BIOCHEMICAL STUDIES OF THE ASCIDIAN, CYNTHIA RORETZI v. DRASCHE III. THE CONSTITUTION OF NEW n-DECADIENOL

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III. THE CONSTITUTION OF NEW *n*-DECADIENOL

By

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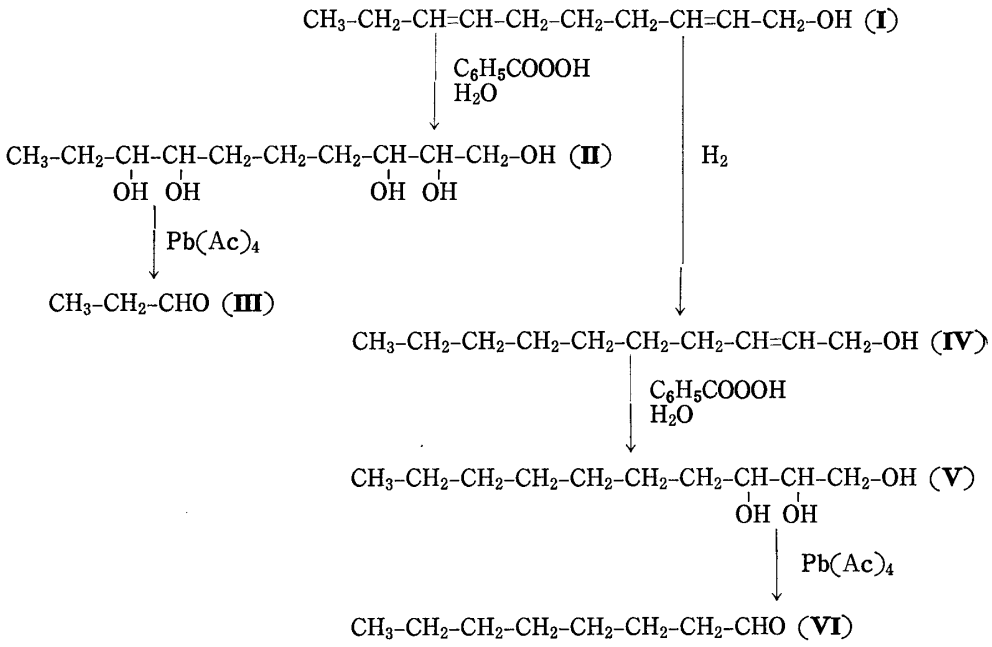
In the previous report (1) the author investigated the peculiar odriferous compounds of the ascidian and obtained *n*-octanol, 7-decen-1-ol and new *n*-decadienol, b.p. 105–108°C/12mm, n_D^{20} 1.4636, d_4^{20} 0.8641. *n*-Octanol has already been found in free form in the marine tube worm, *Eudistylla vancouveri*, by Idler and Fagerlund (2). 7-Decen-1-ol has also been isolated in a mixture of *cis* and *trans* isomers, with predominancy in the former, from the unsaponifiable fraction of the ascidian by Kita (3). He has found that it carries an odour common to such marine invertebrates as sea squirts, sea cucumbers and sea snails. However, *n*-decadienol has not been found in nature to date. Therefore, the author named it "cynthiaol".

The positions of ethylenic linkages of the new *n*-decadienol were determined by the lead tetraacetate cleavage of the glycols (**II**), (**V**) (4) obtained through the actions of perbenzoic acid upon the decadienol and its half-hydrogenated one. The propionaldehyde (**III**) identified as its 2, 4-dinitrophenylhydrazone was only obtained from the decadienol, and the other aldehyde such as dialdehyde and hydroxyaldehyde could not be found in this cleavage product. This fact indicates that one of the ethylenic linkages locates at the 7 position. The decadienol was then half-hydrogenated to give the decenol by catalytic reduction. As the cleavage of its glycol gave *n*-caprylic aldehyde (**VI**) identified as its 2, 4-dinitrophenylhydrazone, the decenol is 2-decen-1-ol (**IV**). The new *n*-decadienol is, therefore, proved to be 2, 7-decadien-1-ol (**I**).



Four forms (2-*trans*, 7-*trans*; 2-*cis*, 7-*cis*; 2-*trans*, 7-*cis* and 2-*cis*, 7-*trans*) are considered on the stereochemical configuration of the 2, 7-decadien-1-ol. The infra-red spectra of the *cis*- and *trans*-hex-3-enols have been recorded and discussed by Crombie and Harper (5) and Sondheimer (6). It has been stated that observation of the band at 10.3μ (*trans*), 11.5μ (*cis*) and 13.9μ (*cis*) may be of considerable assistance in the assignment of the stereochemical configurations. On the 7-decen-1-ol, Kita (3) has also applied the band at 7.1μ which was indicated as *cis* configuration by Sheppard and Simpson (7). The infra-red

