Volatile Components of Cumin Seed Oil

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Volatile components of preground cumin seeds and distilled commercial cumin seed oil were investigated. The volatile oil was isolated from preground cumin seeds by high-vacuum distillation. Individual components were separated from this oil and from a commercial cumin seed oil by gas chromatography. Infrared, ultraviolet, and, where necessary and applicable, mass and NMR spectroscopy were used to identify α-pinene, β-pinene, myrcene, α-phellandrene, α-terpinene, limonene, β-phellandrene, 1,8-cineol, p-cymene, γ-terpinene, 3-p-menthen-7-al, myrtenal, cuminaldehyde, phellandral, 1,3-p-menthadien-7-al, cis-sabinene hydrate, trans-sabinene hydrate, α-terpineol, cuminyl alcohol, β-caryophyllene, β-farnesene, and β-bisabolene.

C umin (*Cuminum cyminum* L.) is an annual plant of the family Umbelliferae. Crushed cumin seeds are used as a condiment in many South and Central American dishes, and cumin is an important ingredient of curries and chili powder. Previous investigations (Guenther, 1950; Gupta and Patwardhan, 1958; deMayo, 1959; El-Hamidi and Ahmed, 1966; El-Hamidi and Richter, 1965) have revealed that the ethereal oil of cumin seeds is rich in aldehydes (up to 60%), the most prominent of which is cuminaldehyde. Constituents reported to be present in cumin oil are listed in Table I. This paper describes the isolation and characterization of additional major and minor constituents of cumin seed oil.

EXPERIMENTAL

Apparatus. The oil was fractioned using a Varian Aerograph Model 202 gas chromatograph with a thermal conductivity detector and two 25-foot × 0.25-inch o.d. stainless steel columns. The primary separation was accomplished on a column containing acid-washed, DMCS-treated, 70–80 mesh Chromosorb G coated with 1% SF-96(50) admixed with 0.02% Triton X-305 to reduce tailing. Further purification was done using 5% Carbowax 20M coated on the same solid support. In most instances, the combination of these two columns provided adequate purification. The injector port temperature was maintained at 175° C. and the detector temperature at 230° C. Except as noted, the initial oven temperature during primary separation was 50° C. and the column temperature was programmed linearly at 4° C. per minute up to 250° C. The flow rate of the carrier gas (helium) was maintained at 50 ml. per minute. Purity of individual isolated peaks was monitored with a Varian Aerograph 1200 gas chromatograph modified for capillary columns and equipped with a flame ionization detector and a 500-foot × 0.03-inch i.d. stainless steel capillary column coated with SF-96(50) admixed with 5% Triton X-305. The components were trapped from the exhaust ports of the chromatograph as described by Jennings et al. (1964).

The infrared spectra of thin films of pure samples held between two sodium chloride plates were obtained using a Perkin-Elmer 257 spectrophotometer with a beam condenser. A Beckman DB-G spectrophotometer was used to obtain the ultraviolet spectra of samples dissolved in methanol and placed in 10-mm. silica cells. Mass spectra were obtained with a Varian M-66 mass spectrometer. Capillary tubes, those used for sample collection, were inserted directly into the sample inlet system. Accurate mass determinations were made using a Varian V5560 reference kit. Nuclear magnetic resonance spectra were obtained using either a Varian HA-100 or a Hitachi-Perkin-Elmer R-20 spectrometer. Tetramethyl silane was used as an internal standard and carbon tetrachloride was used as the solvent. Standard NMR tubes were used with the Hitachi-Perkin-Elmer R-20 instrument; however, microcells were used with the Varian HA-100 instrument.

