

A Revised Structure of Pyrolumisantonin¹⁾

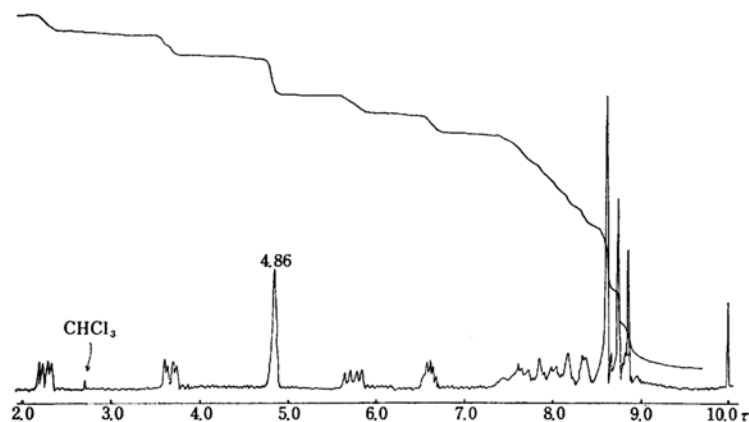
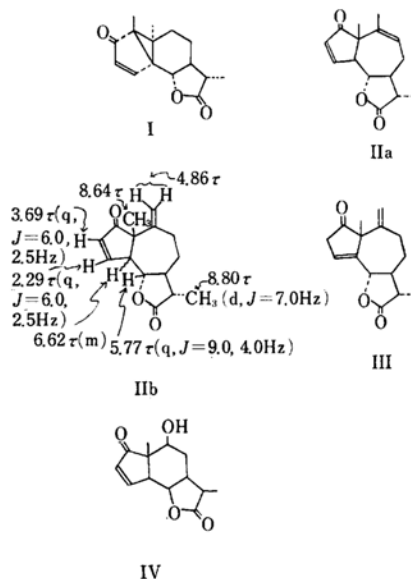
Tadashi SASAKI and Shoji EGUCHI

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya

(Received June 27, 1969)

The structure of pyrolumisantonin was given for the first time by Arigoni and his coworkers as IIa in 1957 on the basis of an ozonized product IV without NMR spectral evidence²⁾ and has been adopted again quite recently by Fisch and Richards.³⁾ During the course of our studies on the synthesis of some double bond derivatives of lumisantonin (I),⁴⁾ we have obtained pyrolumisantonin as a by-product, mp 127—129°C (lit.,²⁾ mp 126—127°C). It gave a satisfactory analysis (Found: C, 72.89; H, 7.30%. Calcd for C₁₅H₁₈O₃: C, 73.14; H, 7.37%) and had almost the same spectral data as those reported: $[\alpha]_D = -170^\circ$ (CHCl₃, $c = 0.265$, lit.,²⁾ -171°); $\lambda_{\text{max}}^{\text{EtOH}}$ 219 m μ , $\log \epsilon$ 4.06 (lit.,²⁾ $\lambda_{\text{max}}^{\text{EtOH}}$ 220 m μ , $\log \epsilon$ 4.07); $\nu_{\text{max}}^{\text{KBr}}$ 3090, 1843, 1635 and 920 (C=CH₂), 1769 (γ -lactone), 1705 and 1600 (cyclopentenone) cm⁻¹ (the spectrum was superimposable on that reported²⁾). In the NMR spectrum (Fig. 1), however, no signals due to an expected allylic methyl protons in the proposed structure IIa were observed but instead a sharp singlet integrated for two protons appeared at τ 4.86 which should be assigned to two *end*-methylene protons and all other signals were compatible with the structure IIb. This led us to revise the structure of pyrolumisantonin from IIa to IIb. A double bond isomer (III) of pyrolumisantonin has been shown to isomerize to pyrolumi-

santonin by chromatography on alumina (neutral, grade II).³⁾ Our sample was treated similarly on an alumina (neutral, grade II) column using benzene as an eluent to afford needles, mp 128—130°C which showed no depression of a mixed melting point with a specimen before chromatography.

Fig. 1. NMR spectrum of pyrolumisantonin CDCl₃ (60 MHz).

1) Studies on Reactions of Isoprenoids. Part X. Part IX: T. Sasaki, S. Eguchi and T. Ishii, submitted to *J. Org. Chem.*

2) D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732

(1957).

3) M. H. Fisch and J. H. Richards, *J. Am. Chem. Soc.*, **90**, 1547, 1553 (1968).

4) T. Sasaki and S. Eguchi, *J. Org. Chem.*, **33**, 4389 (1968).