Analysis of Volatile Components Derived from Raw and Roasted Earth-Almond (*Cyperus esculentus* L.)

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Volatile aroma components of raw earth almond and those developed in a roasting process were analyzed by gas chromatography/mass spectrometry to determine the identity of compounds that would indicate the degree of roasting. In all, 143 components (ca. 90% of the total isolate) were positively identified, of which 138 are reported as earth almond volatiles for the first time. The main flavor compounds identified in raw earth almond were alcohols, whereas in roasted earth almond, the majority of the volatiles identified suggest the flavor formation is via the Maillard reaction, with pyrazines contributing directly to the roasted flavor of earth almond.

INTRODUCTION

Cyperus esculentus L. is a weedlike plant native to Africa and Southern Europe and has been cultivated since early times (Linssen *et al.*, 1989). This plant is characterized by its creeping rootstocks, which produce small sweet tubers called in Spanish "chufa" (Morell and Barber, 1983). Because of the almond-like flavor, these tubers are also known as "earth-almonds". They are used as human food in several countries around the Mediterranean Sea, particularly in Spain (Linssen *et al.*, 1989).

The successful use of earth-almond as a flavoring agent is considered with reference to nut roasting, ice cream formulation, and other applications. Sometimes, it is roasted and added as a flavoring material for biscuits and other similar products (Soliman *et al.*, 1982; Cantalejo, 1996).

The best known application of chufa in the food industry is in the production of "horchata de chufa". Horchata is a sweetened milklike aqueous extract of chufa tubers, mainly produced in Spain during the summertime, although horchata made with other ingredients is consumed in South America (Cavanilles, 1981). In the last few years, the popularity of horchata has extended to other countries, i.e. Great Britain. Horchata's flavor is developed after appropiate drying of chufa tubers and is a mixture of vanilla, nutty, and earthy notes. Horchata made from roasted tubers could be used as a caffeine-free coffee substitute. Because flavor and aroma are fundamental attributes of such products, the present work has focused on the analysis of the volatile fraction of earth-almond to determine important contributors to its aroma, which has scarcely been reported in literature (Soliman *et al.*, 1982).

MATERIALS AND METHODS

Materials. Earth-almonds (*C. esculentus* L.) for the present study were obtained from Ferrer Segarra Co. in Xativa, Valencia, and provided to us by Deprovesa Co. in Carcaixent, Valencia (Spain).

Isolation of Volatile Compounds. Raw and roasted volatiles were isolated by three different well-established procedures: high-vacuum distillation, steam distillation, and simultaneous distillation−extraction (Cronin, 1982; Parliment, 1986; Wild GmbH, private communication).

For the isolation and fractionation of roasted earth-almond volatiles, raw earth-almonds were roasted in a roasting apparatus (MVS GmbH, Garching, Germany) at 120 °C over a period of time (from 10 to 60 min). The analyses were carried out on dry earth-almonds homogenized and ground (Moulinette, Moulinex) to pass through a 0.5 mm sieve.

The method described by Cronin (1982) and based on the principle of Likens-Nickerson was used for the volatile constituents isolated using simultaneous distillation−extraction. In a modified Likens-Nickerson distillation−extraction apparatus (Normag GmbH, Germany), ground earth-almonds (500 g) were blended with 850 mL of water placed in a 2 L round-bottom flask and 20 μL of internal standard (100 mg of pseudocumol plus 10 mg of diethyl methylmalonate in 10 mL of pentane/dichloromethane) was added. The volatiles from the distillation flask were condensed and extracted into the organic solvent (90 mL of 2:1 ether/pentane), from which they flow via a right arm into the solvent flask, while the condensed water, largely free from volatiles, returns via the left arm to the distillation flask. Thus, the aroma compounds are transferred from the aqueous phase to the organic phase. The mixture was subjected to distillation−extraction for 3−4 h. Residual organic solvent was removed by filtering the extract through sodium sulfate, and the extract was concentrated to 100−200 μL of a residual colorless liquid on a water bath at 40 °C using a Vigreux column.

The method described by Parliment (1986) was used for the volatiles isolated using water−steam distillation. Grounded earth-almond (500 g) containing as internal standard 50 μL of 100 mg of pseudocumol plus 10 mg of diethyl methylmalonate in 10 mL of dichloromethane was placed in a pear-shaped flask, and to it was added 700 mL of boiling water. Steam was generated externally and introduced through inlet assembly into the bottom of the flask. Steam-distillate compounds were condensed in the spiral condenser and collected in a 100 mL graduated cylinder. Afterward, the aqueous condensate was extracted by means of a Mixxor (Wild GmbH, HD, Germany). Distillate (10 mL) was placed in the lower vessel, and pentane/dichloromethane (2:1) was added. The sample was mixed by moving the piston up and down. Phases were allowed to separate, and the piston was slowly depressed, forcing the solvent into the upper collecting chamber. The organic phase was taken with a Pasteur pipette and transferred to a long and thin column to be concentrated to 100−200 μL on a water bath at 40 °C.

