

THERMAL ISOMERISATION BETWEEN (-)- δ -ELEMENOL AND (+)-EPI- δ -ELEMENOL

K. Morikawa and Y. Hirose

The Institute of Food Chemistry

2-chome 43, Dojima-naka, Kita-ku, Osaka, Japan

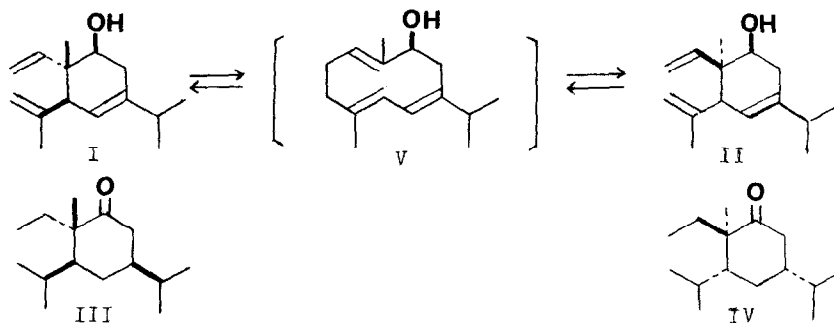
(Received in Japan 16 January 1969; received in UK for publication 1 February 1969)

In addition to the previous report,¹⁾ recently it has been observed that thermal isomerisation between (-)- δ -elemenol (I), $[\alpha]_D^{24} -47.9^\circ$ (C, 0.513 in MeOH)* and (+)-epi- δ -elemenol (II), $[\alpha]_D^{24} +182.5^\circ$ (C, 0.520 in MeOH) does occur.

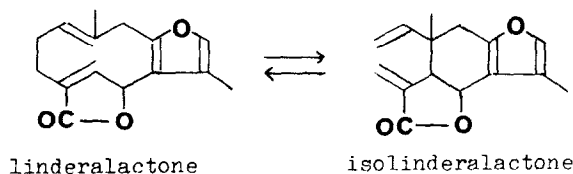
Previously it was suggested that I and II have enantiomeric elemene skeletons, and now the supplementary proof of it is presented as follows. Both hexahydroketones III and IV derived from the corresponding alcohols (I and II respectively) show the same following spectral data, IR (ν_{\max}^{liq} 1705 cm^{-1}), NMR ($\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.63 ~ 1.02, 6 Me), UV ($\lambda_{\max}^{\text{MeOH}}$ 290 $\text{m}\mu$, $\epsilon = 34.5$), MS (M^+ , m/e 224). They show also the same GLC-retention time (Hitachi Golay column HB-2000 : 0.25 $\text{mm} \times 45 \text{ m}$), but show opposite ORD and CD curves which are in accord with their absolute structures III and IV, respectively, and this supports in turn the previously postulated structures I and II¹⁾; III (C, 0.19 in MeOH) : $[\phi]_{317} -231^\circ$, $[\phi]_{275} +239^\circ$ and $[\theta]_{340} 0^\circ$, $[\theta]_{296} -11.2^\circ$, $[\theta]_{240} 0^\circ$, $f/2$ 18.5 $\text{m}\mu$, IV (C, 0.21 in MeOH) : $[\phi]_{317} +254^\circ$, $[\phi]_{275} -253^\circ$ and $[\theta]_{340} 0^\circ$, $[\theta]_{296} +12.1^\circ$, $[\theta]_{240} 0^\circ$, $f/2$ 18.5 $\text{m}\mu$.

When I or II was allowed to stand at 200°C for 3 hr in a sealed tube, it gave the same equilibrium mixture of I and II in a ratio of 54 : 46. This enantiomeric isomerisation between I and II is explained by the following mechanism via a compound (V) which is ready to take a Cope rearrangement²⁾ and gives I and II.

*) This higher $[\alpha]_D$ value than previously reported is authentic because of improved purity of the sample



In 1964, it was reported that a reversible thermal rearrangement was observed between linderalactone and isolinderalactone.³⁾



Thus, it is suggested that such rearrangement is universal and, in a case of some elemene compounds which have no substituent group that decides their elemene skeleton specifically, enantiomeric isomerisation can occur.

It is very interesting that the proportion of I and II is nearly the same both in thermal equilibrium mixture and in the original oil which was obtained from the ripe fruits of *Kadsura japonica* by steam-distillation for 3 - 4 hr and also by extraction-evaporation at room temperature.

Either I or II in a sealed tube scarcely isomerizes on heating at 150°C for 1 hr, and therefore, both alcohols in the oil are the products due not to thermal isomerisation but to thermal rearrangement of a precursor (V), though the presence of which has not been proved yet.

REFERENCES

- 1) K. Morikawa and Y. Hirose, Tetrahedron Letters, 24, 2899 (1968).
- 2) A. S. Rao, A. Paul, Sadgopal and S. C. Bhattacharyya, Tetrahedron, 13, 319 (1961).
H. Ishii, T. Tozyo, M. Nakamura and K. Takeda, Tetrahedron, 24, 625 (1968).
R. V. H. Jones and M. D. Sutherland, Aus. J. Chem. 21, 2255 (1968).
- 3) K. Takeda, H. Minato and M. Ishikawa, J. Chem. Soc. 4578 (1964).