via Girard's P reagent to give 0.5 g of light yellow oil which was 98+% pure by analytical gc (DC-710 column): ir 1720, 896, 1623, 2710, 1570, 1596 cm^{-1}; nmr δ 2.35–3.00 (m, 4 H), 5.06 (s, 1 H), 5.30 (s, 1 H), 7.32 (m, 5 H), 9.77 (s, 1 H); mass spectra *m/e* 118 (100), 29 (48), 117 (43), 103 (32), 91 (30), 77 (30), 160 (2).

5-Phenyl-2-pentenal (9). A solution of 1.34 g of 3-phenylpropionaldehyde and 3.25 g of formylmethylenetriphenylphosphorane (Trippett and Walker, 1961) in 10 ml of benzene was heated at reflux overnight. The solvent was evaporated and the residue was extracted several times with isopentane. Evaporation of the combined extracts gave 0.90 g of yellow oil from which the major component was isolated by preparative gc (W-98 column): ir 1686, 1632, 1599, 2720 cm^{-1}; nmr δ 2.45–3.00 (m, 4 H), 6.09 (d of d, J = 16 and 8 Hz, 1 H), 6.81 (d of t, J = 16 and 7 Hz, 1 H), 7.05–7.45 (m, 5 H), 7.46 (d, J = 8 Hz, 1 H); mass spectra *m/e* 91 (100), 116 (18), 65 (15), 92 (10), 160 (7).

5-Phenyl-4-pentenal (10). A solution of the lithium salt 3 (from 1.30 g of imine) was treated at Dry Ice temperature with 2.00 g of cinnamyl bromide. After 5 hr at room temperature, water was added followed by 10% H_2SO_4 to give pH 1. After 15 min of stirring, the crude product was isolated from the separated organic layer and purified *via* Girard's P reagent to provide 0.64 g of yellow oil which was 99.5% pure by gc (DC-710): ir 1720, 963, 2720, 1595 cm^{-1}; nmr δ 2.54 (m, 4 H), 6.12 (m, 1 H), 6.42 (d, J = 16 Hz, 1 H), 7.25 (m, 5 H), 9.78 (s, 1 H); mass spectra *m/e* 104 (100), 91 (55), 29 (51), 117 (46), 115 (44), 160 (39).

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The Synthesis and Properties of Alkylated Five- and Six-Membered Alicyclic Pyrazines

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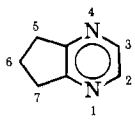
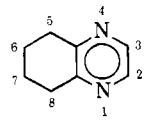
A series of mono-, di-, and trialkyl derivatives of 6,7-dihydro-5*H*-cyclopentapyrazine and 5,6,7,8-tetrahydroquinoxaline was prepared either by condensation of α,β-dicarbonyls with α,β-diamines and subsequent oxidative aromatization or by alkylation of the bicyclic pyrazines. The gas chromatographic retention indices and ir, uv, nmr, and mass spectral data of these derivatives are presented, together with a summary of their natural occurrence to date.

During our gas chromatographic and mass spectroscopic investigations of the volatiles of roasted peanuts and roasted filberts, we encountered a series of compounds which appeared to be pyrazine derivatives with molecular weights two units lower than the alkyl-substituted pyrazines, namely 120, 134, 148, and 162. The data suggested that these compounds probably contained either an unsaturated side chain or else possessed an alicyclic structure. Johnson *et al.* (1971) had encountered similar components in roasted peanut volatiles, and from the mass spectral and uv data they tentatively assigned structures of isopropenyl- and methyl isopropenylpyrazine to the compounds of mol wt 120 and 134, respectively, and suggested also that a methyl-substituted cyclopentapyrazine (mol wt 134) was present. However, when a comparison was made of authentic isopropenylpyrazine, synthesized from ethylpyrazine *via* the Mannich base (Kamal *et al.*, 1962), its mass fragmentation and gc retention time were quite different from the mol wt 120 compound reported by Johnson *et al.* but were identical with our data for an earlier eluting roasted peanut component. Because of the lack of similarity between the properties of the isopropenylpyrazine and the roasted peanut and filbert "unknowns," we concluded that the latter probably were in fact unique bicyclic pyrazines. Various alkyl derivatives of five- and six-membered alicyclic pyrazines (structures I and X, respectively) were synthesized and their gas chromatographic and spectral properties determined. With the availability of these reference data it has been possible to establish the natural occurrence of bicyclic pyrazines not only in roasted peanuts (Walradt *et al.*, 1971) and filberts (Kinlin *et al.*, 1972) but also in cooked beef (Mussinan *et al.*, 1973) and cooked pork liver (Mussinan and Walradt, 1973).