The high-vacuum distillation was performed as follows (Wild GmbH, private communication). A mixture of 1 kg of earth-almonds and 1.7 L of water was stirred and distilled at 40 °C under a 5×10^3 Pa pressure. The distillation apparatus was provided by Wild GmbH (HD, Germany). From 1 kg of earth-

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Table 1. Aroma Compounds Identified by GC/MS in the Extract Obtained by High-Vacuum Distillation in Raw and Roasted Earth-Almond

| | | raw earth-almond | | roasted earth-almond | | | | | | | | | | | | |
| | | | | 10 min roasting | | 20 min roasting | | 30 min roasting | | 40 min roasting | | 50 min roasting | | 60 min roasting | |
no.	compounds	presence	% area	presence	% area	presence	% area	presence	% area	presence	% area	presence	% area	presence	% area
hydrocarbons															
1	limonene	+	4.2	+	2.1	+	0.1	+	0.04	+	0.03	+	0.03	+	0.03
ketones															
2	3-pentanone	−		+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
3	2,3-pentanedione	*b*		+	1.3	+	0.9	+	0.6	+	0.6	+	0.6	+	0.6
4	2,3-butanedione	−		+	0.06	+	0.06	+	0.06	+	0.06	+	0.06	+	0.06
5	3-penten-2-one	−		+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.09
6	2-heptanone	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2
7	acetoin	+	0.1	−		−		−		−		−		−	
8	3-octen-2-one	+	0.1	−		−		−		−		−		−	
9	3(4)-octanone	−		+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.09
10	2-nonanone	−		+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2
11	2-decanone	−		+	0.07	+	0.07	+	0.06	+	0.04	+	0.03	+	0.03
12	2-methyl-2-cyclopenten-1-one	−		+	0.06	+	0.06	+	0.05	+	0.05	+	0.05	+	0.04
13	methyl 2-methylcyclopent-2-enyl ketone[a]	−		+	0.06	+	0.05	+	0.05	+	0.06	+	0.06	+	0.06
14	3-methylcyclohexanone	−		+	0.05	+	0.06	+	0.06	+	0.07	+	0.06	+	0.05
15	3,5-octadien-2-one	+	0.08	−		−		−		−		−		−	
16	1-phenylethanone[a]	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1
17	methylcyclopentenolone	−		+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2
18	2-hydroxycyclopentadecanone	−		+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
19	carvone	+	0.1	−		−		−		−		−		−	
alcohols															
20	isobutyl alcohol	+	4.2	+	1.0	+	0.2	+	0.04	+	0.04	+	0.02	+	0.02
21	*n*-butyl alcohol	+	1.0	+	0.06	+	0.02	+	<0.01	+	<0.01	+	<0.01	+	<0.01
22	isoamyl alcohol	+	19.1	+	10.9	+	0.9	+	0.5	+	0.2	+	0.09	+	0.09
23	3-methyl-3-buten-1-ol	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3
24	*n*-amyl alcohol	+	6.6	+	2.4	+	0.2	+	0.2	+	0.1	+	0.01	+	0.01
25	prenol	+	0.3	+	0.3	+	0.08	+	0.04	+	0.01	+	<0.01	+	<0.01
26	2-heptanol	+	0.3	+	0.1	+	0.1	+	0.03	+	0.03	+	0.01	+	0.01
27	*n*-hexanol	+	21.6	+	12.1	+	1.2	+	0.7	+	0.03	+	0.03	+	0.03
28	2-methyl-3-pentanol	−		+	0.05	+	0.05	+	0.05	+	0.05	+	0.05	+	0.05
29	1-octanol	+	3.5	+	2.6	+	1.3	+	0.2	+	0.1	+	0.04	+	<0.01
30	3-octanol	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1
31	6-methyl-3-heptanol	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1
32	1-octen-3-ol	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2
33	7-octen-4-ol	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3
34	6-methyl-5-hepten-2-ol	−		+	0.2	+	0.2	+	0.3	+	0.4	+	0.7	+	0.9
35	2-ethyl-1-hexanol	+	0.7	+	0.7	+	0.7	+	0.7	+	0.7	+	0.7	+	0.7
36	2-nonanol	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3
37	linalool	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
38	2-butoxyethanol	+	0.1	−		−		−		−		−		−	
39	cyclohexanol	+	0.2	−		−		−		−		−		−	
40	1-heptanol	+	4.3	+	2.6	+	1.8	+	0.2	+	0.1	+	0.04	+	<0.01
41	ethyl-1-hexanol	+	0.4	−		−		−		−		−		−	
42	4-terpineol	+	0.1	−		−		−		−		−		−	
43	α-terpineol	+	0.1	−		−		−		−		−		−	
44	1-nonanol	+	3.2	+	1.4	+	0.3	+	0.2	+	<0.01	+	<0.01	+	<0.01
45	phenyl ethyl alcohol	+	0.9	+	0.5	+	0.2	+	0.05	+	0.02	+	0.01	+	<0.01
aldehydes															
46	2-butenal	−		+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
47	2-methyl-2-butenal	−		+	0.05	+	0.05	+	0.05	+	0.05	+	0.05	+	0.04
48	*n*-hexanal	+	0.6	+	0.6	+	0.6	+	0.6	+	0.6	+	0.6	+	0.6
49	*n*-heptanal	+	0.03	+	0.03	+	0.03	+	0.03	+	0.03	+	0.03	+	0.03
50	*n*-octanal	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3
51	*n*-nonanal	+	0.4	−		−		−		−		−		−	
52	benzaldehyde	+	5.0	+	2.3	+	0.1	+	0.07	+	0.04	+	0.02	+	0.02
53	2-nonenal	+	0.06	+	0.06	+	0.06	+	0.06	+	0.06	+	0.06	+	0.06
54	4-methylbenzaldehyde	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1
55	vanillin	−		+	0.02	+	0.02	+	0.02	+	0.02	+	0.02	+	0.02
pyridines															
56	pyridine	+	0.05	+	0.06	+	0.05	+	0.05	+	0.05	+	0.05	+	0.05
57	2-methylpyridine	+	0.01	+	0.01	+	0.01	+	0.01	+	0.01	+	0.01	+	0.01
58	2-acetylpyridine	+	0.05	+	0.05	+	0.06	+	0.05	+	0.05	+	0.05	+	0.05
acids															
59	isobutyric acid	+	0.01	+	0.01	+	0.01	+	0.01	+	0.01	+	0.01	+	0.01
60	2-methylpropanoic acid	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3
61	hexanoic acid	*b*		+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1
62	heptanoic acid	*b*		+	0.01	+	0.01	+	0.01	+	0.01	+	0.01	+	0.01
63	octanoic acid	*b*		+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
64	nonanoic acid	*b*		+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
65	decanoic acid	*b*		+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
esters															
66	ethyl butyrate	+	0.4	−		−		−		−		−		−	
67	ethyl caproate	+	0.6	+	0.6	+	0.6	+	0.6	+	0.6	+	0.6	+	0.6

