Table III. Residues (ppmw on Fresh Weight Basis) of Glyphosate and N-Nitrosoglyphosate in Roots and Shoots of Oat Plants Grown in the Treated Soil[a]

treatment level, ppmw	glyphosate		N-nitrosoglyphosate	
	root	shoot	root	shoot
0	ND[b]	ND	ND	ND
5	ND	ND	4.9 ± 0.2	ND
10	ND	ND	9.1 ± 0.2	ND
25	4.8 ± 0.3	ND	21.3 ± 0.9	4.4 ± 0.2
50	8.6 ± 0.7	1.4 ± 0.1	40.3 ± 1.5	7.9 ± 0.6
100	17.0 ± 0.9	3.9 ± 0.1	72.7 ± 5.2	15.4 ± 0.5
200	39.1 ± 1.9	10.1 ± 0.3	135 ± 7.6	25.1 ± 1.1
300	59.8 ± 4.6	16.8 ± 1.0	213 ± 5.8	45.6 ± 1.2

[a] Mean values for triplicate samples with standard errors. The data are not corrected for recovery. [b] Not detected.

is persistent in soil (Khan and Young, 1977). The data presented in this paper indicate that N-nitrosoglyphosate can be assimilated by the roots of oat plants and translocated to the shoots.

Whether the nitrosation of glyphosate in soil to form N-nitrosoglyphosate will occur under natural conditions is still a matter of conjecture. However, based on the previous study (Khan and Young, 1977) we do not expect the formation of detectable amounts N-nitrosoglyphosate in soil under normal field conditions. It was observed that high concentrations of the herbicide glyphosate and nitrite were essential to get measurable amounts of N-nitrosoglyphosate in soil, which amounts in turn were considerably lower than the concentrations of N-nitrosoglyphosate used in this study. Even though soil concentrations were extremely high, the observations that N-nitrosoglyphosate can be taken up by plants should prompt further research to determine whether such a possible hazard is in fact a reality with other pesticides.

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Identification of "Isodihydrolavandulol" by Application of Fourier Transform Nuclear Magnetic Resonance Spectroscopy to Gas Chromatography Eluates

"Isodihydrolavandulol" has been found to be a mixture of two major components. The FT-NMR spectra of each component were obtained on samples collected from a gas chromatograph. On the basis of the evidence from these spectra, the components were identified as 4-methyl-2-propyl-2-hexenol and 2-propyl-2-heptenol.

According to the literature (Arctander, 1969), "isodihydrolavandulol" is either 2-isopropyl-5-methyl-2-hexenol (1) or 2-isopropylidene-5-methylhexanol (2) (Figure 1). As shown in Figure 2a, "isodihydrolavandulol" is a mixture of two compounds whose identification is the subject of this communication.

The isomeric 2-hexenols have been described in the patent literature (Kallianos et al., 1972) as obtained from the base-catalyzed self-condensation of 3-methylbutyraldehyde, followed by sodium borohydride reduction of the unsaturated aldehydes. The mixture obtained in this manner consists predominantly of the cis and trans isomers of 1 and a small amount of 2-isopropyl-5-methyl-3-hexenol (3). As is discussed below, these structure assignments have been confirmed in this study. The gas chromatogram (Figure 2b) of this mixture was distinctly different from that of "isodihydrolavandol".

An unambiguous synthesis of 2-isopropylidene-5-methylhexanol (2) was carried out according to the scheme shown in Figure 3. As shown, the double bond was introduced regiospecfically by means of a Wittig–Horner reaction (Wadsworth and Emmons, 1961). The ^{1}H NMR spectrum of this alcohol (2) clearly showed the presence of the expected isopropylidene group; the gas chromatogram (Figure 2c) of this alcohol (2) did not coincide with either of the major peaks of "isodihydrolavandulol". Thus "isodihydrolavandulol" has neither of the structures by which it is commonly described.

The rapid development of Fourier transform NMR spectroscopy has made possible obtaining spectra on very small quantities of material. It appeared feasible to obtain usable spectra from samples collected from an analytical gas chromatograph. The details of the technique by which the spectra were obtained are presented in the Experimental Section; the interpretation of these spectra follows.

