disulfide, i e $MeSS(CH_2)_4Me$ Methyl pentyl disulfide was synthesized by oxidation of 1-pentanethiol and methanethiol with hydrogen peroxide

2 exhibited an IR absorption at 2500 cm^{-1} attributed to $-S-SH$ The mass spectrum ($[M+2]^+$ ion at *m/z* 138, $[M]^+$ ion at *m/z* 136) showed a base peak at *m/z* 71 due to expulsion of $[M-SSH]^+$ Its ^1H NMR spectrum appeared similar to that of **1**, but the signal at δ2 56 assigned to the methyl had disappeared, and a fresh signal at δ2 15 (1H, *s*) corresponding to $-S-S\underline{H}$ appeared From these data, the only possible structure for this compound is pentyl hydrodisulfide, i e $Me(CH_2)_4SSH$ Pentyl hydrodisulfide was synthesized by oxidation of 1-pentanethiol and sodium sulfide with hydrogen peroxide The natural and synthetic products in both cases agreed entirely in all respects (IR, MS, ^1H NMR, GC)

EXPERIMENTAL

The δ values in the ^1H NMR spectra (200 MHz) are expressed in ppm downfield with TMS as int standard and $CDCl_3$ as solvent The MS were measured at 70 eV

Plant material Allium schoenoprasum L was collected in the Yamaguchi-prefecture, Japan, in June 1981 After steam distillation of 6 48 kg of the green leaves, 2 5 g (0 038%) of the volatile oil was obtained by extraction of the distillate with Et_2O and by the evaporation of the solvent under N_2

Isolation of methyl pentyl disulfide (**1**) *and pentyl hydrodisulfide* (**2**) 2 5 g of the volatile oil was chromatographed on Si gel and eluted with hexane to separate the aliphatic sulfur compounds These were purified by prep GC

Methyl pentyl disulfide (**1**) Colorless liquid $[\alpha]_D^{25}$ 0° IR ν_{max}^{NaCl} cm^{-1} 2975, 2950, 1460, 1380, 1290, 900, 780, 740 MS (probe) 70 eV (rel int) 152 $[M+2]^+$ (4), 150 $[M]^+$ (33), 122 $[Me-SS-CH_2-CH_2-Me]^+$ (58), 108 $[Me-SS-CH_2-Me]^+$ (20), 94 $[Me-SS-Me]^+$ (27), 80 $[Me-SSH]^+$ (70), 43 $[C_3H_7]^+$ (100) ^1H NMR (200 MHz, $CDCl_3$) δ2 87 (2H, *t*, $J = 8$ Hz, $Me-SS-C\underline{H}_2-$), 2 56 (3H, *s*, $\underline{Me}-SS-$), 1 78 (2H, *m*, $J = 8$ Hz, $-SS-CH_2-CH_2-$), 1 54 [4H, *s*, $-(C\underline{H}_2)_2-$], 1 02 [3H, *t*, $J = 8$ Hz, $-(CH_2)_2-Me$]

Pentyl hydrodisulfide (**2**) Colorless liquid $[\alpha]_D^{25}$ 0° IR ν_{max}^{NaCl} cm^{-1} 2900, 2820, 2500, 1460, 1380, 1290, 1270, 1220, 780, 660 MS (probe) 70 eV (rel int) 138 $[M+2]^+$ (5), 136 $[M]^+$ (72), 103 $[M-SH]^+$ (19), 71 $[M-SSH]^+$ (100), 55 $[C_4H_7]^+$ (12) ^1H NMR (200 MHz, $CDCl_3$) δ2 85 (2H, *t*, $J = 8$ Hz, $Me-SS-CH_2-$), 2 15 (1H, *s*, $-SSH$), 1 77 (*m*, 2H, $J = 8$ Hz, $-SS-CH_2-CH_2-$), 1 53 [4H, *s*, $-(CH_2)_2-$,], 1 00 [3H, *t*, $J = 8$ Hz, $-(CH_2)_2-Me$]

Synthesis of methyl pentyl disulfide (**1**) *and pentyl hydrodisulfide* (**2**) A soln of 1-pentanethiol (4 5 g, 0 05 mol) and methanethiol (2 4 g, 0 05 mol) were added to 50 ml 10% NaOH The mixture was stirred at room temp for 4 hr, after the mixture was cooled to 0°, 34 g (32 ml, 0 3 mol) of 30% H_2O_2 was added The reaction mixture was stirred at 0° for 1 hr and extracted with Et_2O The Et_2O layer was separated, washed and dried The Et_2O was removed, and an oily liquid (7 3 g) was obtained which was a mixture of methyl pentyl disulfide and dipentyl disulfide Methyl pentyl disulfide was purified by prep GC and agreed in all its spectral properties with the natural compound

Pentyl hydrodisulfide was synthesized by oxidation of 1-pentanethiol (4 5 g, 0 05 mol) and Na_2S (3 9 g, 0 05 mol) with 34 g 30% H_2O_2 in 50 g 10% NaOH Pentyl hydrodisulfide was purified by prep GC and agreed in all its spectral properties with the natural compound

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n-ALKANES OF *HYPERICUM PERFORATUM*: A REVISION

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Key Word Index—*Hypericum perforatum*, Hypericaceae (Guttiferae), *n*-alkanes

Abstract—A study of the *n*-alkanes of *Hypericum perforatum* L revealed the presence of all members in the series C_{16}–C_{29} Contrary to previous reports the prevailing *n*-alkane was found to be nonacosane which was isolated in the pure state and identified on the basis of physical and spectral properties

INTRODUCTION

The presence of antibacterial substances in species of the genus *Hypericum* has been known for almost 40 years [1–3], extracts of *H perforatum* have been used clinically in Russia to treat infections [4], and in the U S A as a food preservative [3] Recently we reported on the relative stereochemistry [5] of the active principle which has been designated hyperforin [4, 6] As part of our study on the constituents of *H perforatum* which is commercially available as dried plant material from Scandinavian drugstores, we wish to report the results from an examination of the hydrocarbon fraction of the acetone extract

RESULTS AND DISCUSSION

GC/MS and co-chromatography with authentic alkanes revealed the presence of all *n*-alkanes in the series C_{16}–C_{29} Nonacosane ($C_{29}H_{60}$) prevailed and was obtained in virtually pure state (mp 63–64°) and identified beyond doubt on the basis of physical and spectral properties

Except for octacosane, none of these *n*-alkanes have previously been reported to be present in *H perforatum* Mathis and Ourisson claimed to have isolated a mixture of octacosane and triacontane ($C_{30}H_{62}$) judging from its mp, 63–64°, and mass spectrum [7] The former of these *n*-alkanes was present in our material in minute quantities (cf Table 1), while the latter was possibly present but in too small amounts to be identified with certainty Zellner and Porodko [8] reported on the hydrocarbons of *H perforatum* and suggested the presence of $C_{33}H_{68}$ and $C_{36}H_{74}$ on the basis of combustion analysis and MW determination according to Rast Because of the experimental errors associated with these methods, the fact that the mp (63°) of their $C_{33}H_{68}$-sample corresponds well with that of nonacosane, and due to the dominance of nonacosane in our plant material, we have reason to question the previously reported identifications of octacosane, triacontane and $C_{33}H_{68}$

Saturated straight and branched hydrocarbons of shorter chain have previously been reported to be present in the essential oil of *H perforatum* 2-methyloctane [9, 10],