

Table II. Conversion of [^{14}C]-L-Valine and [^{14}C]Isobutyric Acid into Volatiles by Asparagus Tissue Slices

Precursor (50 μCi):	[^{14}C]-L-Valine	[^{14}C]Isobutyric acid
Incubation time, h	5	13
Radioactivity in the aroma extracts, %	1.9	2.3
		3
		15.9
Distribution of Radioactivity among Volatile Components, %		
2-Oxo-3-methylbutyric acid	3.0	17.5
Isobutyric acid	7.0	2.1
Methacrylic acid	0.5	42.5
3-Mercaptoisobutyric acid	65.5	3.2
3-(Methylthio)isobutyric acid	15.1	61.6
Asparagusic acid	0.3	1.5
		28.5
		0.3

discs, but 3-S-acetylthiomethacrylic acid and asparagusic acid showed only small amount of radioactivity. The experiments will be continued. The discussed biosynthetic route is an analogous reaction to the formation of S-1-propenylcysteine sulfoxide in onion (Schwimmer and

Friedmann, 1972; Schwimmer and Guadagni, 1968).

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Formation of Flavor Components in Asparagus. 2. Formation of Flavor Components in Cooked Asparagus

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Aroma components of cooked white asparagus were enriched by liquid-liquid extractions at different pH values and separated by the method of adsorption chromatography into fractions of graduated polarity. Individual components or fractions were isolated and enriched by means of preparative gas chromatography for capillary gas chromatography-mass spectrometry. More than 100 constituents (among them: thiophenes, thiazoles, pyrroles, pyrazines, aldehydes, ketones, alcohols, and phenols) have been identified. Most of the aroma components are formed during heating processes: by thermal degradation of precursors like S-methylmethionine, asparagusic acid, p-coumaric acid, and ferulic acid, by lipid oxidation of linoleic acid and linolenic acid, and via Maillard reactions.

The typical flavor components of asparagus are formed during cooking of the plant material. According to Freytag and Ney (1968, 1972), dimethyl sulfide is formed as a principal aroma constituent in cooked asparagus. S-Methylmethionine is supposed to be the corresponding precursor. This amino acid had been identified by Challenger and Hayward (1954) in uncooked asparagus. Casey et al. (1963) showed that dimethyl sulfide (Me_2S) is formed during the heating of methionine with pectin. The latter reacts to give S-methylmethionine which in turn decomposes to afford dimethyl sulfide. Therefore, Me_2S is known as a common constituent in most cooked vegetable. Besides Me_2S , more than 100 constituents (among them: aldehydes, ketones, alcohols, phenols, and heterocyclics) have been identified by means of liquid-liquid extraction at different pH values, LSC, GLC, and MS.

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These aroma constituents are formed during cooking of asparagus: (1) by thermal fragmentation of precursors like S-methylmethionine, asparagusic acid, p-coumaric acid, and ferulic acid, (2) by oxidative degradation of unsaturated fatty acids, (3) via Maillard reactions.

MATERIAL AND METHODS

Sample Preparation. White asparagus (20 kg) was homogenized with 20 L of phosphate buffer (0.1 M, pH 6.8), refluxed for 30 min, and pressed at 400 atm to give 36 L of filtrate.

Liquid-Liquid Extraction. Eighteen liters of the obtained filtrate was directly extracted with pentane-ether (1:1) for 24 h at pH 6.8 to isolate neutral compounds. The other part of the filtrate was adjusted to pH 8.5, and basic compounds were isolated in the same way. Both extracts were dried over Na_2SO_4 , concentrated to a definite volume (3 mL), and separated by adsorption chromatography.

