94 000 are more evident in the DS fraction of young leaves than in that of old leaves (Figure 4). Overall, there are fewer differences in young leaves and old leaves of the DS fraction than in those of the BS fraction. In addition to the 96 000 and 94 000 molecular weight bands, band 13 500 is most prominent in young leaves. The bands most distinct in the DS fraction of older leaves have the molecular weights of 61 000, 62 000, and 14 000, and the entire complex of bands in the molecular weight range of 23 000–29 000. This complex of proteins may be part of the light harvesting complex (LHC) of chloroplast thylakoid membranes which has been identified as a group of proteins within this molecular weight range in a wide variety of plants (Grebanier et al., 1979).

From the results, it is apparent that the overall leaf protein composition changes very little with age of the leaf, but some age-specific changes in the polypeptide profiles occur. These data should be considered in evaluation of peanut leaf protein for human consumption; likewise, the leaf age may affect the quality of the leaf protein concentrate in other plant species. The nutritional value of the proteins obtained from different age leaves and cellular fractions should be analyzed and used in determining processing methods of peanut leaves as a dietary supplement.

LITERATURE CITED

Betschart, A.; Kinsella, J. E. *J. Agric. Food Chem.* **1973**, *21*, 60.
Bradford, M. M. *Anal. Biochem.* **1976**, *72*, 248.
Downton, J.; Slatyer, R. O. *Planta* **1971**, *96*, 1.
Edwards, R. H.; Miller, R. E.; deFremery, D.; Knukles, B. E.; Bickoff, E. M.; Kohler, G. O. *J. Agric. Food Chem.* **1975**, *23*, 620.
Grebanier, A. E.; Steinback, K. E.; Bogorad, L. *Plant Physiol.* **1979**, *63*, 436.
Highfield, P. E.; Ellis, R. J. *Nature (London)* **1978**, *271*, 420.
Laemmli, U. K. *Nature (London)* **1970**, *224*, 680.
Neucere, N. J.; Godshall, M. A. *J. Agric. Food Chem.* **1979**, *27*, 1138.
Pallas, J. E., Jr.; Samish, Y. B. *Crop Sci.* **1974**, *14*, 478.
Switzer, R. C.; Merril, C. R.; Shifrin, S. *Anal. Biochem.* **1979**, *98*, 231.

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Mass Spectra and Sensory Properties of Some 4,5-Dialkyloxazoles

Fifteen 4,5-dialkyloxazoles have been synthesized by the reaction of corresponding bromo ketones with formamide. Mass spectra data and preliminary odor descriptions of synthesized 4,5-dialkyloxazoles are given. The general molecular structure for bell pepper like aroma compounds proposed by Buttery et al. could be extended to 4,5-dialkyloxazoles.

Among about 3000 known constituents of aroma (Ohloff and Flament, 1978), heterocyclic compounds deserve particular attention. Due to their characteristic odor, heterocyclic compounds contribute significantly to the flavor of processed foods. Alkyloxazoles are heterocyclic compounds containing both nitrogen and oxygen. The report of Stoffelsma and Pypker (1968) was the first identifying an oxazole as naturally occurring in a food. Since then, alkyloxazoles have been found in several foods, including roasted coffee (Stoffelsma et al., 1968; Vitzthum and Werkhoff, 1974), roasted cocoa (Vitzthum et al., 1975), roasted barley (Harding et al., 1978), baked potato (Coleman et al., 1981), roasted peanut (Lee et al., 1981), and meat products (Chang and Peterson, 1977; Mussinan and Walradt, 1974).

The published mass spectra data of oxazoles are very limited (Bowie et al., 1968; Vitzthum and Werkhoff, 1974). In this paper, mass spectra and sensory properties of 15 4,5-dialkyloxazoles, which have not yet been found in foods, are reported.

EXPERIMENTAL SECTION

Materials. Aliphatic ketones, bromine, and formamide were obtained from reliable sources.

Bromo Ketones. The method used was that of Catch et al. (1948). In most cases where two isomeric bromo ketones were formed, they were not separated but taken through the oxazole synthesis, and the isomeric oxazoles were separated by gas–liquid chromatography.

4,5-Dialkyloxazoles. These were all synthesized by the general method of Lindberg et al. (1970). The bromo ketone was allowed to react with formamide. Yields were all satisfactory at about 50–60%. In the cases where a mixture of two isomeric bromo ketones was used, the isomeric 4,5-dialkyloxazoles were separated by GLC using a 12 ft. long × $^1/_8$ in. o.d. stainless steel column packed

