Tetrahedron Letters No. 13, pp 1019 - 1020, 1976. Pergamon Press. Printed in Great Britain.

STRUCTURE OF DICLAUSENAN A AND B

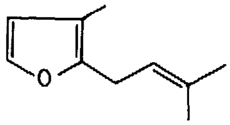
G.S.R.Subba Rao*, K.Srinivasa Rao and B. Ravindranath
Department of Organic Chemistry, Indian Institute of Science,
Bangalore 560012, India

(Received in UK 12 February 1976; accepted for publication 20 February 1976)

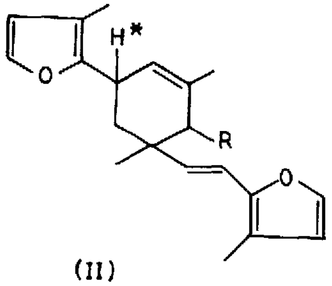
The isolation of α,β- and γ-clausenans and diclausenan from Clausena willdenovii was reported earlier[1]. During a reexamination of the steam-volatile constituents of the dried leaves, we have isolated γ-clausenan (0.5%) and diclausenan (0.1%), γ-Clausenan, $C_{10}H_{14}O$, b.p.102°/50 mm, was identified as rosefuran (I)[2] from its spectral data and by comparison with authentic sample.

Diclausenan, $C_{20}H_{24}O_2$ (M^+296), b.p.140°/5 mm, was separated into two isomeric compounds, diclausenan-A and diclausenan-B, by preparative GLC (3:2). The PMR spectrum of diclausenan-A showed the presence of a tertiary methyl group at δ 1.2(s,3H), a vinylic methyl at 1.74(s,3H), two β- and two α-protons of the furan rings at δ 6.15 and 7.15 respectively and signals due to protons on a trans disubstituted double bond (AB pattern centred around 6.0, J=16Hz), a vinylic proton (δ5.35,m) and a doubly allylic proton (δ3.30,m). The data clearly indicated that the compound is a dimer of an isoprenyl-substituted methylfuran, probably formed by an oxidative dimerisation of rosefuran. The inference was supported by the mass spectrum which showed the base peak at m/e 148. Of the two possible structures for the dimer, (II, R=H) was preferred for diclausenan-A since, in its PMR spectrum, the doubly allylic proton (H*) appeared as a multiplet at δ 3.30 and not a doublet. Further, irradiation at δ 5.35 collapsed the signal at 3.30 to a doublet of doublets thus confirming the presence of two methylene protons on the adjacent carbon.

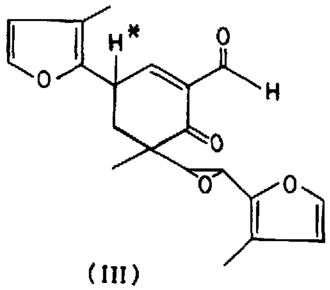
The spectral data of diclausenan-B were very similar to those of diclausenan-A, except that in the PMR spectrum, the tertiary methyl signal appeared at δ 0.9 compared to 1.2 in the latter; the two compounds are thus considered diastereomers. The above conclusions have been confirmed by chemical evidence. In view of the difficulty in the separation of the two isomers, chemical



(I)



(II)



(III)

reactions have been carried out using the mixture.

Reduction of the diclausenan mixture with sodium in liquid ammonia gave the dihydroderivative, $C_{20}H_{26}O_2$ (M^+298), indicating a double bond conjugated to the furan ring. The presence of a double bond in the carbocyclic ring was proved by hydroboration and oxidation to give a six-membered ketone (ν_{max}1710 cm^{-1}) SeO_2 oxidation gave two compounds, one of which was identified as (II,R=OH) from its spectral data; its PMR spectrum showed a singlet at δ 4.0 for the proton $\underline{H}-\overset{|}{\underset{|}{C}}-OH$ indicating that the adjacent carbons do not bear a proton. The other product, $C_{20}H_{20}O_5$, was assigned the epoxide structure (III), based on its PMR spectral data, which showed the absence of the *trans* disubstituted olefinic proton and, instead, showed the epoxide protons at δ 2.6(d,J=1Hz,1H) and 3.4(broad, 1H). The doubly allylic proton (H*) in this case appeared as a triplet of doublets (δ3.64) supporting our preference of structure (II,R=H) over the alternative. Further, the PMR spectrum of (III) showed only one signal (at δ 1.1) for the tertiary methyl group indicating that equilibration of methine proton at the activated allylic position occurred during oxidation, confirming our postulation that diclausenans A and B are diastereomers.

References

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