Adsorption Chromatography. A separation according to polarity of components was carried out by liquid-solid chromatography. Ten 300- μL fractions of the extracts were separated on two different columns. Column A (250 \times 12 mm i.d.) was filled with two parts of Al_2O_3 90 (acidic,

Table I. Components Characterized in Cooked Asparagus

Compound	LSC	I_R (UCON)	Mass spectral data	Approx concn, ppb
Sulfur components				
(1) Dimethyl sulfide			62* 47 61 43 46	3300
(2) Dimethylsulfone	A VI	1483	79 94* 45 29 48 63	30
(3) 3-(Methylthio)propanal	B III	1228	48 57 56 61 85 104*	Tr
(4) 3-(Methylthio)propanol	B IV	1350	57 58 61 106* 48	10
(5) Methyl 1,2-dithiolane-4-carboxylate	A II	1742	164* 41 104 45 78 59	7000
(6) Ethyl 1,2-dithiolane-4-carboxylate	A II	1778	178* 41 104 105 86 73	50
(7) Methyl 3-S-acetylthiomethacrylate	A V	1586	43 73 100 142 105 174*	15
(8) 1,2-Dithiocyclopentene	B I	1284	103 45 104* 71 39 72 64	70
(9) 3-Vinyl-3,6-dihydro-1,2-dithiine	B I	1482	72 71 111 45 144* 97 103	Tr
(10) 3-Vinyl-3,4-dihydro-1,2-dithiine	B I	1561	72 71 45 144* 111 97 103	20
(11) 2-Formylthiophene	B I	1383	111 112* 39 45 83	10
(12) 3-Methyl-2-formylthiophene	B I	1443	125 126* 97 45 53	70
(13) 2-Acetylthiophene	B I	1479	111 126* 39 43 45 83	Tr
(14) 2-Hydroxymethylthiophene	B IV	1619	114* 85 97 45 113 81	20
(15) 4-Methylthiazole	B I	1149	99* 71 72 45 39 69	Tr
(16) 2-Acetylthiazole	B I	1382	43 127* 99 58 57 112	10
(17) Benzothiazole	B I	1627	135* 108 69 63 45 82	20
Pyrroles, pyridines, pyrazines, furans				
(18) 1-Methyl-2-formylpyrrole	B II	1348	109 108* 80 78 53 39	Tr
(19) 1-Methyl-2-acetylpyrrole	B II	1417	80 123* 53 43	Tr
(20) 2-Formylpyrrole	B IV	1645	95* 94 39 66	60
(21) 2-Acetylpyrrole	B IV	1623	94 109* 66 39 43	90
(22) 5-Formyl-6-methyl-2,3-dihydro-1H-pyrrolizine	B III		148 149 120 66 134 77 93	10
(23) Pyridine	B II	1010	79* 52 51 50	10
(24) 2-Ethylpyridine	B II	1123	106 107* 79 78 52 51	Tr
(25) Pyrazine	B II	1037	80* 53 26 52	Tr
(26) Methylpyrazine	B II	1082	94* 67 39 40 53	300
(27) 2,5-Dimethylpyrazine	B II	1150	108* 42 39 40 81 28	35
(28) 2,6-Dimethylpyrazine	B II	1156	108* 42 40 39 38 67	200
(29) Ethylpyrazine	B II		107 108* 80 53 52 39	Tr
(30) 2,3-Dimethylpyrazine	B II	1165	67 108* 80 42 40 26	Tr
(31) 2-Ethyl-6-methylpyrazine	B II	1217	121 122* 39 94 56 40	Tr
