[CONTRIBUTION FROM THE INDUSTRIAL RESEARCH INSTITUTE, OSAKA, JAPAN]

Isolation of 7-Decen-1-ol from an Ascidian

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From the unsaponifiable fraction of *Halocynthia roretzi* v. Drasche a compound was isolated which was shown by oxidation to propionaldehyde and hydrogenation to *n*-decanol to be 7-decen-1-ol. Comparison of the compound with synthetic *trans*-7-decen-1-ol indicates that the natural material is probably a mixture of *cis* and *trans* isomers, with the *cis* isomer predominating.

During the course of an investigation of the unsaponifiable matter of the sea squirt, *Halocynthia roretzi* v. Drasche, a decenol was isolated. Its properties, b.p., 90° (7 mm.), d_4^{25} 0.8526; n_D^{25} 1.4534, are different from those of a decenol of unknown structure which Ueno and Koyama[1] have described as one of the minor constituents of blubber oil; b.p. 100–102° (15 mm.); d_4^{25} 0.8340; n_D^{25} 1.4417. Upon hydrogenation the new decenol took up one mole to give *n*-decanol, identified as the 3,5-dinitrobenzoate. The position of the ethylenic linkage was determined by the periodate cleavage of the glycol obtained through the action of hydrogen peroxide and formic acid[2] upon the decenol. There was obtained propionaldehyde, identified as its 2,4-dinitrophenylhydrazone. The new alcohol is therefore a 7-decen-1-ol.

The infrared spectrum[3] of the decenol shows a distinct although weak band at 10.3μ characteristic of *trans* configuration,[4,5] and bands at 13.9μ and 7.1μ which seem to be associated with a *cis* substituted double bond.[5,6] The possibility therefore exists that the natural decenol is a mixture of its *cis* and *trans* isomers. To settle this question a synthesis of a 7-decen-1-ol of known configuration was undertaken. A suitable starting material for the *cis* form appeared to be the naturally occurring leaf alcohol which after a long dispute had been shown to be the *cis*-3-hexen-1-ol.[5,7] At present, however, the tailings of Japanese peppermint oil, said to be the best source of *cis* hexenol, were not available, and a synthesis of this alcohol is more complicated than that of its *trans* isomer.[7] It was therefore decided to prepare the *trans*-7-decen-1-ol starting from *trans*-hex-3-enoic acid, which was prepared by the Knoevenagel condensation of *n*-butyraldehyde with malonic acid using triethanolamine as a catalyst. The acid was reduced to the corresponding alcohol with lithium aluminium hydride according to Nystrom and Brown.[8]

The *trans*-hexenol was converted into the bromide which was then condensed with diethylmalonate. From the condensation product the *trans*-octenoic acid was obtained which was reduced with lithium aluminium hydride to *trans*-5-octen-1-ol. It has the odor characteristic of sea cucumbers. A by-product of the malonic ester synthesis, probably the hexenyl ethyl ether, had a very strong odor reminiscent of broad beans and green peas. The octenol was converted to the bromide and this was reacted with magnesium and ethylene oxide to give the desired decenol. This method, however, was less satisfactory than a repetition of the malonic ester synthesis. The *trans*-7-decen-1-ol obtained by this method, b.p. 92° (7 mm.); d_4^{25} 0.8520; n_D^{25} 1.4518, has a peculiar odor, but quite different from that of the natural product. The infrared spectrum of the synthetic product, when compared with that of the natural alcohol, shows a stronger band at 10.3μ, a weakening of the band at 13.9μ and disappearance of the band at 7.1μ. These spectra are in general in good agreement with those of the *cis*- and *trans*-hexenols reported by Crombie and Harper.[5] This evidence then permits the conclusion that the decenol isolated from the ascidian is essentially the *cis*-isomer of 7-decen-1-ol mixed with some of the *trans*-isomer.

