sitate a great investment of heat energy to produce a dry product.

One approach to lowering the water content of the coagulated protein complexes is to use organic solvents, such as methanol or acetone, to remove the protein. Organic solvents, due to their high vapor pressure, should produce a product which is easy to dry. The resulting dried product would be almost totally composed of protein. In addition, the organic solvent could be recovered from the mother liquor after the coagulation step, or during the drying step, and recycled.

Methanol and acetone each acts as a protein coagulant in diluted blood solutions at acidic pH values. As displayed in Figure 4, methanol has an optimum in the range of pH 2–3, while acetone is effective in the pH range 2.5–3.5 when used at final concentrations of 20% (v/v) in blood diluted 1 to 3. Methanol is significantly more effective than acetone for removal of protein from diluted blood (Figure 5). At a 20% (v/v) concentration in diluted blood (pH 3.0) methanol removes 98.5% of the total Kjeldahl nitrogen, whereas acetone removes 89% of the Kjeldahl nitrogen at a 28% (v/v) concentration (Figure 5). For both the acetone and methanol products 83% of the weight of the complex is lost upon drying.

In spite of the effectiveness of methanol as a blood protein coagulant, the amount of methanol required is significant. Other approaches to lowering the water content of the coagulant–protein complexes are currently being investigated in our laboratory. In addition, we are currently determining the identity and percent of the components present in the coagulant–protein complexes produced by the above described techniques. We believe that cold blood processing by chemical coagulation holds promise as an economical technique for the production of dried blood suitable for use as an animal feed ingredient.

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LITERATURE CITED

Folin, O., Denis, W., *J. Biol. Chem.* **11**, 527 (1912).
Kramer, S. L., Waibel, P. E., Behrends, B. R., El Kandelgy, S. M., *J. Agric. Food Chem.* **26**, 979 (1978).
Merrill, M. H., Fleisher, M. S., *J. Gen. Physiol.* **16**, 243 (1932).
Sanders, M. D., *Ind. Eng. Chem.* **6**, 1151 (1948).
Somogyi, M., *J. Biol. Chem.* **86**, 655 (1930).
Vandergrift, V., Ratermann, A. L., *J. Agric. Food Chem.* **27**, 1252 (1969).
Waibel, P. E., Cuperlovic, M., Hurrell, R. F., Carpenter, K. J., *J. Agric. Food Chem.* **25**, 171 (1977).

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Substituted 4-Methyl-1,3-dioxolanes: Solvent Interaction Products in Some Commercial Beef Flavorings

Glesni MacLeod,* Mehdi Seyyedain-Ardebili, and Alexander J. MacLeod

By use of a modified Likens and Nickerson extraction procedure followed by low-temperature/high-vacuum distillation, representative samples of aroma volatiles were obtained from some commercial beef flavorings. Prefractionation of concentrates by preparative gas chromatography facilitated subsequent analysis by combined gas chromatography/mass spectrometry. One fraction provided a number of similar mass spectra exhibiting intense characteristic peaks at m/e 87. It was considered that these could be 2-substituted-4-methyl-1,3-dioxolanes, but dioxolanes have not been reported as volatile components of meat. Selected 1,3-dioxolanes were synthesized and comparison of their mass spectra and GC retention times confirmed the identities of the unknown components of the simulated meat flavor isolate. Their origin may be explained by interaction of propane-1,2-diol, a commonly used solvent for commercial flavors, with carbonyl aroma components—interactions which can modify the flavor characteristics of the product.

Results of recent work undertaken at our laboratory involving the chemical and sensory analysis of cooked beef aroma have been reported (MacLeod and Coppock, 1976, 1977, 1978). As part of this continuing program, some commercial beef flavorings have been analyzed; these were mainly based on natural materials of plant or animal origin. Aroma extraction and concentration was achieved using previously reported techniques, optimized for cooked beef aroma isolation (MacLeod and Coppock, 1976), and the extracts obtained were analyzed by routine gas chromatography (GC). However, due to the complexity of the gas chromatograms, the total isolate was then fractionated by preparative GC into three fractions. The first of these, comprising the more volatile components, provided some initially unexpected results and these are the subject of this paper.