The structures of the three components of the mixture derived from 3-methylbutyraldehyde were confirmed by NMR spectroscopy. The proton and ^{13}C spectra of the two major components were consistent in all respects with cis and trans isomers of 2-isopropyl-5-methyl-2-hexenol (1).

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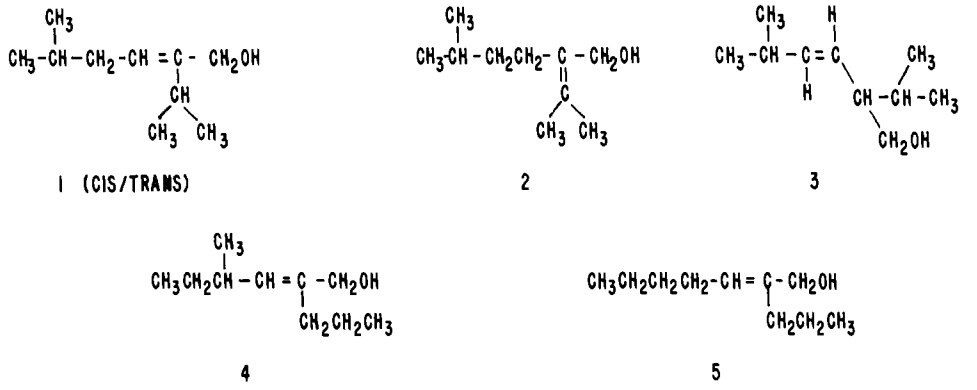

Figure 1. Isomeric C_{10} alkenols.

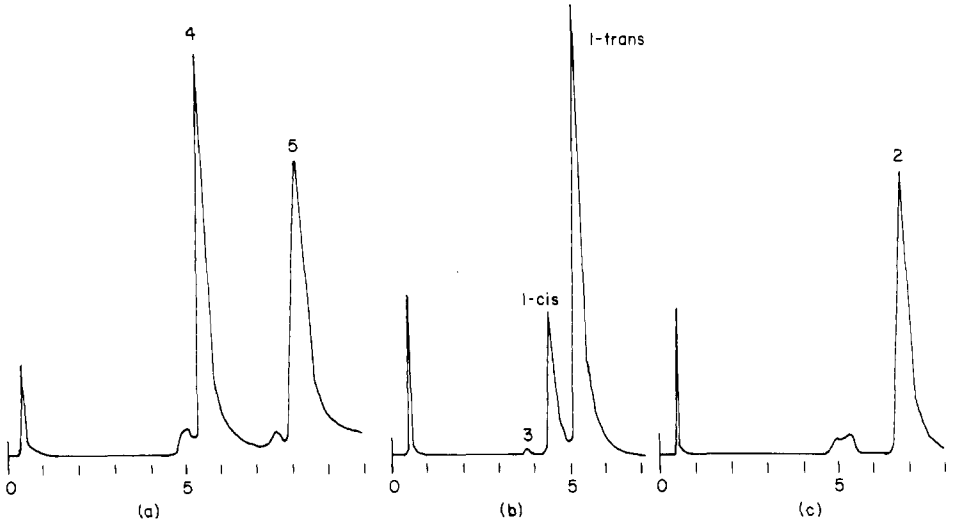

Figure 2. Gas chromatogram of (a) "isodihydrolavandulol", (b) 2-isopropyl-5-methylhexenols, and (c) 2-isopropylidene-5-methylhexanol. The numbers refer to the structural formulas shown in Figure 1.

