the nitro group in the 3-*endo* position[21] and that $J_{1,4} = 4.8$ c.p.s. is of the correct magnitude. However, proton H_1 appears as an extremely crude triplet and coupling constants $J_{1,2}$ and $J_{1,3}$ are not obtainable. The sodium salt, XIV, effectively removes H_4 and allows the spectrum to be simplified such that proton H_1 occurs as a doublet with $J_{1,3} = 3.6$ c.p.s. and $J_{1,2} = 0$ c.p.s.

$$\underset{\text{XV}}{HOCH_2CH{=}NO_2^-Na^+} \qquad \underset{\text{XVI}}{O_2N{-}CH_2CH_2O^-Na^+}$$

The sodium salt of 2-nitroethanol is a mixture of salts of both possible anions, the *aci*-nitro anion XV and the alkoxy anion XVI. The n.m.r. spectrum of the mixture shows a symmetric triplet centered at 6.27 p.p.m. and another triplet at 4.20 p.p.m. The center peak of the triplet at 4.20 p.p.m. is much larger and represents XVI, while the remainder of the spectrum (see Table I) represents XV.

It is of interest to note that none of the nitro form is present in any of the spectra of the salts except that of XIII. Although the spectrometer is not sensitive beyond 2–3%, it is reasonable that the nitro form is present in only very small amounts.

The observance of the nitronate anion by n.m.r. has practical significance. The base condensation of nitro paraffins with carbonyl compounds in aqueous media can now be observed directly both as to rate of reaction and product formation. It is hoped that further use of this technique will provide a better understanding of these reactions.

Experimental

The n.m.r. spectra were obtained from a Varian A-60 spectrometer using solutions that contained 10–15% of each salt in deuterium oxide. The spectra were calibrated using acetone as an internal standard. The sodium salts of the nitro paraffins were prepared according to known procedures.[3,4] The following preparation of the sodium salt of 1-nitropropane illustrates the procedure used in this study.

An ice-cold solution containing 7.0 g. (0.13 mole) of sodium methoxide in 25 ml. of absolute methanol was added in one portion to an ice-cold solution of 1-nitropropane (12.0 g., 0.13 mole) in absolute methanol (25 ml.). A very small amount of white solid precipitated, and after standing 30 min., ether (100 ml.) was added to precipitate the salt. The white solid was quickly filtered and washed well with anhydrous ether. After drying in a desiccator under high vacuum, the salt weighed 7.6 g. (53%). The infrared spectrum of the salt showed λ_{max}^{KBr} 2.94, 3.38, 3.47, 6.27, 6.85, 7.30, 8.59, 8.85, 9.61, 10.08, 11.03, and 14.28 μ, while absorption in the ultraviolet occurred at $\lambda_{max}^{H_2O}$ 232 mμ (ε 9650).

As the procedures for the preparation of the remaining salts were basically identical with the above, only the physical data for each salt are listed below.

Sodium Salt of Nitromethane (VI).—Infrared spectrum (KBr) 2.93, 6.36, 6.93, 7.90, 8.51, 9.74, 10.19, 10.51, and 13.55 μ.

Sodium Salt of Nitroethane (VII).—Infrared spectrum (KBr) 2.95, 3.47, 6.03, 6.22, 7.17, 7.53, 7.86, 8.44, 8.95, 9.55, 11.28, and 13.91 μ; ultraviolet spectrum λ^{H_2O} 228 mμ (ε 9030), 340 (224), and 375 (316).

Sodium Salt of 2-Nitropropane (XII).—Infrared spectrum (KBr) 3.05, 3.42, 6.00, 7.72, 8.63, 10.58, and 12.87 μ; ultraviolet $\lambda_{max}^{H_2O}$ 222 mμ (ε 10,500).

Sodium Salt of 2-Nitroethanol (XV and XVI).—Infrared spectrum (KBr) 3.10, 3.38, 3.51, 6.40, 7.07, 7.23, 7.57, 8.06, 8.60, 9.22, 9.62, 10.20, 11.52, 12.05, and 13.20 μ.