(32) 2-Ethyl-5-methylpyrazine	B II	1221	121 122* 39 56 94	Tr
(33) Trimethylpyrazine	B II	1234	42 122* 39 81	Tr
(34) 2-Ethyl-3,5-dimethylpyrazine	B II	1283	136* 135 39 108 53 56	Tr
(35) 2-Methyl-5-vinylpyrazine	B II	1287	120* 52 54 39 93 79	Tr
(36) 6,7-Dihydro-5H-cyclopentapyrazine	B II		120* 119 39 41 66 65	Tr
(37) 5-Methyl-6,7-dihydro-5H-cyclopentapyrazine	B II	1406	119 134* 133 39 52 78	Tr
(38) 2-Ethylfuran	B I	904	81 39 96* 41 51 65	Tr
(39) 2-Pentylfuran	B I	1140	81 82 138* 53 39 41	165
(40) 2-Furfural	B II	1206	96* 95 39 29 38	10
(41) 2-Acetylfuran	B II	1266	95 110* 43 39 46 68	Tr
(42) 5-Methyl-2-furfural	B II	1313	110* 109 53 51	Tr
(43) Furfuryl alcohol	B IV	1388	98* 41 39 53 81 97	350
Aldehydes				
(44) Pentanal	A II	887	44 29 41 27 ... 86*	Tr
(45) Hexanal	A III	975	41 43 44 56 57 82 67 72*	100
(46) 2-Hexenal	A III	1048	39 41 69 55 57 83 98*	Tr
(47) 2-Heptenal	A III	1169	41 55 56 83 ... 112*	30
(48) 2-Octenal	A III	1273	41 39 70 83 55 57 69 ... 126*	Tr
(49) 2-Nonenal	A III	1375	41 39 43 70 55 57 69 83 ... 140*	10
(50) 2,4-Nonadienal	A III	1494	81 41 39 67 65 53 95 ... 138*	Tr
(51) 2,4-Decadienal	A III	1600	81 41 39 67 55 95 83 ... 152*	Tr
(52) 2,4,7-Decatrienal	A III	1598	121 77 91 83 94 150* 65 79	15
(53) Benzaldehyde	A III	1274	77 106* 105 51	Tr
(54) 2-Phenylacetaldehyde	A III	1378	91 120* 92 65	Tr
(55) 2-Phenyl-2-butenal	A III	1623	117 115 91 146*	10
Ketones				
(56) 2-Pentanone	A III	890	43 27 29 57 86* 41	Tr
(57) 2-Hexanone	A II	968	43 58 29 41 ... 100*	10
(58) 2-Heptanone	A III	1068	43 58 71 55 83 ... 114*	15
(59) 2-Nonanone	A II	1263	43 58 71 ... 142*	Tr
(60) 2-Undecanone	A II	1469	58 43 71 ... 170*	Tr
(61) 2-Pentadecanone	A III	1868	58 43 71 ... 226*	Tr
(62) 2-Hepten-4-one	A III	1163	69 41 39 97 84 ... 112*	Tr
(63) 3-Octen-2-one	A III	1249	55 43 111 41 97 39 ... 126*	10
(64) 3-Nonen-2-one	A III	1312	41 43 55 97 111 84 ... 140*	50
(65) 3,5-Octadien-2-one	A III	1363	95 67 81 55 39 105 110 124*	70
(66) 3,5-Nonadien-2-one	A III	1470	95 138* 123 77 52 65 41 43	10
(67) 3,5-Decadien-2-one	A III	1537	95 109 152 123 110 96 67	10
(68) 2,5-Hexandione	A IV	1436	43 99 71 55 ... 114*	90
(69) 3-Hydroxy-2-butanone	A IV	1315	45 43 27 29 ... 88*	6400
(70) 3-Hydroxy-2-pentanone	A IV		59 31 43 45 41 58 ... 102*	80