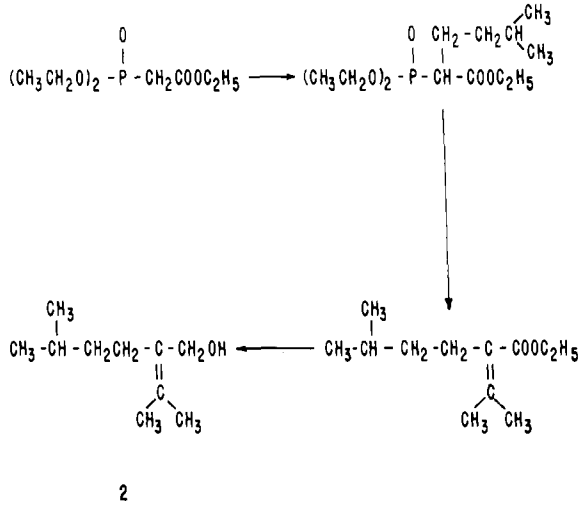

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Figure 3. Preparation of 2-isopropylidene-5-methylhexanol (**2**).

The proton NMR spectrum of the minor component, estimated to arise from approximately 50 μg of sample in the capillary sample tube, could be interpreted unequivocally in accord with 2-isopropyl-5-methyl-3-hexenol (**3**). Figure 4a shows the full spectrum of the compound, and Figure 4b shows an expansion of the region between 3.2 and 5.7 ppm. The large coupling constant, $J_{3,4}$ = 15.5 Hz, in the multiplet centered around 5.3 ppm is characteristic of coupling between trans olefinic protons. The multiplet centered at 3.5 ppm displays a coupling constant $J_{1,1'}$ which is equal to 10.5 Hz, typical of the coupling between a nonequivalent pair of protons on a carbon atom to which an oxygen is attached. The chemical shift is consistent with a $-CH_2OH$ group. The nonequivalence arises from the asymmetry of C_2 in this molecule. In addition, the methyls of the isopropyl substituent on C_2 become nonequivalent and give rise to four lines between 0.85 and 1.0 ppm. Both of the protons on C_1 and the olefinic proton on C_3 show spin–spin coupling to the proton on C_2, and the olefinic proton on C_4 shows coupling to the isopropyl proton on C_5.

The identification of the two major components of "isodihydrolavandulol" was based on the following evidence. The component eluting first showed a doublet for the olefinic proton at 5.2 ppm, indicating coupling to a methine proton. The methyl region of the proton spectrum (0.85–1.05 ppm) showed two triplet methyl resonances with a superimposed doublet. A group of three protons between 2.0 and 2.5 ppm appeared as a superposition of a triplet and a multiplet. These data are consistent with 4-methyl-2-propyl-2-hexenol (**4**).

The proton spectrum of the other component showed only two triplet methyl groups which indicated the presence of straight chain substituents. A multiplet at 1.4 ppm appeared to be three methylene groups; two other methylene groups appeared further downfield at 2.1 ppm, suggesting they are adjacent to a double bond. The olefinic proton at 5.4 ppm appeared as a triplet, confirming an adjacent methylene group. These data are consistent with 2-propyl-2-heptenol (**5**).

The two components of "isodihydrolavandulol" can be derived from the crossed-aldol condensation of valer-

