

**cis-Hept-4-en-2-ol in Corn Volatiles: Identification and Synthesis**

*cis*-Hept-4-en-2-ol was synthesized in 60% overall yield by the oxidation of *cis*-hex-3-enol to *cis*-hex-3-enal which was then reacted with methylmagnesium iodide. The infrared absorption spectrum of the synthetic sample was identical with that of a sample isolated from corn husk volatiles, confirming that the corn husk hept-4-en-2-ol is in the *cis* form.

The authors recently reported a study (Buttery et al., 1978) of the volatiles of corn husks and corn kernels. A similar study on corn silk volatiles has been reported by Flath et al. (1978). In all three parts of the corn plant, hept-4-en-2-ol was both a unique and major component. It was not established, however, whether the double bond was *cis* or *trans*. There seemed a possibility that such a compound might be an important corn ear worm (*Heliothis zea*) attractant. Having the correct isomer can be an important factor in insect attraction. The synthesis of the *cis*-hept-4-en-3-ol was desirable to compare with the sample obtained from corn husks using infrared absorption spectrometry. It was also necessary to have sufficient amount of the compound available for insect attractancy testing.

**EXPERIMENTAL SECTION**

**Synthesis of *cis*-Hept-4-en-2-ol.** *cis*-Hex-3-enal was synthesized following the method of Kajiwara et al. (1975) from 60 g of Cr<sub>2</sub>O<sub>3</sub>, 95 mL of pyridine, 1500 mL of CH<sub>2</sub>Cl<sub>2</sub>, and 10 g of *cis*-hex-3-enol (Aldrich No. H1290-0). It was not isolated but added in the concentrated (100 mL), dried, CH<sub>2</sub>Cl<sub>2</sub> solution to excess methylmagnesium iodide (from 4.8 g of Mg, 12 mL of MeI in 100 mL of ether). Following the usual Grignard workup, removal of solvent gave 8.5 g of crude *cis*-hept-4-en-2-ol, which was purified by gas-liquid chromatography (GLC) using a 3 m long by 0.64 cm o.d. Carbowax 20-M column at 100° C. GLC analysis showed an overall yield of 60% pure *cis*-hept-4-en-2-ol, the only other major product being unreacted *cis*-hex-3-enol.

**GLC Separation from Corn Husk Oil.** Components were separated from corn husk volatile oil using a 3 m long by 0.64 cm o.d. stainless steel GLC column packed with Chromosorb G-DMCS coated with 2% Silicone SF96(50). The column was temperature programmed from 50–170 °C at 2 °C/min and held at the upper limit. Samples were collected in 3 mm o.d. × 14 cm long Pyrex tubes.

**Infrared Absorption (IR) Spectra.** The IR spectra were measured in the pure state as a film on ultramicro salt plates or in CS<sub>2</sub> solution using ultramicrocavity cells and a reflecting beam condenser with a Perkin-Elmer Model 237 instrument.

**RESULTS AND DISCUSSION**

A few years ago *cis*-hex-3-enal could only be obtained in very poor yield (ca. 5%, e.g., Buttery et al., 1971) from oxidation of *cis*-hex-3-enol (which is commercially available). Recently, however, a method using chromium trioxide and pyridine in methylene chloride solution was reported by Kajiwara et al. (1975), whereby *cis*-hex-3-enol can be oxidized to *cis*-hex-3-enal in better than 70% yield. This method was used in the present work to provide the *cis*-hex-3-enal which was not isolated but simply reacted in solution with methylmagnesium iodide. This gave an overall yield of 60% of pure *cis*-hept-4-en-2-ol, quite sufficient for preparing enough material for insect tests. A different more complex synthesis of *cis*-hept-4-en-2-ol, using aluminum alkyl compounds, which gave poorer yields

(ca. 34%) than the present method, was recently reported by Malpass et al. (1977).

The GLC purified *cis*-hept-4-en-2-ol had a mass spectrum as follows (two major ions each 14 mass units above *m/e* 34, intensities in parentheses, molecular ion in boldface): 42 (44), 45 (100); 53 (7), 55 (77); 70 (71), 71 (7); 79 (0.6); 81 (7); 96 (7), 99 (0.6); 114 (0.5). This mass spectrum was very similar to that of the *trans* form (Buttery et al., 1978). The IR spectrum showed absorption bands at *s* (3.0, 3.3, 3.4, 3.5, 6.9, 7.1, 7.3, 8.9, 9.3, 10.6), *m* (7.1, 7.4, 7.6, 8.2, 11.8), *w* (6.02, 9.8, 10.1, 10.3, 10.6, 11.2, 11.5, 12.3, 12.6) μm<sup>-1</sup>. This IR spectrum was quite different from that of the *trans* form which showed a strong absorption band at 10.3 μm<sup>-1</sup> characteristic of a *trans*-CH=CH- group. The <sup>1</sup>H NMR spectrum (90 MHz, CDCl<sub>3</sub>) showed δ 0.92 (t, 3 H, CH<sub>3</sub>CH<sub>2</sub>), 1.18 (d, 3 H, CH(OH)CH<sub>3</sub>), 1.53 (s, 1 H, OH), 1.8–2.3 (m, 4 H, CH<sub>2</sub>CH=CHCH<sub>2</sub>), 3.78 (m, 1 H, CH<sub>2</sub>CH(OH)CH<sub>3</sub>), 5.4 (m, 2 H, CH=CH), the olefinic splitting at δ 5.4 being consistent with the *cis* form. The GLC Kovats Retention Index on a 150 m long by 0.64 mm i.d. Pyrex glass capillary column coated with Tween 20 was 1230 for the synthetic *trans* form and 1261 for the synthetic *cis* form.

**Isolation from Corn Husk Volatile Oil.** The vacuum steam volatile oil was obtained from corn husks as described previously (Buttery et al., 1978), and components were isolated by packed column GLC separation. Measurement of the infrared spectrum of the component corresponding to hept-4-en-2-ol showed that it was identical with that of the synthetic *cis*-hept-4-en-2-ol and quite different from that of the *trans* isomer. The capillary GLC retention time of the isolated material was also more consistent with the *cis* form.

Other components isolated from corn husk volatile oil whose identification (Buttery et al., 1978) was confirmed by comparison of the infrared spectra of the isolated samples with that of authentic samples were hexanal, hex-2-enal, hex-*cis*-3-enol, heptan-2-ol, 2-pentylfuran, oct-2-enal, nonanal, nonan-2-ol, non-2-enal, decanal, *trans,trans*- and *trans,cis*-deca-2,4-dienal, and β-ionone.

**LITERATURE CITED**

- Buttery, R. G., Ling, L. C., Chan, B. G., *J. Agric. Food Chem.* **26**, 866 (1978).  
 Buttery, R. G., Seifert, R. M., Guadagni, D. G., Ling, L. C., *J. Agric. Food Chem.* **19**, 524 (1971).  
 Flath, R. A., Forrey, R. R., John, J. O., Chan, B. G., *J. Agric. Food Chem.* in press (1978).  
 Kajiwara, T., Harada, T., Hatanaka, A., *Agric. Biol. Chem.* **39**, 243 (1975).  
 Malpass, D. B., Watson, S. C., Yeargin, G. S., *J. Org. Chem.* **42**, 2712 (1977).

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