Tetrahedron Letters No.42, pp. 4417-4419, 1968. Pergamon Press. Printed in Great Britain.

THERMAL REARRANGEMENT OF CURZERENONES

H. Hikino, K. Agatsuma, C. Konno, and T. Takemoto

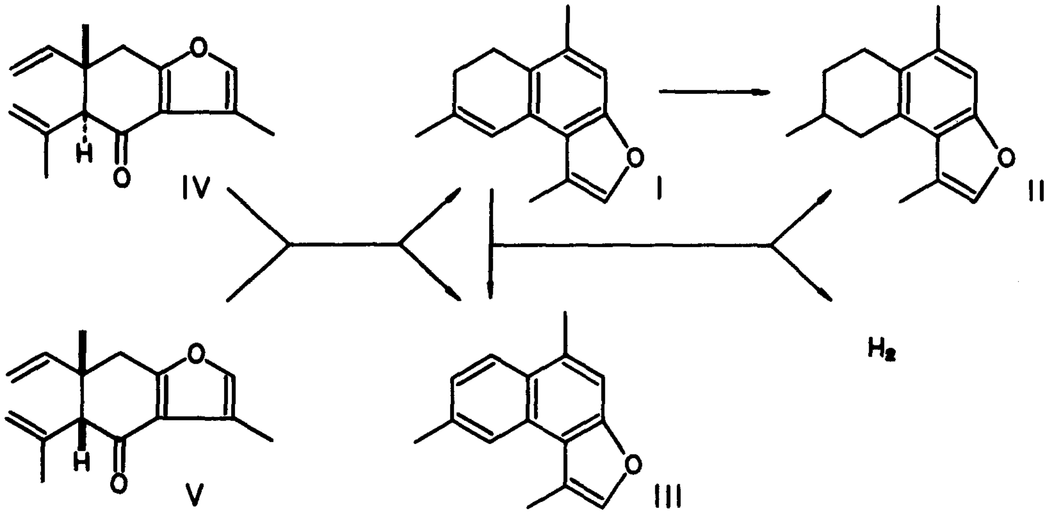
Pharmaceutical Institute, School of Medicine, Tohoku University, Sendai, Japan.

(Received in Japan 25 June 1968; received in UK for publication 19 July 1968)

Quite recently, we have reported the isolation of two new sesquiterpenoids, curzerenone and epicurzerenone, from the rhizome of zedoary, Curcuma zedoaria Roscoe (Zingiberaceae), and the assignment of the structures IV and V to them, respectively.1)

We have more recently isolated another new furan-containing sesquiterpenoid for which the term pyrocurzerenone is given. Pyrocurzerenone, m.p. 76.5~77.5°, $[\alpha]_D \pm 0°$, possesses the composition $C_{15}H_{16}O$.*1 The NMR spectrum*2 shows the presence of an α-hydrogen (7.10) and a β-methyl (2.31) on a furan ring (J=1.2), a hydrogen (6.91) and a vicinal methyl (2.25) on a benzene ring (J=small), a hydrogen (6.69) and a methyl (1.92) on an ethylenic linkage (J=1.4), and four allylic hydrogens (2.05~2.75); all the hydrogens being accounted for. Further, the occurrence of an intramolecular nuclear Overhauser effect was observed between the β-methyl of the furan (2.31) and the hydrogen on the ethylenic linkage (6.69), demonstrating that both are very close together in space.2) The UV spectrum (λ_{max} 233, 239, 249, 283, and 293 mμ (log ε 4.75, 4.72, 4.62, 4.40, and 4.40)) is suggestive of a benzofuran further conjugated with an ethylene bond.3) Hydrogenation of pyrocurzerenone over platinum catalyst in methanol gave the dihydro-derivative (II), m.p. 72~73°, whose NMR spectrum exhibited the disappearance of the trisubstituted double bond present in pyrocurzerenone and the formation of a secondary methyl group (1.08). The UV spectrum (λ_{max} 216, 248, 254, 262, 281, and 291 mμ (log ε 4.47, 4.23, 4.25, 3.76, 3.76, and 3.64)) indicates it to have a benzofuran chromophore.3)

On the other hand, after the deduction of the structures of the curzerenones, curzerenone (IV) was subjected to pyrolysis in the hope of obtaining the Cope rearrangement product, furanodienone (VI). Heating at 200° under nitrogen for 10 hours afforded a pyrolyzed product which was not that expected but was identified as pyrocurzerenone. When the temperature was raised to 350° and heating continued for 30 minutes, two main products were obtained in the ratio 1:4. The minor product was identified as pyrocurzerenone. The major product, $C_{15}H_{14}O$, m.p. 98~100°,