Table I (Continued)

Compound		I_K	LSC (UCON)	Mass spectral data	Approx concn, ppb
Alcohols					
(71) Butanol	A IV	1004	41 43 45 31 56 55 74*		160
(72) 3-Methyl-1-butanol	A III	1062	41 55 70 43 31 39 57		80
(73) Pentanol	A IV	1101	41 42 55 70 31 39 57		2300
(74) Hexanol	A IV	1198	56 43 41 55 31 39 69 84		8400
(75) Heptanol	A IV	1301	70 56 41 55 43 69 83 98		25
(76) Octanol	A IV	1400	56 41 69 70 55 83 43 31 112		70
(77) Nonanol	A IV	1498	56 41 43 57 69 84 98 ... 126		60
(78) Decanol		1597	41 43 55 57		Tr
(79) 2-Pentanol	A IV	994	45 31 43 55 59 74		25
(80) 2-Octanol	B III	1281	45 55 41 43 97 112		Tr
(81) 2-Nonanol	B III	1397	45 41 43 69 55 98 ... 126		Tr
(82) 2-Decanol	B III	1496	45 41 43 ...		Tr
(83) 1-Penten-3-ol	A IV	1016	57 39 41 43 55		80
(84) 1-Octen-3-ol	A III	1298	57 41 43 72 39 85		300
(85) 2-Pentenol	A IV	1144	57 41 43 68 71 86		100
(86) 2-Hexenol	A IV	1246	57 41 43 82 67 69 71		240
(87) 2-Heptenol	A IV	1342	57 41 43		300
(88) 2-Octenol	A IV	1434	57 41 39 67 68 81		300
(89) 2-Nonenol	B III	1526	57 41 43 67 68 81		20
(90) 2,4-Hexadienol	A IV	1363	41 39 55 43 83 69 79		20
(91) 2,4-Heptadienol	A IV	1459	41 55 39 59 74 83 79		65
(92) 2,4-Heptadienol	A IV	1464	41 55 83 68 39 79 67		270
(93) 2,4-Nonadienol	A IV	1656	41 55 39 67 79 83 84		50
(94) 2,4-Decadienol	A IV	1747	55 41 83 67 84 79 81		70
(95) 2,4-Decadienol	A IV	1753	41 55 83 84 67 79 81		140
(96) Benzyl alcohol	A IV	1569	79 108* 107 77 91		410
(97) 2-Phenylethanol	A IV	1603	91 92 122* 65 39		440
Phenols					
(98) Phenol	B III	1661	94* 66 39 65		40
(99) <i>O</i> -Cresol	B III	1681	108* 107 79 77 39		10
(100) <i>m</i> -Cresol	B III	1744	107 108* 77 79		20
(101) <i>p</i> -Cresol	B III	1750	107 108* 77 79		20
(102) 4-Vinylphenol	B III	1981	120* 91 119 65 39		260
(103) 4-Hydroxybenzaldehyde	B IV		107 122* 121 77 91		40
(104) Guaiacol	B II	1544	109 81 124*		50
(105) Veratrol	B II	1484	138* 95 123 77 52 51		10
(106) 4-Vinylguaiacol	B III	1832	135 150* 107 77		850
(107) Vanillin	B IV		152* 151 91 109		1200
(108) Acetovanillone	B IV		151 166* 123 77		80
Lactones					
(109) γ -Hexalactone	A V	1628	85 29 27 41 56 ... 114*		Tr
(110) 2-Hexen-4-olid		1357	83 55 27 29 112* 39		70
(111) γ -Heptalactone		1721	85 29 27 56 100		100
(112) γ -Octalactone		1831	85 29 27 56 100		10
(113) γ -Nonalactone		1939	85 56 29 27 100 114		10
Acids					
(114) Methacrylic acid		910	41 100* 39 69		
(115) 2-Oxopropionic acid		995	43 29 42 59 102*		
(116) 2-Oxo-3-methylbutyric acid		1129	43 71 29 41 59 39 130*		15
(117) 2-Oxo-3-methylpentanoic acid		1215	57 85 41 29 144* 39 74		190
(118) 2-Oxo-4-methylpentanoic acid		1230	57 85 41 43 144* 29 59		830
(119) 9-Oxononanoic acid			74 41 55 87 111 83 143 155 ... 186*		
(120) 12-Oxododecenoic acid			55 41 98 74 83 87 166 ... 194*		
(121) Azelaic acid		1788	55 74 59 152 185 143		20
(122) Furoic acid		1211	95 39 126*		15
(123) Pyrrolic acid			94 125* 39 66		

activity V, Merck 1078) and one part of silica gel 60 (activity II-III, Merck 7734) to separate neutral compounds. Six fractions (90 mL each) were eluted with solvents of increasing polarity: (I) pentane (P)-methylene chloride (MC) (9:1), (II) P/MC (3:1), (III) P/MC (1:1), (IV) P/ether (E) (9:1), (V) P/E (1:1), (VI) ether. Column B (200 \times 9 mm i.d.) was filled with Al₂O₃ 90 (acidic, activity V, Merck 1078) to separate basic compounds. Five fractions (30 mL each) were eluted with solvent: (I) P/MC (9:1), (II) P/MC (3:1), (III) P/E (9:1), (IV) P/E (1:1), (V) ether. The different fractions were concentrated to a definite volume and analyzed by gas chromatography.

Gas Chromatography. Gas chromatography conditions were as Tressl et al. (1977) described in Part 1. One additional column was used for preparative separations

(column 4: 4 m (4 mm i.d.) 10% CW20M on Chromosorb WAW/DMCS, 60-80 mesh, temperature program 60-210 $^{\circ}$ C, 4 $^{\circ}$ C/min).