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EXPERIMENTAL SECTION

Sample Preparation. A concentrated total isolate of the aroma components of the commercial, simulated beef flavor was prepared as follows, based on the previously reported method for genuine cooked beef aroma isolation

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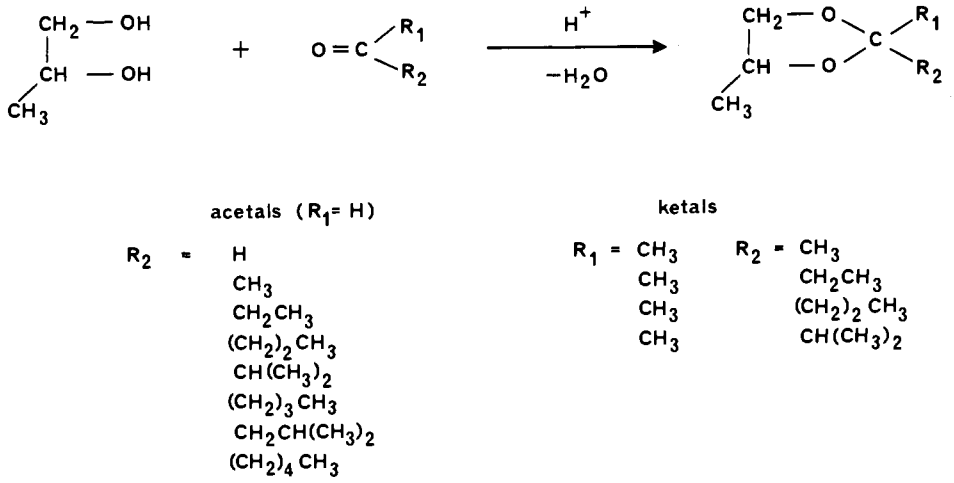


Figure 1. Synthesis of 2-alkyl-4-methyl-1,3-dioxolanes (acetals) and 2-alkyl-2,4-dimethyl-1,3-dioxolanes (ketals).

(MacLeod and Coppock, 1976, 1977). The commercial sample (300 g) in distilled water (300 mL) was submitted to continuous distillation/solvent vapor extraction using the modified Likens and Nickerson apparatus developed by MacLeod and Cave (1975). The solvent employed was 2-methylbutane (30 mL) and the extraction period was 4 h. A "use-level" total isolate was prepared in a similar manner, but using a 3.75-g sample and 750 mL of distilled water (equivalent to recommended manufacturer's use level concentration) and extracting for 1 h. The extracts thus obtained were concentrated to a volume of ca. 400 μL by high-vacuum/low-temperature distillation (MacLeod and Coppock, 1976, 1977). The first isolate was sufficiently concentrated to facilitate identification of its individual components. The second isolate served to confirm that the same compounds were also present at use-level concentrations.

Fractionation of Total Isolate. Using the concentrated total isolate, a Pye–Unicam Series 104 gas chromatograph with heated fid was used, equipped with a Pye-Unicam manual preparative system. After extensive evaluation, the following procedure provided superior fractionation. A glass preparative column (5 m × 7 mm i.d.) was packed with 20% PEG 20M coated on 60–70 BSS mesh acid-washed Diatomite C. An outlet split ratio of 100:1 was employed and a short heated (220 °C) glass tube led the major portion of the column eluant to glass U-shaped traps cooled in liquid N_2. Using a nitrogen carrier gas flow rate of 30 mL/min and a temperature program of 70 °C for 9 min, followed by a 6 °C/min increase to 115 °C for 30 min, followed by a 6 °C/min rise to 150 °C for the remainder of the run, the concentrated total isolate was thus separated into three broad fractions by repeated injections of 200-μL aliquots. The individual fractions collected were then separately rechromatographed to afford further purification and to ensure no qualitative nor quantitative variation in the fractions compared with the total isolate as a result of the preparative GC.

Analytical Gas Chromatography. The first fraction (F1) was analyzed by GC using a Pye-Unicam Series 104 dual-column instrument with heated fid. Optimum resolution for subsequent gas chromatography/mass spectrometric (GC/MS) analysis on a packed column was obtained using a glass column (6 m × 4 mm i.d.) packed with 20% PEG 20M coated on 100–120 mesh acid-washed Diatomite C and using a nitrogen carrier gas flow rate of 30 mL/min. The best temperature program was 70 °C for 20 min, followed by a 2.5 °C/min increase to 150 °C for the remainder of the run. Retention times and peak areas were measured using a Hewlett Packard integrator Model 3370B, and internal standards used were butanone and dimethyl disulfide. Synthesized 1,3-dioxolanes were analyzed in an identical manner.

