

Identification and Characterization of 1,4-*p*-Menthadien-7-al

Isolated from Cumin Seeds

P. T. Varo¹ and D. E. Heinz

A previously unreported aldehyde, 1,4-*p*-menthadien-7-al, was isolated from fresh, whole cumin seeds. Infrared, ultraviolet, nuclear magnetic resonance, and mass spectra were used to characterize the compound. The chemical reactivity of the

aldehyde was studied in basic and acidic conditions. The reaction products indicate that many of the previously reported aldehydes in cumin oil may be artifacts.

Varo and Heinz (1970) reported the major and some minor volatile constituents found in oil extracted from ground cumin seeds and in commercial cumin oil. In subsequent studies of fresh, whole cumin seeds, it was observed that the aldehyde fraction contains a major constituent not identified in previous investigations. Identification and chemical reactivity of this constituent, 1,4-*p*-menthadien-7-al, are discussed in this paper.

EXPERIMENTAL

The cumin oil used was distilled from freshly ground, whole seeds (Spice Islands of Leslie Foods Inc.) using the procedure of Varo and Heinz (1970). The gas-liquid chromatograph, infrared spectrum, and mass spectrum apparatus were also essentially the same as described previously. The nuclear magnetic resonance spectrum of 1,4-*p*-menthadien-7-al was obtained using a Varian A-60 spectrometer. Spectrophotometric methods (Beckman DB-G) were used to follow reactions of the compound and of 1,3-*p*-menthadien-7-al. The reactants were added directly into a cuvette with methanol as the solvent. After the zero time spectrum was determined, a drop of 10% acid or base was added and the contents were mixed. The spectrum was then scanned from 350 to 200 nm. at pertinent time intervals. Gas chromatographic methods were used to follow some reactions involving 1,4-*p*-menthadien-7-al.

RESULTS

The approximate composition of the oil of fresh cumin seeds is shown in Table I. Peak numbers are identical to those of the preceding paper (Varo and Heinz, 1970). Although peak 18 from preground seeds is pure 1,3-*p*-menthadien-7-al, the oil obtained from whole seeds contains another aldehyde, designated 18^s, in peak 18. The latter compound has identical retention times with 1,3-*p*-menthadien-7-al on both columns

used in the investigation. The infrared spectrum of peak 18^s (Figure 1) reveals a strong carbonyl band at 1691 cm.⁻¹, indicating less extensive conjugation than in 1,3-*p*-menthadien-7-al. A doublet centered at 1375 cm.⁻¹ for a gem-dimethyl group and a medium strong band at 842 cm.⁻¹, indicating a trisubstituted double bond, are also present. The ultraviolet spectrum of peak 18^s has λ_{\max} at 315, 257, and 221 nm. ($\epsilon_{221} = 7300$) with the intensities of each increasing in the same order. When peak 18^s is collected and then reinjected onto the gas chromatograph, three completely

Table I. Approximate Content of Volatile Oil from Whole, Fresh Cumin Seeds

Peak Number ^a	Compound	% of Total ^{c,d}
1	α -Pinene	1.3
2	β -Pinene	20.1
3	Myrcene	0.2
4	α -Phellandrene	t
5	<i>p</i> -Cymene, Limonene, β -Phellandrene, 1,8-Cineol, and α -Terpinene	11.1
7	δ -Terpinene	18.5
8	<i>trans</i> -Sabinene hydrate	t
10	<i>cis</i> -Sabinene hydrate	t
13	Unknown	0.1
14	3- <i>p</i> -Menthen-7-al, Myrtenal, and α -Terpineol	0.1
16	Cuminaldehyde	16.4
17	Phellandral	t
18 ^b	1,3- <i>p</i> -Menthadien-7-al and 1,4- <i>p</i> -Menthadien-7-al	31.5
20	Cumyl alcohol	t
22	Unknown	0.2
24	β -Caryophyllene	0.1
26	β -Farnesene	0.2
27	Unknown	0.1
28	β -Bisabolene	t
33	Unknown	t

^a Peak in Figure 1 of Varo and Heinz (1970).

^b Approximately pure 1,4-*p*-menthadien-7-al.