6,7-dihydro-5*H*-cyclopentapyrazine
I



5,6,7,8-tetrahydroquinoxaline
X

International Flavors & Fragrances, R&D, Union Beach, New Jersey 07735.

Table I. Properties of Bicyclic Enaminimines

Compound	Mp, °C	λ_{max}, nm	Ir, cm^{-1}	Ms *m/e*, %[b]	Nmr, δ ppm
5-Methyl-3,4,6,7-tetrahydro-2*H*-cyclopentapyrazine	121–123	283	3260, 2920, 2840, 1640, 1435, 1405, 1325, 1205, 1165, 1100, 990[a]	*136* (*100*), 135 (63), 94 (41), 109 (35), 41 (29), 108 (28), 121 (22), 39 (20)	See Figure 1A
2,3,5-Trimethyl-3,4,6,7-tetrahydro-2*H*-cyclopentapyrazine	115–116	285	3230, 2960, 2920, 2840, 1665, 1640, 1405, 1375, 1330, 1205, 1195, 1175, 1105, 1000[a]	*164* (*100*), 149 (100), 123 (35), 108 (33), 95 (32), 41 (28), 163 (21), 44 (20), 135 (19)	See Figure 1B
5,7-Dimethyl-2,3,4,7,8-hexahydroquinoxaline		280	3300, 2945, 2850, 1650, 1630, 1610, 1460, 1400, 1375, 1330, 1205, 1150, 990, 930	*164* (*100*), 163 (70), 149 (62), 41 (43), 122 (28), 39 (28), 137 (20)	1.04 (m, 3 H) CH_3; 1.66 (s, 3 H) $CH_3C{=}C$; 1.09, 2.92 (m, 5 H) CH_2CHCH_2; 3.08 (t, 2 H) CH_2N; 3.68 (t, 2 H) $CH_2N{=}$
5,7,7-Trimethyl-2,3,4,7,8-hexahydroquinoxaline		285	3300, 2950, 2850, 1640, 1615, 1460, 1400, 1395, 1370, 1330, 1200, 975, 935	*178* (*100*), 163 (47), 177 (36), 148 (30), 41 (27), 135 (23), 39 (17), 136 (16), 150 (15)	0.96 (s, 6 H) $(CH_3)_2C$; 1.62 (s, 3 H) $CH_3C{=}C$; 2.05 (s, 2 H) $CH_2C{=}C$; 2.22 (s, 2 H) $CH_2C{=}N$; 3.05 (t, 2 H) CH_2N; 3.67 (t, 2 H) $CH_2N{=}$

[a] Recorded in carbon tetrachloride. [b] AEI MS9 probe.

Table II. Synthesis and Properties of Alicyclic Pyrazines

		Synthetic route used	Natural occurrence, filbert (F), peanut (P), beef (B), pork liver (L)	Retention index, I_E	Uv λ_{max}^{MeOH}, nm	Uv $E \times 10^{-3}$	Ir, cm^{-1}	Ms, *m/e*, %
I	5,7-Dihydro-5*H*-cyclopentapyrazine	A	F, P, B, L	10.2	275 281 310 (s)[c]	10.8	3050, 2950, 2840, 1465, 1455, 1425, 1380, 1310, 1245, 1190 1145, 1105, 1050, 1200, 900, 840	*120* (*100*), 119 (86), 39 (25), 41 (18), 65 (18), 52 (17), 66 (16), 93 (13)
II 2-Methyl-		A	F, P, B, L	10.73	287 305 (s)	9.4	3030, 2950, 2910, 2830, 1450, 1440, 1415, 1365, 1300, 1260, 1150, 1110, 1020, 955, 895, 825	*134* (*100*), 133 (74), 39 (64), 66 (42), 40 (22), 107 (20), 65 (19), 41 (17)
III 5-Methyl-		A	F, P, B,[d] L	9.94	277 (s) 282 308 (s)	9.7	3050, 2960, 2930, 2870, 1455, 1430, 1385, 1330, 1155, 1125, 1090, 1075, 1015, 870, 845	119 (100), *134* (*48*), 133 (25), 39 (21) 27 (18), 52 (16), 78 (12), 41 (12)
IV 2-Ethyl-		D	F, P	11.42	210 286 308 (s)	9	3040, 2965, 2920, 1460, 1450, 1370, 1235, 1155, 1115, 1050, 900	147 (100), *148* (*83*), 39 (19), 120 (14), 65 (9), 66 (8), 53 (8), 133 (6), 41 (6)[a]
V 5-Ethyl-		A	F, P	10.82	210 (s) 275 (s) 282 307 (s)	9.6	3050, 2960, 2930, 2870, 1455, 1430, 1385, 1345, 1145, 1130, 845	120 (100), 119 (60), 39 (15), 27 (15), *148* (*11*), 78 (11)
VI 2,3-Dimethyl		A	F, P	11.54	210 (s) 287 305 (s)	8.0	2945, 2920, 1440, 1390, 1370 1320, 1220, 1165, 975, 835, 715	*148* (*100*), 66 (64), 147 (45), 39 (44), 107 (34), 42 (24), 65 (22), 53 (21)
VII 2(or 3), 5-Dimethyl-		A, C	F	10.26	211 (s) 286 306 (s)	9.4	2950, 2920, 2865, 1440, 1365, 1325, 1310, 1260, 1150, 1135, 1075, 1020, 990, 890	133 (100), *148* (*55*), 39 (27), 147 (24)[a]
VIII 3(or 2), 5-Dimethyl-		A, C	F	10.39			2950, 2920, 2865, 1450, 1435, 1330, 1300, 1285, 1260, 1150, 1135, 1070, 965, 890	133 (100), *148* (*41*), 39 (26), 147 (13)[a]