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Table 1. (Continued)

		raw earth-almond		10 min roasting		20 min roasting		30 min roasting		40 min roasting		50 min roasting		60 min roasting	
no.	compounds	pres-ence	% area	pres-ence	% area	pres-ence	% area	pres-ence	% area	pres-ence	% area	pres-ence	% area	pres-ence	% area
esters (continued)															
68	butanoic acid, ethenyl ester	+	0.04	+	0.04	+	0.04	+	0.04	+	0.04	+	0.04	+	0.04
69	ethyl caprylate	+	0.1	−		−		−		−		−		−	
70	3-methyl-3-butenyl isovalerate	+	0.04	+	0.04	+	0.04	+	0.04	+	0.04	+	0.04	+	0.04
71	ethyl nonanoate	+	0.2	−		−		−		−		−		−	
72	methyl cinnamate	*b*		+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
73	ethyl oleate	+	0.07	−		−		−		−		−		−	
lactones															
74	γ-valerolactone	+	0.01	+	0.01	+	0.01	+	0.01	+	0.01	+	0.01	+	0.01
75	butyrolactone	+	0.4	+	0.4	+	0.4	+	0.4	+	0.4	+	0.4	+	0.4
76	γ-hexalactone	+	0.4	+	0.4	+	0.4	+	0.4	+	0.4	+	0.4	+	0.4
77	γ-octalactone	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2
78	γ-nonalactone	+	0.4	+	0.3	+	0.1	+	0.04	+	0.02	+	0.01	+	<0.01
79	γ-decalactone	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
80	γ-undecalactone	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
81	δ-dodecalactone	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
pyrazines															
82	pyrazine	−		+	0.2	+	0.4	+	0.2	+	0.1	+	0.08	+	0.03
83	methylpyrazine	−		+	0.8	+	4.5	+	3.6	+	3.1	+	2.4	+	1.8
84	2-methylpyrazine	+	0.2	+	6.0	+	11.5	+	9.8	+	3.3	+	2.8	+	1.2
85	2,5-dimethylpyrazine	+	0.3	+	8.9	+	15.6	+	10.7	+	5.9	+	4.7	+	3.2
86	2,6-dimethylpyrazine	+	1.1	+	3.4	+	9.8	+	3.8	+	2.5	+	2.5	+	1.5
87	2-ethylpyrazine	+	<0.01	+	1.0	+	2.1	+	2.2	+	2.1	+	1.9	+	1.3
88	2,3-dimethylpyrazine	+	0.01	+	0.4	+	0.7	+	1.6	+	0.9	+	0.8	+	0.4
89	2-ethyl-3,5-dimethylpyrazine	+	0.05	+	0.2	+	1.7	+	0.9	+	0.6	+	0.6	+	0.1
90	2,3-dimethyl-5-methylpyrazine	*b*		*b*		+	0.04	+	0.04	+	0.04	+	0.04	+	0.03
91	2-ethyl-6-methylpyrazine	+	0.1	+	1.0	+	2.1	+	1.9	+	1.1	+	1.1	+	0.5
92	2-ethyl-5-methylpyrazine	−		+	0.1	+	1.5	+	3.3	+	2.7	+	2.4	+	0.6
93	2-ethyl-3-methylpyrazine	*b*		+	1.4	+	1.7	+	1.7	+	1.0	+	0.8	+	0.5
94	trimethylpyrazine	+	0.1	+	2.5	+	4.4	+	4.7	+	2.3	+	2.0	+	1.6
95	ethenylpyrazine	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2
96	2,6-diethylpyrazine	+	0.05	+	0.08	+	0.1	+	0.2	+	0.6	+	0.07	+	0.06
97	3-ethyl-2,5-dimethylpyrazine	+	2.3	+	2.5	+	2.6	+	2.0	+	1.3	+	0.9	+	0.8
98	2,3-diethylpyrazine	*b*		+	0.02	+	0.02	+	0.02	+	0.02	+	0.02	+	0.02
99	tetramethylpyrazine	−		+	<0.01	+	0.01	+	0.03	+	0.02	+	0.01	+	<0.01
100	isopropenylpyrazine	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1
101	2,3-diethyl-5-methylpyrazine	−		+	0.04	+	0.04	+	0.04	+	0.04	+	0.04	+	0.04
102	2-ethenyl-6-methylpyrazine	+	0.1	+	0.6	+	1.5	+	1.3	+	1.0	+	0.9	+	0.5
103	3,5-diethyl-2-methylpyrazine	+	0.06	+	0.06	+	0.06	+	0.06	+	0.06	+	0.06	+	0.06
104	2-ethenyl-5-methylpyrazine	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3	+	0.3	+	0.2
105	2-methyl-5-(1-propenyl)pyrazine	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
106	2-methyl-6-(1-propenyl)pyrazine	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.09
107	5-methyl-6,7-dihydro-5*H*-cyclopentapyrazine	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2
108	2-acetylpyrazine	+	0.08	+	0.08	+	0.08	+	0.08	+	0.08	+	0.07	+	0.07
109	2,5-dimethyl-6,7-dihydro-5*H*-cyclopentapyrazine	+	0.05	+	0.05	+	0.05	+	0.05	+	0.05	+	0.05	+	0.04
110	2-acetyl-3-methylpyrazine	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2