Capillary Gas Chromatography-Mass Spectrometry. See Part 1, Tressl et al. (1977). Additional column: 100 ft (0.02 in. i.d.), stainless steel S.C.O.T. column P4G 1540 (Perkin-Elmer), 12 mL He/min, temperature program 70-140 $^{\circ}$ C, 2 $^{\circ}$ C/min.

Reference Compounds. Reference samples were purchased as far as possible or were gifts from Haarman and Reimer, Holzminden, Firmenich, Geneva, Oril, Paris. The aldehydes *trans*-2-heptenal, 2,4-hexadienal, and 2-phenyl-2-butenal, as well as 3,5-octadien-2-one, 3,5-nonadien-2-one, and 3,5-decadien-2-one were synthesized by aldol condensations. Acetaldehyde (0.05 mol) in 20 mL

LIQUID-LIQUID-EXTRACTION		
pH=2,5 Methylation	pH=6,8 —	pH=8,5 —
LIQUID-SOLID-CHROMATOGRAPHY		
SiO ₂	SiO ₂ /Al ₂ O ₃	Al ₂ O ₃
Aliphatic Acids	Alkylfuranes	Thiophenes, Thiazoles
Aromatic Acids	Ketones, Esters (sac)	Pyrazines, Ketones
Oxacids	Ketones, Aldehydes (unsat.)	Alcohols, Phenols
Sulphur Containing Acids	Alcohols, Phenols	
Hydroxyacids	Pyrazines	
Dicarboxylic Acid Lactones Mercaptaoacids		
GAS-LIQUID-CHROMATOGRAPHY		
MASS SPECTROMETRY		

Figure 1. Scheme for isolation, separation, and identification of the complex aroma of asparagus.

of ether was stirred with 2 mL of KOH (50%) and refluxed with propanal, *trans*-2-butenal, pentanal, and phenylacetaldehyde to give the corresponding aldehydes. Acetone (20 mL) was refluxed with *trans*-2-pentenal, *trans*-2-hexenal, and *trans*-2-heptenal to yield the dienones. Alcohols were obtained by reducing the corresponding aldehydes with LiBH₄. The synthesized substances were purified and isolated by means of LSC and preparative GC and identified by comparison of MS, IR, and GC retention with published data (Schreiber, 1974; Buttery, 1975).

RESULTS AND DISCUSSION

The investigation of essential trace components in complex mixtures like heated vegetable aroma concentrates is rendered extremely difficult because these compounds are masked by the more strongly concentrated fatty acids and by other constituents. Figure 1 shows a research scheme of the methods by means of which trace compounds in asparagus were investigated. By means of liquid-liquid extraction, enriched aroma concentrates of cooked asparagus were separated by the method of adsorption chromatography (LSC) into fractions of graduated polarity. These separations occur strictly according to functional groups. This procedure was followed by further separation of the compounds by means of gas chromatography in combination with selective detectors (FPD), preparative gas chromatography, and capillary gas chromatography-mass spectrometry. As the separated compounds left the GC column, they were subjected to a sensorial "sniff test" in order to determine whether or not they contribute to aroma. The organic acids were extracted with pentane-ether (1:1) at pH 2.5, transformed into the methyl esters, and separated on silica gel as Tressl et al. (1977) described in Part I. Alkylfuranes, ketones, esters, aldehydes, alcohols, and phenols were extracted at pH 6.8 and separated on silica gel-aluminium oxide (2:1). By this method the acids were eliminated. Thiophenes, thiazoles, pyrazines, pyrroles, and phenols were extracted at pH 8.5 and cleanly separated on aluminum oxide. Trace constituents were isolated and enriched by preparative gas chromatography for capillary gas chromatography-mass spectrometric investigation. In our opinion, these simple methods are most effective in tracing essential components in complex mixtures. On the other hand, the extraction, liquid-solid chromatographic separation, and gas chromatographic separation were carried out with internal standards. Therefore, most of the constituents were determined semiquantitatively. The results are summarized in Table I.