MATERIALS AND PROCEDURE

Ground cumin seed (Cal-Compack Foods, Inc.) was the main source of the ethereal oil used. Steam-distilled cumin oil (Fritzsche Bros., Inc.) was an additional source for some components. The oil of the ground seeds was distilled in a one-plate vacuum distillation pot. The powdered seed material was placed on the bottom of the apparatus and the volatiles were collected on a cold finger filled with dry ice–methanol slush. Temperature of the powdered seeds was

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Table I. Reported Constituents of Cumin Oil

Compound	Reference
Terpenes	
α-Pinene	Guenther (1950)
β-Pinene	Guenther (1950)
p-Cymene	Guenther (1950); Gupta and Patwardhan (1958)
Dipentene	Guenther (1950); Gupta and Patwardhan (1958)
β-Phellandrene	Guenther (1950)[a]
α-Terpinene	deMayo (1959)
γ-Terpinene	deMayo (1959)
Terpene aldehydes	
Cuminaldehyde	Guenther (1950); Gupta and Patwardhan (1958); El-Hamidi and Richter (1965); El-Hamidi and Ahmed (1966)
Perillaldehyde	Guenther (1950); Gupta and Patwardhan (1958); El-Hamidi and Richter (1965); El-Hamidi and Ahmed (1966)
Terpene alcohols	
Cuminyl alcohol	Guenther (1950); Gupta and Patwardhan (1958); El-Hamidi and Richter (1965); El-Hamidi and Ahmed (1966)
Others	
Cryptone	El-Hamidi and Richter (1965)[a]

[a] Tentative identification.

Table II. Concentrations of Volatile Oil from Preground Cumin Seeds and Commercial Steam-Distilled Cumin Oil

Peak No.[a]	Preground		Commercial oil		Compounds Identified	Evidence[e]
	% Found in[b,c,d]					
1	0.5		1.2		α-Pinene	IR
2	13.0		13.6		β-Pinene	IR, RT
3	0.3		0.3		Myrcene	IR, UV
4	t		t		α-Phellandrene	IR, UV
5	9.5		18.6			
a		8.5		17.6	p-Cymene	IR, UV
b		0.5		0.5	Limonene	IR
c		0.3		0.3	β-Phellandrene	IR, UV
d		0.2		0.2	1,8-Cineol	IR
e		t		t	α-Terpinene	IR, UV
7	29.5		14.0		γ-Terpinene	IR
8	t		t		trans-Sabinene hydrate	IR
10	t		1.2		cis-Sabinene hydrate	IR
13	t		2.4		Unknown hydrocarbon	IR
14	0.7		0.8			
a		0.7		0.8	3-p-Menthen-7-al	IR, MS, NMR
b		t		t	Myrtenal	IR, UV
c		t		t	α-Terpineol	IR
16	32.4		32.0		Cuminaldehyde	IR, UV, MS, RT, CD
17	t		t		Phellandral	IR, UV, CD
18	5.6		13.0		1,3-p-Menthadien-7-al	IR, UV, MS, NMR
20	2.8		2.5		Cuminyl alcohol	IR, UV, RT
22	1.4		0.2		Unknown sesquiterpene h.c. (mixt)	IR
24	0.8		0.1		β-Caryophyllene	IR
26	1.1		t		β-Farnesene	IR
27	1.3		0.2		Unknown sesquiterpene h.c. (mixt)	IR
28	0.9		t		β-Bisabolene	IR
33	0.6		t		Unknown hydrocarbon	IR

[a] Refers to peak number in Figure 1. [b] Data collected with a Varian digital integrator (model 480) and digital peak area readout was used to estimate composition without correction factors. [c] All other peaks present at trace amounts only. [d] t = trace (less than 0.1%). [e] IR = infrared spectrum, UV = ultraviolet spectrum, MS = mass spectrum, NMR = nuclear magnetic resonance spectrum, RT = retention time, CD = chemical derivative.
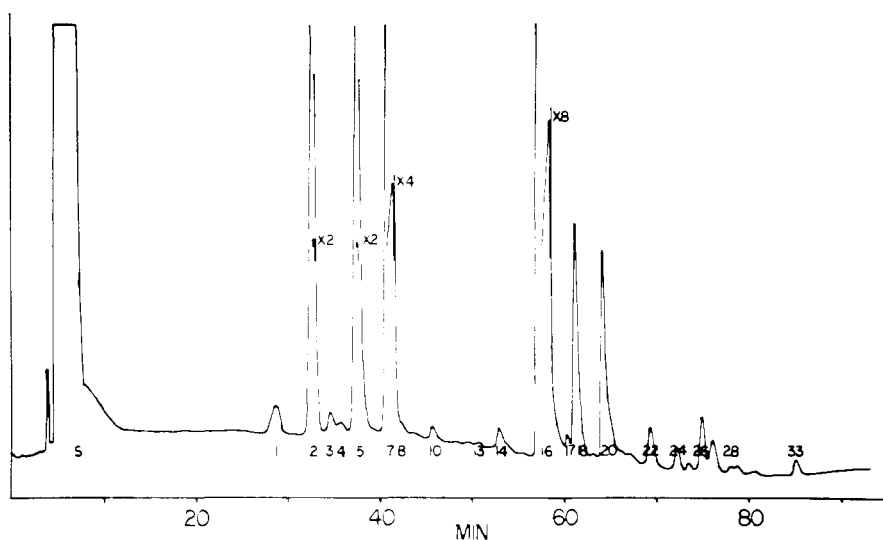