The *cis*-7-decen-1-ol carries the odor common to such marine invertebrates as sea squirts, sea cucumbers, and sea snails. This odor is pervasive as Carson states in her book,[9] and seems to be essential to these animals and also to be one of the components of the smell of a low tide. The decenol is a new addition to the list of odoriferous unsaturated alcohols. Takei *et al.*[10] have detected the presence of hexenol in the growing leaves of a number of plants, and Murahashi[11] has found 1-octen-3-ol in Japanese mushrooms. These alcohols have the characteristic odor of green leaves and mushrooms, respectively. A 5-octen-1-ol has not yet been detected in natural

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(1) Ueno and Koyama, *J. Chem. Soc. Japan*, **57**, 1, (1936).

(2) Swern, *Org. Reactions, VII*, 398 (1953).

(3) The author is indebted to Mr. K. Maito, the National Bureau of Industrial Science and Technology, Osaka, for his kind determination of the infrared spectra.

(4) Raa and Daubert, *J. Am. Chem. Soc.*, **70**, 1102 (1948).

(5) Crombie and Harper, *J. Chem. Soc.*, 873 (1950).

(6) Sheppard and Simpson, *Quart. Rev.* (*London*), **6**, 17 (1952).

(7) Sonderheimer, *J. Chem. Soc.*, 877 (1950).

(8) Nystrom and Brown, *J. Am. Chem. Soc.*, **69**, 1198 (1947).

(9) Carson, *The Edge of the Sea*, Staples, London, 1955, p. 41.

(10) Takei, *J. Agr. Chem. Soc., Japan*, **14**, 709 (1938).

(11) Murahashi, *Sci. Papers Inst. Phys. Chem. Research*, (*Tokyo*), **30**, 263 (1936).

products but the fact mentioned above that synthetic *trans*-5-octen-1-ol has the pervasive odor of sea cucumbers seems to tell us of its occurrence in nature, and particularly in marine products. It may also be added here that Takei *et al.* have synthesized 2,6-nonadien-1-ol which has an odor very similar to the scent of sea cucumbers, and which they believe to occur in natural products. Higher unsaturated alcohols from decenol to docosenol have been isolated from sperm head and blubber oil[12] and recently from sea anemones.[13] None of them has been reported to possess characteristic odors. The relationships between molecular size, position of the double bond and odoriferous properties still remain to be determined.

EXPERIMENTAL

All melting points and boiling points are uncorrected.

Isolation. The material used in this study was collected on the coast of Ishinomaki, northern part of Honshu Island. The outer covers of sea squirts were peeled off and the animals preserved by deep-freezing; the total amount, 6.9 kg. Prior to extraction, they were cut in half and dried for a while in an oven under 80°. The partially dried material (1.7 kg.) was then ground and extracted in a large Soxhlet extractor with acetone for 48 hr. The acetone was then distilled, the residue taken up in ether, and the solution was filtered. After removal of the ether there remained 180 g. of a red-brown vaseline-like material, semisolid at room temperature, d_4^{25}, 0.9540; n_D^{25}, 1.4830; acid number, 32.5; saponification value, 144.9; iodine value (Wjis), 145.0; unsaponifiable matter, 14.3%.

The lipid was saponified by the usual method, and the unsaponifiable matter was extracted with ether. The ether soluble part was then dissolved in hot methanol and the methanol solution was decanted to remove a small amount of resinous substance. After cooling, 12.53 g. of crude sterol was obtained, m.p., 127–129°, $[\alpha]_D^{25}$ $-4.1°$ (in chloroform).

The methanol filtrate was found to contain another 3.69 g. of sterol by the digitonide method. From the methanol solution, after almost all methanol was distilled and solid substance was filtered, there was obtained about 12 g. of liquid. This was distilled under reduced pressure and 5.5 g. of pale yellow liquid was obtained, b.p., 90° (7 mm.); d_4^{25}, 0.8520; n_D^{25}, 1.4534; M_D, 49.49 (calcd. for $C_{10}H_{19}OH$, 49.38); iodine value (Wjis), 170.3 (calcd. for $C_{10}H_{19}OH$, 163); hydroxyl value, 357.3 (calcd. for $C_{10}H_{19}OH$, 359).

Anal. Calcd. for $C_{10}H_{19}OH$: C, 76.85, H, 12.90. Found: C, 76.81, H, 12.80.