111	2,3-dimethyl-6,7-dihydro-5*H*-cyclopentapyrazine	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
112	2-furylpyrazine[a]	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2	+	0.2
113	acetyldimethylpyrazine	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
114	2-acetyl-3-ethylpyrazine	*b*		+	0.01	+	0.01	+	0.01	+	0.01	+	0.01	+	0.01
115	2-butyl-3,5-dimethylpyrazine	*b*		*b*		*b*		+	<0.01	+	<0.01	+	<0.01	+	<0.01
116	2-methyl-5-(1-methylethyl)pyrazine	*b*		*b*		*b*		+	<0.01	+	<0.01	+	<0.01	+	<0.01
furans															
117	furfural	+	1.2	+	5.6	+	9.8	+	23.8	+	33.5	+	38.5	+	46.5
118	2,5-dimethyl-3-(2*H*)-furanone	−		+	0.01	+	0.01	+	0.01	+	0.01	+	0.01	+	0.01
119	2-acetylfuran	+	0.1	+	0.8	+	1.6	+	3.4	+	3.4	+	4.6	+	2.6
120	furfuryl acetate	+	0.01	+	0.03	+	0.06	+	0.3	+	0.5	+	0.7	+	0.9
121	allyl furoate	+	0.2	−		−		−		−		−		−	
122	α-methylfurfural	−		+	0.9	+	2.4	+	5.9	+	10.6	+	18.4	+	21.2
123	furfuryl alcohol	+	0.2	+	1.5	+	2.7	+	2.8	+	2.8	+	2.2	+	1.1
124	2-methyltetrahydrofuran	−		+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
125	7-methylbenzofuran	−		+	0.02	+	0.02	+	0.02	+	0.02	+	0.02	+	0.02
126	2,3-dihydrobenzofuran	−		+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1
127	hydroxymethylfurfural	−		−		+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
pyrroles															
128	1-ethyl-1*H*-pyrrole	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1
129	1-ethyl-1*H*-pyrrole-2-carboxaldehyde[a]	−		−		+	0.1	+	0.1	+	0.1	+	0.1	+	0.1
130	1-(2-furanylmethyl)-1*H*-pyrrole[a]	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
131	*n*-methyl pyrrol aldehyde[a]	−		+	0.1	+	0.1	+	0.1	+	0.1	+	0.1	+	0.1
132	2-acetylpyrrol	+	0.1	+	0.7	+	0.8	+	1.3	+	1.6	+	0.7	+	0.4
133	1*H*-pyrrole-2-carboxaldehyde[a]	−		+	0.03	+	0.03	+	0.03	+	0.03	+	0.03	+	0.03
134	1-methyl-2-pyrrolecarboxaldehyde[a]	−		+	0.04	+	0.04	+	0.04	+	0.04	+	0.04	+	0.04

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Table 1. (Continued)

no.	compounds	raw earth-almond		10 min roasting		20 min roasting		30 min roasting		40 min roasting		50 min roasting		60 min roasting	
		pres-ence	% area	pres-ence	% area	pres-ence	% area	pres-ence	% area	pres-ence	% area	pres-ence	% area	pres-ence	% area
phenols															
135	*p*-allylphenol (chavicol)	*b*		*b*		*b*		+	0.03	+	0.03	+	0.03	+	0.03
136	guaiacol	+	0.08	+	0.08	+	0.08	+	0.08	+	0.08	+	0.08	+	0.08
137	phenol	−		−		+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
138	2-ethylphenol	−		−		−		+	<0.01	+	<0.01	+	<0.01	+	<0.01
139	*p*-vinylguaiacol	+	<0.01	+	0.1	+	0.6	+	0.9	+	0.5	+	0.3	+	0.1
oxazoles															
140	4,5-dimethyloxazole	*b*		*b*		*b*		+	<0.01	+	<0.01	+	<0.01	+	<0.01
141	trimethyloxazole	*b*		*b*		*b*		+	<0.01	+	<0.01	+	<0.01	+	<0.01
thiazoles															
142	thiazole	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
143	benzothiazole	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01	+	<0.01
identified peaks (%)			90.3		87.5		94.7		98.3		92.0		99.7		97.2

[a] Tentatively identified. [b] Not quantifiable.

almonds, 110−120 mL of extract was obtained. The distillate was pressed through a Chromabond HR-P cartridge (polystyrol−divinylbenzol, 40−120 μm particle size) (Macheney-Nagel GmbH, Düren, Germany) for absorption and eluted with a pentane/dichloromethane (Protochem GmbH, Wesel, Germany) (2:1) solvent system for the extraction. The extract was concentrated to 100−200 μL of a residual colorless liquid on a water bath at 40 °C using a Vigreux column.