^c Data collected with Varian digital integrator (Model 480) and digital peak area readout used to estimate percentage composition without correction factors.

^d t = trace (less than 0.1%).

Department of Consumer Sciences, University of California, Davis, Calif. 95616

¹ Present address, Alko, Itämerenkatu 51, Helsinki 18, Finland.

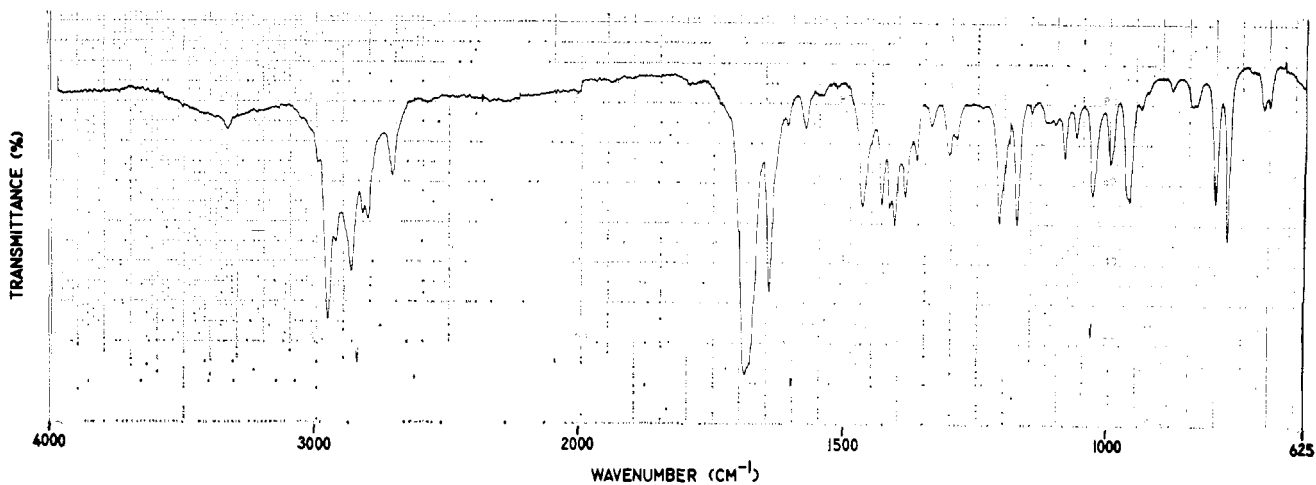


Figure 1. Infrared spectrum 1,4-*p*-menthadien-7-al (isolated from peak 18)