Figure 1. Gas chromatogram [obtained on a SF-96(50) column] of 25 μl. of volatile oil distilled from preground cumin seeds

maintained at 60° to 75° C. during distillation. The cold finger was removed after 2 hours and the condensed mixture of water and volatiles was melted by replacing the cooling mixture with water. The ether-soluble fraction obtained from this mixture was subsequently concentrated by distillation, and 25-μl. aliquots of the concentrate were injected into the SF-96(50) column. Fractions were collected and reinjected into the Carbowax 20M column.

Primary separation of the terpenes and sesquiterpenes from the polar constituents occurred on a short alumina column (Muller and Jennings, 1967). The microscale lithium aluminum hydride reductions of the aldehydes took place in 5-ml. centrifuge tubes (Fieser and Fieser, 1962).

RESULTS

Figure 1 indicates the general gas chromatographic profile of cumin oil obtained from preground seeds using the SF-96(50) column. The major components found in the two oils used are given in Table II, along with the percentage of total volatiles represented by each peak. Five major peaks
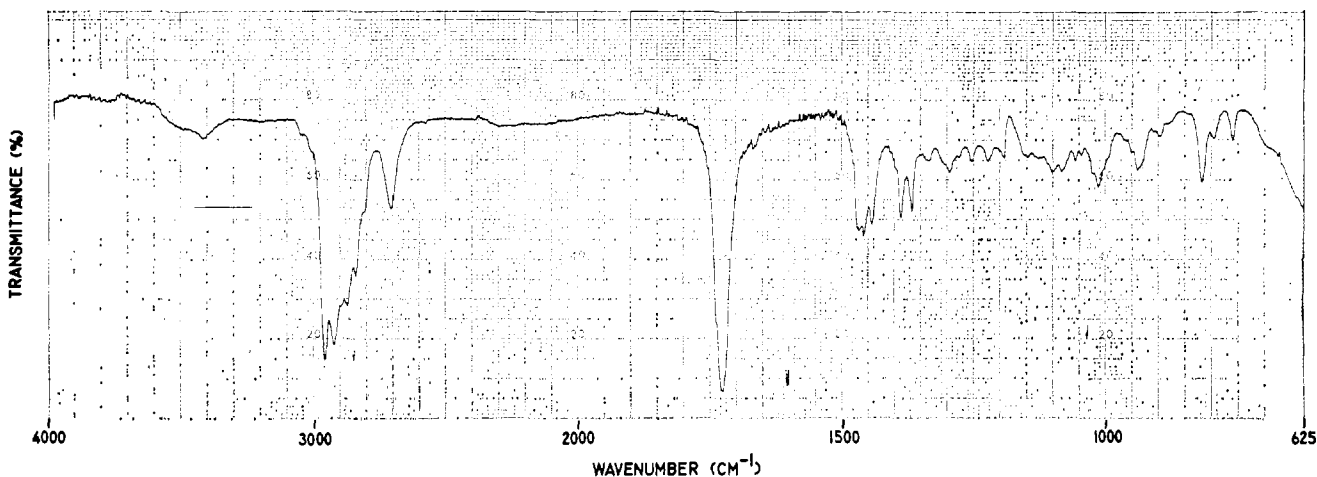
Figure 2. Infrared spectrum of 3-p-menthen-7-al (isolated from peak 14)

represent 90 to 97% of the total volatiles in cumin oil. Peaks 2, 5, and 7 are terpene hydrocarbons and 16 and 18 are aldehydes.