Sodium Salt of *α-d*-Nitrocamphor (XIV).—Infrared spectrum (KBr) 2.89, 5.93, 6.74, 7.51, 7.68, 7.96, 8.18, 9.07, 10.71, and 11.12 μ; ultraviolet $\lambda_{max}^{H_2O}$317 mμ (ε 13,100) and 227 mμ (ε 4540).

Acknowledgment.—The authors wish to thank J. E. McKeon and C. B. Strow, Jr., for their suggestions and helpful discussions.

---

[21] R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

Volatiles from Oranges. III. The Structure of Sinensal[1]

K. L. STEVENS, R. E. LUNDIN, AND R. TERANISHI

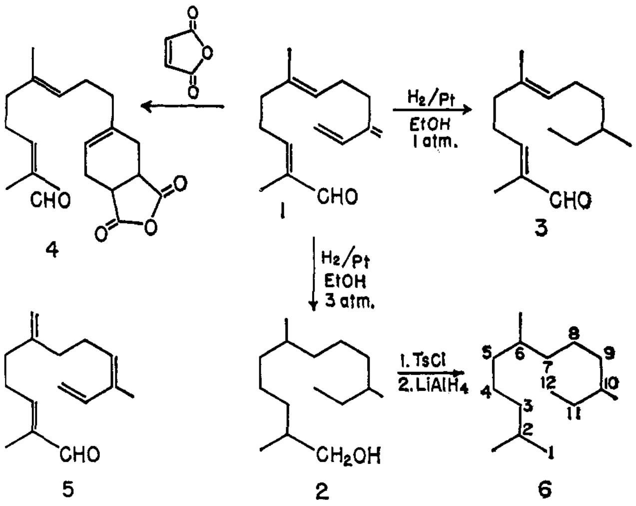
Fruit Laboratory, Western Regional Research Laboratory,[2] Albany, California

Received November 30, 1964

A new sesquiterpene aldehyde, sinensal ($C_{15}H_{22}O$), has been isolated from orange oil (*Citrus sinensis L.*) and shown to be **1**. Sinensal is a colorless liquid, b.p. ~180° (1 mm.), optically inactive, and has a molecular weight of 218 determined by mass spectrometry. The ultraviolet spectrum shows λ_{max}^{EtOH} 227 mμ (ε 31,000). Preparation of the 2,4-dinitrophenylhydrazone of sinensal gave a red-orange product with m.p. 87–88°.

Reduction of sinensal with Adams catalyst in ethanol at three atmospheres gave octahydrosinensol (**2**) as an oil. Preparation of the tosylate then reduction with lithium aluminum hydride gave a saturated hydrocarbon with infrared, n.m.r., and mass spectra identical with those of an authentic sample of farnesane (**6**) (see Scheme I).

SCHEME I



An infrared spectrum of sinensal showed peaks at 3.70 and 5.94 μ thus indicating an *α,β*-unsaturated aldehyde.[3] The n.m.r. spectrum (Figure 1) shows a singlet at 9.33 p.p.m. (1H) which confirms an unsaturated aldehyde[4] and also establishes the fact that there are no *α*-protons. This information may also

---

[1] Part II: T. H. Schultz, R. Teranishi, W. H. McFadden, P. W. Kilpatrick, and J. Corse, *J. Food Sci.*, **29**, 790 (1964).

[2] One of the laboratories of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[3] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 133.

[4] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p. 62.

be obtained by an examination of the n.m.r. spectrum of octahydrosinensol (2) in which the carbinyl protons occur as a doublet at 3.33 p.p.m. (J = 5.5 c.p.s.). Had an α-proton been present in the α,β-unsaturated aldehyde, the low-field methylene of octahydrosinensol would have been a triplet.

A doublet at 1.70 p.p.m. ($J \sim 1$ c.p.s., 3H) in the n.m.r. spectrum of sinensal shows a paramagnetic shift of 0.24 p.p.m. on preparation of the 2,4-dinitrophenylhydrazone (2,4-DNP) indicating the α-substituent on the α,β-unsaturated aldehyde to be a methyl group. An α,β-unsaturated aldehyde with an α-methyl group unequivocally places the aldehyde moiety at C-1 of the farnesane skeleton (6).