Both 3,5-dinitrobenzoate and benzoate of the alcohol were liquid at room temperature. But when they were cooled strongly with Dry Ice and acetone, leaflets were obtained from ethanol.

Hydrogenation of the decenol. The alcohol (0.873 g.) was taken up in absolute alcohol and hydrogenated by the usual method using platinum oxide as catalyst. One hundred-thirty ml. of hydrogen (theoretical amount; 125 ml.) was absorbed to give a saturated alcohol with an iodine value of 2.0. One-tenth gram of the hydrogenated alcohol was treated with 0.5 g. of 3,5-dinitrobenzoyl chloride and 3 ml. of pyridine to give white crystals, m.p. 50°. Recrystallization five times from ethanol gave material, m.p. 55–57° (lit.[14] 57°). A mixed melting point with authentic decanyl 3,5-dinitrobenzoate showed no depression.

Anal. Calcd. for $C_{17}H_{24}O_6N_2$; C, 57.95, H, 6.81, N, 7.95. Found: C, 57.64, H, 6.68, N, 8.11.

Position of the ethylenic linkage. To a well stirred solution of 1.2 g. of decenol in 5 ml. of formic acid at 25°, 0.5 g. of 30% hydrogen peroxide solution was added during a 15 min. period. After about 2 hr. formic acid was removed by distillation under reduced pressure. The residue was saponified with aqueous sodium hydroxide.

The dihydroxydecanol was subjected to the glycol cleavage with periodic acid without being isolated. After a large volume of water, excess amounts of potassium periodate and sulfuric acid were added, and the reaction mixture was kept at room temperature overnight. The volatile aldehyde was steam-distilled into a freshly prepared 2,4-dinitrophenylhydrazine solution. Red crystals which formed were collected and recrystallized from ethanol; 90 mg., m.p., 149–153.5°, (m.p. of 2,4-dinitrophenylhydrazone of propionaldehyde, 154°).[11]

Anal. Calcd. for $C_9H_{10}N_4O_4$: N, 23.52. Found: N, 23.22.

Preparation of trans-3-hexenoic acid. This was prepared by the method of Linstead, Noble, and Boorman.[15] One hundred grams (1.4 mole) of freshly distilled *n*-butyraldehyde, 140 g. (1 mole) of triethanolamine, and 160 g. (1.5 mole) of malonic acid were shaken under cooling to a homogeneous solution in a 1-l. flask. After 2 days standing it was heated overnight on a water bath and then cooled and acidified with 50% sulfuric acid.

The reaction product was digested in sodium carbonate solution and the mixture was then shaken with ether to remove unreacted aldehyde and other impurities. The aqueous layer was again acidified and the hexenoic acid was distilled under reduced pressure; colorless liquid, 105–120° (20 mm.). It was purified by partial freezing and rejection of the liquid layer. The *trans*-3-hexenoic acid was redistilled, b.p., 110° (15 mm.), yield, 65 g. (41%).

Preparation of trans-3-hexen-1-ol. An ether solution of the acid (65 g.) was added slowly under stirring to lithium aluminium hydride (13 g.) dissolved in anhydrous ether (850 ml.). The mixture was then refluxed for 1 hr. on water bath. After cooling, water was added and the ethereal solution was washed with 10% sulfuric acid, with water, and then dried over sodium sulfate. Forty grams (70%, yield) of trans-3-hexen-1-ol was distilled under reduced pressure, 58–59° (20 mm.). As noticed by Crombie and Harper,[5] the alcohol developed a very strong smell of chrysanthemum leaf. The melting point of the 3,5-dinitrobenzoate was 47–48°, in agreement with that reported by these authors.[5]

Preparation of 1-bromo-3-hexene. According to the method of Goering *et al.*,[16] the *trans*-hexenol was brominated with phosphorus tribromide and dry pyridine. A solution of 40 g. (0.4 mole) of *trans*-hexenol and 10 g. of dry pyridine was placed in a 200 ml. three-necked flask fitted with a sealed stirrer, dropping funnel, and thermometer. Phosphorus tribromide, 45 g. (0.16 mole), was then added dropwise to the hexenol solution which was chilled to −10°. The temperature was maintained below 0°.