The purified monoterpene hydrocarbons were identified by comparing the obtained infrared spectra to the reported ones (Mitzner et al., 1965) and, where available, to the infrared spectra of authentic samples. The ultraviolet spectra were also used, where applicable, to confirm the proposed structures. β-Phellandrene and 1,8-cineol in peak 5 were never resolved, but were tentatively identified by subtracting the values of infrared spectrum of pure 1,8-cineol (Matheson) from the combined infrared spectrum. Several other unidentified monoterpene hydrocarbons were present in lesser amounts under peaks 1, 2, and 5.

The infrared spectrum of peak 13 indicates neither hydroxyl nor carbonyl functional groups. Since the retention time of this compound is considerably greater than that of monoterpene hydrocarbons, but less than that of sesquiterpene hydrocarbons, it may contain oxygen as an ether or be nonterpenoid.

Several alcohols are present in the volatile oil of cumin, but the quantities are small compared to those of the major constituents. The alcohols are distributed from peak 8 to peak 20. The infrared spectrum of a white solid obtained from peak 8 is identical to that of a solid alcohol identified as a trans-sabinene hydrate (5-isopropyl-2-methylbicyclo [3.1.0] hexan-2-ol) (Russell and Jennings, 1970). The infrared spectrum of peak 10 corresponds to that of cis-sabinene hydrate (Russell and Jennings, 1970).

Peak 14 contained a very minor alcoholic constituent identified as α-terpineol by its infrared spectrum which matches that reported by Mitzner et al. (1968). Peak 20, the biggest alcoholic peak, constituted about 2% of all volatile material. It was identified as cuminyl alcohol by comparing its infrared spectrum to that reported by Mitzner et al. (1968) and to one obtained after reduction of cuminaldehyde and by its ultraviolet spectrum which has low-intensity maxima at 260, 266, and 274 nm.

Major portions of peaks 14 to 18 are terpene aldehydes which constitute up to 50% of all volatiles present in cumin oil. This aldehyde fraction is responsible for most of the characteristic odor of the oil.

Two aldehydes were identified from peak 14 in addition to α-terpineol. The strong band at 1725 cm.⁻¹ in the infrared spectrum (Figure 2) of one indicates a nonconjugated carbonyl moiety. The peak at 2710 cm.⁻¹ is assigned to the

C—H stretching of an aldehydic proton. The region 3000 to 3050 cm.⁻¹ represents unsaturation. The doublet centered at 1375 cm.⁻¹ indicates the possibility of an isopropyl group, and the medium strong peak at 817 cm.⁻¹ can be assigned to a trisubstituted double bond. This compound has no ultraviolet spectrum which is in agreement with the infrared spectrum. Its mass spectrum has a parent peak at 152 m/e. This confirms that there are three degrees of unsaturation, probably consisting of one double bond, one carbonyl moiety, and one ring. A mass spectrum fragment at 109 m/e (P-43) indicates an ion resulting from the loss of the isopropyl group, and a fragment at 81 m/e indicates an ion of a bare ring system. The nuclear magnetic resonance spectrum of 25 scans (Figure 3) has a doublet at 1.0 p.p.m., confirming the isopropyl group. The broad group of peaks centered at 2.0 p.p.m. is assigned to all the saturated ring protons and the tertiary proton from the isopropyl group. The small peak at 5.4 p.p.m., which looks like a very weakly resolved triplet with a spacing of about 1 cps, is assigned to the ethylenic protons. The doublet at 9.7 p.p.m. is due to the aldehydic proton split by the ring proton at carbon 1. The peak at 7.3 p.p.m. represents chloroform, which is an impurity in the solvent. The integration curve indicates that the ratio between the aldehydic and the ethylenic protons is 1 to 1. This ratio confirms that there is only one ethylenic proton in the molecule and that structure is 3-p-menthen-7-al.