A single β-vinyl proton can be seen as a broad triplet (superimposed on other lines) at 6.31 p.p.m. (J = 6 c.p.s., 1H)[5] indicating the presence of a 4-methylene group. The triplet was shifted upfield to 5.93 p.p.m. in the 2,4-DNP derivative of sinensal. To confirm the assignment of peaks, a decoupling experiment was carried out by irradiating the triplet at 6.31 p.p.m. The doublet at 1.70 p.p.m. collapsed to a singlet thus showing the low-field methyl group (1.70 p.p.m.) and the low-field triplet (6.31 p.p.m.) to be coupled.

The high intensity of the peak in the ultraviolet spectrum of sinensal indicated the presence of an additional chromophore.[6] Further examination of the n.m.r. spectrum of sinensal shows a typical X portion (superimposed on a triplet) of an ABX system observed with substituted ethylenes.[7] A first-order analysis shown in Figure 1, gives the center at 6.21 p.p.m. (J = 17 and 10 c.p.s., 1H) which corresponds to the internal proton of a 2-substituted 1,3-butadiene.[8] Owing to accumulation of protons in the region of 4.9–5.3 p.p.m., we are unable to assign the terminal vinyl protons to specific peaks. Hydrogenation of sinensal with Adams catalyst in ethanol at 1 atm. gave tetrahydrosinensal (3) as a colorless liquid. Ultraviolet [$\lambda_{\max}^{\text{EtOH}}$ 230 mμ (ϵ 13,000)] and infrared (3.70 and 5.92 μ) spectral analysis showed the α,β-unsaturated aldehyde to be intact. Confirmation was obtained by observing a singlet (1H) at 9.31 p.p.m. and a triplet (J = 6.5 c.p.s., 1H) at 6.34 p.p.m. in the n.m.r. spectrum. In contrast to the seven vinyl protons shown by sinensal (Figure 1), tetrahydrosinensal showed only two such protons. Hydrogenation with the uptake of 2 moles of hydrogen along with the "loss" of five vinyl proton necessitates the presence of a mono and a disubstituted double bond. That the two bonds are indeed in conjugation was shown by an examination of the n.m.r. spectrum of the Diels–Alder adduct **4** of sinensal and maleic anhydride in which three vinyl protons were found to be present. The adduct of **5**, the alternate structure, would have shown four vinyl protons. The 2-substituted 1,3-butadiene must therefore be as shown in **1**.

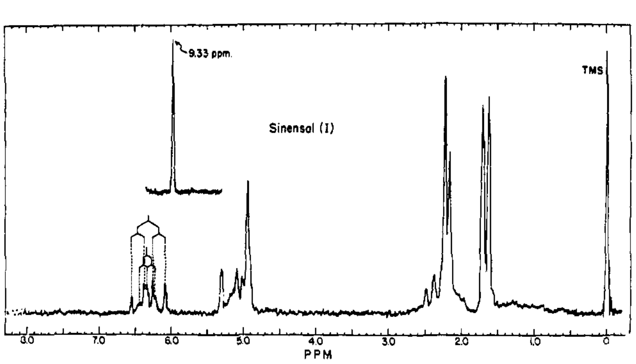


Figure 1.—N.m.r. spectrum of sinensal (1) in carbon tetrachloride at 60 Mc.

For sinensal to have the correct number of vinyl protons, the final double bond must be located at either C-5 or C-6. The C-8 protons on a Δ^5 structure would be expected to occur in the region of 1.3–1.5 p.p.m., since they would be more shielded than the allyl protons. Also a Δ^5 double bond would be expected to show an absorption in the region of 2.9 p.p.m. for $=CH-CH_2-CH=$. The absence of any peaks in this region again necessitates the placement of the double bond at Δ^6. In both tetrahydrosinensal (**3**) and the Diels–Alder adduct **4** a broad triplet was present at 5.13 and 5.03 p.p.m., respectively, which has been assigned to the C-7 vinyl proton. A spin-decoupling experiment showed that irradiation at 5.18 p.p.m. collapsed the doublet at 1.61 p.p.m. to a singlet thus confirming the attachment of the C-6 methyl group to a nonconjugated system. Sinensal (**1**) has thus been shown to be 2,6-dimethyl-10-methylene-2,-6,11-dodecatrienal.

