Tetrahedron Letters No. 34, pp 2909 - 2910, 1974. Pergamon Press. Printed in Great Britain.

# ISOMERIZATION AND TRANSFORMATION OF TRANS-TRANS EPOXYFARNESOL BY DRESCHLERA SOROKINIANA.

L.W. van Broekhoven*, M.W. van Maarschalkerweerd,

R.J.J.Ch. Lousberg and C.A. Salemink.

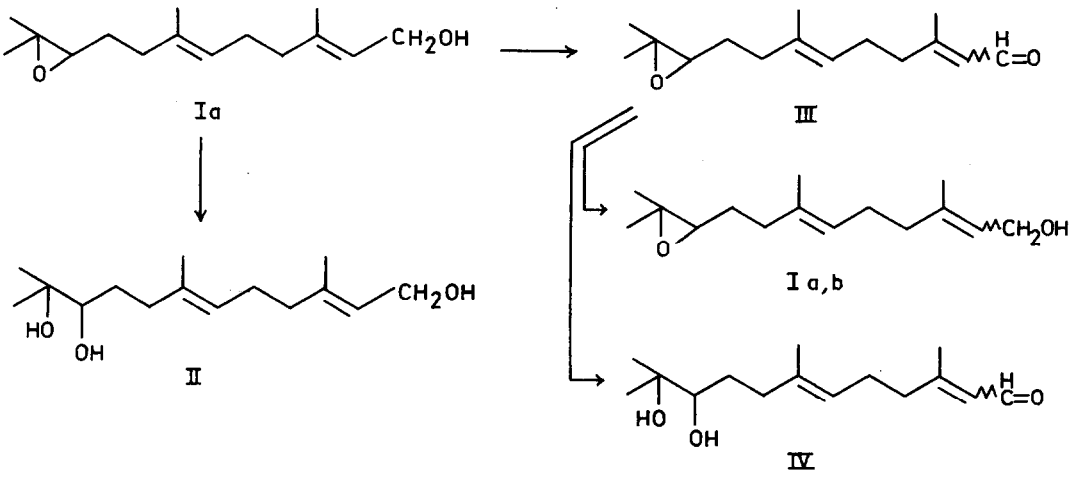
Organic Chemical Laboratory, State University

Croesestraat 79, Utrecht, Holland.

(Received in UK 25 June 1974; accepted for publication 3 July 1974)

Suzuki and Marumo[1] proved that the fungus Helminthosporium sativum[+] was able to more readily consume (+)-epoxyfarnesol than its (-)-enantiomer when the racemic material (I) was added during incubation. The authors also reported[2] that the trans-to-cis-2,3-double bond isomerization of (I) was likely to take place through the intermediate epoxyfarnesal, although they never could isolate this product. Because of our interest in the synthesis of optically active juvenile hormones, we examined the above mentioned fungal transformation of racemic trans-trans-epoxyfarnesol (Ia).

The cultures and the fermentations of (I) were carried out as described by Suzuki and Marumo[1]. After 45 hours the culture filtrates were extracted with ethyl acetate. TLC ($SiO_2$; $CHCl_3$/MeOH=9/1) revealed the presence of four products with Rf 0.75 (III,8%); 0.63(I,68%); 0.50(IV,3%) and 0.39(II,6%).




[+] This fungus, recently classified as Dreschlera sorokiniana, was obtained from the Centraal Bureau voor Schimmelcultures, Baarn, Holland.

The starting material was partly isomerized into its cis-trans isomer (Ib) (δC-3 Me-trans 1.66 and cis 1.73 ppm). In addition to the expected dihydroxyfarnesol (II) we were also able to identify both isomers of epoxyfarnesal (III) as well as those of dihydroxyfarnesal (IV). The compounds were purified from the ethyl acetate extract by column chromatography ($SiO_2$). Compounds I and III were eluted with hexane/ethyl acetate(65/35). Products II and IV were collected by washing with ethyl acetate. Re-chromatography using chloroform/methanol(19/1) afforded pure II and IV.

Spectral data of II were in agreement with those in literature[2].

Compound III was obtained as an oil; m/e 236($M^+$,$C_{15}H_{24}O_2$)

$\nu^{CCl_4}$: 2860(C-H ald.) and 1680 $cm^{-1}$(α,β conj.ald.);

$\delta^{CCl_4}_{TMS}$: 1.24,1.27(each 3H,s,two $C_{11}$-$CH_3$), 1.69(5H,C-9 $CH_2$ and C-7 $CH_3$)
2.06(d,C-3 $CH_3$ cis), 2.25(d,C-3 $CH_3$trans), 2.58(1H,t,C-10 H)
5.30(1 H,broad s,$C_6$ vinyl H),5.95(1H,d,$C_2$ vinyl H),9.89(d,H ald. cis) 9.99(d,H ald. trans)

Compound IV was also obtained as an oil; m/e 254($M^+$,$C_{15}H_{26}O_3$);

$\nu^{CCl_4}$: 3450 (OH),2850( C-H ald.) and 1680 $cm^{-1}$(α,β unsat. ald.);

$\delta^{CCl_4}_{TMS}$: 1.15,1.22(each 3H,s,two $C_{11}$-$CH_3$),1.65(5H,C-9 $CH_2$,C-7 $CH_3$)
2.00(d,C-3 $CH_3$ cis)2.25(d,C-3 $CH_3$ trans),2.50(2H,OH),5.15
(1H broad s,C-6 vinyl H)5.90(1H,d,C-2 vinyl H),9.90 (d,H ald. cis),10.10(d,H ald. trans)

The data on III and IV were in good agreement with those of the synthetic products. Epoxyfarnesal was produced by treatment of epoxyfarnesol with active $MnO_2$[3]; dihydroxyfarnesal was derived from epoxyfarnesal by acid hydrolysis[4].

The present findings strongly support the proposed mechanism of Suzuki and Marumo, that the isomerization of epoxyfarnesol into a mixture of trans-trans and cis-trans-isomers during fermentation can indeed take place through the intermediate farnesal. Preliminary findings indicate, that prolonged fermentation does considerably influence the nature of the products, which are formed. Further results will be the subject of a forthcoming report.

Acknowledgement: Our thanks are due to Miss G.J.J. Holland for performing the microbiological part of the experiments.

## REFERENCES

1. Y. Suzuki and S. Marumo, Tetrahedron L. 19 1887 (1972).
2. Y. Suzuki and S. Marumo, Tetrahedron L. 50 5101 (1972).
3. E.J. Corey et al. J. Amer. Chem. Soc. 90 5617 (1968).
4. M. Slade and C.H. Zibitt, Insect Juvenile Hormones, 155-175 Ed. by J.J. Menn and M. Beroza, Acad. Press, 1972, New York.