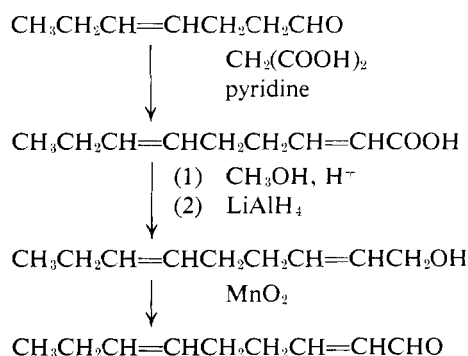


Convenient Synthesis of Nona-*trans*-2,*cis*-6-dienal

A convenient synthesis of the cucumber aldehyde, nona-*trans*-2,*cis*-6-dienal, starting from hept-*cis*-4-enal was devised. A malonic acid condensation with hept-*cis*-4-enal gave nona-*trans*-2,*cis*-6-dienoic acid.

Methylation of the acid, subsequent LiAlH_4 reduction to the alcohol, and MnO_2 oxidation of the alcohol gave nona-*trans*-2,*cis*-6-dienal.

Nona-*trans*-2,*cis*-6-dienal has been reported (Forss *et al.*, 1962b; Takei and Ono, 1939) to be an important contributor to the aroma of cucumbers. The present studies of volatile components of vegetables indicate that this compound may also be present in vegetables other than cucumbers. Since only small amounts of nona-*trans*-2,*cis*-6-dienal could be isolated from cucumbers, a simple method of synthesis was sought to provide larger quantities. The authors had previously obtained hept-*cis*-4-enal and from it were able to combine several simple reactions to synthesize nona-*trans*-2,*cis*-6-dienal by the following scheme:



Some of the principal contributors to the synthesis of this compound (Jutz, 1959; Sondheimer, 1952; Takei *et al.*, 1938) devised routes which either were longer or required a more involved procedure to obtain starting material or intermediates. The steps of the synthesis are easy to carry out and capable of giving satisfactory yields. The scheme is also useful in the general synthesis of 2-enals. A similar scheme has been applied (Forss and Hancox, 1957; Nobuhara and Matsui, 1966) in the synthesis of 2,4-dienals.

EXPERIMENTAL

The products of each step were analyzed by gas-liquid chromatography (GLC), infrared absorption spectrometry, and in some cases mass spectrometry (MS) to confirm their identity.

Hept-*cis*-4-enal. 1-Bromohex-*cis*-3-ene was prepared by adding PBr_3 (21.6 grams) to a cooled, stirred solution of

hex-*cis*-3-enol (20 grams) and pyridine (4.4 grams), and allowing the mixture to stand 18 hours at 25° C. The hex-*cis*-3-enol was commercially obtained (Aldrich Chemical Co., Milwaukee, Wis.). A pentane extract of the mixture was distilled, yielding 22 grams of crude product. The fraction distilling at 63° C. at 26 mm. of Hg (12.3 grams) was allowed to react with magnesium (1.7 grams) in ether and refluxed 45 minutes. Triethyl orthoformate (8 grams) was added to the cooled (5° C.) mixture, refluxed 4 hours, and allowed to stand 18 hours at 25° C. The diacetal obtained from the mixture was hydrolyzed with 100 ml. of 5% H_2SO_4 and steam-distilled. The distillate was simultaneously extracted with pentane. Removal of the solvent gave 5.3 grams of crude hept-*cis*-4-enal.

Nona-*trans*-2,*cis*-6-dienoic Acid. The hept-*cis*-4-enal (5.3 grams) was added to malonic acid (5.5 grams) in 12 ml. of pyridine at room temperature and let stand 4 days. The mixture was poured into 250 ml. of ice water and extracted with pentane (3 × 50 ml.). This extract was washed with ca. 15 ml. of 5% H_2SO_4 , then with ice water (5 × 75 ml.), dried over Na_2SO_4 , and concentrated to 5.08 grams of crude product. Distillation through a spinning band column gave 3.6 grams of nona-*trans*-2,*cis*-6-dienoic acid (b.p. 102–2.5° C. at 0.5 mm. of Hg). Nona-*trans*-2,*cis*-6-dienoic acid was methylated in 93% yield with methanol and 0.3% H_2SO_4 . The methyl ester provided an intermediate of high purity more easily checked by GLC analysis than the acid.