Superior resolution of F1 was obtained using a 100 ft × 0.02 in. i.d. SCOT column coated with PEG 20M, a N_2 carrier gas flow rate of 3 mL/min, and the temperature program already described.

Gas Chromatography/Mass Spectrometry. A Kratos/AEI MS30 double focussing mass spectrometer was employed, equipped with a Pye-Unicam series 104 gas chromatograph linked via a heated membrane separator interface. The system was connected on-line to a dedicated data processing system (Kratos/AEI DS 50). For analysis of F1, the same (analytical) GC conditions as detailed above for the packed column were applied, but using a helium carrier gas. Total elution time was 90 min. Significant mass spectrometer operational parameters were as follows: ionization potential, 70 eV; ionization current, 300 μA; source temperature, 200 °C; resolution, 1500; scan speed, 3 s/decade (repetitive throughout GC run). For optimum sample transfer, an interface temperature of 170 °C was adopted. The background subtraction facility, various scale expansions, and, most importantly, the retrospective single ion monitoring (RSIM) facility of the data system were extensively employed in evaluating the mass spectral data from this sample.

Synthesized 1,3-dioxolanes were analyzed in identical manner.

Synthesis of Substituted 4-Methyl-1,3-dioxolanes. A method based on that of Marshall and Williams (1967) was adopted, which involved acid-catalyzed condensation of propane-1,2-diol with the appropriate aldehyde or ketone (see Figure 1). Details are given here of only one synthesis in exemplification.

2,4-Dimethyl-1,3-dioxolane. All reactants and reagents were carefully dried (with anhydrous $MgSO_4$). Equimolar quantities of propane-1,2-diol (15.2 g) and acetaldehyde (8.8 g) were mixed at 0 °C and then refluxed together with 0.5 g of toluene-*p*-sulfonic acid (catalyst) and 40 mL of benzene. The water produced during the reaction was azeotropically distilled from the mixture and collected in a Dean and Stark water separator protected by a $CaCl_2$ drying tube. Completion of reaction was indicated when the stoichiometric volume of water had been collected. In this preparation the reaction time was only 1 h, but for other dioxolanes synthesized, times of up to 6.5 h were necessary. The reaction mixture was cooled to room temperature and neutralized with solid $NaHCO_3$. Using a fractional distillation Vigreaux column at atmospheric pressure, the benzene was first removed at ca. 80 °C, and

