Ambrosial, a Dehydrocitral Isolated from the Leaf Oil of *Ambrosia confertiflora* D.C. (Ragweed)

The structure for Ambrosial, a component of the volatile oil from *Ambrosia confertiflora* D.C., is deduced to be dehydrocitral.

Some of the difficulties encountered in identifying dehydrocitral as a natural product have been anticipated. After synthesizing this compound by the self-condensation of β-methylcrotonaldehyde, Fischer said that if dehydrocitral were a more stable molecule it would probably have already been reported as a natural product (Fischer and Hultzsch, 1935). He reported on an isomer which formed fine needles, with a bright lemon-yellow color and a melting point of 40.5–41°. More recently, the synthesis was improved by Young and an absorption maximum of 338 mμ for their oil was reported (Young and Linden, 1947). Later, some confusion arose when a precursor to dehydrocitral, 4-ethoxycitral, was reported to have absorption maxima at 240 and 327 mμ (Nazarov and Krasnaya, 1958), which are consistent with expected maxima for dehydrocitral, but not its precursor.

Small samples of one of the larger components in the oil that is steam distilled from the leaves of *Ambrosia confertiflora* D.C. (AWT Texas), were isolated by gas chromatography (Payne *et al.*, 1972). The nmr and ir spectra indicated an unsaturated aldehyde. The mass spectrum showed a molecular weight of 150, and this material was initially believed to be a previously reported natural product, Safranal. However, comparison with the nmr, mass, and infrared spectra from an authentic sample of Safranal (Russell, 1972) proved that the two materials were not identical. Some of the physical properties and the deduction of the structure of this naturally occurring acyclic monoterpene aldehyde are reported in this communication.

EXPERIMENTAL SECTION

Washed leaves were ground in a Waring Blendor and steam distilled under reflux using a Clevenger collection trap for oils lighter than water.

A Varian Model 1520 chromatograph with either a 20% LAC 446 (diethylene glycol adipate cross-linked with pentaerythritol) or a 4% Carbowax 20M, with 1% DEGA (diethylene glycol adipate) on 60–80 mesh Chromosorb W in 205 × 0.635 o.d. × 0.457 i.d. (cm) stainless steel column, was used. The injector and thermal conductivity detector temperatures were 210°, and the column temperature was programmed from 50 to 182°. A 20-point matrix temperature programmer with 5.9-min intervals used the following settings: 6 (6°); 7 (hold); 10 (4°); 11 (hold); 15 (2°). A fraction of oil, peak 11, eluting at 62 min, was collected in a 1.8 × 100 mm melting point capillary tube at the exhaust port using Dry Ice (Payne *et al.*, 1972).

Infrared absorption spectra were obtained in carbon tetrachloride with a Beckman IR-12 using a 0.05-mm path microcell with a neutral density in the reference beam. Ultraviolet absorption was determined with a Beckman DB spectrophotometer. Nmr spectra were obtained with a Varian Model T spectrometer using a 30-μl sample tube and carbon tetrachloride as the solvent. Mass spectra were obtained from a LKB 9000 mass spectrometer at the Graduate School of Public Health, University of Pittsburgh, Pittsburgh, Pa.

The hydrogenation of approximately 10 mg of oil was carried out at atmospheric pressure for 48 hr using platinum oxide as the catalyst. Citral, obtained from Givaudan Corp., was reduced under the same conditions.

These two reduction products and an authentic sample of 3,7-dimethyloctanol-1, also from the Givaudan Corp. (Clifton, N.J.), were found to chromatograph identically. Additional checks using a Beckman GC-4 with a 183 × 0.635 o.d. × 0.216 i.d. (cm) 10% HI-EFF-2 BP (ethylene glycol succinate on Chromosorb W AW, 100–120 mesh) at 120° or a 122 × 0.635 o.d. × 0.216 i.d. (cm) 3% SE-52 on Diatom-W, 80–100 mesh at 90°, also gave identical chromatograms.

RESULTS AND DISCUSSION

Immediately apparent features from the spectra are: ir (cm^{-1} in CCl_4) 2730, 2770, 1670 (conjugated aldehyde), 1380 (CH_3), 1642, 1604 (conjugated double bonds); nmr (CCl_4) δ 10.0 (d, J = 7 Hz, CH=O), 2.09 (s, CH_3), 1.86 (s, $[CH_3]_2$); uv max (absolute ethanol) 332 and 235 mμ; mass spectrum (70 eV) m/e 150 parent ion with approximately a 5% contamination at m/e 166.

From the nmr absorption for an aldehyde hydrogen and the location of the intense uv absorption the molecule should have a basic structure of $CH_3(CH{=}CH)_3CHO$ (Blout and Fields, 1948; Jaffe and Orchin, 1962). Two additional methyl substitutions would fit the molecular weight and also shift this parent absorption maximum from 312 to the observed value of 332 which is in reasonable agreement with the value reported by Young and Linden (1947). The absorption for 4-ethoxycitral, which was reported by Nazarov and Krasnaya (1958), is undoubtedly due to dehydrocitral. When they heated 4-ethoxycitral (which probably was actually crude dehydrocitral from the reported uv) with toluenesulfonic acid, this could have completed an elimination reaction or isomerized it to a form which crystallizes. The absence of a terminal methylene is evident from the ir spectrum, and the appearance of only singlet nmr resonances in the expected regions for vinyl methyl groups lead to the conclusion that a terminal dimethyl grouping exists in our oil.

The presence of a strong ir absorption at 1380 cm^{-1} allowed us to recognize that the strong singlets in the nmr were due to methyl groups even though a precise integration of the nmr spectrum was not possible.

The only remaining problem was the location of the third methyl group of the trienal skeleton. There are only five possible sites available on 7-methyl-2,4,6-octatrienal (the 2, 3, 4, 5, and 6 carbons). Position 2 is ruled out, by the aldehyde hydrogen doublet. Position 5 is ruled out by the absence of a vinyl hydrogen singlet. Of the remaining three possibilities, position 3 is consistent with the "isoprene rule." Direct confirmation of this was found by the catalytic reduction of Ambrosial with platinum oxide and conducting a gas chromatograph comparison of this product with authentic 3,7-dimethyloctanol-1 as well as with the reduction product obtained from citral. The sample of reduction product was insufficient for ir analysis. Although attempts to synthesize this compound by the method of Young and Linden (1947) have been unsuccessful, we conclude that our oil is a dehydrocitral. Of the four possible isomers, the all trans would be the expected isomer for this natural component.

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Junji Kumamoto*
Rainer W. Scora
Willard W. Payne[1]

Department of Plant Sciences
University of California
Riverside, California 92502
[1] Botany Department
University of Florida
Gainesville, Florida 32601

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Correction

TOTAL ^{14}C RESIDUES AND DIELDRIN RESIDUES IN MILK AND TISSUES OF COWS FED DIELDRIN-^{14}C

In this article by John C. Potter, Ronald L. Marxmiller, George F. Barber, Robert Young, Josef E. Loeffler, William B. Burton, and Lloyd D. Dixon [*J. Agr. Food Chem.* 22(5), 889 (1974)], on page 890, column 2, paragraph 2, line 7, the detergent solution Udder-Du is a product of the An-Fo Manufacturing Co., Oakland, Calif., not the Kendell Company as indicated.