P, B,[d] L[e]

IX 2,3,5-Trimethyl-		A		11.26	210 (s)		2950, 2920, 2865, 1450, 1385,	147 (100), *162* (*51*), 161 (14),
					288	8.8	1330, 1220, 1165, 1100, 1000,	148 (13), 53 (10), 79 (10)[b]
					305 (s)		975, 895, 795	
X	5,6,7,8-Tetrahydro-quinoxaline	A, B	F, P, B,[d] L	11.14	273		3040, 3000, 1475, 1445, 1405,	*134* (*100*), 133 (46), 106 (18),
					278	9.2	1165, 1120, 1070, 850, 755	52 (17), 39 (14), 119 (14), 41 (11)
					302 (s)			
XI 2-Methyl-		B	F, B,[d] L	11.30	208		3040, 2950, 2860, 1460, 1380,	*148* (*100*), 147 (39), 39 (30),
					282	8.6	1350, 1315, 1270, 1185, 1160,	52 (26), 120 (22), 79 (18), 27 (16),
					302 (s)		1135, 990, 835, 740	133 (15)
XII 5-Methyl-		C		10.98	272		3040, 2930, 1445, 1430, 1400,	*148* (*100*), 133 (79), 147 (47),
					278	9.4	1365, 1230, 1170, 1155, 1140,	39 (20), 41 (14), 66 (13)[a]
					305 (s)		1100, 1060, 1040, 960, 865, 850	
XIII 2,3-Dimethyl-		B		12.32	212		2920, 2850, 1440, 1400, 1210,	*162* (*100*), 52 (43), 161 (30), 79 (28),
					283	9.0	1185, 1140, 1010, 980, 930,	121 (22), 53 (21), 39 (18)
					300 (s)		865, 775	
XIV 5,7-Dimethyl-		A		11.13	272		3040, 2950, 2970, 2770, 1450,	147 (100), *162* (*79*), 119 (69),
					278	8.0	1430, 1400, 1375, 1225, 1165,	39 (32), 41 (27), 161 (26), 27 (25)
					304 (s)		1145, 1070, 1060, 850	
XV 5,8-Dimethyl-		C		10.73	272		3040, 2950, 2930, 2860, 1450,	*162* (*100*), 147 (74), 161 (28),
					279	11.7	1395, 1370, 1325, 1190, 1155,	119 (24), 133 (22), 39 (15),
					310 (s)		1145, 1065, 1035, 995, 950, 850	41 (11)[b]
XVI 5,7,7-Trimethyl-		A		11.12	205 (s)		3040, 2950, 2920, 2870, 1460,	161 (100), *176* (*95*), 133 (66),
					272		1450, 1425, 1400, 1365, 1190,	119 (65), 41 (42), 39 (40), 27 (32),
					278	8.6	1130, 1065, 1015, 975, 885,	29 (24)
					308 (s)		845	

[a] Hitachi RMU-6E. [b] AEI MS9. [c] S = shoulder. [d] Tentative. [e] Only one isomer identified.