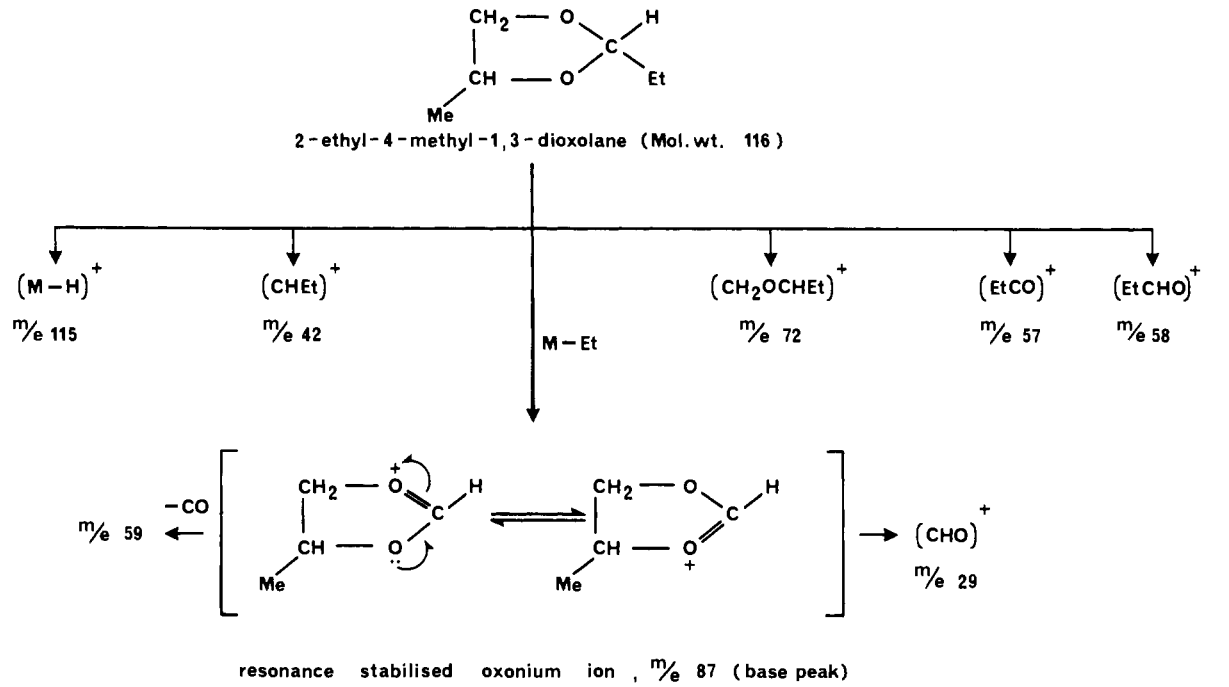


Figure 2. Principal mass spectral cleavages of propylene acetals.

then the resulting dioxolane was distilled and collected, bp 90–1 °C [lit. bp 92.8 °C; Lucas and Guthrie (1950)]. For some of the higher members of the series it was necessary to carry out this final distillation under reduced pressure.

Separation of Syn and Anti Isomers of 2-Isopropyl-4-methyl-1,3-dioxolane. For one synthesized dioxolane, syn and anti isomers were separated by preparative GC using the equipment and column described earlier. The column was maintained at 110 °C, and for satisfactory resolution only 100-μL aliquots could be injected. Further (complete) purification of the separated isomers was then achieved using an analytical column (6 m × 4 mm i.d.), but otherwise identical conditions, and injecting 20 μL each time.

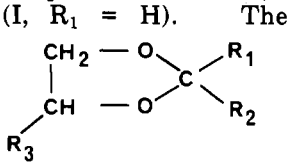
Nuclear Magnetic Resonance Spectroscopy. ^1H NMR spectra of the pure syn and anti isomers of 2-isopropyl-4-methyl-1,3-dioxolane were carefully recorded in CCl_4 solution using a Perkin-Elmer R12B spectrometer operated at 60 MHz.

Sensory Analysis of Synthesized Dioxolanes. This was accomplished by the technique of odor port assessment of the pure separated dioxolane isomers as they eluted from the analytical GC column. Gas chromatography instrumentation and conditions were as already described under the heading "Analytical Gas Chromatography", with the exception that the column was operated isothermally at 125 °C. A 50% solution (in triply distilled 2-methylbutane) of each synthesized dioxolane (usually a mixture of syn and anti isomers) was prepared, and 5 μL was injected into the GC column. The eluant from the column was split in a 10:1 ratio, with the major portion passing through a heated (220 °C) glass line to the odor port exit for sniffing by a total of five untrained assessors during replicate assessments.

RESULTS AND DISCUSSION

The first fraction of the total isolate from the commercial beef flavor was still a relatively complex mixture containing at least 90 components resolved on the SCOT column. When analyzed by combined GC/MS, many of these components were identified, but four—all major constituents of the sample—provided unusual mass spectra which bore no relationship to those of compounds previously obtained from genuine cooked beef aroma isolates. The spectra were very similar, suggesting a common, and novel group of compounds. A significant feature of all four spectra was a characteristic base peak at m/e 87. Using the RSIM facility of the data system following GC/MS, a single ion trace based on mass 87 was produced, and in addition to the four GC peaks already mentioned, a further six peaks were obtained. On careful examination of the spectra indicated by these extra peaks, four spectra showed m/e 87 as the base peak. Without the RSIM facility it would have been difficult in most cases, and impossible in a few, to detect these further components. Some were minor components whose GC peaks were barely visible on the total ion current trace and two coeluted with other major components, and certainly their presence would not have been suspected without RSIM.

Summaries of the mass spectra of these ten peaks are given in Table I. A base peak at mass 87 is comparatively unusual and suggests the presence in the sample of a series of closely related compounds possessing a readily formed and stable common "nucleus" characterized by a fragment mass of 87. The spectra exhibited no molecular ion peaks. From application of basic mass spectrometry fragmentations and by comparison with literature compilations (Eight Peak Index of Mass Spectra, 1974), it was considered that these compounds could be 2,4-disubstituted-1,3-dioxolanes (I, R_1 = H). The class of 2-