The reaction product was kept at room temperature overnight. It was taken up in ether and washed with dilute sodium bicarbonate solution and ice water. After drying over sodium sulfate, ether was evaporated and the 1-bromo-3-hexene was distilled under reduced pressure, b.p. 47° (20 mm.), yield 31 g. (47%).

Malonic ester synthesis.[17] A 200 ml. three necked flask was fitted with a liquid-sealed mechanical stirrer, reflux condenser, dropping funnel, and thermometer. In the flask was

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[12] Toyama and Akiyama, *Bull. Chem. Soc. Japan*, **10**, 579 (1935); **11**, 29 (1936).

[13] Bergmann, Creighton, and Stokes, *J. Org. Chem.*, **21**, 721 (1956).

[14] Shriner and Fuson, *Identification of Organic Compounds*, John Wiley and Sons, New York, 1948.

[15] Linstead, Noble, and Boorman, *J. Chem. Soc.*, 557 (1933).

[16] Goering, Cristol, and Dittmer, *J. Am. Chem. Soc.*, **70**, 3314 (1948).

[17] Reid and Riihoff, *Org. Syntheses*, **Coll. Vol. II,** 474 (1948).

placed 100 ml. of absolute alcohol and 5.6 g. (0.2 g. atom) of sodium cut in small pieces was added at one time. After the sodium had dissolved completely, 32 g. (0.2 mole) of ethyl malonate was added rapidly with stirring. And then 31 g. (0.2 mole) of 1-bromo-3-hexene was added slowly. The mixture was refluxed gently for about 1 hr. After saponification the mixture was acidified with hydrochloric acid. The water layer was discarded. The oil was then transferred to a 100 ml. round bottomed flask and heated under an air-cooled reflux condenser in an oil bath at about 170°. When the evolution of carbon dioxide ceased, the residue was distilled under diminished pressure, 110° (5 mm.), 20 g. (74%). In this malonic ester synthesis, besides the 5-octenoic acid, a small amount of neutral liquid, b.p., 55° (17 mm.) was obtained. It had a strong smell of broad beans and green peas. Although it was not investigated further, it seemed to be the by-product, hexenyl ethyl ether.

Preparation of 5-octen-1-ol. Twenty grams of 5-octenoic acid was reduced with 4 g. of lithium aluminium hydride. Distillation under reduced pressure gave 11 g. (61%) of 5-octen-1-ol, 79° (8 mm.) d_4^{25}, 0.8496, n_D^{25}, 1.4451, M_D (calcd.), 40.10, M_D (found), 40.10.

The odor of the alcohol was very similar to that of sea cucumber.

Bromination of trans-5-octen-1-ol. The solution of 10 g. of octenol and 4 ml. of dry pyridine was treated with phosphorus tribromide as described previously for the preparation of 1-bromo-3-hexene. Six grams (38%) of 1-bromo-5-octene was obtained, b.p., 75° (10 mm.).

Preparation of 7-decenoic acid. Six grams of 1-bromo-5-octene was treated with 20 ml. of absolute alcohol, 1 g. of sodium, and 9.6 g. of ethyl malonate. Five grams (90%) of 7-decenoic acid was obtained, 135–140° (10 mm.).

Trans-7-decen-1-ol. After 5 g. of 5-octenoic acid was reduced with lithium aluminum hydride, the colorless liquid was distilled to yield 3 g. (66%; 4.4%, calcd. from trans-3-hexen-1-ol), b.p., 92° (7 mm.), d_4^{25}, 0.8520, n_D^{25} 1.4518, M_D (calcd.), 49.43, M_D (found), 49.35. The synthetic decenol (0.3 g.) was heated on a water bath with 1 g. of 4′-iodobiphenylisocyanate[12] in 20 ml. of benzene. 4′-Iodobiphenylurethane (0.26 g.) was obtained, m.p., 125°; after two crystallization from acetone, the m.p. was raised to 138–139°.

Anal. Calcd. for $C_{23}H_{28}INO_2$: C, 57.86; H, 5.87; N, 2.93. Found: C, 58.60; H, 5.91; N, 2.73.[13]

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