Autoxidation Products of 2,4-Decadienal[1]

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Abstract

2,4-Decadienal was autoxidized by purging a purified sample with oxygen. An analysis of the autoxidative degradation products was made with tandem gas chromatography-mass spectrometry. Additional information was obtained from the determination of the melting point of the dinitrophenylhydrazone derivatives and IR absorbency data. Pentane, furan, ethanal, hexanal, acrolein, butenal, 2-heptenal, 2-octenal, benzaldehyde, glyoxal, *trans*-2-buten-1,4-dial, acetic acid, hexanoic acid, 2-octenoic acid, 2,4-decadienoic acid and benzene were identified.

Introduction

Many workers who have studied the autoxidation of lipids recognized the importance of degradation of secondary products. However, relatively little information is available in the literature regarding this phenomenon. Kimoto and Gaddis (1) recently found very little 2,4-decadienal when autoxidized linoleate was decomposed by dilute acid, but found considerably larger amounts when autoxidized linoleate was decomposed by heat, alkaline conditions or copper. Lillard and Day (2) indicated that 2,4-heptadienal oxidized rapidly with the formation of shorter carbon chain alkanals, α-keto alkanals, glyoxal, malonaldehyde and *cis*-2-buten-1,4-dial. 2,4-Dinitrophenylhydrazones (DNP-hydrazones) of these compounds were formed and characterized. Sulzbacher et al. (3) identified hexanal and 2-octenal from autoxidized 2,4-decadienal by forming their DNP-hydrazones. Nonaka et al. (4) revealed that *p*-xylene, *n*-propyl- and *n*-butylbenzene, and *n*-butyl and *n*-pentyl furan were oxidation products of *trans-trans*,2,4-decadienal.

In this study, purified 2,4-decadienal was autoxidized and its degradation products studied primarily by gas liquid chromatography (GLC) and mass spectrometry (MS).

Experimental Procedures

Materials

Commercially available 2,4-decadienal was purified by vacuum distillation. Mineral oil which had been previously vacuum-stripped was used as a diluent to reduce polymerization during purification. Photochemical degradation was inhibited by excluding ambient light. Analysis by GLC showed that the purity of the 2,4-decadienal with a distillation range of 65–68 C at 1 mm of Hg was 95%. The major impurity was estimated to be about 5%, and additional analyses revealed that this impurity was always present to the extent of 5–6% of the total sample before and after autoxidation.

There are four possible geometric isomers for 2,4-decadienal. Although attempts to determine the amount of each isomer were inconclusive, GC and IR evidence indicated that the predominate isomer present in our sample was *trans,trans*-2,4-decadienal (5).

Process of Autoxidation

The purified 2,4-decadienal was stored under oxygen overnight then subjected to a 2 hr purge in which oxygen was bubbled through a glass capillary tube submerged in the sample. The purge was carried out at room temperature and light was excluded. The purified oxygen had been passed through a filter of Linde Type 4A molecular sieve before it came in contact with the sample.

Analysis of Autoxidation Products

An Atlas CH 4 rapid scanning mass spectrometer connected directly to an F + M model 810 GLC was used to identify the components of autoxidized 2,4-decadienal. A 4.27 m × 0.218 cm o.d. stainless steel column, packed with 15% DEGS on 60–80 mesh Gaschrom Q was used to separate the components of autoxidized 2,4-decadienal. The flow rate was 25 ml of helium per min at 115 C. The injector temperature was 130 C, detector 215 C and column temperature 50 C and linear programmed to 200 C at 2 C/min. The GLC was fitted with an effluent splitter which allowed 17% of the effluent to go to the GLC flame ionization detector with the remainder going to the MS. About 10% of this was admitted to the ion source through the EC-1 throttle valve and the residual was vented to the atmosphere.

IR spectra were recorded with a Beckman IR 5 with a 5x beam condenser. The components that were liquid at room temperature were analyzed as a thin film on a NaCl plate. The solid components were diluted 1 to 20 with KBr and compressed into a micro pellet.