I

monosubstituted-1,3-dioxolanes was dismissed since these show a base peak at m/e 73 (Marshall and Williams, 1967; Eight Peak Index of Mass Spectra, 1974). Furthermore, fragmentation patterns suggested a methyl substituent present on the C-4 position (I, R_3 = CH_3) (Beynon, 1960; Marshall and Williams, 1967). Figure 2 shows the principal cleavages expected to be undergone by this group of compounds (propylene acetals) in the mass spectrometer, taking as an example 2-ethyl-4-methyl-1,3-dioxolane. The

Table I. Summaries of Mass Spectra of Some Components of the First Fraction of an Isolate from a Commercial Simulated Beef Flavor

GC peak 26	*m/e*	87	31	58	43	59	41	44	45	
	% rel int	100	77	75	71	64	43	40	36	
GC peak 29	*m/e*	87	31	58	59	41	43	44	45	101
	% rel int	100	81	75	73	44	41	34	25	1
GC peak 39	*m/e*	87	59	31	41	43	57	42	72	
	% rel int	100	73	64	62	31	22	12	7	
GC peak 41	*m/e*	87	59	31	41	57	42	43	72	
	% rel int	100	72	55	53	22	21	20	12	
GC peak 43	*m/e*	87	59	41	43	31	56	57	71	
	% rel int	100	52	46	42	34	30	16	2	
GC peak 44	*m/e*	87	41	39	59	31	65	43	56	
	% rel int	100	72	62	49	42	40	30	18	
GC peak 57	*m/e*	87	59	41	31	55	57	70		
	% rel int	100	51	44	32	5	5	2		
GC peak 58	*m/e*	87	59	41	31	43				
	% rel int	100	42	36	25	9				
GC peak 40	*m/e*	43	71	87	60	41	45	42	72	57
	% rel int	100	95	47	31	22	19	15	5	2
GC peak 51	*m/e*	43	71	41	87					
	% rel int	100	54	32	2					

resonance stabilized oxonium ion explains the base peak at *m/e* 87, and most other fragmentations shown were also typified by the mass spectral evidence obtained (see Table I).

2,2-Disubstituted-1,3-dioxolanes (I, R_1 and $R_2 \neq H$) had also been considered as possible identities for this group of compounds, but published spectra again indicated that this was unlikely since such ketals tend to give intense peaks in their mass spectra characteristic of the second (smaller) alkyl substituent on the C-2 position. For example, methyl ketones condensed with diols give 1,3-dioxolanes (I, $R_1 = CH_3$, R_2 = alkyl), which show characteristic intense peaks, often the base peak, at *m/e* 43 due to $CH_3C{\equiv}O^+$ (Marshall and Williams, 1967; Schormüller and Kochmann, 1969; Ferretti and Flanagan, 1971). Clearly, however, by analogy with the first group of compounds, these methyl ketals were possibilities for the two other compounds whose mass spectra are given at the bottom of Table I.

On the basis of the above deductions, an extensive series of 2-monosubstituted-4-methyl-1,3-dioxolanes (propylene acetals) and a more limited range of 2,2-disubstituted-4-methyl-1,3-dioxolanes (propylene ketals) were synthesized in order to confirm the suspected identities and to determine the particular substituents. Figure 1 shows the particular dioxolanes which were synthesized and for which GC relative retention measurements were then calculated. For each acetal, two GC peaks were obtained, representing syn and anti isomers, except for the first member of the series (I, $R_1 = R_2 = H$). In all cases, the first isomer of the pair to be eluted (isomer 1) was the one which predominated under the conditions of synthesis and analysis. The GC peak area ratio for isomer 1 compared with isomer 2 was consistently approximately 1.6:1. Similarly such isomers were obtained for the ketals, but only for those prepared from unsymmetrical ketones (I, $R_1 \neq R_2$).

Proton nuclear magnetic resonance (^1H NMR) spectra and refractive indices obtained for the individual separated and purified isomers of 2-isopropyl-4-methyl-1,3-dioxolane are compared with the corresponding literature values (Willy et al., 1970) in Table II. According to Willy and his co-workers (1970), who studied the configurations of numerous 2,4-disubstituted-1,3-dioxolanes, the syn isomer consistently is thermodynamically more stable, displays an upfield chemical shift for the C-2 proton (I, $R_1 = H$), and, with the exception of one compound only, exhibits a lower refractive index, in comparison with the anti isomer. By correlation with the literature (Table II) it is clear that for 2-isopropyl-4-methyl-1,3-dioxolane, isomer 1 has the syn configuration while isomer 2 has the anti stereochemistry. From these results, and also bearing in mind that for all other synthesized dioxolanes which exhibited syn and anti isomers, the main product of synthesis was also always eluted first from the GC column, it can be deduced that for all such synthesized dioxolanes, the thermodynamically more stable syn isomer is always eluted before the corresponding anti compound.