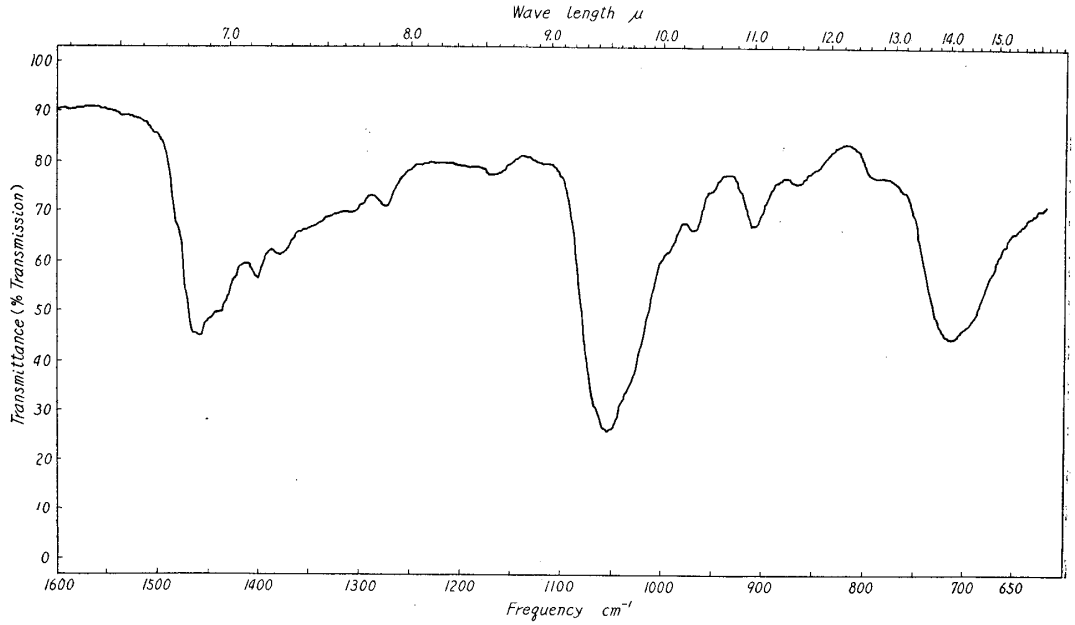


Fig. 1. The infra-red spectrum of 2-*trans*, 7-*cis*-decadien-1-ol.

spectrum of the 2, 7-decadien-1-ol shows a weak band at 10.3μ of *trans* configuration, as indicated in Fig. 1, and also shows strong band at 13.9μ and weak bands at 7.1 and 11.5μ of *cis* configuration. It is suggested that one of the double bonds is *trans* form and the other is *cis* form. The spectrum of the 2-decen-1-ol obtained by half-hydrogenation of the decadienol shows typical *trans* absorption band at 10.3μ which its intensity is markedly higher than that of the decadienol, as indicated in Fig. 2. It also shows a weakening of the band at 13.9μ and disappearance of the band at 7.1 and 11.5μ for *cis* form. The 2-decen-1-ol is, therefore, *trans* form. From the above mentioned evidence, it is concluded that the *n*-decadienol isolated from the ascidian is 2-*trans*, 7-*cis*-decadien-1-ol.

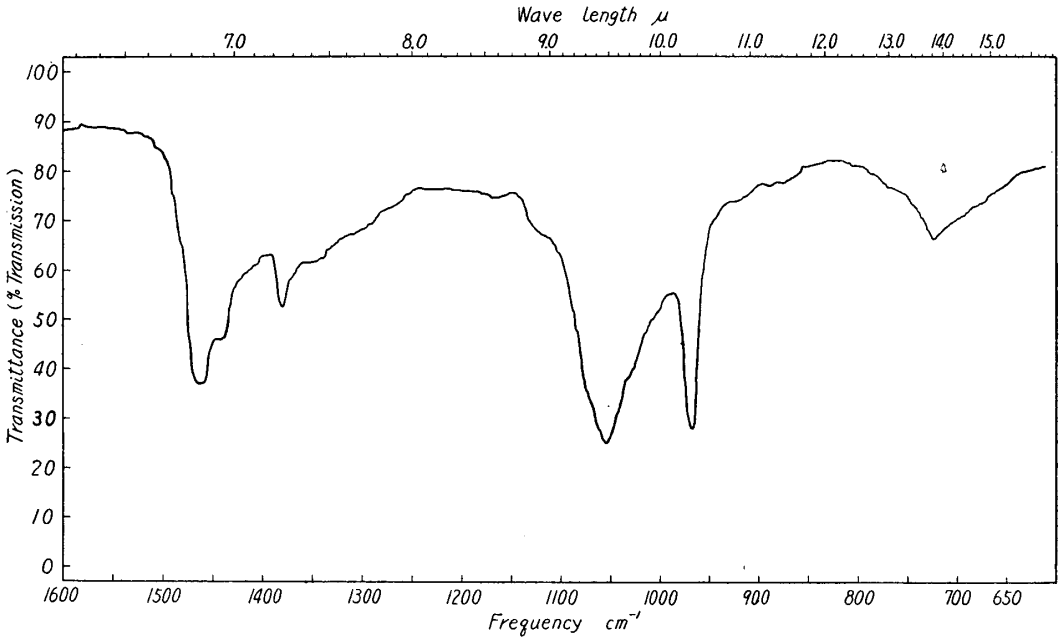


Fig. 2. The infra-red spectrum of 2-*trans*-decen-1-ol.