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Table I. Mass Spectral Data and Odor Descriptions of 4,5-Dialkyloxazoles

compound	mass spectra,[a] m/e (rel intensity)	odor descriptions[b]
I, 4-methyl-5-propyloxazole	27 (16), 29 (4), 41 (13), 42 (15), 54 (4), 55 (6), 67 (1), 68 (10), 82 (2), 83 (2), 96 (100), 97 (6), 125 (17), 126 (2); M = 125	vegetable-like, green
II, 4,5-diethyloxazole	27 (93), 29 (100), 43 (25), 45 (30), 55 (14), 59 (38), 68 (8), 74 (19), 82 (4), 83 (4), 96 (3), 97 (1), 110 (19), 111 (1), 125 (7), 126 (1); M = 125	green, vegetable-like
III, 4-propyl-5-methyloxazole	29 (49), 31 (67), 39 (21), 43 (100), 55 (12), 59 (27), 69 (36), 74 (12), 82 (3), 83 (5), 96 (67), 97 (57), 110 (11), 124 (3), 125 (18), 126 (3); M = 125	green, weak bell pepper like
IV, 4-butyloxazole	31 (5), 33 (3), 34 (16), 41 (22), 54 (21), 55 (12), 68 (5), 69 (4), 82 (16), 83 (100), 96 (58), 97 (7), 110 (23), 111 (2), 124 (1), 125 (16); M = 125	vegetable-like, green
V, 4-methyl-5-butyloxazole	27 (13), 29 (5), 41 (12), 42 (11), 54 (5), 55 (6), 68 (8), 70 (4), 82 (1), 83 (3), 96 (100), 97 (12), 110 (1), 139 (14), 140 (1); M = 139	vegetable-like, green
VI, 4-ethyl-5-propyloxazole	27 (32), 29 (18), 39 (37), 41 (42), 54 (12), 55 (44), 68 (8), 69 (12), 82 (22), 83 (13), 96 (7), 97 (4), 110 (100), 111 (8), 124 (7), 139 (21), 140 (3); M = 139	vegetable-like, green
VII, 4-propyl-5-ethyloxazole	27 (21), 29 (43), 39 (14), 41 (14), 55 (26), 57 (35), 67 (2), 68 (6), 82 (12), 83 (32), 94 (1), 96 (8), 110 (100), 111 (50), 119 (1), 124 (12), 138 (2), 139 (24); M = 139	celery-like, green
VIII, 4-butyl-5-methyloxazole	27 (14), 29 (6), 41 (16), 43 (68), 54 (19), 55 (8), 69 (31), 70 (7), 82 (2), 83 (1), 96 (68), 97 (100), 110 (8), 111 (3), 124 (7), 139 (16), 140 (3); M = 139	bell pepper like
IX, 4-ethyl-5-butyloxazole	27 (11), 29 (12), 39 (13), 41 (21), 54 (7), 55 (22), 69 (7), 70 (5), 82 (14), 83 (12), 96 (16), 97 (8), 110 (100), 111 (12), 124 (3), 138 (1), 153 (21), 154 (2); M = 153	vegetable-like, green
X, 4-pentyl-5-methyloxazole	27 (10), 29 (8), 41 (13), 43 (48), 54 (8), 55 (7), 69 (22), 70 (5), 82 (3), 83 (2), 96 (59), 97 (100), 110 (15), 111 (8), 124 (9), 125 (1), 138 (5), 153 (13), 154 (3); M = 153	bell pepper like
XI, 4-methyl-5-hexyloxazole	27 (14), 29 (10), 41 (16), 43 (17), 54 (6), 55 (12), 68 (7), 69 (4), 80 (5), 83 (5), 96 (100), 97 (18), 110 (3), 111 (3), 122 (1), 124 (2), 138 (1), 152 (1), 167 (11), 168 (1); M = 167	vegetable-like, green
XII, 4-butyl-5-propyloxazole	29 (16), 30 (2), 41 (55), 43 (11), 53 (11), 55 (33), 69 (23), 71 (16), 82 (16), 83 (15), 96 (94), 97 (100), 110 (18), 111 (3), 124 (44), 125 (54), 138 (19), 139 (2), 152 (9), 153 (1), 167 (19), 168 (2); M = 167	bell pepper like
XIII, 4-ethyl-5-pentyloxazole	27 (6), 29 (10), 39 (8), 41 (15), 54 (5), 55 (19), 68 (4), 69 (10), 82 (14), 83 (14), 96 (14), 97 (10), 110 (100), 111 (15), 122 (1), 124 (2), 138 (8), 139 (1), 167 (17), 168 (3); M = 167	vegetable-like, green
XIV, 4-hexyl-5-methyloxazole	27 (2), 29 (5), 41 (6), 43 (22), 54 (5), 55 (4), 69 (13), 70 (3), 81 (1), 82 (2), 96 (44), 97 (100), 110 (14), 111 (8), 122 (1), 124 (9), 138 (12), 139 (1), 152 (2), 167 (11), 168 (3); M = 167	vegetable-like, green
XV, 4-heptyloxazole	29 (9), 41 (19), 43 (18), 54 (13), 55 (11), 67 (3), 69 (3), 82 (15), 83 (100), 96 (19), 97 (9), 110 (23), 111 (3), 122 (4), 124 (18), 137 (2), 138 (7), 152 (1), 167 (2), 168 (1); M = 167	vegetable-like

[a] The two most intense ions every 14 mass units above 20 are listed. [b] Odor descriptions were only considered as preliminary.

with 10% SP-1000 on 80–100-mesh Chromosorb W. Each oxazole separated and purified by GLC was accumulatively collected according to the method of Thompson et al. (1978). The purified oxazoles were then subjected to GC–mass spectrometry determination.