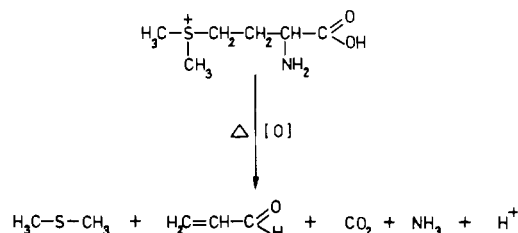


Figure 2. Thermal fragmentation of *S*-methylmethionine.

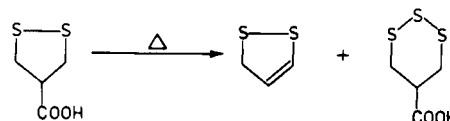


Figure 3. Thermal fragmentation of asparagusic acid during cooking of asparagus.

Formation of Constituents during Cooking of Asparagus and Thermal Fragmentation of Precursors. During cooking of asparagus, Me₂S is formed as a principal aroma constituent (Freitag and Ney, 1968, 1972). Dimethyl sulfide amounts to 3 to 10 ppm during a heating period of 20 to 30 min. In this concentration, Me₂S acts as a contributing aroma constituent. *S*-Methylmethionine is supposed to be the corresponding precursor. As the respective model tests showed, Me₂S is formed during heating of this amino acid. In the presence (Figure 2) of α -diketones, acrolein had been characterized. The latter presumably reacts with H₂S, forming the two isomeric dihydrovinylthiines which had been characterized in model tests by heating *S*-methylmethionine, cysteine, and α -diketones. During cooking of asparagus, asparagusic acid is decomposed as shown in Figure 3. Decarboxylation of the acid leads to a cyclic compound (1,2-dithiacyclopentene). This constituent is not very stable and delivers a pleasant smell like cooked asparagus. During this reaction 1,2,3-trithiane-5-carboxylic acid is formed. The methyl ester of asparagusic acid is more stable and is obviously not decomposed during heating. The amount of asparagusic acid decreased from 3500 to 150 ppb during a heating period of half an hour. On the other hand, 1,2,3-trithiane-5-carboxylic acid and 1,2-dithiacyclopentene amount to 300 and 100 ppb, respectively. In our opinion, this is an important reaction in the formation of cooked asparagus flavor.

p-Coumaric acid and ferulic acid are transformed into phenols by thermal fragmentation. This seems to be a general reaction in heat-processed plant material. During the heating-up period, enzymes may split the bound phenolic acids. As the respective model tests showed, only the free phenolic acids were converted into the corresponding phenols (Tressl, 1975, 1976). Eleven phenols were characterized in cooked asparagus. These compounds are of high odor intensity and have very low thresholds. The thermal fragmentation of ferulic and *p*-coumaric acid was proved by means of model tests. In the first step the acid is decarboxylated to the corresponding *p*-vinylphenol which may undergo oxidation to form an aldehyde.

Formation of Volatiles by Oxidative Degradation of Unsaturated Fatty Acids. Most of the volatile constituents identified in asparagus arise through oxidative degradation of linoleic and linolenic acids. Alkanals, 2-alkenals, 2,4-alkadienals, saturated and unsaturated ketones, as well as the corresponding alcohols, are the predominant components. During crushing of the plants or during the heating-up period, lipoxygenases, alcohol-dehydrogenases, and other enzymes may catalyze these

Table II. Enzymatic Splitting of [$U-^{14}C$]Linoleic Acid into Volatiles in Homogenates^a

	Extraction analysis	
	Asparagus	Cucumber
Radioactivity in the extract, %	9.3	5.0
Distribution of radioactivity among volatiles, %		
Pentanal	9.5	0.5
Hexanal	57.7	12.6
2-Heptenal, hexanol	6.5	1.4
Pentanol	3.9	9.1
2-Nonenal	3.3	33.0
2,4-Decadienal	1.3	22.5
2-Nonenol	6.0	2.0
9-Oxononanoic acid	1.5	13.0

^a 12.5 μ L of [$U-^{14}C$]linoleic acid homogenized with 50 g of tissue for 5 min.

reactions, but chemical reactions are also involved (Eriksson, 1975; Grosch et al., 1974; Ohloff, 1973).