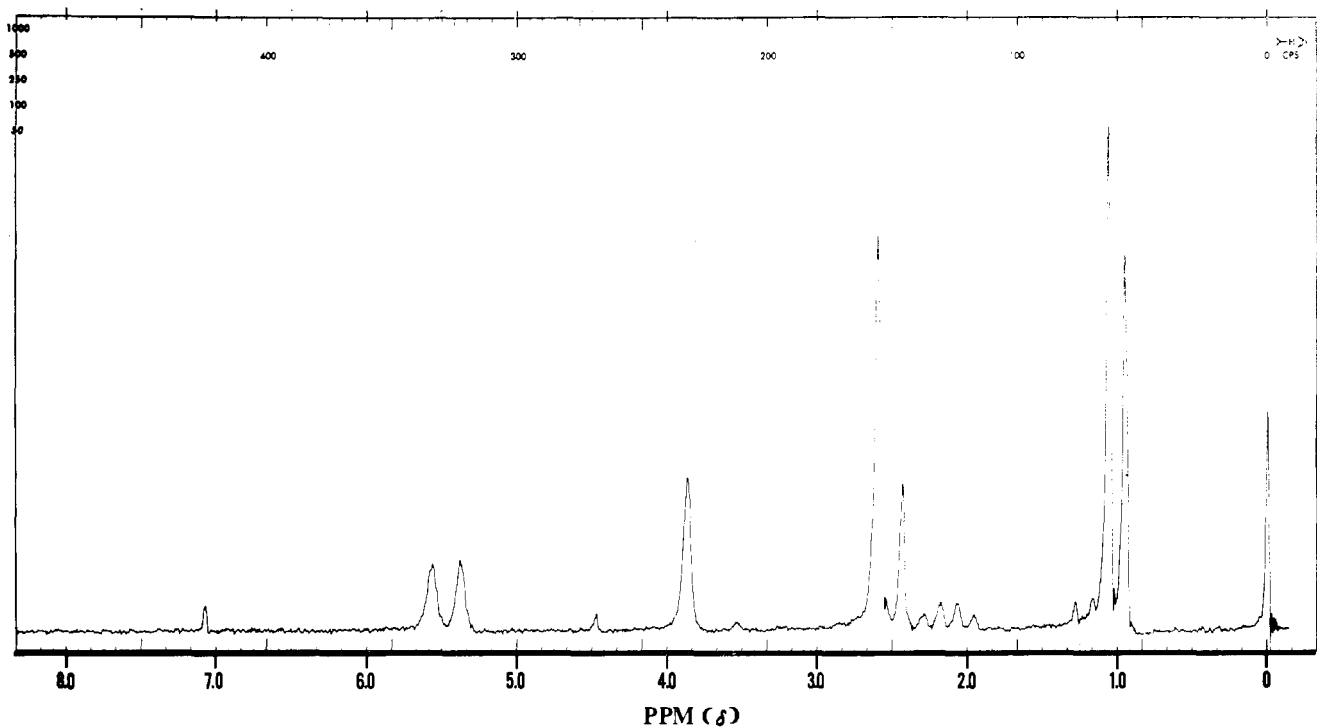


Figure 2. NMR spectrum of 1,4-*p*-menthadien-7-al

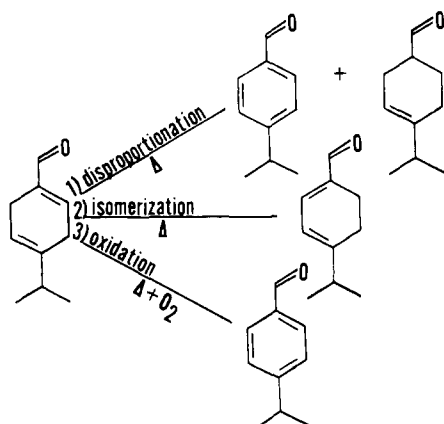
resolved peaks are observed, no matter how many times the collections and reinjections are repeated. The first peak, approximately 5% of peak 18, has the same retention time and infrared spectrum as 3-*p*-menthen-7-al; the second peak, approximately 10% of peak 18, has the same retention value and infrared spectrum as cuminaldehyde. Cuminaldehyde most likely accounts for the absorption maximum at 257 nm. in the ultraviolet spectrum of peak 18^s. Peak 18^s is seemingly isomerized to 1,3-*p*-menthadien-7-al as evidenced by the fact that samples obtained from subsequent reinjection onto the gas chromatograph have an increase in the maximum at 315 nm. The above information indicates that peak 18^s may be 1,4-*p*-menthadien-7-al. Attempts to isolate the pure compound from peak 18^s for spectral analysis were unsuccessful. However, a mass spectrum of the major aldehyde under peak 18^s was arrived at by subtracting from the spectrum of peak 18 the spectrum of the major impurity, cuminaldehyde. The mass spectrum obtained in this manner reveals a parent peak at 150.15 *m/e*, in agreement with the proposed structure.

The base peak is at 107.06 *m/e* (P-43) and probably corresponds to the loss of the isopropyl fragment. Fragments 135 and 129 *m/e* (P-15 and P-29) may result from the loss of methyl and H—C=O fragments, respectively. The peak 79 *m/e* could indicate the fragment of the bare ring system.