The second aldehyde isolated from peak 14 has an infrared spectrum identical to that of myrtenal (Lawrence and Terhune, 1969). This aldehyde's ultraviolet absorption maximum at 246 nm. agrees with that reported for myrtenal (Moore and Fisher, 1956).

Peak 16 was identified as cuminaldehyde by comparing its infrared and mass spectra to those of the authentic sample (Matheson). Peak 16 also has an ultraviolet spectrum (λmax at 257 nm. ε = 14,800) which is consistent with the structure. When the compound was reduced with lithium aluminum hydride, an alcohol was obtained, the infrared spectrum of which matches the one reported for cuminyl alcohol (Mitzner et al., 1968).

The minor peak 17 is an aldehyde. Its infrared spectrum (Figure 4) has a carbonyl band at 1688 cm.⁻¹ which indicates conjugation, and an isopropyl moiety as evidenced by the doublet centered at 1380 cm.⁻¹ A fairly weak band at 817 cm.⁻¹ indicates a proton attached to a trisubstituted ethylenic bond. The compound has an absorption maximum at 232 nm. which verifies the conjugation. When the compound
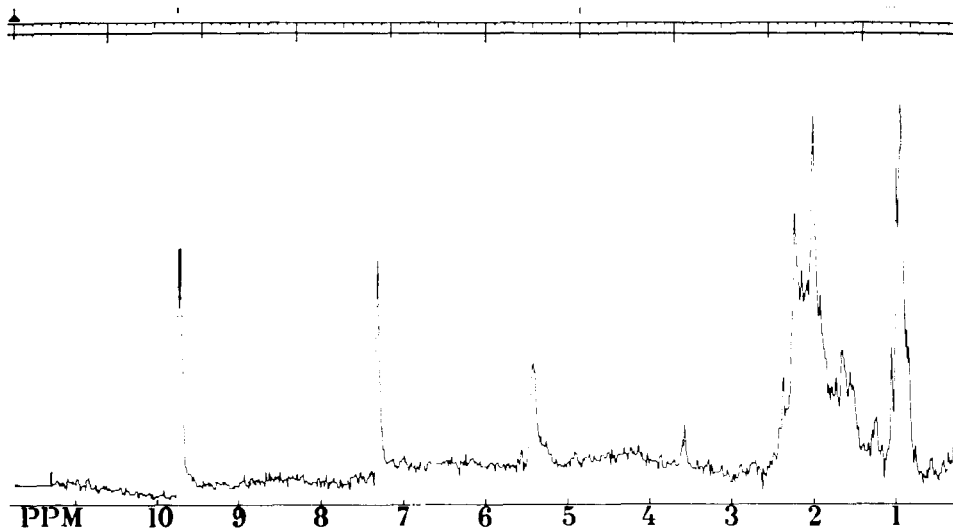
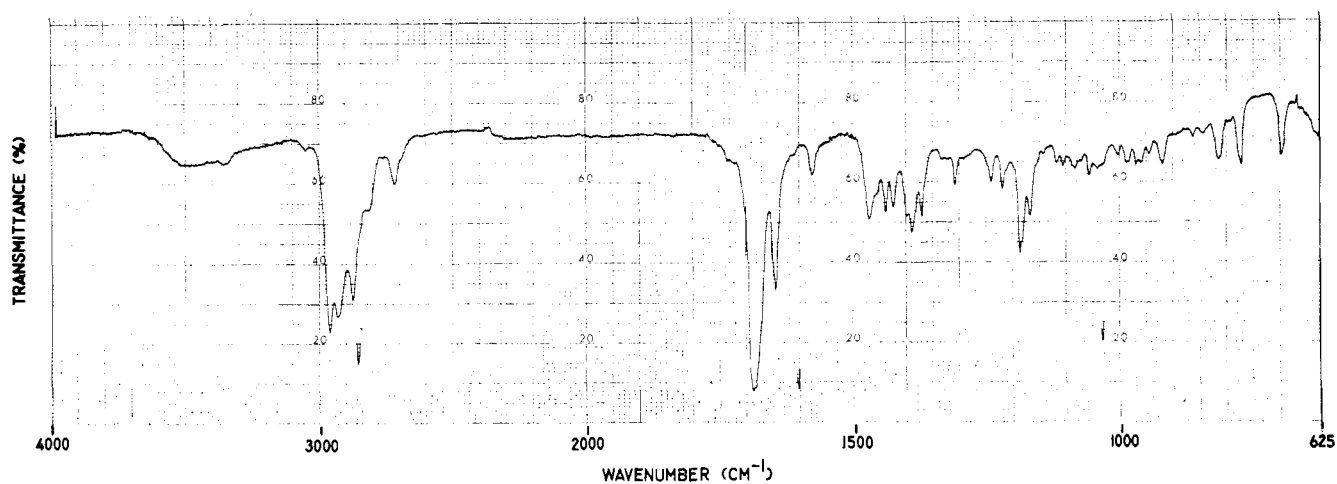Figure 3. NMR spectrum of 3-p-menthen-7-al (isolated from peak 14)