This paper reports the syntheses, gas chromatographic retention indices (I_E values), and spectral properties of these bicyclic pyrazines and summarizes their known natural occurrence. Much of our information, including synthetic procedures and the structure of the alkyltetrahydro-2*H*-cyclopentapyrazines, has been presented in preliminary publications (Pittet *et al.*, 1971, 1972a,b) and has now been duplicated in part by other research workers (Flament *et al.*, 1973).

MATERIALS

The materials used in the synthesis of the bicyclic pyrazines were obtained from the following commercial sources or prepared by the literature methods cited: 2-hydroxy-3-methyl-2-cyclopenten-1-one (Cyclotene, Dow Chemical, Midland, Mich.); 1,2-diaminocyclohexane, 2-chlorocyclopentanone, and 2-chlorocyclohexanone (Aldrich Chemical Co., Cedar Knolls, N. J.); Sodamide (Alfa Chemicals, Berkley, Mass.); 3-ethyl-2-hydroxy-2-cyclopenten-1-one (Gianturco and Friedel, 1963); 2-hydroxy-3-methyl-2-cyclohexen-1-one (Harries, 1902); 2-hydroxy-3,5-dimethyl-2-cyclohexen-1-one (Wallach, 1924); 2-hydroxy-3,5,5-trimethyl-2-cyclohexen-1-one (Payne, 1959); 2,3-butylenediamine (Wyandotte, UK Patent 858,698).

Other chemicals used in the syntheses are readily obtainable from chemical supply houses.

SYNTHETIC ROUTES

A. Condensation of an Alicyclic α,β-Diketone with an α,β-Diamine. *Preparation of 5-Methyl-6,7-dihydro-5H-cyclopentapyrazine (III).* A mixture of 116 g of 2-hydroxy-3-methyl-2-cyclopenten-1-one, 72 g of ethylenediamine, and 3 l. of benzene was heated under reflux for 2.5 hr; the water formed in the reaction was continuously removed by means of a Bidwell trap. Evaporation of the solvent yielded a brown crystalline solid (124 g), a small portion of which was purified by sublimation to yield colorless crystals with mp 121–123° and was characterized as 5-methyl-3,4,6,7-tetrahydro-2*H*-cyclopentapyrazine (see Figure 1A and Table I). The major portion of the material was dissolved in 3.75 l. of ethanol and after the addition of 40 g of potassium hydroxide, oxygen was passed through the solution, initially at −20° for 1 hr, then at 50° for 2 hr. The solvent was removed by evaporation and the product distilled to yield 35.8 g of colorless liquid with bp 47° at 0.7 mm; yield was 26%.

B. Condensation of an Alicyclic α,β-Diamine with an α,β-Dicarbonyl. *Preparation of 5,6,7,8-Tetrahydroquinoxaline (X).* To 5.5 l. of ethanol was added simultaneously 228 g of 1,2-diaminocyclohexane and 319 g of 40% aqueous glyoxal over 4 hr while maintaining the temperature at −20°. When the addition was complete, 80 g of potassium hydroxide was added and oxygen passed through the solution at −20° for 1 hr and then for 1 hr at 50°. After removal of the solvent the residue was dissolved in water and extracted with 7 × 400 ml of ether. The combined dried (anhydrous magnesium sulfate) extracts were evaporated and the residue was distilled under reduced pressure to yield 67 g (25%) of 5,6,7,8-tetrahydroquinoxaline with bp 85° at 3 mm.

C. Alkylation in Liquid Ammonia. *Preparation of 5-Methyl-5,6,7,8-tetramethylquinoxaline (XII).* To a continuously stirred suspension of 8 g of sodamide in 300 ml of liquid ammonia, 26.8 g of 5,6,7,8-tetrahydroquinoxaline (X) was added dropwise over a 10-min period, during which time a deep red color developed, indicating the formation of the anion. After 15 min, methyl iodide (28.4 g) diluted with an equal volume of diethyl ether was slowly added. After stirring for 1 hr the reaction was terminated by the addition of 20 g of ammonium chloride. The reaction product was worked up in the usual manner (Behun and Levine, 1961) and distilled under reduced pressure. The main fraction (18.8 g) distilled at 72° (3 mm) and by