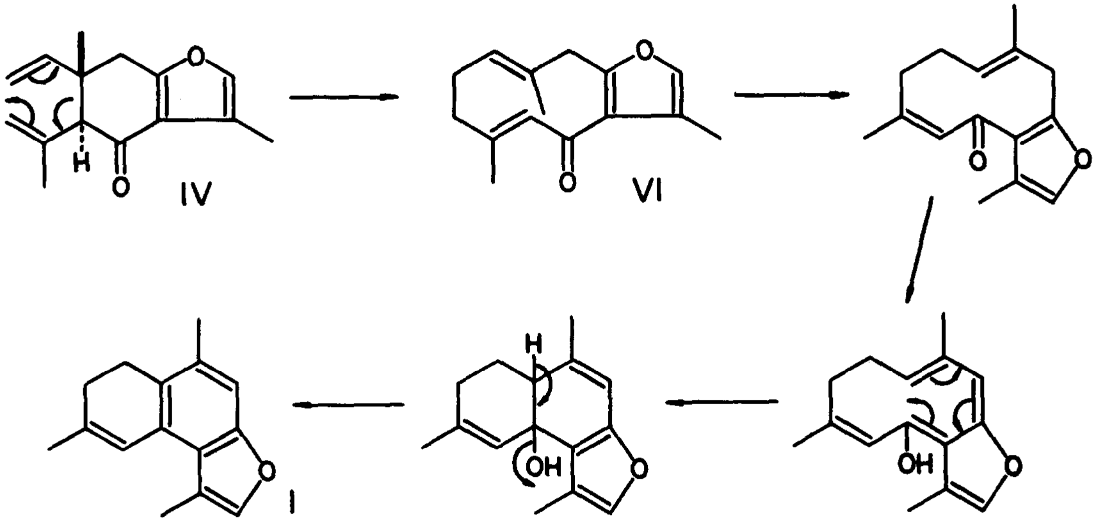


which is named furanocadinene, shows in the NMR spectrum signals originating from an α-hydrogen (7.29) and a β-methyl (2.53) on a furan ring (J=1.2), two sets of hydrogens (7.98 and 7.27) and vicinal methyls (2.51 and 2.64) on benzene rings (J=0.7 and 0.9, respectively), and two vicinal hydrogens (7.16 and 7.80) on a benzene ring (J=8.5); the aromatic proton (7.98) is further spin-coupled with the other aromatic protons (7.16 and 7.80) (J=1.8 and 0.6, respectively). Intramolecular nuclear Overhauser effects were again noted between the β-methyl of the furan (2.53) and the aromatic hydrogen (7.98), and between the aromatic methyl (2.64) and the aromatic hydrogen (7.80). The UV spectrum (λ_{max} 233, 239, 249, 283, and 293 mμ (log ε 4.53, 4.57, 3.94, 3.82, and 3.53)) suggests that it has a naphthofuran chromophore.3)

Pyrolysis of epicurzerenone (V) was also carried out under similar conditions to give essentially the same results.

The above evidence leads us to conclude that the structures of pyrocurzerenone and furanocadinene are represented by formulas I and III, respectively.

The transformation from curzerenone (IV) to pyrocurzerenone may be rationalized if it be assumed that a preliminary Cope rearrangement takes place to give furanodienone (VI) which further undergoes a second Cope rearrangement and dehydration. It seemed most likely that furanocadinene would be formed from pyrocurzerenone by a transfer of hydrogen to another molecule of pyrocurzerenone or the starting substance, curzerenone (IV). In confirmation, pyrolysis of pyrocurzerenone at 350° resulted in the formation of dihydropyrocurzerenone (II) together with furanocadinene. However, the yield of the former was much less than that of the latter. Compensat-



ing for this discrepancy, hydrogen was detected in the reaction mixture, indicating that liberation of hydrogen from pyrocurzerenone on pyrolysis also occurred.

To the best of our knowledge pyrocurzerenone is the first sesquiterpenoid of the cadinane type containing furan ring.

We thank Dr. M. C. Woods, Varian Associates, for measurements of the NMR spectra, and Prof. N. Tamiya, this University, for determination of hydrogen.

FOOTNOTES AND REFERENCES

[*1] Elemental analyses are in accord with the molecular formulas shown.

[*2] NMR spectra were recorded on a Varian HA-100 spectrometer in CCl_4 solution. Chemical shifts are given in p.p.m. downfield from the internal TMS, and coupling constants (J) in Hz.

1) H. Hikino, K. Agatsuma, and T. Takemoto, *Tetrahedron Letters*, **1968**, 2855.

2) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965).

3) *cf*. J. Romo and P. Joseph-Nathan, *Tetrahedron*, **20**, 2331 (1964).