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64. **Isao Ogura**: Structure of Longifolene.

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Simonsen and others[1] formerly submitted the structural formula (I) for longifolene, but later Moffett and Rogers[2] proposed the structure (II) for longifolene hydrochloride, consisting of two five-membered rings and a seven-membered ring from the result of its X-ray investigation. Based on this research in company with Naffa and Ourisson,[3] they suggested formula (III) for longifolene on the assumption that longifolene underwent Wagner-Meerwein rearrangement, and confirmed from Raman spectra that the double bond in this molecule was present as a methylenecyclopentano chain and that the presence of a *gem*-dimethyl group was indicated from its infrared spectrum. Moreover, they obtained by oxidation longicamphenylone (IV), a C_{14}-monoketone having a five-membered ring, and longidione (IX), a C_{15}-diketone, along with longifolic acid. (IV) was cleaved when treated with sodium amide according to Semmler's method[4] and by saponification it was transformed into a C_{14}-monobasic acid (VI). When the latter was oxidized with hydrogen peroxide, α-longifolic acid (X), a C_{15}-dibasic acid, was obtained. In addition, they confirmed that longidione (IX) was obtained from longifolene through longihomocamphenylone, and determined the existence of a five-membered ring with a double bond.

On the other hand, Zeiss and Arakawa,[5] and Nayak and Sukh Dev[6] attempted structural determination of longifolene and the latter workers tried to obtain azulene derivatives by the degradation of longifolene.

The author[7] had previously concluded that longifolic and isolongifolic acids are endo-exo isomers. In order to obtain chemical evidence of five- and seven-membered rings in the molecule besides the five-membered ring that was determined by Naffa and Ourisson, longifolene was oxidized and a monobasic and α-longifolic acids were obtained. Then each acid was submitted to dehydrogenation, using about 1.5 times the excess of selenium and heated on a sand bath at 340∼360°. The compounds having saturated rings generally resist dehydrogenation,[8] and a carboxyl group is ordinarily decomposed at about 340∼350°, while that attached to a secondary carbon atom is extremely stable.[9] These facts show that a large quantity of the sample is generally required to gain the products of dehydrogenation reaction.

In the present experiment, the yield of monobasic acid (VI) from longicamphenylone (IV) was very small, 5 g. of it affording only 0.2 g. of a light violet-colored oil, which did not give a picrate. On the other hand, 2 g. of brownish violet oil and 0.12 g. of deep blue-violet oil were obtained by fractionation from 18 g. of α-longifolic acid (X), heated for 28 hours. Application of picric acid to the deep blue-violet oil gave a

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1) J.L. Simonsen: J. Chem. Soc., **117**, 578(1920); *ibid.*, **125**, 2642(1923); A.E. Bradfield, E.M. Francis, J.L. Simonsen: *Ibid.*, **1934**, 188.
2) R.H. Moffett, D. Rogers: Chem. & Ind.(London), **1953**, 916.
3) P. Naffa, G. Ourisson: *Ibid.*, **1953**, 917; P. Naffa, G. Ourisson: Bull. soc. chim. France, **1954**, 1115.
4) F.W. Semmler: Ber., **39**, 2577(1906).
5) H.H. Zeiss, M. Arakawa: J. Am. Chem. Soc., **76**, 1633(1954).
6) U.R. Nayak, Sukh Dev: Chem. & Ind.(London), **1954**, 989.
7) I. Ogura: Bull. Chem. Soc. Japan, **29**, 393(1956).
8) J.W. Cook, C.L. Hewett: J. Chem. Soc., **1936**, 62.
9) L. Ruzicka: Helv. Chim. Acta, **19**, 419(1936).

picrate of purple-black needles, m.p. 156∼158°. From the mixed melting point determination with the authentic picrate of 4,8-dimethylazulene, which was surmised from Naffa and Ourisson's formation, it was confirmed that 4,8-dimethylazulene was produced by these treatments.

Since a derivative of azulene was obtained in this experiment, it was confirmed that five- and seven-membered rings existed in α-longifolic acid (X). Thus, according to the structural formula proposed by Naffa and Ourisson, these degradations can be represented as shown in Chart 1. Consequently, it was concluded that the structural formula suggested by them is correct.