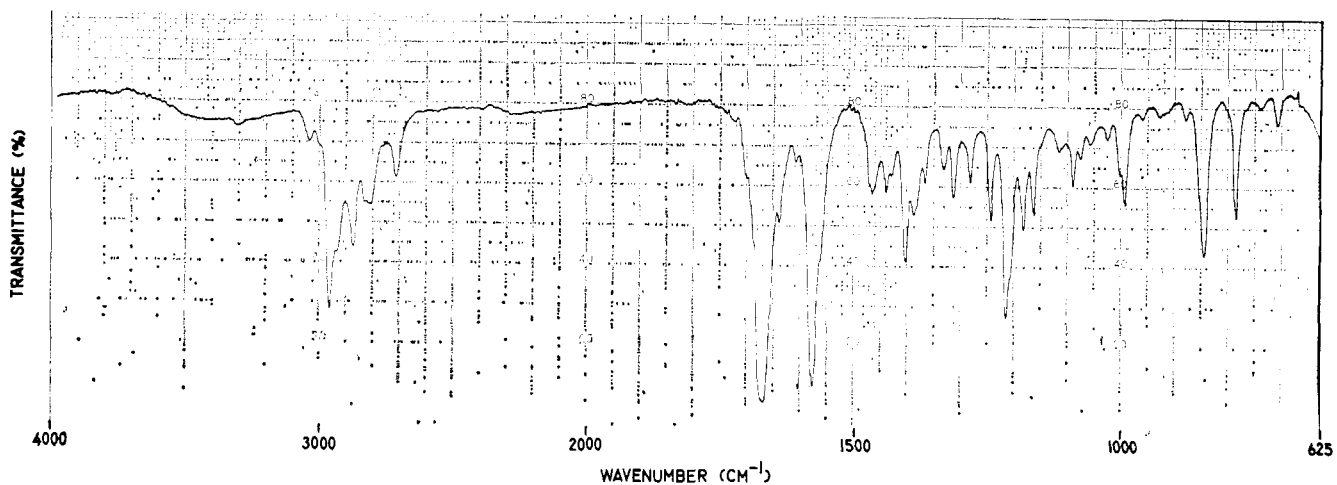Figure 4. Infrared spectrum of phellandral (isolated from peak 17)

Figure 5. Infrared spectrum of 1,3-p-menthadien-7-al (isolated from peak 18)

was reduced with lithium aluminum hydride, the infrared spectrum of the resulting alcohol was identical to the spectrum reported for phellandrol (Mitzner et al., 1968), thus establishing compound 17 as phellandral.

The infrared spectrum (Figure 5) of the major fraction under peak 18 has a strong carbonyl peak at 1670 cm.$^{-1}$, indicating extensive conjugation. This is supported by the