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Experimental

Position of the ethylenic linkage of n-decadienol

To a solution of perbenzoic acid (1.03 g) (8) in chloroform (20 *ml*) was added the decadienol (0.50 g). The solvent was kept at 0°C for 24 hours, and

was shaken frequently during the first hour. The benzoic acid was removed from the chloroform solution by shaking with an excess of 10 per cent sodium hydroxide solution, the alkali was then removed by washing with water, and the chloroform solution was dried with anhydrous sodium sulfate. After the distilling off of the solvent, the residual oil was treated with aqueous sodium hydroxide for one hour on the water bath, and the solution acidified with dilute sulfuric acid was then thoroughly extracted with ether. After the ethereal solution was dried with anhydrous sodium sulfate, the solvent was distilled off. Lead tetraacetate (0.80 g) (9) was added to the solution of tetrahydroxydecanol (0.33 g) in benzene (20 *ml*), and the mixture was allowed to stand over night at room temperature. The solvent containing volatile aldehyde was then distilled off, and 2, 4-dinitrophenylhydrazine was added to this distillate to make phenylhydrazone, the crude crystal of 2, 4-dinitrophenylhydrazone thus obtained was recrystallised six times from ethanol. It formed orange needles, having m.p. 152–153°C; this m.p. was not depressed on admixture with a specimen obtained from authentic propionaldehyde. Anal. Calcd. for $C_9H_{10}O_4N_4$; N, 23.52, Found: N, 23.50.

The above residue was steam-distilled until the distillate ceased to give the smell perceptibly of an aldehyde. The distillate saturated with sodium chloride was then thoroughly extracted with ether. After the ethereal solution was dried with anhydrous sodium sulfate, 2, 4-dinitrophenylhydrazine was added. Although, after distilling off of the ether the residual oily 2, 4-dinitrophenylhydrazone was attempted to crystallise, this trial was unsuccessful.

Half-hydrogenation of n-decadienol

The decadienol (0.5086 g) in ethanol (20 *ml*) was stirred in hydrogen in the presence of palladium-calcium carbonate (0.05 g) (10) at room temperature. After the absorption of 80 *ml* of hydrogen (theoretical amount of saturation; 156.4 *ml*) the remaining hydrogen was immediately removed by the suction. The catalyst was filtered off, and the solvent was removed. A small amount of half-hydrogenated alcohol was treated for the determination of infra-red spectrum. The other part (0.41 g) was converted into the glycol through the action of perbenzoic acid by the above mentioned method. Lead tetraacetate was added to the solution of dihydroxydecanol in benzene, and the mixture was allowed to stand over night at room temperature. After removal of the solvent by distillation the residue was steam-distilled until the distillate ceased to give the smell perceptibly of a *n*-caprylic aldehyde. The distillate saturated with sodium chloride was thoroughly extracted with ether, the ethereal solution was dried with anhydrous sodium sulfate, and 2, 4-dinitrophenylhydrazine was added. After distilling off of the solvent, the residual crystal of 2, 4-dinitrophenylhydrazone was recrystallised five times from ethanol. It formed yellow needles, having m.p. 106°C; this m.p. was not depressed on admixture with a specimen

(m.p. 106°C) obtained from authentic *n*-caprylic aldehyde. On admixtures with the 2, 4-dinitrophenylhydrazone of authentic *n*-caproic aldehyde (m.p. 104°C) and *n*-heptoic aldehyde (m.p. 107–108°C), the m.p. were 85–89°C and 90–95°C respectively. Anal. Calcd. for $C_{14}H_{20}O_4N_4$; N, 18.17, Found: N, 18.38.

Summary

The constitution of a new *n*-decadienol isolated from *Cynthia roretzi* v. DRASCHE was determined. The lead tetraacetate cleavage of the glycols obtained from the decadienol and the decenol which was obtained by half-hydrogenation of the decadienol gave propionaldehyde and *n*-caprylic aldehyde respectively. The new alcohol is, therefore, 2, 7-decadien-1-ol. The infra-red spectra of the decadienol and the decenol show that the new alcohol is 2-*trans*, 7-*cis*-decadien-1-ol.

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