The DNP-hydrazones of four components were prepared by the method described by Attaway et al. (6). The purity of the derivatives was checked by thin layer chromatography (TLC) using 5% ethyl acetate in benzene (v/v) for development. Melting points of the derivatives were measured on a Kofler micro hot stage.

Results and Discussion

A typical chromatogram for autoxidized 2,4-decadienal is shown in Figure 1. Table I correlates the peaks of the chromatogram with the identified components. Relative retention times in Table I are based relative to the retention time of hexanal; this compound had been previously identified in autoxidized 2,4-decadienal (3,7).

The diethyl ether found in peak 1 could be a contaminant since this was the solvent used to clean the syringe. The ethanol in peak 6 should be disregarded as the commercially available 2,4-decadienal was supplied as a 50% solution in ethanol.

Peak 10 was identified as *trans*-2-buten-1,4-dial

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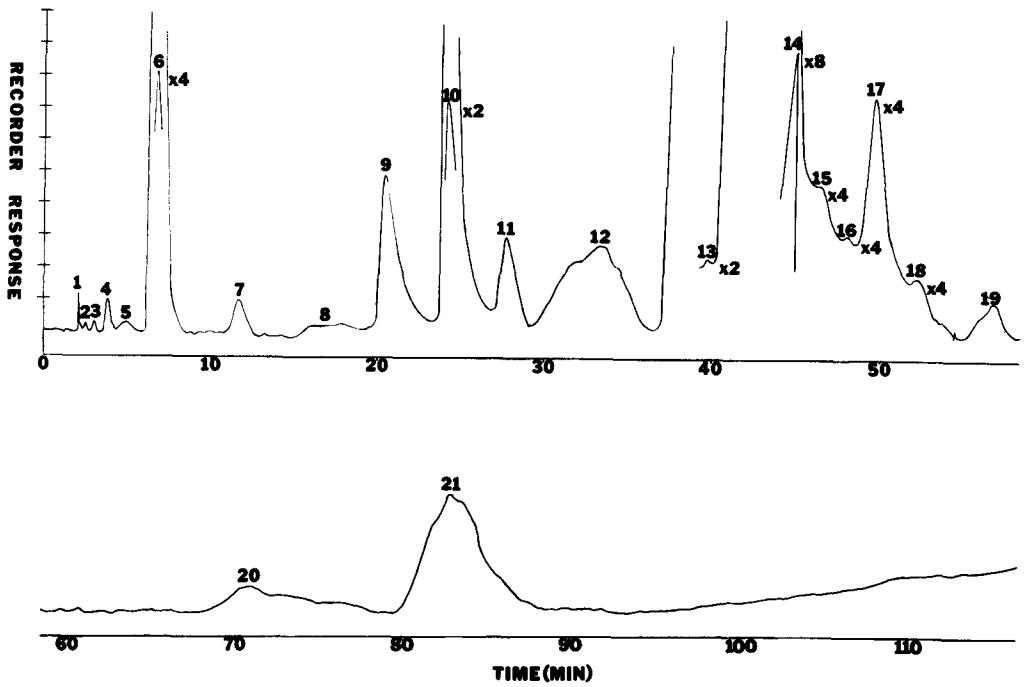

FIG. 1. Gas chromatogram of autoxidized 2,4-decadienal.

(fumaraldehyde). Since no authentic mass spectrum had been reported and the authentic compound was not commercially available, the (bis) DNP-hydrazone derivative of peak 10 was prepared and studied. The reported decomposition points for the (bis) DNP-hydrazone of the *cis* and *trans* isomers are 293 C and 382 C, respectively (8). The temperature of thermal decomposition of the derivative of the component responsible for peak 10 was 380 C, consequently the component was identified as the *trans* isomer or fumaraldehyde. The IR spectrum of the derivative was identical to a spectrum reported by Lillard (9) for the *cis* isomer derivative, therefore the possibility exists that Lillard mistakenly identified the *trans* isomer as *cis* 2-buten-1,4-dial. The major ions in the mass spectrum of fumaraldehyde are given in Table II.