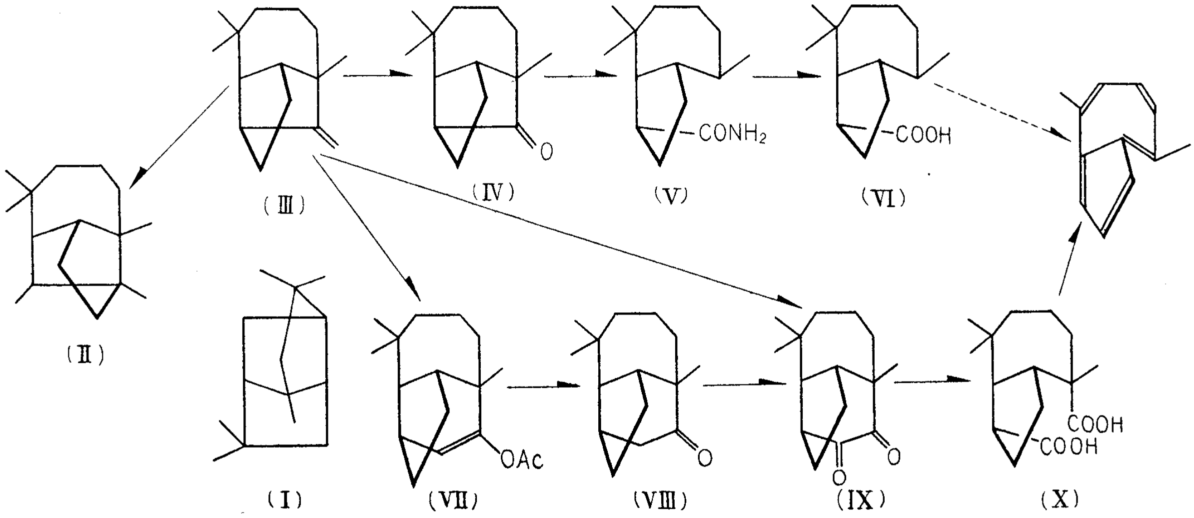

Chart 1.

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Experimental

Longicamphenylone and Longidione—The fraction of b.p$_{36}$ 149∼152° of terpentine oil was oxidized by heating on a water bath with alkaline $KMnO_4$ solution until the color was no longer discharged. Longifolene, further purified by distillation, had the following constants: b.p$_{10}$ 123∼124°; d_4^{25} 0.9301; n_D^{25} 1.4944. Longifolene was oxidized in AcOH with CrO_3, the product was extracted with ether, acid fraction was removed by washing with dil. NaOH solution, and a neutral fraction was distilled under a diminished pressure as shown in Table I.

TABLE I. Fractional Distillation of Neutral Fraction (Sample, 247 g.)

Fraction	b.p$_{11}$(°C)	Yield (g.)	d_4^{25}	n_D^{25}
1	∼120	12	0.9641	1.4849
2	120∼125	43	0.9875	1.4957
3	125∼130	28.5	0.9936	1.4970
4	130∼135	19.5	1.0003	1.4981
5	135∼140	16	(Crystallized)	
6	140∼145	24	〃	
7	145∼150	26.5	〃	
8	150∼160	17	〃	
9	160∼170	18.5	1.0760	1.5029
10	170∼	24.5	Crystals	

Fraction 1 was a colorless oil and was thought to be the unchanged longifolene. Other fractions were yellow and crystals separated from fractions 5, 6, 7, 8, and 10 on leaving them to cool. Fractions 5∼8 corresponded to longicamphenylone, m.p. 50∼51° (*Anal.* Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.35; H, 10.79), and 10 to longidione, m.p. 93∼94° (*Anal.* Calcd. for $C_{15}H_{22}O_2$: C, 76.85; H, 9.50. Found: C, 76.88; H, 9.46), which was a viscid, yellow oil and crystallized immediately when it distilled out.

α-Longifolic Acid and Monobasic Acid—Longidione (20 g.) was dissolved in 550 cc. of acetone, 660 cc. of 1*N* NaOH solution and 55 cc. of 30% H_2O_2 were added to it, and oxidized by the method of Naffa and Ourisson. α-Longifolic acid (19.5 g.) was obtained as white crystals, m.p. 222~223°. *Anal.* Calcd. for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02. Found : C, 67.02; H, 9.11.

Treatment of longicamphenylone (21 g.) with sodium amide (5 g.) produced a monobasic acid amide (V), a viscid brown oil (18 g.) which formed colorless crystals. (V) was saponified by refluxing in conc. HCl-EtOH. The reaction mixture was extracted with ether, the extract was washed with water, and extracted with NaOH solution. The acid (5 g.) thereby obtained was a monobasic acid, m.p. 77~78°.

Dehydrogenation—A mixture of α-longifolic acid (18 g.) and Se (26 g.) was heated on a sand bath at 270~280° for 5 hrs. and at 340~360° for 28 hrs. After the reaction ended, Se was removed and a brownish violet-colored oil (2 g.) was obtained. Distillation afforded first a colorless oil (b.p$_{13}$ 100~106°; 1.0 g.; d_4^{25} 0.9579; n_D^{25} 1.4900), then, one drop of light violet oil (b.p$_{13}$ 160~165°), and finally deep blue-violet oil (above 165°; 0.12 g.). The deep blue-violet oil formed a picrate of violet-black needles, m.p. 156~158°, which agreed with 4,8-dimethylazulene picrate by the mixed melting point determination with the authentic picrate, produced by the Plattner and Wyss' method.[10]

On the other hand, when the monobasic acid (5 g.) was treated for 10 hrs. with Se (7 g.) in the same manner as above, only a light violet-colored oil (0.2 g.) was obtained, which did not form a picrate.

Summary

Naffa and Ourisson proposed a structure of longifolene from the investigation of its X-ray, infrared, and Raman spectra, and from chemical reactions of five-membered ring having a double bond. For the purpose of chemical certification of five- and seven-membered rings in the molecule, other than those verified by Naffa and others, examination was made on dehydrogenation of α-longifolic acid and a monobasic acid which was obtained from longicamphenylone by decomposition. 4,8-Dimethylazulene was obtained from α-longifolic acid in this experiment confirming the structural formula suggested by Naffa and Ourisson.

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[10] A. Plattner, J. Wyss : Helv. Chim. Acta, **24**, 483(1941).