

BIOCHEMICAL STUDIES OF THE ASCIDIAN, CYNTHIA RORETZI v. DRASCHE II. ISOLATION OF n-OCTANOL, n-DECENOL AND n-DECADIENOL

著者	SUZUKI Yoshio
journal or publication title	Tohoku journal of agricultural research
volume	10
number	1
page range	65-69
year	1959-07-30
URL	http://hdl.handle.net/10097/29266

BIOCHEMICAL STUDIES OF THE ASCIDIAN,
CYNTHIA RORETZI v. DRASCHE

II. ISOLATION OF *n*-OCTANOL, *n*-DECENOL
AND *n*-DECADIENOL

By

Yoshio SUZUKI

*Department of Fisheries, Faculty of Agriculture,
Tohoku University, Sendai, Japan*

(Received February 21, 1959)

In the previous report (1) the author investigated the nitrogenous extracts of the ascidian and found 15 amino acids, two purine bases and choline. Among them glycine, alanine, glutamic acid and glycine betaine were considered to be the savoury substances of the ascidian. With respect to its volatile compounds Iida and Murata (2) have detected monomethyl-, dimethyl- and trimethyl amine, and formic- and acetic acid by paper chromatography. Kita (3) has isolated 7-decen-1-ol which was a mixture of *cis* and *trans* isomers, with predominancy in the former, from the unsaponifiable fraction of the ascidian, and found that it carries the odour common to such marine invertebrates as sea squirts, sea cucumbers and sea snails.

The author obtained pale yellow oil by steam-distillation from the ascidian. After removal of the acidic and alkaline compounds on treatment with potassium hydroxide and sulfuric acid, the neutral oil was separated into three fractions by fractional distillation. Each of them was positive to Nessler's reagent and diazo reagent. Being oxidized with chromic acid, they reacted positively upon Schiff's reagent and Tollens' reagent. When bromine was added to them in acetic acid solution, fraction 1 did not decolorize it but the other two did. Therefore, it seems that fraction 1 is saturated primary alcohol and the others are unsaturated primary alcohols.

Fraction 1, b.p. 85~87°C/12 mm., n_D^{20} 1.4360, d_4^{20} 0.8354, was identified to be *n*-octanol through the 3, 5-dinitrobenzoate and allophanate.

The properties of fraction 2, b.p. 96~98°C/12 mm., n_D^{20} 1.4542, d_4^{20} 0.8531, were very similar to those of 7-decen-1-ol, n_D^{25} 1.4534, d_4^{25} 0.8526, which was already obtained by Kita. The allophanate derived from this fraction had m.p. 141°C and the propionic acid identified as its *p*-bromphenacyl ester was obtained by oxidizing with potassium permanganate by Hilditch's method (4).

Fraction 3, b.p. 105~108°C/12 mm., n_D^{20} 1.4636, d_4^{20} 0.8641, was hydrogenated by catalytic reduction, the alcohol took up two moles of hydrogen to give *n*-decanol identified as its 3, 5-dinitrobenzoate and allophanate. Moreover, the iodine value 343 and molecular refraction 49.15 of this alcohol correspond with those of values calculated from *n*-decadienol in iodine value 329 and molecular refraction 48.97 respectively. The unsaturated alcohol was, therefore, proved to be *n*-decadienol. The allophanate, m.p. 126~127°C, was also obtained as a derivative of it.

The author newly found *n*-octanol and *n*-decadienol from the ascidian. Idler and Fagerlund (5) have already found free *n*-octanol in the marine tube worm, *Eudistylla vancouveri*, and it seems to occur as one of the common odoriferous components in the marine invertebrates. However it is supposed that *n*-decadienol is not so common as *n*-octanol or *n*-decanol, but characteristically occurs in the ascidian which is accepted as a local flavorful food in the northeastern districts and Hokkaido of Japan. The author named it "cynthiaol."

The author expresses his gratitude to Dr. Y. Tsuchiya, Professor of Department of Fisheries, Tohoku University, for his kind advice and criticism, and is indebted to Asist. Prof. Y. Hashimoto, Department of Fisheries, Tokyo University, for his help in nitrogen micro-analysis. The expense for this study was partly defrayed by a Grant in Aid for Miscellaneous Scientific Research.

Experimental

Isolation

37.5 g of essential oils were obtained by steam-distillation from 160 kg of minced fresh materials removed from their tests. The oil was dissolved in ether, washed with dilute sulfuric acid, potassium hydroxide and water to remove the acidic and alkaline compounds. After drying over anhydrous sodium sulfate the neutral oil was finally fractionated into three parts by distillation under reduced pressure. The fractions and their properties are indicated in Table 1.

The determinations for radicals in each fractions were made by various reactions as shown in Table 2.

Preparation of 3, 5-dinitrobenzoate of *n*-octanol

Fraction 1 (0.2 g) and anhydrous pyridine (0.5 ml) were added to a solution of 3, 5-dinitrobenzoyl chloride (0.5 g) in anhydrous benzene (2 ml), and the mixture was allowed to stand over night at room temperature. It was then diluted with anhydrous ether, washed with dilute hydrochloric acid, sodium hydroxide and water, and dried over anhydrous sodium sulfate. After the solvent distilled off, the residual crude 3, 5-dinitrobenzoate was recrystallised three times from ligroine. The 3, 5-dinitrobenzoate of *n*-octanol was obtained

Table 1. Fractions of oil and their properties.

	b.p. (°C/12mm.)	n_D^{20}	d_4^{20}	M_D	Iodine value (wijs)	Yield (g)
Fraction 1	85-87	1.4360	0.8354	40.69 *(40.67)		10.8
	87-96	1.4477			124	3.7
Fraction 2	96-98	1.4542	0.8531	49.66 ***(49.38)	182 ***(163)	3.4
	98-105	1.4591			257	4.5
Fraction 3	105-108	1.4636	0.8641	49.15 ***(48.97)	343 ***(329)	2.5

* Calcd. for $C_8H_{18}O$ ** Calcd. for $C_{10}H_{20}O$ *** Calcd. for $C_{10}H_{18}O$

Table 2. Detection of the radicals.