Gas Chromatography/Mass Spectrometry (GC/MS). The analyses were performed on raw and roasted earth-almond concentrated extracts and carried out in a Hewlett-Packard 5890 Series II gas chromatograph coupled with a HP 5985 mass spectrometer. One microliter of aroma extract was injected onto a Carbowax 20 M capillar column (50 m × 0.25 mm i.d., film thickness of 0.4 μm) (CS-Chromatographie Service GmbH, Langerwehe, Germany) using a split injector. The column inlet pressure was 10^5 Pa, and hydrogen was used as a gas carrier (split 1:30). The oven temperature was programmed as follows: the first 5 min at 50 °C, then from 50 to 110 °C at 3 °C/min followed by 110 to 230 °C at 5 °C/min, and finally remaining at 230 °C for 40 min; the detector temperature was 230 °C. The conditions of the programmable temperature vaporizer (PTV) injector (Fa. Gerstel) were the following: from 40 to 250 °C at 10 °C/s. A mass spectrometer was used as a detector. The MS parameters were as follows: temperature of ion source = 200 °C, mass interval = 40−350 m/e, and ionization energy = 70 eV.

The chufa aroma compounds were identified with reference to Kovats Indices and mass spectra comparison (Kovats, 1965; Stenhagen *et al.*, 1974; Heller and Milne, 1978).

RESULTS AND DISCUSSION

In this paper, the main contributors to the differences in the odors of raw and roasted earth-almond are shown, and the relationships of the different compounds to the odor profiles of earth-almond are discussed. Likewise, a study of the effect of roasting temperature on the aroma components of earth-almond was carried out. The obtained results agree, at least in part, with the limited data published by Soliman *et al.* (1982).

From the comparison of the three methods used for the isolation of volatiles in earth-almond, the yields and appearance of the products were greatly affected by the method employed. In the case of steam distillation and simultaneous distillation−extraction, the yields were much lower than with high-vacuum distillation. This latter was found to give more reproducible results and include higher amount of isolated compounds than that with the other methods of extraction. Likewise, Table 1 refers to the aroma compounds isolated only by high-vacuum distillation.

The majority of the volatiles identified in roasted earth-almond like pyrazines (35), furans (11), and pyrroles (7), together with the fact that earth-almonds contain carbohydrates and lipids in large quantities (Morell and Barber, 1983), suggest the possibility of flavor formation via the Maillard reaction. This reaction is one of the most important routes to flavor compounds in cooked foods. The initial stages of the reaction involve the condensation of the carbonyl group of a reducing sugar with an amino compound, followed by the degradation of the condensation products which gives a number of different oxygenated compounds. The subsequent stages of the Maillard reaction involve the interaction of these compounds with other reactive components such as amines, amino acids, and aldehydes. These additional reactions lead to many important classes of flavor compounds, including furans, pyrazines, pyrroles, oxazoles, thiazoles and other heterocyclic compounds, which are shown to be present in this paper.

The volatile components in roasted earth-almond are similar to those from other roasted products, such as peanuts (Mason *et al.*, 1966; Walradt *et al.*, 1971), coffee (Bondarovich *et al.*, 1967; Friedel *et al.*, 1971; Stoll *et al.*, 1967), filbert (Kinlin *et al.*, 1972; Sheldon *et al.*, 1972), almond (Takei *et al.*, 1974), pecan (Wang and Odell, 1972), and pistachio nut (Soliman *et al.*, 1981). Thus, pyrazines, pyridines, pyrroles, and furan derivatives are generally major components of roasted earth-almond aroma. Heterocyclic compounds increase in both number and concentration when earth-almond is roasted, creating an odor more reminiscent of cocoa or chocolate.

Concerning the indicator compounds for evaluation of the degree of earth-almond roasting, Table 1 shows the identified aroma compounds grouped according to their chemical structure. The main flavor compounds identified in raw earth-almond were alcohols which represent about 67.9%: *n*-hexanol (no. 27) (21.6%), isoamyl alcohol (no. 22) (19.1%), *n*-amyl alcohol (no. 24) (6.6%), isobutyl alcohol (no. 20) (4.2%), 1-heptanol (no. 40) (4.3%), 1-octanol (no. 29) (3.5%), and 1-nonanol (no. 44) (3.2%). Among hydrocarbons, limonene (no. 1) represented 4.2%, whereas in the case of aldehydes (6.4% in total), benzaldehyde (no. 52) plays the main role (5%) in raw earth-almond (Figure 1A).

Roasted earth-almond (Figure 1B) contained more furans, pyrazines, and pyrroles, as formed by the Maillard reaction during the roasting process. Thus,

over 35 pyrazines have been identified in roasted earth-almond aroma. They arise from amino acids and sugars in Maillard and Strecker reactions.

