Tetrahedron Letters No.23, pp. 2017-2019, 1970. Pergamon Press. Printed in Great Britain.

(-) PARABENZLACTONE, A NEW PIPEROLIGNANOLIDE ISOLATED FROM PARABENZOIN TRILOBUM NAKAI

Kojiro Wada and Katsura Munakata

Laboratory of Pesticide Chemistry,
Department of Agricultural Chemistry,
Nagoya University, Nagoya, Japan

(Received in Japan 8 April 1970; received in UK for publication 21 April 1970)

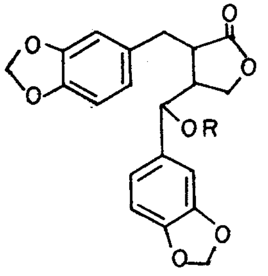
In the course of the isolation of the insect feeding inhibitors from Parabenzoin trilobum Nakai1), we isolated a new piperolignanolide, for which we proposed the name (-)parabenzlactone. In this communication we wish to report the structure determination of this lignanolide.

(-)Parabenzlactone (I) mp. 159-161°C, $(\alpha)_D^{25}$ -11°(c, 1.15 $CHCl_3$), $C_{20}H_{18}O_7$ 2) had IR absorptions at 3480 and 1725 cm^{-1}. The UV spectrum, λ_{max}^{MeOH} 237 and 286 mμ (logε= 3.87 and 3.87), indicated the presence of substituted benzene chromophore in I. I was readily acetylated to give acetylparabenzlactone (II), mp. 142-145°C, $C_{22}H_{20}O_8$ 2), ν_{max}^{KBr} 1750, 1735, 1250 and 935 cm^{-1}. The NMR spectrum3) exhibited proton signals ascribed to a methylene group of five-membered lactone ($\delta_{Me_4Si}^{CDCl_3}$ 3.90, 2H, d, J=7.5 cps) which is also suggested from an absorption band at 1750 cm^{-1} in the IR spectrum of II, a secondary acetoxyl group (5.63, 1H, d, J=6.3 cps), two methylenedioxy groups attached on aromatic rings (5.85, 2H, s and 5.87, 2H, s), aliphatic methylene or methine groups (4H, signals overlapped at 2.5-2.9), and substituted aromatic rings(6H, signals overlapped at 6.4-6.7).

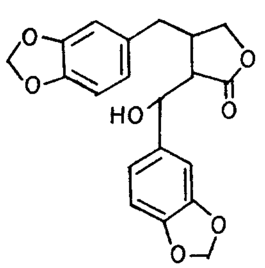
Oxidation of I with chromic acid-pyridine complex gave oxo-parabenzlactone (III) mp. 113-115°C, $C_{20}H_{16}O_7$ 2). The IR and UV spectra of III had characteristic absorption band of phenylketone group (ν_{max}^{KBr} 1660 cm^{-1}; λ_{max}^{MeOH} 232, 279, 286 sh., and 313 mμ (logε=4.32, 3.98, 3.94, and 3.94), indicating that I has a benzyl alcohol group.

These findings suggest that (-)parabenzlactone could be represented by the structure (I) or (I'), which have the same skelton as that of (-)hinokinin4)

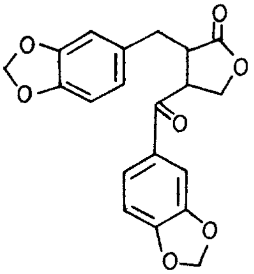
K. Ohta in our laboratory have recently isolated a 2,3-naphthalide lignan, justicidin E (V) as one of the piscicidal components of Justicia procumbens and synthesized V and VI which is different from V only in the orientation of the lactone ring[5]. Thus, we intended to confirm the structure of (-)parabenzlactone by transforming it to a 2,3-naphthalide lignan, V or VI.



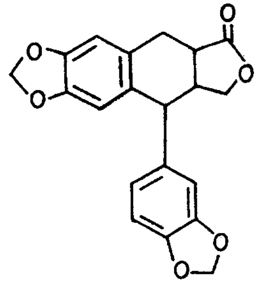
I R = H
II R = Ac



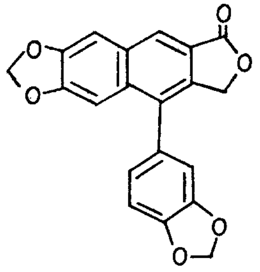
I'



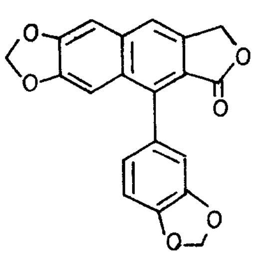
III



IV



V



VI

I was transformed to a 1,2,3,4,-tetrahydro-2,3-naphthalide derivative (IV), mp. 235-236°C, $C_{20}H_{16}O_6$, ν_{max}^{KBr} 1788 and 935 cm^{-1}, with acid treatment (hydrochloric acid in acetic acid at room temperature)[6]. Dehydrogenation of IV with N-bromosuccinimide[7] gave justicidin E (V), mp. 265-269°C, $C_{20}H_{12}O_6$[2], $\lambda_{max}^{CHCl_3}$ 252, 259, 297, 315, and 348 mμ (logε= 4.65, 4.69, 4.11, 4.13 and 3.72), ν_{max}^{KBr} 1770, 945 and 937 cm^{-1}, $\delta_{Me_4Si}^{DMSO}$ 3)

5.28 (2H, s, one methylene group of α,β-unsaturated lactone), 6.14, 6.20 (2H x 2, s x 2, two methylenedioxy groups), 6.90, 7.12, 7.02, 7.07, 7.65 and 8.37 (1H, dd, J=8, 1 cps, 1H, d, J=8 cps, 1H, s, 1H, s, 1H, s, and 1H, s, six protons on aromatic rings). This dehydrogenated product was identified by comparing its physical constants (mp., IR, UV, and NMR) with those of an authentic sample of justicidin E (V), which was given by K. Ohta.

On the basis of these data, the structure (I) was reasonably assigned to (-)parabenzlactone.

Acknowledgements : The authors are indebted to Dr. K. Ohta in their laboratory for useful discussions. They are also grateful to Mrs. H. Nishiyama for microanalysis.

Footnotes and References

1) K. Wada, Y. Enomoto, K. Matsui, and K. Munakata, Tetrahedron Letters No.45, 4673 (1968).

2) Satisfactory elemental analysis were obtained.

3) The NMR spectra were measured with a JNM-4H-100.

4) R.D. Haworth and L. Wilson, J. Chem. Soc., 71 (1950).

5) This work was presented at the Annual Meeting of the Agricaltural Chemical Society of Japan, held at Fukuoka, April 4, 1970.

6) K. Freudenberg and L. Knof, Chem. Ber., **90**, 2857 (1957).

7) M. E. Cisney, W.L. Shilling, W.M. Rearon, and D.W. Goheen, J. Amer. Chem. Soc. **76**, 5086 (1954).