To obtain the nuclear magnetic resonance spectrum of the aldehyde in peak 18^s, the compound was reduced with lithium aluminum hydride to the corresponding alcohol, because it was thought that the alcohol might be less inclined to isomerize or oxidize than the aldehyde. The resulting spectrum (Figure 2) is in agreement with the proposed structure. The six-proton doublet ($J = 6$ c.p.s.) at 1.02 p.p.m. indicates a gem-dimethyl in the isopropyl group. The proton multiplet ($J = 6$ c.p.s.) centered at 2.14 p.p.m. results from the tertiary proton in the isopropyl group. The hydroxyl proton contributes a peak at 2.43 p.p.m., and the four-proton peak at 2.60 p.p.m. corresponds to the two methylene groups adjacent to the two double bonds. The two-proton singlet at 3.85 p.p.m. results from the methylene group next to the oxygen

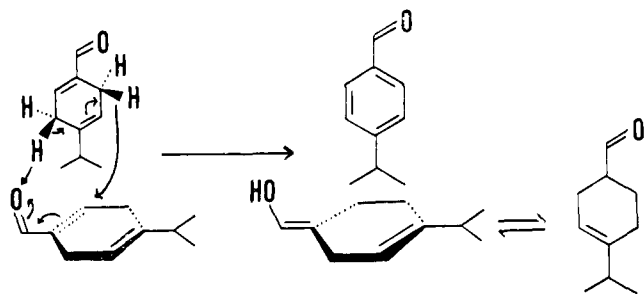
atom. Two one-proton, broad peaks at 5.38 and 5.56 p.p.m. assigned as the ethylenic protons reflect, with a very low coupling constant ($J = 1.5$ c.p.s.), the expected triplet-like formation resulting from secondary splitting from the adjacent methylene groups.

The reactivity of 1,4-*p*-menthadien-7-al during gas chromatographic analysis indicates that this compound is unstable and is capable of undergoing disproportionation and isomerization reactions simultaneously. Where these reactions occur during the chromatographic procedure is a matter of dispute. The solvents—methanol, diethyl ether, and pentane—which were used in handling the compound between collections and reinjections did not appear to affect the proportions of the products of the reactions. Approximately 0.3% of 3-*p*-menthen-7-al was found with respect to the amount of 1,4-*p*-menthadien-7-al in the fresh cumint seed oil, while the purified 1,4-*p*-menthadien-7-al produced 5% of the reduced aldehyde during gas chromatographic analysis. These observations imply that during the analysis of the whole oil the disproportionation occurs only to a minor degree, or some other material present in the oil is reduced while the 1,4-*p*-menthadien-7-al is being oxidized to cuminaldehyde. At least during the chromatographic analysis of the purified 1,4-*p*-menthadien-7-al, the excessive amount of aromatic product formed compared to that of the reduced one indicates that some oxidation, most likely with trapped oxygen contained on the sample, is also occurring. Possible reactions are summarized in the following scheme:



Scheme I

The disproportionation reaction may involve a concerted proton transfer:



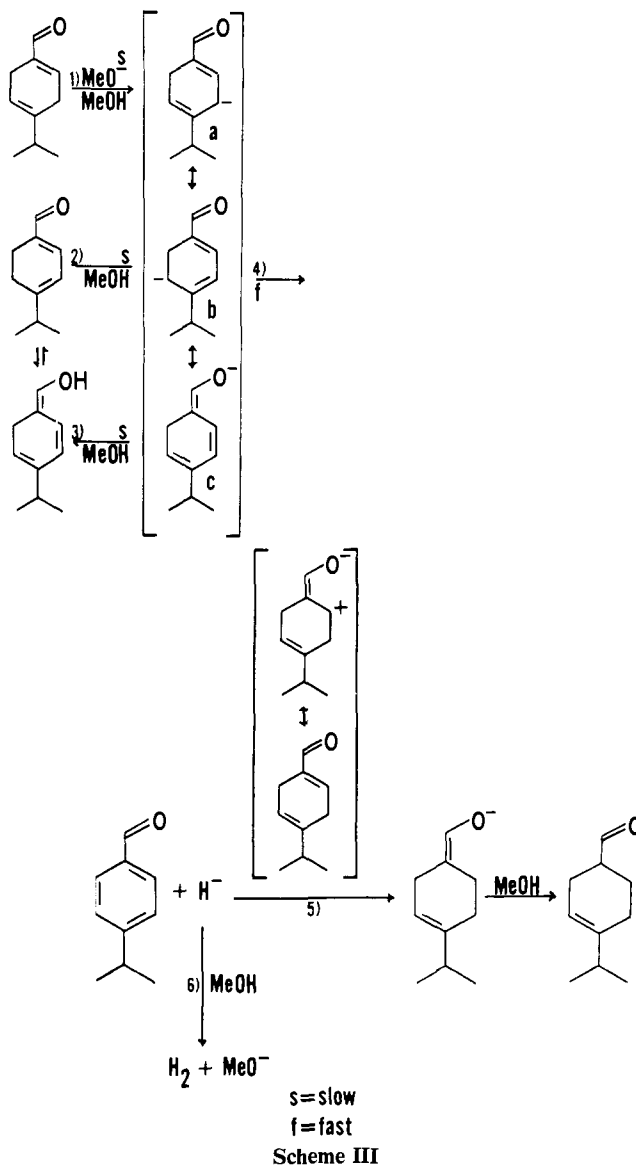
Scheme II

It is evident from the chromatographic experiments that 1,4-*p*-menthadien-7-al is oxidized to the aromatic aldehyde more easily than from aldehyde to the corresponding acid, since the acid was never obtained. On the other hand, cuminaldehyde oxidizes in air readily to cuminic acid which emerges as a broad peak from the SF-96(50) column after cuminyl alcohol. To learn more about the chemical properties of

1,4-*p*-menthadien-7-al, the compound was added in alkaline and acidic methanol solutions and kept at room temperature. After 2 hours in the alkaline reaction, the starting material completely disappeared. The products, as determined by gas chromatographic and ultraviolet and infrared spectroscopic analyses, were 3-*p*-menthen-7-al, cuminaldehyde, and a very small amount (about 2%) of 1,3-*p*-menthadien-7-al. The ratio of 3-*p*-menthen-7-al to cuminaldehyde was approximately 1 to 2.

No phellandral (peak 17) was found among the alkaline reaction products, which implies that the carbonyl group has a directing effect on the reduction. When the base-catalyzed reaction was done in a helium atmosphere to exclude air oxidation, the ratio of products remained the same. The reaction was monitored by observing the appearance or disappearance of the absorption maxima of both the reactant and two of the products, cuminaldehyde and 1,3-*p*-menthadien-7-al (Figure 3). Cuminaldehyde ($\lambda_{max} = 257$ nm.) increased rapidly during the reaction and the maximum was reached in 1 $\frac{1}{2}$ hours. Simultaneously, the absorption maximum at 221 nm. (1,4-*p*-menthadien-7-al) completely disappeared while the maximum at 315 nm. (1,3-*p*-menthadien-7-al) increased only slightly.

The following mechanism could summarize the base-catalyzed reaction:



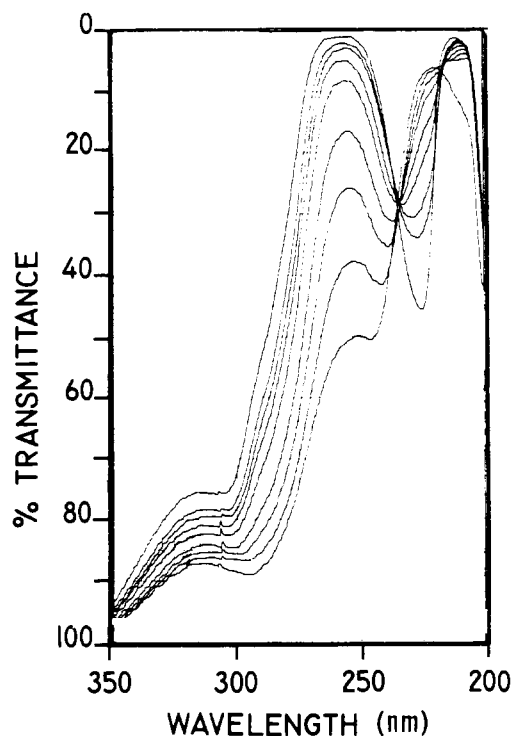


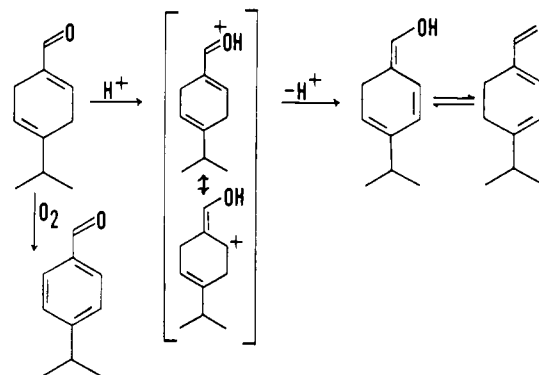
Figure 3. Alkaline-induced spectral changes in 1,4-*p*-menthadien-7-al as a function of time