Among the most abundant products of Maillard reaction are oxygenated furans and pyrans, such as furfural, α-methylfurfural, and 2-acetylfuran. In their own right, oxygenated furans may contribute to caramel-like, sweet aromas in heated foods; however, they are important intermediates to other flavor compounds, including thiophenes, furanthiols, and other sulfur-containing compounds. Hodge *et al.* (1972) divided Maillard reaction flavors into four main groups by correlating their aromas, their molecular shape structures, and their routes of formation. The first two groups are the nitrogen heterocyclics, which give corny, nutty, roasted, or bready aromas, and the cyclic enolones which give rise to caramel aromas. These groups give the characteristic flavors to heated foods, whereas the other two groups, the polycarbonyls and monocarbonyls, include the more volatile supplementary flavors.

Among the identified compounds, it is pointed out that acetoin (no. 7) and 2,3-pentanedione (no. 3) are well-known sugar degradation products which contribute to the sweet, buttery, and caramel odors perceived. Likewise, hexanal (no. 48), heptanal (no. 49), nonanal (no. 51), and nonenal (no. 53) are indicators of lipid oxidation. Also, the ketone 2-heptanone (no. 6) could have originated from lipid as well (Ho and Carlin, 1989).

With respect to degradation products of carbohydrates, cyclopentenolones are formed by condensation of degradation products thermally generated from reducing sugars. Some cyclopentenolones can act as precursor compounds and can undergo condensation with α-amino ketones and ammonia to form bicyclic pyrazines such as the peanutty smelling 5-methyl-6,7-dihydro-5*H*-cyclopentapyrazine (no. 107).

Koehler *et al.* (1969) found that the carbohydrate source affected the total yield of pyrazines formed. Both the type of amino acid and type of sugar had an effect on the total yield and relative distributions of pyrazines.

On the other hand, within the range of technical roasting processes, the concentration of pyrazine itself (no. 82), methylpyrazines (itself, 2-, 2-ethyl-6-, and 2-ethenyl-6-) (nos. 83, 84, 91, and 102), dimethylpyrazines (2,5-, 2,6-, 2-ethyl-3,5-, and 3-ethyl-2,5-) (nos. 85, 86, 89, and 97), and trimethylpyrazine (no. 94) increases at the beginning of overroasting but decreases from 30 min of roasting onward, possibly due to volatilization.

Quantitatively, furfural was the major peak of furans in all of the samples along the roasting process. Furfural (no. 117) and α-methylfurfural (no. 122) increased characteristically as a function of time, from 5.6 and 0.9%, respectively, after 10 min of roasting to 46.5% in the case of furfural and 21.2% α-methylfurfural after 60 min of roasting.

On the other hand, a decrease and then an increase were observed with several other furan compounds like 2-acetylfuran (no. 119) and furfuryl alcohol (no. 123), as the extent along the roasting process of deamination increased. It is possible that, at the lowest and highest levels of deamidation, sugar activation was enhanced. This could be due to the fact that at low levels of deamidation more ammonia was released, resulting in more sugar being activated. This fact may be due to changes in protein structure brought about by deamidation hydrolysis of peptide bonds (Izzo and Ho, 1993). This trend was not found to be true with furfural.

Likewise, the ratio between pyrazines and furans became smaller as roasting time increased, as after 20 min of roasting the content of pyrazines was about 61.8% whereas furans represented 16.7%; on the other hand, after 60 min of roasting, pyrazines decreased to 15.5% in contrast with the content of furans, which rose to 72.4%. Pyrazines are one of the major classes of compounds formed in the Maillard reaction. They contribute directly to the roasted flavor of earth-almond. Pyrazine itself is formed only to a very small extent. Factors such as time and temperature of reaction are important variables in determining the nature and quantity of the products from such reactions (Shibamoto and Bernhard, 1976). Several mechanisms have been proposed for the formation of pyrazines in food flavors (Vernin and Párkányi, 1982; Maga, 1982), and one important route is the Strecker degradation, which is one of the most important reactions associated with the Maillard reaction, and involves the oxydative deamination and decarboxylation of an α-amino acid in the presence of a dicarbonyl compound. This leads to the formation of amino ketones, which are important intermediates in the formation of several classes of heterocyclic compounds (Vernin and Párkányi, 1982).

Various volatiles derived from Strecker degradation are important odorants in roasted earth-almond. α-Dicarbonyls, which are generated by a side pathway of the Maillard reaction, are highly reactive and condense with free amino groups of amino acids. Self-condensation of the amino ketones, or condensation with other amino ketones, forms dihydropyrazines (nos. 107, 109, and 111) that can be oxidized to the pyrazine.

Besides pyrazine itself (no. 82), the most widespread monosubstituted pyrazines included 2-methyl, 2-ethyl, 2-acetyl, and 2-furyl derivates (nos. 84, 87, 108, and 112). Among the di-, tri-, and tetrasubstituted derivates, dimethylpyrazine isomers (nos. 85, 86, and 88) as well as their methylethyl homologues (no. 116) trimethyl-, 2,5-dimethyl-3-ethyl-, and tetramethylpyrazines (nos. 94, 97, and 99) were also frequently detected. Previous studies have shown these to occur in roasted nut products (Kinlin *et al.*, 1972; Walradt *et al.*, 1971).