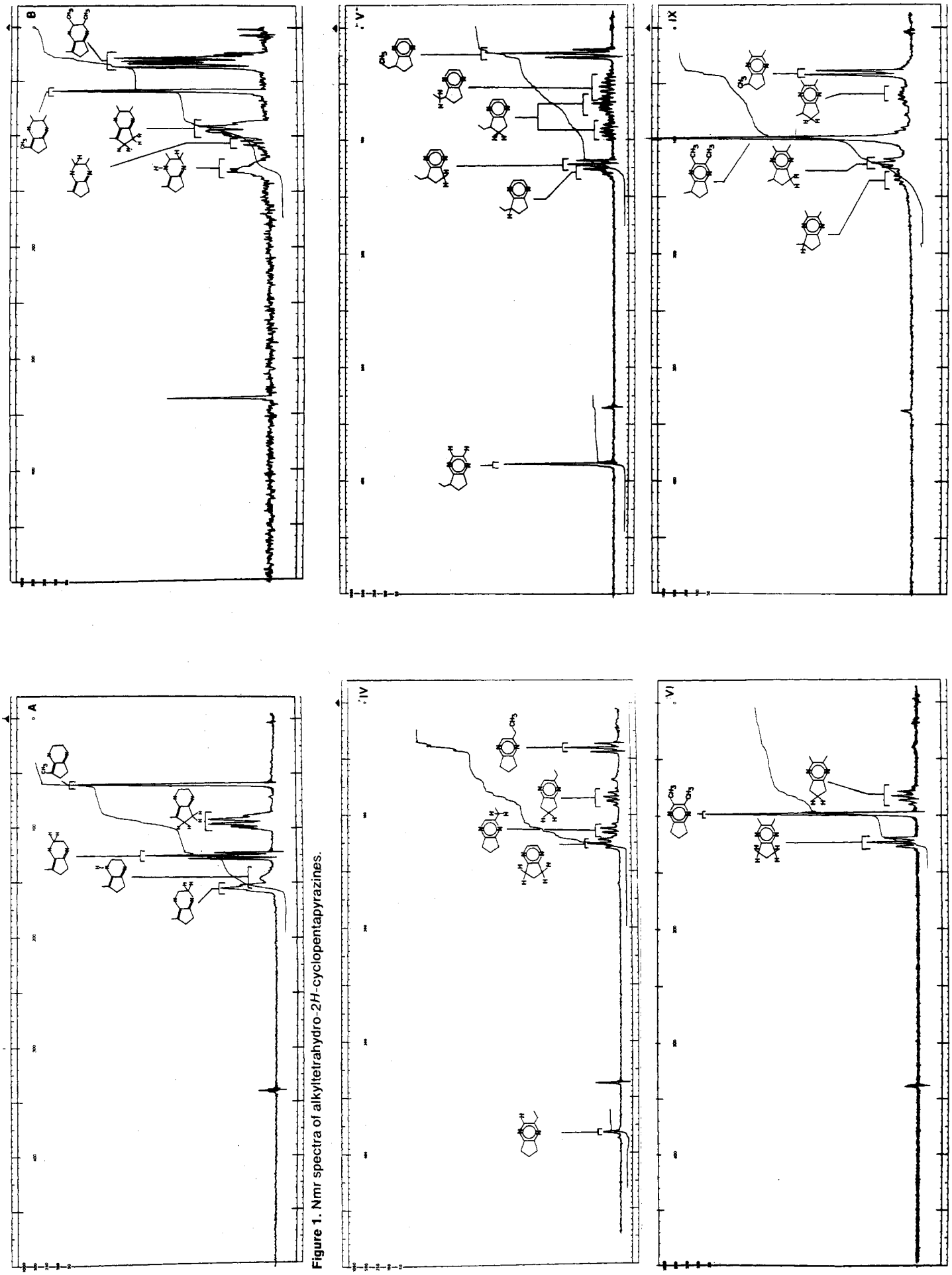


Figure 1. Nmr spectra of alkyltetrahydro-2*H*-cyclopentapyrazines.