The maxima at 257 nm. have progressively higher absorptions with reaction time. Spectra were determined at 0, 1, 5, 10, 20, 30, 45, 60, and 145 minutes

In the first step of the reaction, methoxide ion extracts the ring proton that is flanked by the double bonds. Three resonance structures (*a*, *b*, and *c*) can be drawn for the resulting carbanion. When protonated, structure *b* yields 1,3-*p*-menthadien-7-al (reaction 2) while *c* yields its tautomer (reaction 3). Since cuminaldehyde forms very rapidly while only small amounts of 1,3-*p*-menthadien-7-al are formed, reaction 4 must be fast compared to reactions 1, 2, and 3. Since the ratio of cuminaldehyde to 3-*p*-menthen-7-al is not 1 to 1, the hydride ion must react at least along two different paths, for instance, reactions 5 and 6. Hydrogen gas was never observed, perhaps because the experiments were done on a micro scale. Since 1,3-*p*-menthadien-7-al was observed to be stable in basic conditions, it is not formed and subsequently oxidized to cuminaldehyde during the base-catalyzed reaction of 1,4-*p*-menthadien-7-al.

1,4-*p*-Menthadien-7-al was more stable in acidic than in basic conditions. In acidic milieu, about 75% of the reactant remained unchanged after 2 hours. Gas chromatographic analysis indicated that the volatile products of this reaction were cuminaldehyde and 1,3-*p*-menthadien-7-al. When the acid reaction was monitored by ultraviolet spectroscopy, the absorption at 315 nm. (1,3-*p*-menthadien-7-al) increased first at a moderate rate but at 257 nm. (cuminaldehyde) remained very low. After about 15 hours, the absorption at

315 nm. started to decline slowly while the absorption at 257 nm. increased at a steady, slow rate. When pure 1,3-*p*-menthadien-7-al is subjected to acidic conditions, it reacts slowly; but according to ultraviolet analysis, no cuminaldehyde is formed. Cuminaldehyde, therefore, may arise from direct oxidation of 1,4-*p*-menthadien-7-al as summarized below:



Scheme IV

The major naturally occurring aldehyde in fresh cumin seeds may be 1,4-*p*-menthadien-7-al and most of the other aldehydes may be artifacts, except myrtenal and phellandral. In freshly ground cumin seeds, the concentration of 1,4-*p*-menthadien-7-al is very high while the concentration of cuminaldehyde is comparatively low, and 1,3-*p*-menthadien-7-al and 3-*p*-menthen-7-al are present only in negligible amounts. In preground seeds and in the commercial oil, the predominant aldehyde is cuminaldehyde; and the concentrations of 1,3-*p*-menthadien-7-al and 3-*p*-menthen-7-al are fairly high, but there is no 1,4-*p*-menthadien-7-al (Varo and Heinz, 1970). The loss of this compound might have taken place during the storage period of the preground seeds or during the heat treatment associated with distillation of the commercial oil.

There are also reasons to believe that cuminy alcohol may be an artifact. It is present in moderate amounts in the preground seeds and in the commercial oil (Varo and Heinz, 1970), but is missing from the whole seeds. Cuminy alcohol was not found in the products of either acid- or base-catalyzed reactions. But when a mixture of pure cuminaldehyde and aluminum oxide was allowed to stand for 1 hour and the organic material then isolated, considerable amounts of both cuminy alcohol and cuminic acid, as well as starting material, were present in the mixture. This indicated that a Cannizzaro-type disproportionation had taken place on aluminum oxide. A similar enzymatic reaction could be postulated. The reason no cuminic acid was isolated from the preground seed oil may be that the acid is ionized in the seed material or its low vapor pressure prevents its isolation by distillation.

LITERATURE CITED

Varo, P. T., Heinz, D. E., *J. AGR. FOOD CHEM.* **17**, 234 (1970).

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