Nona-*trans*-2,*cis*-6-dienol. The methyl ester (3.3 grams) in 10 ml. of ether was added over a 10-minute period to stirred LiAlH_4 (0.43 gram) in 30 ml. of ether. Reflux was maintained an additional 15 minutes, and the mixture was cooled and poured slowly into 150 ml. of ice water. A 4% solution of H_2SO_4 (50 ml.) was added with stirring until the solid dissolved. The mixture was extracted with ether (3 × 75 ml.). Ether extracts were washed with water (2 × 50 ml.) and once with dilute NaHCO_3 solution, dried over Na_2SO_4 , and concentrated to 3.3 grams of crude nona-*trans*-2,*cis*-6-dienol, 62% pure by GLC.

Nona-*trans*-2,*cis*-6-dienal. Nona-*trans*-2,*cis*-6-dienol (0.33 gram, purified by GLC to 87% purity) in 0.4 ml. of pentane was added to stirred MnO_2 (3.25 grams) in 30 ml.

of ether and stirred 10 minutes. The MnO_2 was prepared by the method of Henbest *et al.* (1957). The mixture was centrifuged and the liquid decanted. Pentane (40 ml.) was added to the solid MnO_2 , stirred, and decanted. The supernatants were combined, filtered, dried over Na_2SO_4 , and concentrated to a crude product (weight 0.242 gram). GLC analysis showed the crude product was 80% pure. The infrared and MS data were consistent with those of nona-*trans*-2,*cis*-6-dienal which the authors isolated from cucumbers. The MS data were consistent with those furnished by Forss (1967). The infrared spectra were consistent with published data (Forss *et al.*, 1962a; Jutz, 1959).

The MS of the purified compound were run on a Consolidated 21-620 mass spectrometer. The molecular ion was 138 (low intensity), the base peak was 41, and the major ions in order of intensity were 70, 69, 81, 79, 94, 109, and 95. The infrared data were obtained on a Perkin-Elmer 237 double-beam grating instrument. The infrared spectra are reported in microns with the size of the maxima abbreviated as S meaning strong, M medium, and W weak. The infrared spectra found for the purified compound in the 5- to 15-micron range were: S (5.9), M (6.11, 6.88, 8.51, 8.85, 9.05, 10.25), W (6.78, 7.05, 7.15, 7.3, 7.52, 7.69, 7.94, 9.35, 9.90, 11.43, 12.1, 12.48, 13.89).

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Correction

SOME CHEMICAL PROPERTIES OF *MUNIDA GREGARIA* AND *EUPHAUSIA SUPERBA*

In this article by P. R. Burkholder *et al.* [*J. AGR. FOOD CHEM.* **15**, 718 (1967)], because of some errors in decimal points in Table I, the following corrected Table I is published.

Table I. Proximate Composition of *Munida gregaria* and *Euphausia superba*

	Results ^a	
	<i>Munida</i>	<i>Euphausia</i>
	%	
Ash	17.61	13.13
Crude protein ^b	(14.13)	(63.87)
Protein (amino N $\times$ 6.25)	13.19	37.75
Fat (ether extract)	38.08	17.79
Fiber (chitin) ^c	19.77	12.31
Carbohydrate	11.34	19.02
	Per 100 G.	
Caloric value ^d	441	387

^a Calculated to moisture-free basis.

^b Values in parentheses are based on the untenable common assumption that Kjeldahl N $\times$ 6.25 = protein.

^c Lovell *et al.*, *J. AGR. FOOD CHEM.* **16**, 204 (1968).

^d Based on caloric equivalents of 9, 4, and 4 per gram for fat, protein, and carbohydrate, respectively. Chitin is assumed to be noncalorigenic.

Also, in the text, page 718, second column, line 27 should read 11.34 and 19.02% rather than 44.98 and 57.92%, respectively, and page 719, first column, line 2 should read 17.79% rather than 1.77%.