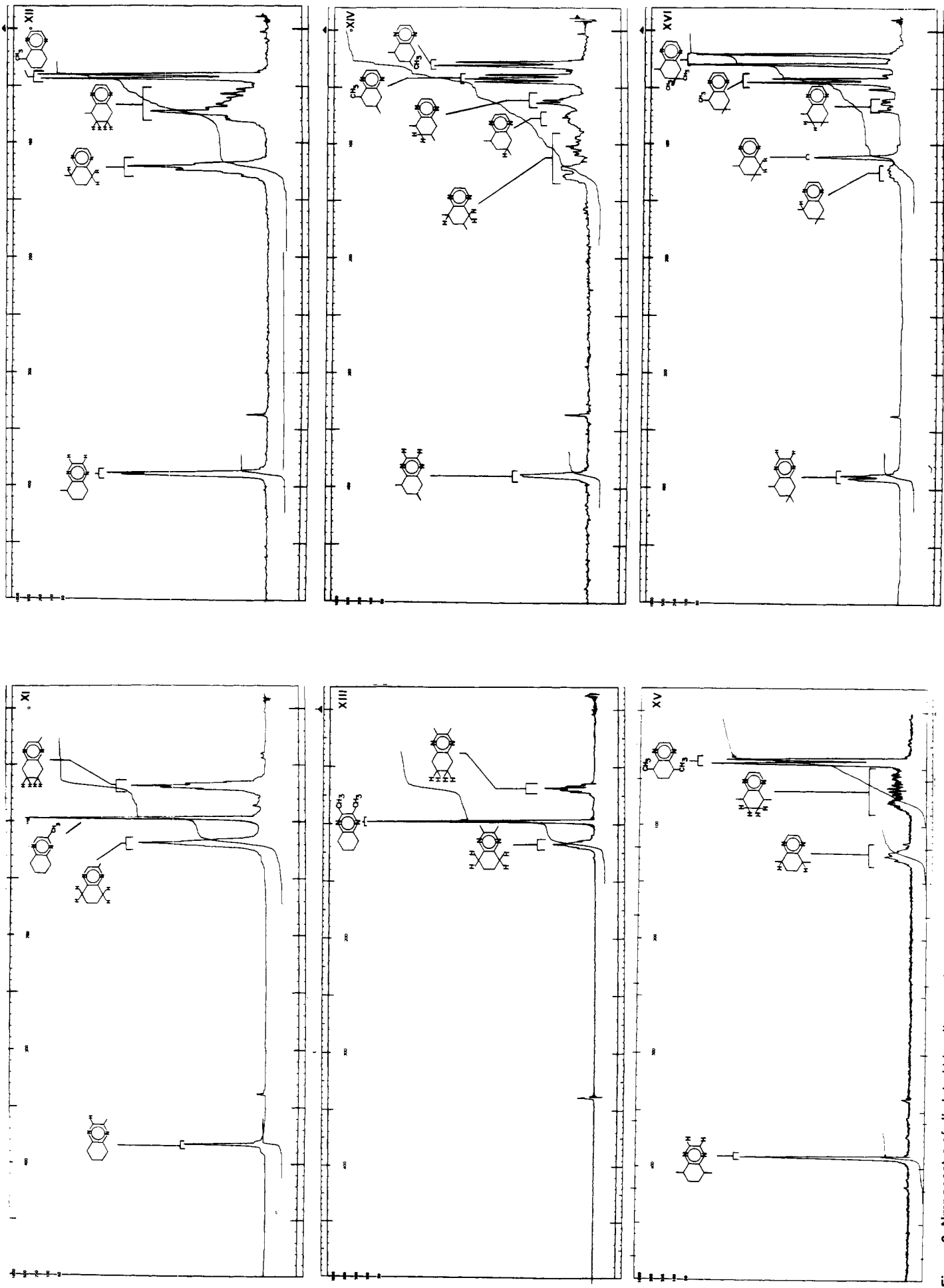


Figure 2. Nmr spectra of alkylated bicyclic pyrazines.

computerized gc–ms analysis had the following composition: 5,6,7,8-tetrahydroquinoxaline (X) 26.8%, 5-methyl-5,6,7,8-tetrahydroquinoxaline (XII) 63%, 5,8-dimethyl-5,6,7,8-tetrahydroquinoxaline (XV) 3% and, tentatively, 5,5-dimethyl-5,6,7,8-tetrahydroquinoxaline (2.9%).

D. Nuclear Alkylation. *Preparation of 2-Ethyl-6,7-dihydro-5H-cyclopentapyrazine (IV).* To a stirred mixture of 1.2 g of 6,7-dihydro-5*H*-cyclopentapyrazine (I), 2.1 g of acetaldehyde (dried over sodium sulfate) and 5 g of pulverized glass and 45 ml of toluene (previously dried over potassium) was added 1.4 g of potassium in small pieces over 1.5 hr. The temperature was kept between 28–30°. The slurry was stirred under nitrogen for 20 hr, worked up according to the procedure of Bramwell *et al.* (1971), and, from the products, 2-ethyl-6,7-dihydro-5*H*-cyclopentapyrazine was isolated by preparative gc.

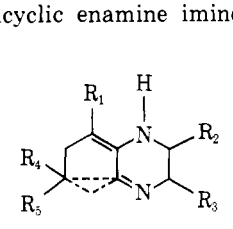
INSTRUMENTAL ANALYSES

Ir spectra were obtained on neat samples, except where otherwise stated, using a Beckman IR4 spectrophotometer. Uv spectra were measured on methanolic solutions using a Beckman DK-2A spectrophotometer. Nmr spectra were recorded in deuteriochloroform with tetramethylsilane as the internal standard using a Varian HA 100 spectrometer. The sweep width was 1000 Hz sweep with a 50 Hz offset. Mass spectra were determined on a CEC 21 103C mass spectrometer, unless otherwise stated.