R. B. Bates[9] has shown that the configuration around a trisubstituted double bond, in which one of the substituents is a methyl, can be ascertained by an examination of the chemical shift of the vinyl methyl. However, an attempt to assign a configuration without the n.m.r. spectrum of the other isomers would be risky. For convenience, the structures have been drawn with a *trans-trans* configuration.

Experimental[10]

All n.m.r. spectra were run at 60 Mc. using carbon tetrachloride as the solvent with tetramethylsilane as an internal standard.

Isolation of Sinensal (1).—Cold-pressed orange oil was separated into various groups as discussed in an earlier paper.[11] The fraction containing the oxygenated terpenes was distilled in a short-path distillation apparatus to separate the terpenes from the sesquiterpenes. Sinensal was then separated from the high-boiling (180° 1 mm.) mixture by gas chromatography using a 1 in. × 12 ft. column packed with 10% Carbowax 20M on 60–70-mesh Anakrom AB. The helium flow rate was 5.3 cm./sec. and the temperature was programmed from 175–190° over a period of 20 min. Sinensal emerged in 23 min. Analysis on several columns showed the material to be homogeneous: mol. wt. (mass spectrum) 218; $\lambda_{\max}^{\text{EtOH}}$ 227 mμ (ϵ 31,000); λ^{CCl_4} 3.26 (m), 3.44 (s), 3.52 (w), 3.63 (w), 3.70 (m), 5.6 (broad, w), 5.94 (s), 6.10 (s), 6.28 (s), 6.95 (s), 7.14 (m), 7.23 (m), 7.37 (m), 8.08 (m), 8.39 (w), 8.62 (m), 9.21 (m), 9.2 (sh), 10.08 (s), 11.05 (sh), and 11.18 (s) μ. The 2,4-dinitrophenylhydrazone gave m.p. 87–88°.

Anal. Calcd. for $C_{21}H_{26}N_4O_4$: C, 63.3; H, 6.58. Found: C, 63.2; H, 6.51.

---

(5) The triplet is more easily seen in tetrahydrosinensal (**3**) or the Diels–Alder adduct **4**.

(6) For instance, crotonaldehyde has $\lambda_{\max}^{\text{EtOH}}$ 220 mμ (ϵ 14,700): E. R. Blout and M. Fields, *J. Am. Chem. Soc.*, **70**, 189 (1948).

(7) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **38**, 2066 (1960).

(8) J. A. Pople, W. G. Schneider, and H. J. Berstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 245.

(9) R. B. Bates and D. M. Gale, *J. Am. Chem. Soc.*, **82**, 5749 (1960).

(10) Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

(11) R. Teranishi, T. H. Schultz, W. H. McFadden, R. E. Lundin, and D. R. Black, *J. Food Sci.*, **28**, 541 (1963).

Tetrahydrosinensal (**3**).—Sinensal (250 mg., 1.15 mmoles) dissolved in 20 ml. of 95% ethanol was hydrogenated at 1 atm. and room temperature using 40 mg. of platinum oxide as a catalyst. After 145 min. the uptake of hydrogen had stopped with 1.45 equiv. of hydrogen being consumed. Removal of the catalyst and ethanol left an oil which was purified by gas chromatography to give 110 mg. of tetrahydrosinensal (**2**). Mass spectral analysis gave a parent molecular ion, *m/e* 222: λ_{max}^{EtOH} 230 mμ (ϵ 13,000); λ^{CCl_4} 3.40 (sh), 3.43 (s), 3.50 (sh), 3.70 (m), 5.92 (s), 6.09 (m), 6.90 (m), 713 (w), 7.25 (m), 7.37 (w), 8.02 (m), 8.39 (w), 8.63 (w), and 11.58 (ms) μ; n.m.r. (CCl_4) δ 0.85–0.95 (d, t, 6H), 1.1–1.5 (broad, 5H), 1.63 (s, 3H), 1.73 (s, 3H), 1.8–2.6 (m, 6H), 5.13 (t, 1H), 6.34 (t, 1H), and 9.31 (s, 1H).