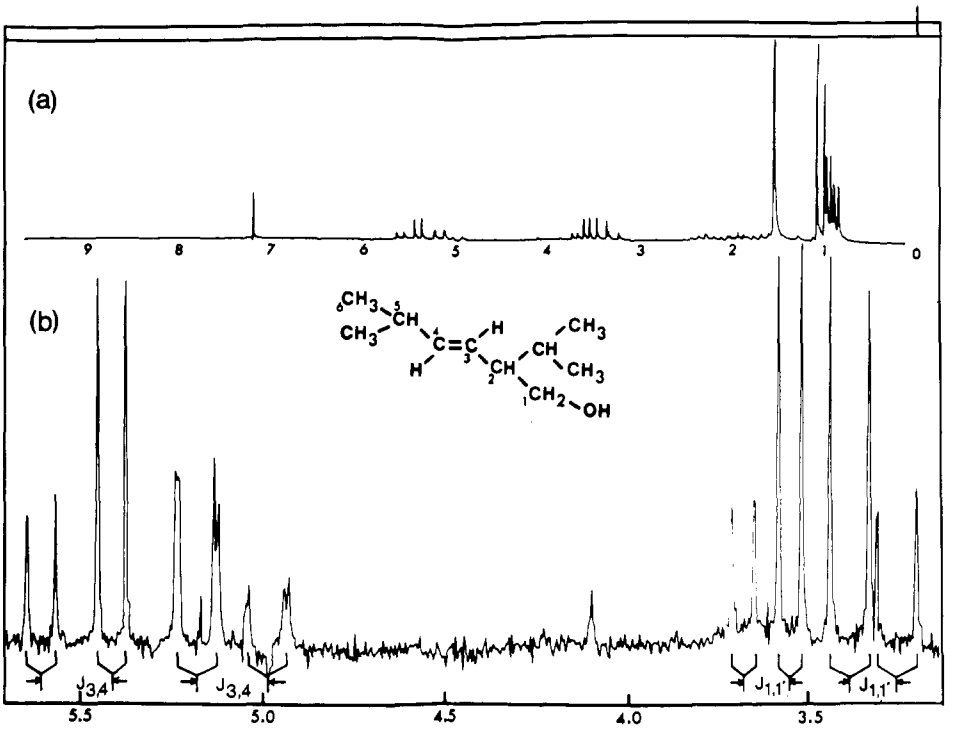

Figure 4. (a) Full proton spectrum of 2-isopropyl-5-methyl-3-hexenol (3), minor product from 3-methylbutyraldehyde. Scale is 10 ppm relative to Me_4Si. Peak at 7.2 ppm is residual $CHCl_3$. Peak at 1.5 is due to H_2O plus the hydroxyl proton. Sample size is approximately 50 μg. (b) Expansion of the 3.2–5.7 ppm region of the spectrum, showing the trans coupling, $J_{3,4}$, the geminal coupling, $J_{1,1'}$, and further splitting of all lines due to each of the four protons having one proton on an adjacent carbon.

aldehyde and 2-methylbutyraldehyde. Of the four possible aldol condensation products, only two appear in the distilled product. The other two, if formed, apparently do not dehydrate as readily since there is no evidence of a nonconjugated aldehyde in the distillate. Reduction of the mixture of aldehydes with $NaBH_4$ gave a mixture of alcohols which was identical in all respects with "isodihydrolavandulol".

EXPERIMENTAL SECTION

Materials. "Isodihydrolavandulol" was obtained from Fritzsche, Dodge and Olcott. The isomeric 2-hexenols were prepared as described in the literature (Kallianos et al., 1972). The aldol condensation of valeraldehyde and 2-methylbutyraldehyde and subsequent reduction were carried out by standard methods. The preparation of 2-isopropylidene-5-methylhexanol (2) was carried out according to the scheme shown in Figure 3; the final product was satisfactorily characterized by spectroscopic techniques.

Apparatus. Infrared spectra were obtained on dilute solutions using a Perkin-Elmer Model 621 grating infrared spectrophotometer. Proton NMR spectra were obtained using a Varian A-60A spectrometer operating at ambient temperatures. Gas chromatograms were obtained using a Varian Series 1800 gas chromatograph equipped with a thermal conductivity detector. The column was 10 ft × $^1/_8$ in. stainless steel packed with 5% Carbowax 20M on 100–120 mesh Gas-Chrom Z. All samples were chromatographed at an oven temperature of 150 °C, injector at 225 °C, and detector at 275 °C with a flow rate of 35 mL/min He.

Collection of Samples. A 1-μL sample of each mixture was injected into the gas chromatograph. Each of the eluates was collected separately in an open-end melting point capillary (1 mm o.d.) cooled with a small piece of dry ice. After collection, the tube was sealed by heating with a microburner.

Fourier Transform Spectra. The proton and ^{13}C NMR spectra were obtained with a Varian Associates CFT-20 NMR spectrometer equipped with a 1.7-mm probe which could be switched from ^1H to ^{13}C operation. The spectrometer was operated in a pulsed-deuterium NMR lock mode, locking on the deuterium in approximately 15 μL of $CDCl_3$ used as solvent. Wide-band noise-modulated proton decoupling was used to obtain fully decoupled ^{13}C spectra of all compounds except the minor component from the condensation of 3-methylbutyraldehyde. Chemical shifts were measured relative to internal Me_4Si, added to the samples as a reference.

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