ultraviolet spectrum (λ_{max} 315 nm. ϵ = 9000) which indicates either an open-chain, tetraconjugated system or a triconjugated, diannular system. The low value of the extinction coefficient favors the latter possibility. The infrared spectrum also favors the cyclic structure, since the spectrum does not have a band at 890 cm.$^{-1}$ typical of a terminal methylene group; but it does have a doublet centered at 1370 cm.$^{-1}$,
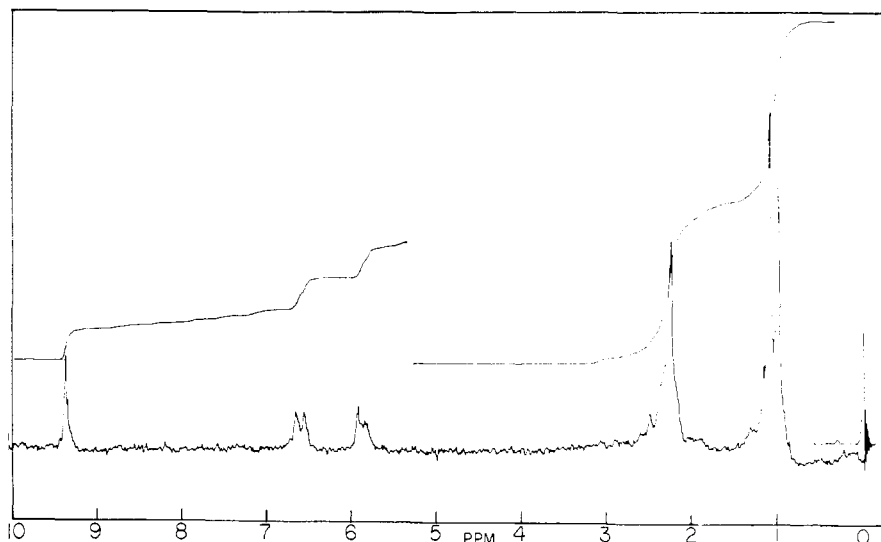
Figure 6. NMR spectrum of 1,3-p-menthadien-7-al (isolated from peak 18)

indicating an isopropyl group. The mass spectrum of peak 18 reveals the parent peak at 150 m/e. The peak at 107 m/e (P-43) indicates the loss of an isopropyl fragment. The nuclear magnetic resonance spectrum of peak 18 (Figure 6) confirms the structure 1,3-p-methadien-7-al. The spectrum includes a six-proton doublet at 1.05 p.p.m. due to the isopropyl group and two, broad, one-proton doublets at 5.87 and 6.61 p.p.m. due to the ethylenic protons. The breadth of the doublets results from the secondary splitting across the ring.

Sesquiterpene hydrocarbons (peaks 22 to 30), as compared to monoterpene hydrocarbons and aldehydes, account for only a small fraction of cumin oil. Peaks 22, 23, 25, 27, 29, and 30 were mixtures not resolvable on the 0.25-inch columns. Peak 24 was identified as β-caryophyllene by its infrared spectrum which matches that reported by Wenninger et al. (1967). The fact that it has no absorption maximum in the ultraviolet region is also consistent with this assignment.

Two other sesquiterpene hydrocarbons were identified: peak 26 as β-farnesene and peak 28 as β-bisabolene. The infrared spectra of these compounds are identical with those reported by Wenninger et al. (1967). Compound 26 has an ultraviolet absorption maximum at 230 nm. as compared to 225 nm. reported by Pinder (1960). Compound 28 does not have an ultraviolet absorption maximum.

The infrared spectrum of peak 33 has no absorption bands above 3100 cm.$^{-1}$ nor in the carbonyl region, indicating that the compound may be a nonterpenoid or that it contains oxygen as an ether or epoxide functional group. Not enough of this material was available for further characterization. Like peak 13, this peak does not appear when the monoterpenes and sesquiterpenes are isolated from the polar constituents using an alumina column.

All constituents previously reported in the literature except perillaldehyde and the tentatively identified nonterpenoid, cryptone, were isolated and identified from these cumin samples. To determine the physical properties of perillaldehyde, it was generated from perillartine (Aldrich Co.) by acid

hydrolysis using 1N HCl. The retention time of perillaldehyde obtained on the SF-96(50) was identical with that of peak 17, phellandrol. The major bands produced in the infrared analysis for perillaldehyde were not observed even in low concentrations in the spectra of any of the aldehydes found in the cumin oil. Therefore, if perillaldehyde is in cumin oils, it must either be in low concentration or in varieties other than those used in this study or it occurs in seeds at a stage of development different from that of seeds used for this study.

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