Retention indices (I_E values) were determined on a 500-ft × 0.03 in. stainless steel open tubular column coated with Carbowax 20M using ethyl esters of *n*-aliphatic acids as standards (van den Dool and Kratz, 1963). The column was programmed from 70° to 190° at 1°/min at a helium gas flow of 10 ml/min.

RESULTS AND DISCUSSION

The procedures used for the synthesis of alicyclic pyrazines were adaptations of previously reported methods for alkylpyrazines. The availability of suitable starting materials largely governed the route(s) used. The reaction conditions were not optimized, since our primary objective was to generate reference compounds which might prove to be of use in the identification of the pyrazine "unknowns" in the volatiles of roasted peanuts and filberts. It may be seen from Table II that the route most frequently used was the condensation of an α,β-alicyclic diketone with an α,β-diaminoalkane (Route A). The 3-alkyl alicyclic 1,2-diketones used in these syntheses exist predominately as the corresponding enolones (Pittet *et al.*, 1970) and, when condensed with α,β-diaminoalkanes, they preferentially form bicyclic enamine imines of the following structure



R_1 to R_5 = H or lower alkyl

rather than the corresponding dihydropyrazines. These compounds exhibit typical >NH absorption (3200–3300 cm^{-1}) in the ir and their nmr spectra are consistent with the proposed structures (see Figure 1 and Table I); these intermediates and the alicyclic pyrazines have similar uv absorption maxima, but the former may be distinguished by their characteristic reversible bathochromic shift of 50 to 100 nm on acidification. The bicyclic enamine imines which have interesting odor properties (Pittet *et al.*, 1972b) could be aromatized to the corresponding pyrazines by oxidation under alkaline conditions.

The synthesis of derivatives of I with no alkyl substituents on the alicyclic ring would be achieved most readily by starting from either 1,2-diaminocyclopentane or 1,2-cyclopentanedione; unfortunately, neither material is commercially available. However, the latter compound may be prepared from cyclopentanone (Acheson, 1956) *via* the 2-bromo compound.

It is noteworthy that condensation of either 2-chlorocyclopentanone or 2-chlorocyclohexanone with ethylenediamine followed by vigorous oxidation under basic conditions did yield the corresponding bicyclic pyrazines but the yields were particularly low, probably due to the lower oxidation state of the initial condensation products compared to those formed *via* route A.

Alkylpyrazines, in the form of the corresponding anions generated in liquid ammonia with sodamide, readily undergo side chain alkylation with alkyl halides by nucleophilic displacement (Behun and Levine, 1961); an application of this procedure for the synthesis of certain alkyl bicyclic pyrazines was investigated. Compound X was alkylated to XII in good yield with the formation of minor byproducts, one of which was identified as XV, and from nmr data another probable byproduct was 5,5-dimethyl-5,6,7,8-tetrahydroquinoxaline but it was not obtained sufficiently pure for full characterization. When the anion of II was reacted with methyl iodide under similar conditions, alkylation again took place on the alicyclic ring since a mixture of VII and VIII was formed, together with traces of higher alkylated products; no IV was identified in the reaction mixture. The latter compound was of interest as we believed it to be a constituent of roasted nuts so it was synthesized by an alternative method, namely, nuclear alkylation (Bramwell *et al.*, 1971) of compound I.

In both the I and X series, the 5-methyl derivatives elute before the parent compounds on a Carbowax open tubular gc column, whereas the 2-methyl derivatives elute significantly later. This unexpected behavior of the 5-methyl derivatives may be attributed to a shielding by the alkyl group of the unbonded electrons of the vicinal nitrogen atom of the pyrazine ring, thus reducing the polarity of the molecule. It has been found that slight variations in the I_E values do occur due to differences in the preparation and age of the gc column but the order of elution is not changed.