GC relative retention times confirmed the suspected identities of the ten unknown components (eight acetals, two ketals) of the simulated meat flavor isolate, and these data are summarized in Table III. The mass spectra of some of these synthesized dioxolanes were also recorded for further confirmation, and these are given in Table IV. Although the mass spectra are not that useful for complete interpretive purposes in this instance, it can be seen that these also agree with those of previously unknown GC peaks (compare Table I).

In summary, the following were therefore conclusively identified in the isolate from the simulated beef flavor sample: 2,4-dimethyl-1,3-dioxolane (syn and anti), 2-ethyl-4-methyl-1,3-dioxolane (syn and anti), 2-isopropyl-4-methyl-1,3-dioxolane (syn and anti), 2-(2-methylpropyl)-4-methyl-1,3-dioxolane (syn and anti) and either the syn or anti isomer (or both) of 2,4-dimethyl-2-ethyl-1,3-dioxolane and 2,4-dimethyl-2-propyl-1,3-dioxolane.

In the case of the latter two ketals, the uncertainty is due to the fact that the isomers of each compound elute so close together on GC that they are not completely resolved, rendering relative retention measurements insufficiently accurate for positive assignment. It is most likely that both isomers occur in the beef flavoring sample, since this was the case with all the acetals found to be present.

Dioxolanes have not been reported as volatile flavor components of meat, but a few have been identified in some foods of plant origin, e.g., grapes and wines (Stevens et al., 1969; Schreier et al., 1976), cranberries and bilberries (Anjou and von Sydow, 1969), and tomatoes (Schormüller and Kochmann, 1969). However, the origin of the di-

Table II. Chemical Shifts[a] and Refractive Indices of Syn and Anti Isomers of 2-Isopropyl-4-methyl-1,3-dioxolane

2-isopropyl-4-methyl-1,3-dioxolane	$\nu_{H(2)}$[b]		$\nu_{R(2)}$[c]		n_D^{20}	
	synthesized	lit.[d]	synthesized	lit.[d]	synthesized	lit.[d]
isomer 1	273.6	273.8 (syn)[e]	54.6	54.6 (syn)[e]	1.4080	1.4083 (syn)[e]
isomer 2	278.9	278.4 (anti)	52.2	53.5 (anti)	1.4105	1.4103 (anti)

[a] ^1H-NMR signals refer to CCl_4 solutions and are in cps downfield from Me_4Si at 60 Mcps. [b] Proton on C-2. [c] Methyl protons of the isopropyl group on C-2. [d] Willy et al. (1970). [e] More stable isomer.

Table III. Substituted 1,3-Dioxolanes: Relative Retention Times and Identifications in Isolate from Simulated Beef Flavor

synthesized substituted 1,3-dioxolanes					components in first fraction of isolate from simulated beef flavor	
R_1[a]	R_2[a]	name (-1,3-dioxolane)		t_R, min	peak no.[b]	t_R, min
H	H	4-methyl-		39.83[c]		
H	CH_3	2,4-dimethyl-	syn	34.50[c]	26	34.48[c]
			anti	37.89[c]	29	37.64[c]
H	CH_2CH_3	2-ethyl-4-methyl-	syn	46.79	39	46.68
			anti	49.50	41	49.60
H	$(CH_2)_2CH_3$	2-propyl-4-methyl-	syn	60.10		
			anti	62.98		
H	$CH(CH_3)_2$	2-isopropyl-4-methyl-	syn	51.06	43	51.32
			anti	53.39	44	53.49
H	$(CH_2)_3CH_3$	2-butyl-4-methyl-	syn	72.46		
			anti	75.12		
H	$CH_2CH(CH_3)_2$	2-(2-methylpropyl)-4-methyl-	syn	65.49	57	65.41
			anti	68.00	58	68.16
H	$(CH_2)_4CH_3$	2-pentyl-4-methyl-	syn	84.73		
			anti	87.90		
CH_3	CH_3	2,2,4-trimethyl-		34.97[c]		
CH_3	CH_2CH_3	2,4-dimethyl-2-ethyl-	syn	47.65	40	47.75
			anti	48.21		
CH_3	$(CH_2)_2CH_3$	2,4-dimethyl-2-propyl-	syn	59.25	51	59.63
			anti	60.16		
CH_3	$CH(CH_3)_2$	2,4-dimethyl-2-isopropyl	syn	53.49		
			anti	54.78		

[a] See Figure 2. [b] See Table I. [c] Retention time relative to butanone (29.27 min); all other retentions relative to dimethyl disulfide (55.2 min).