Tetramethylpyrazine (no. 99) was also found in fermented soy products (Kosuge *et al.*, 1962), whereas ethyl-2,5-dimethyl- and trimethylpyrazines (no. 97 and 94) are formed in relatively large amounts during the deep-fat frying of soy beans, in which they are responsible for the nut-like or peanut butter-like aroma (Wilkens and Lin, 1970).

The alkylpyrazines generally have nutty, roasted aromas with some eliciting earthy or potato-like flavor notes (Fors, 1983). The odor threshold values of the mono-, di-, tri-, and tetramethylpyrazines are all relatively high (>1 ppm), but these pyrazines probably only play minor roles in food aromas. However, replacing one or more of the methyl groups with ethyl can give a marked decrease in the odor threshold value (Guadagni *et al.*, 1972), and some ethyl-substituted pyrazines have threshold values sufficiently low to be important in the roast aroma of earth-almond and cooked foods.

2-Acetylpyrazine and its 3-methyl, 3-ethyl, and dimethyl homologues (nos. 108, 110, 114, and 113) were identified mainly in roasted products, including peanuts (Walradt *et al.*, 1971), filberts (Kinlin *et al.*, 1972), almonds (Takei *et al.*, 1974), etc. Apart from 2-acetylpyrazine (no. 108), relatively few pyrazines with oxygen-containing substituents have been reported as products

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A

B
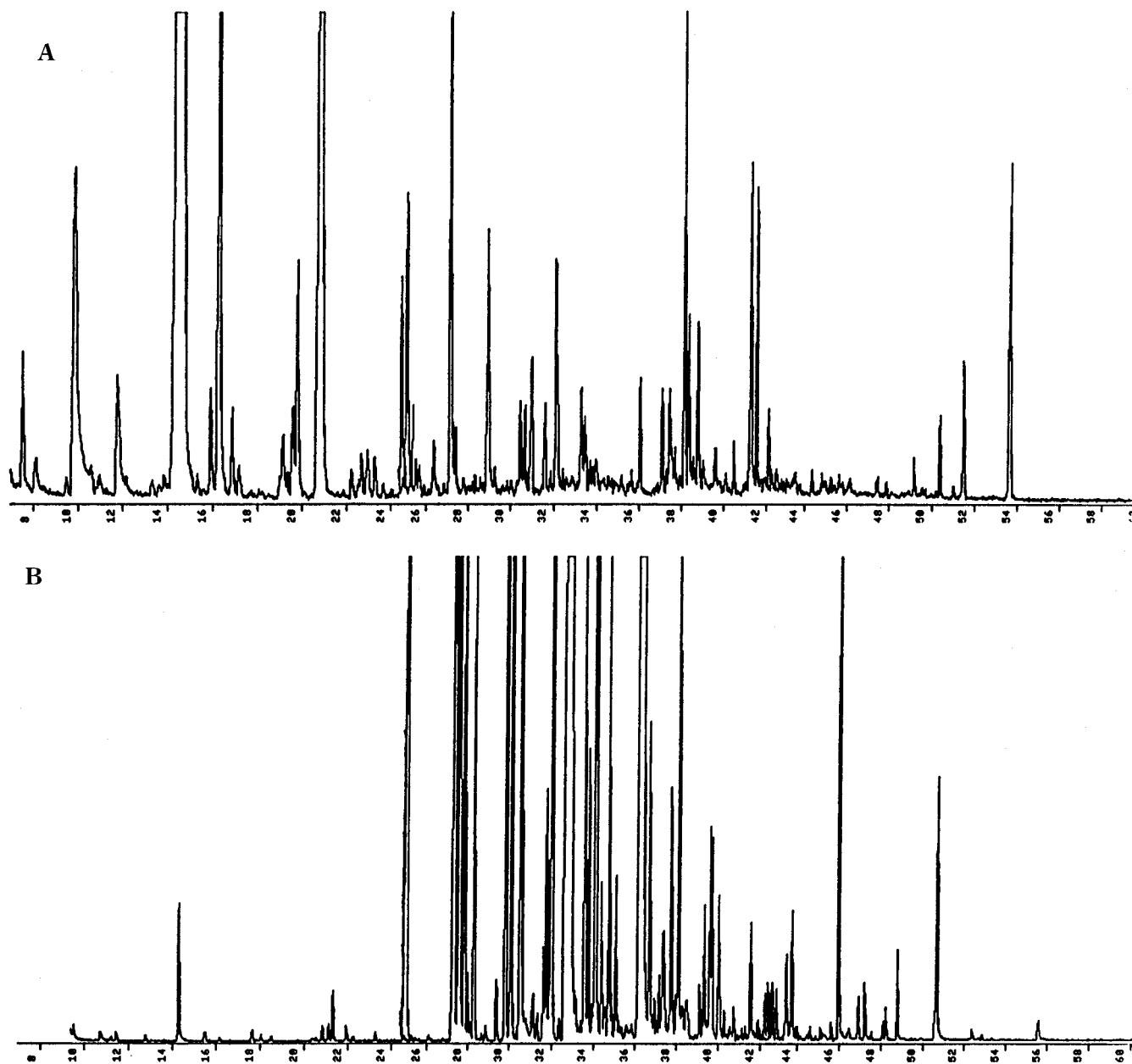
Figure 1. (A) Gas chromatogram of the aroma compounds in the extract obtained by high-vacuum distillation in raw earth-almond. (B) Gas chromatogram of the aroma compounds in the extract obtained by high-vacuum distillation in 60 min-roasted earth-almond.

of the Maillard reaction in foods, although methoxy-pyrazines are important biosynthesized aroma compo-nents in a number of vegetables (Fors, 1983). Numer-ous pyrazines derived from Maillard reactions occur in roasted earth-almond in remarkable amounts and form about 30% of the overall volatile content (40 min-roasted earth-almond).

