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PHOTOCHEMICAL CONVERSION OF ASATONE TO ISOASATONE
THE REVISED STRUCTURE OF ASATONE

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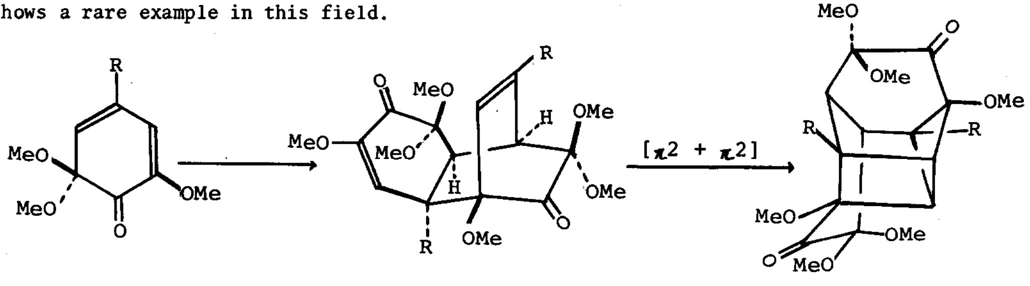
In the previous paper,[1] we reported the tentative structure of asatone (m.p. 101 - 102°; $C_{24}H_{32}O_8$), a main component of Asarum taitonense Hayata. However, in connection with the biogenesis of isoasatone, whose stereostructure has been determined by means of an X-ray crystallographic analysis[2], further study on these unusual lignans has been carried out. In the present paper, we wish to describe the photochemical conversion of asatone to isoasatone, indicating the structure of the former to be I.

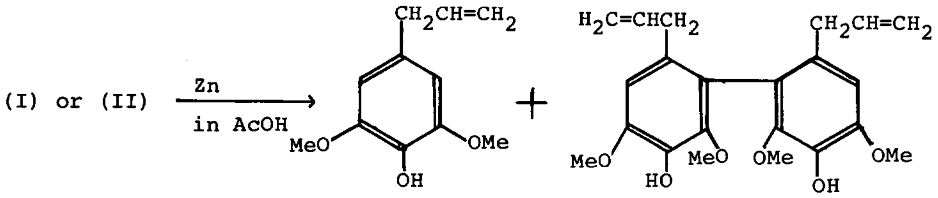
On zinc reduction, asatone (I) and isoasatone (II) both have been known to afford two phenolic compounds (III and IV) in high yields.[1,3] Furthermore, in the light of the stereostructure of isoasatone, which co-occurs with asatone in the plant, asatone (I) can be derived from two C_6-C_3 units and may be a plausible precursor of isoasatone (II), as suggested in the previous paper[2]. Thus, chemical correlation between them was successfully carried out by photochemical reaction of asatone, as follows.

When asatone (I) was irradiated in n-hexane using 0.02% aq.K_2CrO_4 solution as a filter (10°, 54hr), a colourless viscous liquid was obtained, which was subjected to preparative TLC to give isoasatone (II) in 64% yield (m.p., IR, NMR and mass spectra).[4] In the case of V[1], tetrahydroisoasatone (VI) was also produced in 60% yield. Thus, the structure of asatone was established as I.[5] In addition, clearly, asatone must be non-enzymatically produced in vivo from the plausible dienone [A], and then subjected to photochemical

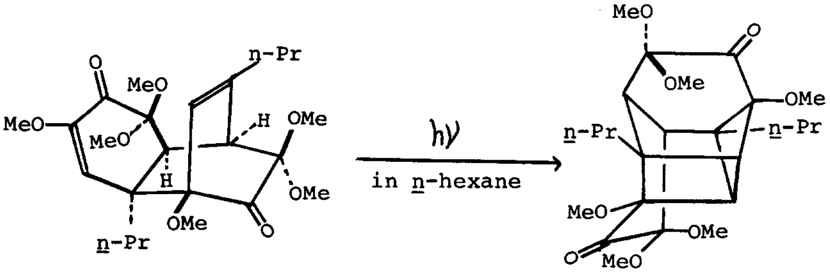
[$\pi 2$ + $\pi 2$]cycloaddition to give isoasatone (II), as shown below. Thus, the present study shows a rare example in this field.



[A] R = $CH_2CH{=}CH_2$ (I) (II)



(III) (IV)



(V) (VI)

REFERENCES AND FOOTNOTES

1. Y.Chen, M.Hong, H.Hsu, S.Yamamura and Y.Hirata, Tetrahedron Letters, 1607 (1972).
2. K.Sasaki, Y.Hirata, S.Yamamura, Y.Chen, M.Hong and H.Hsu, ibid., 4881 (1973).
3. S.Yamamura, K.Sasaki, Y.Hirata, Y.Chen and H.Hsu, ibid., 4877 (1973).
4. On Kieselgel PF_{254} (Type 60) in n-hexane - EtOAc (3 : 1).
5. Of the spectral data of I, two methine protons have the same chemical shift in the NMR spectrum, although these two protons are in different environment to each other. Secondly, the UV absorption band [λ_{max}(MeOH) 278nm (ε, 5100)] is observed at longer wave length than calculated one. This is probably due to some effects of α',α'-dimethoxyl groups as well as of the isolated and trisubstituted double bond.