Table IV. Summaries of Mass Spectra of Some Synthesized 1,3-Dioxolanes

syn-2,4-dimethyl-1,3-dioxolane	*m/e*	87	43	31	41	59	45	58	44	
	% rel int	100	98	72	57	43	19	18	14	
anti-2,4-dimethyl-1,3-dioxolane	*m/e*	87	31	58	59	41	45	44	43	
	% rel int	100	92	81	62	58	50	45	38	
syn-2-ethyl-4-methyl-1,3-dioxolane	*m/e*	87	59	31	41	57	42	43	72	115
	% rel int	100	71	66	55	38	28	23	17	2
anti-2-ethyl-4-methyl-1,3-dioxolane	*m/e*	87	59	31	41	57	42	72	43	115
	% rel int	100	69	57	53	28	22	20	11	3
syn-2-isopropyl-4-methyl-1,3-dioxolane	*m/e*	87	41	59	43	56	31	57	72	71
	% rel int	100	98	55	46	39	37	11	7	5
anti-2-isopropyl-4-methyl-1,3-dioxolane	*m/e*	87	41	59	31	39	43	56	71	72
	% rel int	100	82	55	52	41	36	32	6	3
2,4-dimethyl-2-propyl-1,3-dioxolane	*m/e*	43	101	41	71	42	39	55	87	44
	% rel int	100	28	27	17	15	12	8	7	2

Table V. Odor Port Assessment of Synthesized 1,3-Dioxolanes

1,3-dioxolane	odor quality
	Syn / Anti
2,4-dimethyl-	solvent-like, etherish, petrol, sweet / buttery, creamy, butterscotch, diacetyl-like
	Syn and Anti
2-ethyl-4-methyl-	solvent-like, acetone, eucalyptus, menthol, camphor, slight fruity
	Syn and Anti
2-isopropyl-4-methyl-	solvent-like, etherish, eucalyptus, menthol, camphor, fruity
	Syn and Anti
2-(2-methylpropyl)-4-methyl-	sweet, strong fruity, strong estery, amyl acetate, pear-drops, banana

oxolanes in this instance may be explained by the fact that they are readily formed by condensation of carbonyl compounds with 1,2-diols. Although the former are common aroma components of many foods (including beef), the latter are not, but the source is likely to be propane-1,2-diol (propylene glycol), a commonly used solvent for commercial flavorings. The solvent in this case is therefore not acting as an inert carrier, but instead is reacting to give a series of artifacts which are present at use levels of the commercial flavor.

The dioxolanes identified possess interesting odor qualities, determined by the technique of odor port assessment, and the results for the acetals are given in Table V. The odors of the separated syn and anti isomers were generally similar. The odor qualities of these dioxolanes could well be influencing the sensory properties of the simulated beef flavor.

This study therefore illustrates the need to be aware of potential interactions between solvent and aroma components in commercial flavors—interactions which might well modify the intended flavor characteristics of the product.

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LITERATURE CITED

Anjou, K., von Sydow, E., *Acta Chem. Scand.* **23**, 109 (1969).

Beynon, J. H., "Mass Spectrometry and Its Applications to Organic Chemistry", Elsevier, Amsterdam, 1960, p 367.
"Eight Peak Index of Mass Spectra", 2nd ed, MSDC Aldermaston, United Kingdom, 1974.
Ferretti, A., Flanagan, V. P., *J. Agric. Food Chem.* **19**, 245 (1971).
Lucas, H. J., Guthrie, M. S., *J. Am. Chem. Soc.* **72**, 5490 (1950).
MacLeod, A. J., Cave, S. J., *J. Sci. Food Agric.* **26**, 351 (1975).
MacLeod, G., Coppock, B. M., *J. Agric. Food Chem.* **24**, 835 (1976).
MacLeod, G., Coppock, B. M., *J. Agric. Food Chem.* **25**, 113 (1977).
MacLeod, G., Coppock, B. M., *J. Food Sci.* **43**, 145 (1978).
Marshall, J. T. B., Williams, D. H., *Tetrahedron* **23**, 321 (1967).
Schormüller, J., Kochmann, H. J., *Z. Lebensm.-Unters.-Forsch.* **141**, 1 (1969).
Schreier, P., Drawert, F., Kerenyo, Z., Junker, A., *Z. Lebensm.-Unters.-Forsch.* **161**, 249 (1976).
Stevens, K. L., Flath, R. A., Lee, A., Stern, D. J., *J. Agric. Food Chem.* **17**, 1102 (1969).
Willy, W. E., Binsch, G., Eliel, E. L., *J. Am. Chem. Soc.* **92**, 5394 (1970).