Pyridine (no. 56) and alkyl-substituted pyridines (nos. 57 and 58) have also been isolated from earth-almond, and they appear to result from Maillard reactions. They can be formed via a cyclization of suitable amino sugar derivatives. Watanabe and Sato (1971) suggested that pyridines, like pyrazines, could contribute to the typical roasted flavor of heated foods, although Pittet and Hruza (1974) found that most of the alkyl-substituted pyridines which they investigated had green flavors.

Oxazoles (nos. 140 and 141) have been described as ingredients of coffee and cocoa aroma (Flament, 1991). The contribution of these compounds to the overall aroma of roasted earth-almond is perhaps not as

important as that of the closely related thiazoles (nos. 142 and 143), which have lower threshold values, and only when the substitution is increased do they add nutty, roasted, and sometimes meaty characteristics (Pittet and Hruza, 1974; Ho and Jin, 1984). The nature and number of alkyl substituents appear to be impor-tant in determining the aroma character, and certain di- and trialkyl derivates have roasted notes. A number of thiazoles have been isolated from foods which have undergone heat processing or Maillard-type reactions. These include coffee (Stoll *et al.*, 1967), roasted peanuts (Waldradt *et al.*, 1971), and roasted filberts (Kinlin *et al.*, 1972), among others.

Pyrroles possess mostly burnt aroma notes and are found in the volatiles of most heated foods (Maga, 1981). Some pyrroles may contribute desirable aromas; e.g. 2-acetylpyrrol (no. 132) has a caramel-like aroma, and 1*H*-pyrrole-2-carboxaldehyde (no. 133) is sweet and cornlike (Fors, 1983). Many more volatile pyrroles have been found in coffee than in other foods (Flament, 1991),

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Table 2. Enantiomeric Distribution of γ-Lactones in Earth-Almond[a]

	R (+) (%)	S (−) (%)
γ-hexalactone	34.6	65.4
γ-octalactone	46.3	53.7
γ-nonalactone	43.5	56.5
γ-decalactone	56.8	43.2
γ-undecalactone	47.3	52.7

[a] Mean values of three determinations.

and they are common products of amino acid−sugar model systems. Whereas the typical roasted aromas of the Maillard reaction products appear to be due mainly to the N-heterocyclic compounds, the fragant caramel aroma fraction seems to consist mainly of oxygen heterocyclics.

Likewise, most of the phenol compounds are formed by a thermal degradation cascade of phenolic acids. Among numerous phenolic compounds, only *p*-vinylguaiacol (no. 139) and guaiacol (no. 136) show a considerable impact on roasted earth-almond flavor. One of the intermediate breakdown products, vanillin (no. 55), seems to be of lower sensory importance.

According to the obtained results, pyrazines (in raw earth-almond, 5.8%) and pyrroles (0.2%) significantly increase during the roasting process and reach their maximum levels at optimal roasting conditions (120 °C for 20 min): 61.8% pyrazines and 1.1% pyrroles. On the other hand, pyrroles slightly decrease during overroasting at 60 min (0.7%), perhaps as a result of their reactivity in contact with amino compounds (Maga, 1981), whereas pyrazines decrease steeply, representing 15.5% of the total as a result of the increasing of furans (72.4% at 60 min).

Likewise, whereas pyridines and acids remain more or less unchanged, alcoholes, aldehydes, hydrocarbons, and esters decrease during earth-almond roasting as a result of the Maillard reaction.

Concerning γ-lactones, the importance of chiral γ-lactones as natural flavor and intermediates is well-known in the synthesis of natural products, as well as the chiroptical and sensory properties of their enantiomers. Lactones are ubiquitous in nature and have been isolated from all major food systems (Bernreuther *et al.*, 1989).

With respect to the enantiomeric distribution of γ-lactones in earth-almond, for γ-hexalactone, γ-octalactone, γ-nonalactone, and γ-undecalactone (this was found in traces), the S enantiomer predominated in earth-almond, whereas in the case of γ-decalactone (also found in traces), the R enantiomer was the main constituent (Table 2). Similar results have been described earlier for a limited number of fruits, such as raspberry and strawberry (Bernreuther *et al.*, 1989).

The enantiomeric ratios R (+):S (−) and the concentration of the isolated γ-lactones remained constant over the course of the roasting process (from 10 until 60 min), which means that γ-lactones were not broken down due to roasting temperatures at increasing times. Only γ-nonalactone decreased in concentration from 0.4% in raw earth-almond to <0.01% in 60 min-roasted earth-almond.

Nevertheless, a more thorough study of the effect of roasting temperature on the enantiomeric composition of γ- and δ-lactones is currently in progress in this laboratory in collaboration with P. Schreier from the University of Würzburg, Germany.

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