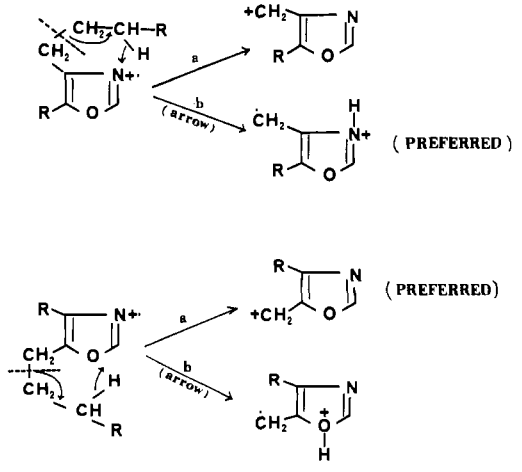
Mass Spectra. Mass spectrometry was performed on a Du Pont 21-490 mass spectrometer with a jet separator interfaced to a Varian Moduline 2700 gas chromatograph fitted with an FID detector and a $^1/_8$ in. o.d. × 12 ft. stainless steel column packed with 10% OV-101 on 80–100-mesh Chromosorb W.

RESULTS AND DISCUSSION

Table I lists the mass spectra and preliminary odor description data of the 4,5-dialkyloxazoles.

Mass Spectra. The important fragmentations which give the base peak for the 4,5-dialkyloxazoles studied are (a) β fission and (b) β fission with hydrogen migration (McLafferty rearrangement). The fragmentation takes place on the longer side chain containing an *n*-propyl or longer alkyl group. Scheme I shows the typical fragmentations of two 4,5-dialkyloxazoles. It is noted that, in Scheme I, where there is a nitrogen atom as the migration terminus, the McLafferty rearrangement is the preferred

Scheme I



fragmentation mode and β scission is of reduced importance. However, with an oxygen atom as the migration terminus, the McLafferty rearrangement is less favored and renders β fission the major fragmentation process.

Odor Properties of 4,5-Dialkyloxazoles. Most of the 4,5-dialkyloxazoles synthesized have green, vegetable-like aroma. It is interesting to note that 4-butyl-5-propyloxazole, 4-butyl-5-methyloxazole, and 4-pentyl-5-methyloxazole were judged to have a strong bell pepper like character. Buttery et al. (1976) found that some 4,5-dialkylthiazoles possessed potent bell pepper aroma. From consideration of this and of the structures of other pyrazine, pyridine, and thiazole compounds, they suggested a general structure for this high potency and character. The general structure is —CH=NC(R)=CX— where R is a hydrocarbon chain about four carbons long and X is oxygen or sulfur. Our observations indicate that the general structure proposed by Buttery et al. (1976) could be extended to 4,5-dialkyloxazoles.

LITERATURE CITED

Bowie, J. H.; Donaghue, P. F.; Dodda, H. J. *Org. Mass Spectrom.* **1968**, *1*, 13.
Buttery, R. G.; Guadagni, D. G.; Lundin, R. G. *J. Agric. Food Chem.* **1976**, *24*, 1.
Catch, J. R.; Hey, D. H.; Jones, E. R. H.; Wilson, W. *J. Chem. Soc.* **1948**, 276.
Chang, S. S.; Peterson, R. J. *J. Food Sci.* **1977**, *42*, 298.
Coleman, E. C.; Ho, C.-T.; Chang, S. S. *J. Agric. Food Chem.* **1981**, *29*, 42.
Harding, R. J.; Wren, J. J.; Nursten, H. E. *J. Inst. Brew.* **1978**, *84*, 41.
Lee, M. H.; Ho, C.-T.; Chang, S. S. *J. Agric. Food Chem.* **1981**, *29*, 684.
Lindberg, U. H.; Bexell, G.; Pedersen, J.; Ross, S. *Acta Pharm. Suec.* **1970**, *7*, 423.
Mussinan, C. J.; Walradt, J. P. *J. Agric. Food Chem.* **1974**, *22*, 827.
Ohloff, G.; Flament, I. *Heterocycles* **1978**, *11*, 663.
Stoffelsma, J.; Pypker, J. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 241.
Stoffelsma, J.; Sipma, G.; Kettenes, D. K.; Pypker, J. *J. Agric. Food Chem.* **1968**, *16*, 1000.
Thompson, J. A.; May, W. A.; Paulose, M. M.; Peterson, R. J.; Chang, S. S. *J. Am. Oil Chem. Soc.* **1978**, *55*, 897.
Vitzthum, O. G.; Werkhoff, P. *J. Food Sci.* **1974**, *39*, 1210.
Vitzthum, O. G.; Werkhoff, P.; Hubert, P. J. *J. Food Sci.* **1975**, *40*, 911.

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