Benzaldehyde, peak 11, has frequently been found as a component of foods when 2,4-decadienal was also present (10–13). The source of benzaldehyde has remained speculative with some authors (14) citing nonenzymatic browning as the source and others (9) suggesting plant metabolism. From this research it appears benzaldehyde could also originate from oxidized unsaturated lipids.

Peak 21, 2,4-decadienoic acid, was identified by comparing its IR spectrum with that reported by Jennings and Creveling (15). The mass spectrum is given in Table III.

It is generally accepted that the initial steps of the autoxidation mechanism differ for conjugated and nonconjugated systems (16–18). The mechanism followed during the autoxidation of conjugated unsaturated molecules is still not known despite con-

TABLE I

Compounds Identified in Autoxidized 2,4-Decadienal

Compound	Peak No.	Approximate quantity, %	Retention time		Method of identification		
			Autoxidation	Authentic	GLC-MS	IR	Dinitrophenylhydrozone, mp
Pentane	1	0.03	0.184	0.182	+		
Diethyl ether	1 (tail)	Trace	0.211	0.215	+		
Acetaldehyde	2	0.02	0.250	0.243	+		
Furan	3	0.02	0.288	0.294	+		
Acrolein	4	0.10	0.382	0.382	+		
Benzene	4	Trace	.....	.....	+		
Glyoxal	5	0.04	0.605	0.619	+		
Ethanol	6	Trace	.....	1.00	+		
Hexanal	6	10.58	1.00	1.00	+		108 C
Butenal	7	0.22	1.95	.....	+		
2-Heptenal	8	0.23	2.86	3.07	+		
2-Octenal	9	1.34	3.69	3.92	+		
Acetic acid	9 (tail)	Trace	.....	4.25	+		
Fumaraldehyde	10	4.62	4.33	.....	+	+	380 C
Benzaldehyde	11	0.68	4.91	5.18	+		
Unknown	12	3.31	5.43	.....			
2,4-Decadienal	13	4.53	6.51	.....	+	+	
Hexanoic acid	13 (tail)	Trace	.....	7.42	+		
2,4-Decadienal	14	60.99	7.70	.....	+	+	136 C
Unknown	15	0.90	7.89	.....			
Unknown	16	0.09	7.98	.....			
Unknown	17	6.58	8.10	.....			116 C
Unknown	18	0.75	9.50	.....			
2-Octenoic acid	19	0.30	11.78	12.23	+		
Unknown	20	1.08	12.40	.....			
2,4-Decadienoic acid	21	3.48	13.82	.....	+	+	

TABLE II

Mass Spectrum of Fumaraldehyde

m/e	Relative intensity
25	11
26	42
27	65
28	100 (base peak)
29	69
32	50
37	10
39	13
41	13
44	27
45	10
46	36
53	10
55	48
56	20
83	4
84	41 (molecular ion)

siderable effort spent trying to elucidate the pathway. Previous workers have postulated either oxygen addition directly across the double bond (16–19) or at an active allylic methylene group (20, 21).

TABLE III

Mass Spectrum of 2,4-Decadienoic Acid

m/e	Relative intensity	m/e	Relative intensity
26	78	69	15
29	93	70	40
39	60	73	12
41	99	77	11
42	72	79	30
43	31	80	8
45	16	81	34
50	4	83	14
51	14	84	15
52	11	86	16
53	25	94	8
54	14	96	17
55	66	97	100 (base peak)
56	9	98	28
57	20	99	40
60	4	100	11
65	20	108	5
66	19	111	8
67	57	168	14 (molecular ion)
68	11		

If allylic hydrogen abstraction were the key step for the autoxidation of 2,4-decadienal, pentanal would have been a major product of dissociation. Since pentanal was not found and hexanal was the primary oxidation product, it can be inferred that oxygen attacks primarily at the olefinic centers. Autoxidative cleavage of the double bond between carbon atoms two and three would yield 2-octenal and glyoxal while attack between carbon atoms four and five would produce hexanal and 2-buten-1,4-dial. All four of these compounds were identified.

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