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A Comparative Study of the Persistence, Movement, and Metabolism of Six Carbon-14 Insecticides in Soils and Plants

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A comparative study was conducted to investigate the fate of six insecticides in two soil types and oat plants grown in these soils. All systems were incubated under identical environmental conditions. The insecticides used, in order of increasing water solubility were [^{14}C]DDT, [^{14}C]lindane, [^{14}C]fonofos, [^{14}C]parathion, [^{14}C]phorate, and [^{14}C]carbofuran. Total amounts of ^{14}C residues recovered from insecticide-treated loam soils plus oats grown in these soils were similar with DDT and carbofuran. They were also higher than those observed with the other insecticides. While most of the [^{14}C]DDT residues remained in the soils, most of the [^{14}C]carbofuran residues were recovered from oat leaves in the form of carbofuran and 3-hydroxycarbofuran. ^{14}C residues of all insecticides were more persistent in loam than in sandy soil and sand-grown oats took up more ^{14}C insecticide residues than loam-grown oats. The more water-soluble insecticides [^{14}C]phorate and [^{14}C]carbofuran were more mobile and were metabolized to a greater extent than insecticides of lower water solubilities. Unextractable (bound) ^{14}C residues in loam soil ranged from 2.8 to 29.1% of the applied doses of [^{14}C]DDT and [^{14}C]parathion, respectively. Bound ^{14}C residues were lower in the sandy soil than in the loam soil; however, plant-bound ^{14}C residues were higher in oats grown in the sandy soil than in loam-grown oats. Insecticide metabolites recovered from soils and plants were identified and quantitated whenever possible. The oxygen analogue metabolites of the organophosphorus insecticides were most abundant in the sandy soil and in oats grown therein. Data illustrate the importance of chemical structure, water solubility, and soil type in predicting the comparative environmental behavior of pesticides.

Insecticides are an indispensable part of modern agriculture. On the basis of environmental considerations, restrictions in their usage have become necessary, yet their production and use is expected to increase (Berg, 1975). Responsible use of these toxicants requires knowledge of their persistence, transport, and transformation in the environment.

There are currently over 60 000 synthetic chemicals in common use which are potential environmental pollutants (Maugh, 1978). Since it would be nearly impossible to gather all the pertinent data on the environmental fate of each of these chemicals, it has been proposed to utilize the physical and chemical properties of these materials in order to predict their environmental behavior (Howard et al., 1978). Since many environmental studies have been conducted with pesticides, this technology is a natural starting point for investigating other potential pollutants. In order to determine which properties of a chemical can be used to predict its environmental behavior, it is first necessary to use existing data for the design and testing of predictive models. Most studies of pesticide behavior have been conducted using only one or two compounds at a given time. Thus, numerous investigations have been performed with various types of soil or plants and the experiments have been conducted under a variety of environmental conditions. While these studies have provided a large volume of data on the environmental fate and behavior of individual pesticides, the *comparative* behavior of different compounds is difficult to assess since the experimental conditions under which these data were obtained differed considerably.

Table I. Water Solubility and Vapor Pressure of the Insecticides Used

insecticide	water solubility, ppm	vapor pressure, mmHg
DDT	0.001[a]	1.9×10^{-7}/20° [b]
lindane	10[b]	9.4×10^{-6}/20° [b]
fonofos	15.7[c]	2.0×10^{-4}/25° [d]
parathion	12.4[c]	3.8×10^{-5}/20° [b]
phorate	17.9[c]	8.4×10^{-4}/20° [b]
carbofuran	320[c]	8.3×10^{-6}/25° [e]

[a] Bowman et al. (1960). [b] Spencer (1973). [c] Bowman and Sans (1979). [d] Menn (1969). [e] Caro et al. (1976).

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