Octahydrosinensol (**2**).—Hydrogenation of sinensal (250 mg., 1.15 mmoles) in 25 ml. of 95% ethanol at 3 atm. and room temperature for 23 hr. using 200 mg. of 5% Pt–C afforded 100 mg. of octahydrosinensol (**2**) after purification by gas chromatography. Mass spectral analysis gave *m/e* 228: λ^{neat} 3.01 (s), 3.40 (sh), 3.45 (s), 3.50 (sh), 6.87 (m), 7.28 (w), and 9.69 (broad, s) μ; n.m.r. (CCl_4) δ 0.83 (s, 3H), 0.90 (s, 3H), 0.93 (s, 3H), 1.0–2.0 (broad, 17H), 2.60 (s, 1H), and 3.33 (d, 2H).

Farnesane (*6*).—Octahydrosinensol (100 mg., 0.44 mmole) was dissolved in 0.5 ml. of pyridine and to this solution, held at 0°, was added 100 mg. (5.3 mmoles) of tosyl chloride. The mixture was stirred at 0° for 1.5 hr. then 1 ml. of concentrated hydrochloric acid with 3 ml. of ice–water was added. An ethereal extract of the mixture was washed with water, 10% sodium bicarbonate solution, and finally with water. After drying over anhydrous magnesium sulfate, the ether was removed, leaving the tosylate as an oil.

To the above oil was added 0.5 ml. of commercial tetrahydrofuran and 20 mg. (0.53 mmole) of lithium aluminum hydride along with an additional 1.5 ml. of tetrahydrofuran. The solution was refluxed for 2.5 hr.; then ether (5 ml.) and water were slowly added. Work-up in the usual manner and purification by gas chromatogography gave 12 mg. (13%) an oil. The compound was found to be identical with farnesane by a comparison of retention times on three different gas chromatographic columns and by infrared, n.m.r., and mass spectral analysis.

Diels–Alder Adduct 4.—Sinensal (218 mg., 1 mmole) was dissolved in 5 ml. of dry benzene and to this solution was added 118 mg. (1.2 mmoles) of resublimed maleic anhydride. The solution was refluxed for 18 hr. after which time the benzene was evaporated under a stream of dry nitrogen. The resulting oil was then chromatogographed on 30 g. of 100–200-mesh Davidson silica gel. Elution with a 1:1 mixture of ether and Skelly B gave 245 mg. of the adduct as an oil: λ_{max}^{EtOH} 229 mμ (ϵ 15,000); λ^{neat} 3.42 (s), 3.50 (w), 3.69 (w), 5.41 (m), 5.62 (s), 5.94 (s), 6.08 (w), 6.93 (ms), 7.12 (w), 7.22 (w), 7.35 (w), 7.41 (w), 7.61 (m), 8.08 (s), 8.22 (w), 8.54 (m), 8.70 (w), 9.16 (s), 9.62 (s), 10.17 (s), and 10.69 (s) μ; n.m.r. (CCl_4) δ 1.61 (d, 3H), 1.70 (d, 3H), 2.0–2.7 (m, 12H), 3.3–3.4 (broad, 2H), 5.03 (t, 1H), 5.60 (broad, 1H), 6.38 (t, 1H), and 9.33 (s, 1H).

Anal. Calcd. for $C_{19}H_{24}O_4$: mol. wt., 316; mol. wt. (by potentiometric titration with 0.1 *N* base), 319 ± 5.

Acknowledgment.—The assistance of D. C. Patterson is gratefully acknowledged. For the many timely and helpful suggestions we wish to thank W. L. Stanley.