The mass spectra of the alkyl derivatives of I and X with no substituents on the alicyclic ring show characteristic *m/e* 66 and 52, respectively, and the base peak is the molecular ion; the only exception is compound IV which exhibits M − 1 as the most abundant ion, typical of the ethyl-substituted alkylpyrazines. The mass fragmentation patterns of compounds VII, VIII, and IX are notable for the few ions observed. The significant ir absorptions (cm^{-1}) and uv spectral data are also given in Table II; the uv λ_{max} occur between 275–290 nm close to the values of the alkenylpyrazines (Bondarovich *et al.*, 1967). The nmr spectra presented in Figure 2 are of the pyrazines not included in our previous publication (Walradt *et al.*, 1971). The nmr spectra of the more highly substituted pyrazines are complex due to the effect of the ring current on nonequivalent protons of the various conformational isomers. The compounds VII and VIII are obtained as a mixture by both synthetic routes A and C. Although the isomers are separable by gc, their nmr spectra are so similar that structural assignments could not be made unequivocally.

SUMMARY

A series of five- and six-membered alicyclic pyrazines was synthesized by adaptation of methods previously reported for simple alkylpyrazines. The gc and spectral data of these compounds were used to facilitate the identification of bicyclic pyrazines in roasted nuts and cooked meat products. As it is unlikely that these compounds, which are formed during heat processing, are unique only to the food products so far analyzed in our laboratories, it is hoped that by publishing data on the properties of these

bicyclic pyrazines it will assist other research workers in identifying them in other natural products.

ACKNOWLEDGMENT

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Formation of *N*-Alkyl-2-acylpyrroles and Aliphatic Aldimines in Model Nonenzymic Browning Reactions

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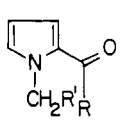
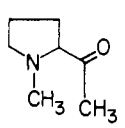
Reactions of α-amino acids with furfural and 2-acetylfuran yielded *N*-alkyl-2-acylpyrroles. The furfural reactions also produced *N*-alkylidenefurfurylamines whose structures were verified by independent syntheses from furfurylamine and aliphatic aldehydes. The pyrroles and aldimines had interesting strong odors, some of which were readily recognized as foodlike.

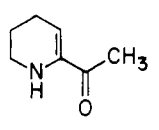
The *N*-alkyl-2-acylpyrroles (I) are a class of organoleptically interesting substances which have been observed in a wide variety of heat-treated foodstuffs including: tea (Yamamoto *et al.*, 1940a,b), cocoa (Dietrich *et al.*, 1964), and coffee (Stoll *et al.*, 1967). In addition, closely related compounds 2-acetyl-1-methylpyrrolidine (II) and 2-acetyl-1,4,5,6-tetrahydropyridine (III) have been reported among bread volatiles (Hunter *et al.*, 1969).



I



II



III

In recent years Japanese investigators (Shigematsu *et al.*, 1972) have been studying the mechanism of acylpyrrole formation in foods *via* detailed examinations of model systems. It was suggested (Kato, 1967) that acylalkylpyrroles are formed by interaction of 3-deoxyosuloses (from sugars) and amines or α-amino acids.

In this connection we wish to report our finding that similar acylalkylpyrroles can be formed by reaction of furfural and its homologs with α-amino acids. Our investigation of furfurals stemmed from a consideration of the known wide occurrence of furans in foodstuffs and the possibility of nucleophilic attack by amines at the electrophilic 5 position on the 2-acylfuran nucleus (Figure 1). In the course of our study we also observed aliphatic aldimine products resulting from attack of α-amino acids at the aldehyde function of furfural. The *N*-alkylidenefurfurylamines isolated from our model reactions comprised a class of stable, aroma-rich compounds which heretofore had not been reported in "natural" food systems.

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EXPERIMENTAL SECTION

Materials. α-Amino acids were high-grade commercial materials which were used without further purification; furfural and diethylene glycol dimethyl ether (diglyme) were freshly distilled before use; simple aldehydes, amines, 2-acetylfuran, pyrrole-2-carboxaldehyde, *N*-methylpyrrole-2-carboxaldehyde, and furfurylamine were commercial samples; other compounds were synthesized by methods exemplified below.

Methods of Analysis. Volatile reaction products were separated by a steam distillation–ether extraction procedure described previously (Rizzi, 1972). Acylalkylpyrroles and aldimines were isolated by fractional distillation or preparative gas chromatography (gc) on 5 ft × 0.25 in. stainless steel columns containing 15% Carbowax 20M or 15% neopentyl glycol succinate on 30–60 mesh Chromosorb W (acid washed). Column temperatures of 100–150° and an He flow rate of *ca.* 50 ml/min were used. Quantitative analyses of reaction products were obtained by planimeter integration of gc curves. Aliphatic amines were isolated by bubbling a stream of N_2 through each reaction mixture and through dilute aqueous HCl. The amine hydrochlorides were identified by paper chromato-