The Photo-synthesis of Anemonin from Protoanemonin

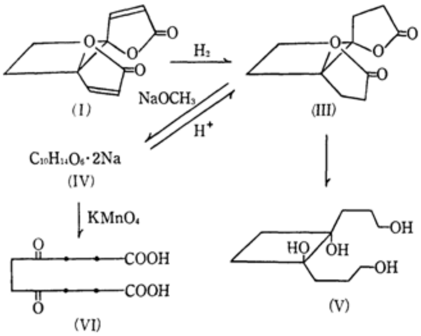
By Hiroshi Kataoka, Kazutoshi Yamada and Noboru Sugiyama

(Received September 7, 1965)

In 1914, Asahina proposed a structure for anemonin[1]; later he confirmed it by the dimerization of synthesized protoanemonin.[2] Later other authors[3] have not, however, paid any attention to the effect of light on the dimerization of protoanemonin.

We have attempted to dimerize protoanemonin to anemonin with radiation of light; we succeeded in getting anemonin in a much better yield than those of the previous reports. As the configuration of anemonin had never been described, we propose that anemonin has a configuration[4] (I).

A methanol solution of protoanemonin[5] (II) was irradiated at $-50°C$ by a high-pressure mercury lamp. The crystals of I deposited were collected (yield, 75%). Colorless needles (from ethanol; m. p. 153°C). IR: 1780, 1755, 935, 900, 810 cm^{-1}. I was catalytically reduced, and tetrahydroanemonin (III) was obtained (from hot water; m. p. 154.5°C). IR: 1775, 930, 900, 810 cm^{-1}. NMR: 7.30 τ (triplet, 4H), 7.89 τ (triplet, 4H), 7.48 τ (quartet, 4H). III was hydrolyzed with sodium methoxide to give sodium dicarboxylate (IV), which was again converted into the lactone III in an acidic solution. The permanganate oxidation of IV gave dilevulinic acid (VI). From these results it was clear that the photodimerization product was identical with Asahina's anemonin.



By letting a methanol solution of I stand at $-50°C$ without irradiation, the formation of I was observed, but the yield was very poor.

Tetrahydroanemonin III was further reduced with lithium aluminum hydride to a tetraol (V). V could not be oxidized by lead tetraacetate and was recovered quantitatively. V showed a shift of the stretching vibration bands of hydroxyl groups when treated by a dilution method. This suggest the existence of a weak inter-molecular hydrogen bond of hydroxyl groups. V had no signal less than 4 τ in the NMR spectrum, indicating the absence of a strong hydrogen bond. These data support the speculation that two hydroxyl groups on the cyclobutane ring of V have a trans configuration. From the trans configuration of V and the fact of the formation of VI, the configuration of I was concluded to be trans and head to head.

Department of Chemistry
Tokyo Kyoiku University
Otsuka, Tokyo

---

1) Y. Asahina, *Ber.*, **47**, 914 (1914).

2) Y. Asahina and A. Fujita, *Acta phytochim. Japan*, **1**, 1 (1922).

3) a) C. Grundman and E. Kober, *J. Am. Chem. Soc.*, **77**, 2332 (1955); b) G. F. D'alelio, C. J. Williams, Jr., and C. L. Wilson, *J. Org. Chem.*, **25**, 1025 (1960).

4) Immediately after our report of this result at the International Conference on Photochemistry, 1965, Tokyo, we received, *J. Am. Chem. Soc.*, **87** (1965), in this volume at page 3252, R. M. Moriarty, C. R. Romain, I. L. Karle and J. Karle described anemonin configuration determined by X-ray analysis.

5) E. Shaw, *J. Am. Chem. Soc.*, **68**, 2510 (1946).