		Fraction 1	Fraction 2	Fraction 3
Schiff's reaction		-	-	-
Tollens' reaction		-	-	-
Sodium nitroprusside reaction		-	-	-
Chloronitroso reaction		-	-	-
Diazo reaction		+	+	+
Nessler's reaction		+	+	+
After oxidation by chromic acid	Schiff's reaction	+	+	+
	Tollens' reaction	+	+	+
	Chloronitroso reaction	-	-	-
Decolorization of bromine		-	+	+

as needles, having m.p. 59°C, this m.p. was not depressed on admixture with a specimen obtained from authentic *n*-octanol. Anal. Calcd. for $C_{15}H_{20}O_6N_2$; N, 8.64, Found: N, 8.56.

Preparation of allophanate of *n*-octanol

Fraction 1 (0.2 g) was saturated by cyanic acid, the crude allophanate solidified was washed with ether, and recrystallised four times from anhydrous ethanol. It formed needles, having m.p. 155~156°C, this m.p. was not depressed on admixture with a specimen obtained from authentic *n*-octanol. Anal. Calcd. for $C_{10}H_{20}O_3N_2$; N, 12.95, Found: N, 12.98.

Oxidation of allophanate of 7-decen-1-ol

Fraction 2 (1.0 g) was converted into allophanate by the above mentioned method. After five times recrystallisation, it formed needles, having m.p. 141°C Anal. Calcd. for $C_{12}H_{22}O_3N_2$; N, 11.47, Found: N, 11.52.

The above allophanate (0.5 g) was dissolved in acetone (20 ml), and finely powdered potassium permanganate (2.0 g) was added to it in the course of one

hour. The solution was gently boiled under a reflux condenser after each addition and, finally, for a further five hours after the addition was complete. The solvent was removed by distillation, the residue was then mixed with a little of water, and the precipitated manganese oxides were reduced and brought into solution by the action of sodium bisulfite and dilute sulfuric acid. The acidified solution was then thoroughly extracted with ether. After distilling off the solvent the residue was steam-distilled until the distillate ceased to smell perceptibly of propionic acid. The distillate was then carefully neutralized with 10 per cent sodium carbonate, concentrated to one *ml*, and a few drops of dilute hydrochloric acid were added until the solution was just acid to litmus. Ethanol (2 *ml*) and *p*-bromphenacyl bromide (0.05 g) were added, the mixture was then heated under reflux for one hour, and allowed to cool at 0°C in the ice box. The precipitated ester was recrystallised four times from ethanol, it formed leaflets, having m.p. 57~59°C, this m.p. was not depressed with a specimen obtained from authentic propionic acid.

The residue of steam-distillation which was insoluble in water, was collected on filter. After four times recrystallisation from ethanol, it formed needles, having m.p. 153~154°C. It seems to be the allophanate of 7-hydroxyoentanitic acid. Anal. Calcd. for $C_9H_{16}O_5N_2$; N, 12.07, Found: N, 12.13.

Hydrogenation of *n*-decadienol

Fraction 3 (0.2586 g) in ethanol (20 *ml*) was stirred in hydrogen in the presence of palladium-calcium carbonate (0.05 g) (6) at room temperature. After the absorption of 81.3 *ml* of hydrogen (theoretical amount; 79.8 *ml*), the uptake practically stopped. The catalyst was filtered off, and the solvent removed. The residual oil was converted into the 3, 5-dinitrobenzoate and allophanate. After four times recrystallisation from ligroine, it formed needles, having m.p. 56°C, undepressed on admixture with authentic 3, 5-dinitrobenzoate of *n*-decanol. Anal. Calcd. for $C_{17}H_{24}O_6N_2$; N, 7.95, Found: N, 7.82. After four times recrystallisation from ethanol, it formed needles, having m.p. 157~158°C, undepressed on admixture with authentic allophanate of *n*-decanol. Anal. Calcd. for $C_{12}H_{24}O_3N_2$; N, 11.47, Found: N, 11.52.

Preparation of allophanate of *n*-decadienol

Fraction 3 (0.2 g) was converted into the allophanate. After five times recrystallisation from ethanol, it formed needles, having m.p. 126~127°C. Anal. Calcd. for $C_{12}H_{20}O_3N_2$; N, 11.66, Found: N, 11.56.

Summary

n-Octanol, 7-decen-1-ol and *n*-decadienol were isolated by steam-distillation from *Cynthia roretzi* v. Drasche. *n*-Octanol and *n*-decadienol were newly found from the asidian, especially the latter has not been found in nature to date,

and the author named it "cynthiaol."

References

- 1) Suzuki, Y. (1955). *Tohoku J. Agr. Res.*, **6**, 85.
- 2) Iida, U. and K. Murata (1955). Reported on the Occasion of the Meeting of the Scientific Fisheries of Japan.
- 3) Kita, M. (1957). *J. Org. Chem.*, **22**, 436.
- 4) Armstrong, E.F. and T.P. Hilditch (1925). *J. Soc. Chem. Ind.*, **44**, 43T.
- 5) Idler, P.R. and U.F.M. Fagerlund (1953). *Progress Rept. Pacific Coast Sta. Fisheries Res. Board Canada*, **95**, 52.
- 6) Busch, M. and H. Stöve (1916). *Ber.*, **49**, 1063.