Tetrahedron Letters No. 26, 2297 - 2298, 1978.	0040-4039/78/0622-2297$02.00/0

ISOLATION AND STRUCTURE OF ALFLABENE FROM ALPINIA FLABELLATA RIDL.

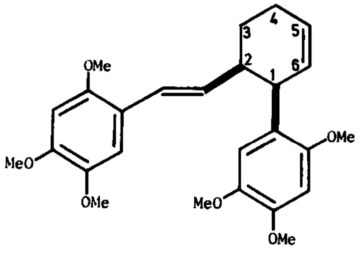
Iwao Mori and Yumiko Nakachi
Department of General Education, University of the Ryukyus, Naha 903, Japan
Katsuhiro Ueda, Daisuke Uemura, and Yoshimasa Hirata
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan

(Received in Japan 27 March 1978; received in UK for publication 27 April 1978)

Studies on the chemical constituents of the native plants in the Ryukyus have been carried out. Now, we wish to report herein the isolation and structure of a new cyclohexene derivative, which has been named alflabene, from *Alpinia flabellata* Ridl. (*Zingiberaceae*).

Fresh roots of the title plant were washed with methanol and extracted with petroleum ether for a period of a few days. The filtrate was concentrated under reduced pressure to give a crystalline material. Recrystallization from methanol afforded a pure sample of alflabene (1): $C_{26}H_{32}O_6$; m.p. 130-131°; UV (EtOH) 261 (ε 17600), 300 (9230), 305 (8890), 310 nm (8630); m/e 440 (M^+), 220; IR ($CHCl_3$) 1605, 1505 cm^{-1}; PMR (100 MHz, $CDCl_3$) 1.78 (2H, m), 2.22 (2H, m), 2.82 (1H, m), 3.69 (3H, s), 3.72 (3H, s), 3.80 (6H, s), 3.85 (6H, s), 4.14 (1H, m), 5.80 (1H, dd, J= 8, 16 Hz), 5.6-6.1 (2H, m), 6.47 (1H, d, J= 16 Hz), 6.44 (1H, s), 6.74 (1H, s), 6.79 (1H, s) ppm.

The pmr spectrum of alflabene reveals the presence of two isolated double bonds, and multiplicities of the cmr signals obtained by SFORD experiments indicate that four carbon atoms



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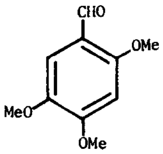

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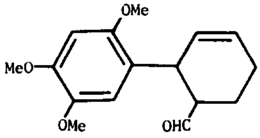

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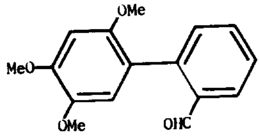

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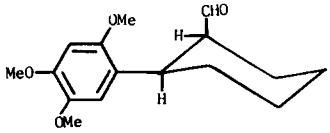

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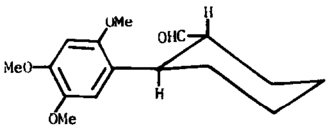

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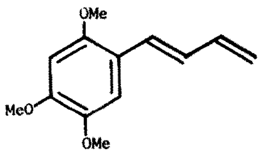
in these double bonds possess one proton each. The trans double bond (J= 18 Hz) was distinguishable from the other by the treatment with an equivalent amount of OsO_4 in pyridine. Oxidation of alflabene (1) in the above condition gave a diol, which was cleaved with $NaIO_4$ in acetone-H_2O to give 2,4,5-trimethoxybenzaldehyde (2)$^{1)}$ and an aldehyde (3): PMR (100 MHz, $CDCl_3$) 1.76 (2H, m, H-3), 2.20 (2H, m, H-4), 2.80 (1H, m, H-2), 3.80 (6H, s, $-OC\underline{H}_3$), 3.87 (3H, s, $-OC\underline{H}_3$), 4.33 (1H, br.dd, $J_{1,6}$= 4 Hz, $J_{1,2}$= 5 Hz, H-1), 5.72 (1H, br.dd, $J_{6,1}$= 4 Hz, $J_{6,5}$= 10 Hz, H-6), 6.05 (1H, br.d, $J_{5,6}$= 10 Hz, H-5), 6.48 (1H, s), 6.78 (1H, s), 9.45 (1H, d, J= 2 Hz, $-C\underline{H}O$). Furhtermore, the aldehyde (3) was converted to a biphenyl derivative (4) on oxidation with DDQ in benzene at 80°. The substitution pattern in the benzene ring generated by oxidation could be recognized to be ortho-relationship from the result that the signal of the proton at C-3 appeared at δ 8.00 as a double doublet (J= 2 and 8 Hz) in the spectrum. Therefore, the planar structure of the aldehyde (3) was proved by this result and analysis of the pmr spectrum of aldehyde (3) secured by decoupling procedures. The configuration at C-1 and C-2 was determined by the following observation. The aldehyde (3) was converted to the cyclohexane (5) by catalytic hydrogenation in ethyl acetate by the use of Pd-C as a catalyst. This compound (5) was converted to the epimer (6) under equilibrium condition with NaOH in methanol. The coupling constants between H-1 and H-2 of compounds (5) and (6) are 4 Hz and 11 Hz, respectively. From these results it is suggested that relationship between two groups attached at C-1 and C-2 is cis in alflabene.

The fact that alflabene is optically inactive suggests non-enzymic process might be involved during its formation. It could be assumed that alflabene is derived from the compound (7) by Diels-Alder type dimerization.$^{2)}$ Feasibility of this consideration has been demonstrated by the synthesis of alflabene from the compound (7) as follows. The aldehyde (2) was converted to an alcohol (8) with allyl magnesium chloride in ether. Treatment of the alcohol (8) with 10% H_2SO_4 gave trans-1-(2,4,5-trimethoxyphenyl)-butadiene (7). However, Wittig reaction$^{3)}$ between the aldehyde (2) and sodium allyl triphenylphosphorane gave cis-1-(2,4,5-trimethoxyphenyl)-butadiene (9) in good yield. Dimerization of the trans-isomer (7) in toluene under reflux for 12 hours afforded a crystalline (1), which was identical with the natural sample of alflabene in all physical and spectral data.



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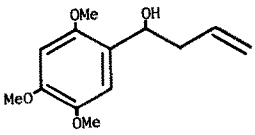

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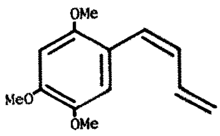

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REFERENCES

1) L. Gattermann and F. Eggers, Ber., 32, 289 (1899).
2) K. Alder, J. Haydn, and W. Vogt, Chem. Ber., 86, 1302 (1953).
3) L. Crombie, P. Hemesley, and G. Pattenden, J. Chem. Soc., (C), 1016 (1969).