Table II shows volatile constituents which result from linoleic acid during homogenization of uncooked asparagus in the presence of oxygen. It can be seen that hexanal and pentanal are the major carbonyls in asparagus, while hexanal, 2-nonenal, and 2,4-decadienal are major components in the homogenates of cucumbers. In cooked asparagus the amounts of aldehydes decrease and the corresponding alcohols are determined as the major components. Most of the aldehydes characterized in cooked asparagus (Table I) arise through oxidative degradation of linoleic and linolenic acids. Recently, 2,4,7-decatrienal had been tentatively identified by Buttery and Ling (1972) in potato chips. 2-Phenylethanal might be formed via Strecker degradation from phenylalanine. 2-Phenyl-2-butenal may arise from 2-phenylethanal and acetaldehyde via aldol-type condensation. Most of the ketones characterized in cooked asparagus had been identified in roasted filberts (Kinlin et al., 1972), in potato chips (Buttery and Ling, 1972), and in dry red beans (Buttery et al., 1975). 3,5-Octadien-2-one, which is present in two isomers, probably *cis,trans* and *trans,trans*, is the major component. This ketone might be derived from linolenic acid by enzymatic oxidative reactions as shown by Grosch (1975) in model tests.

Pentanol, hexanol, and 1-octen-3-ol are the major alcohols. These compounds are derived from linoleic acid. The 2-alkenols as well as the 2,4-alkadienols may arise from the corresponding aldehydes by enzymatic reduction or chemical disproportionation, respectively. The results show that most of the identified constituents in cooked asparagus are lipid oxidation products.

Formation of Volatiles via Maillard Reactions.

During cooking of asparagus, reducing sugars and amino components undergo Maillard reactions. Besides flavorless high molecular melanoidines, volatiles, especially heterocyclics, are formed. The experiments of Hodge (1953, 1967) and Mills et al. (1969) showed that 1-amino-1-deoxy-2-ketoses (Amadori compounds) are formed as intermediates. These compounds are heat labile and decompose via 1-deoxyosones and 3-deoxyosones, respectively. Amadori compounds are supposed to be the essential precursors. 1-Deoxyosones are transformed into α -dicarbonyls with which amino acids can undergo Strecker degradation. Some of the Strecker aldehydes are known to be potent aroma components. During these reactions, the formed amino ketones may be transformed into pyrazines or thiazoles, respectively. At least 20 to 30% of the volatile constituents characterized in cooked asparagus are formed by these reactions. Among them are thiophenes, thiazoles, pyrroles, pyrazines, and furanes.

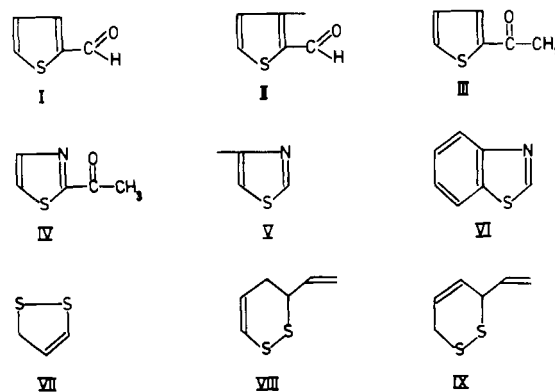


Figure 4. Sulfur-containing heterocyclics characterized in cooked asparagus.

Figure 4 illustrates the results for certain sulfur-containing heterocyclics. By means of liquid-solid chromatography, these compounds were transferred into one fraction, which had a strong aroma like cooked asparagus. Besides the breakdown product of asparagusic acid, 2-acetylthiazole seems to be a contributing constituent. The latter component may be formed from cysteine or cysteamine according to Mulders (1973). 2-Acetylthiazole had been identified by Buttery et al. (1975) as an important compound in cooked red beans. The characterized furanes, pyrroles, and pyrazines are common constituents in heated vegetable and plant material. The 5-formyl-6-methyl-2,3-dihydro-1*H*-pyrrolizine had been identified by Shigematsu et al. (1975) on heating L-proline with glucose.

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