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RING D IN NIMBIN[*] [+]

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Elucidation of the size and attachment of ring D in nimbin was the more difficult part in its structure determination[1], and for which more evidence was still desirable. We had indicated α-configuration for the furan sidechain at C_{17} on biogenetic analogy, and β-configuration for the C_{15}-H since a potential all cis fusion of the five membered rings was considered more natural. Now we have obtained clearer evidence to show that ring D is five membered. Evidence is also obtained for the α-configuration of the furan sidechain, but our results now show that the C_{15}-H is α-oriented.

Hexahydronimbin[1] (I), on cautious treatment with BF_3-etherate and acetic anhydride gave a diene, m.p. 188°, λ_{max} 251 mμ, ε, 4400 (unsubstituted cyclopentadiene[2], λ_{max} 239 mμ, ε, 3400), which correctly analysed[3] for $C_{28}H_{38}O_6(OAc)_2$. The variation of its m.p. from 185-202° and $(\alpha)_D$ +34 to +39° (chf) and UV maximum at about 250 mμ from ε, 4000 to 5000, and the variations in its PMR spectrum in different preparations and even on recrystallization showed that the cyclopentadiene derivative (II) is a mixture of double bond isomers. The characteristic J values of about 3 and 12 cps for the C_6-H at τ 4.93 in the PMR spectrum and the presence of the R-band of the C_1-ketone at λ_{max} 292 mμ in the UV spectrum of the compound showed

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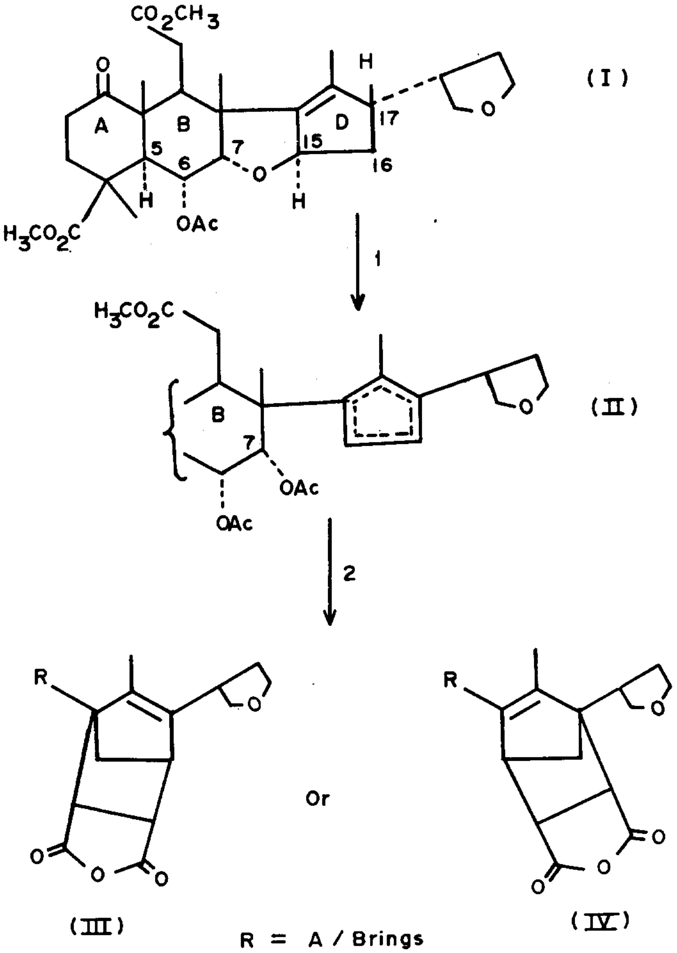

R = A / B rings

1 BF_3 - Ac_2O

2 Maleic anhydride

that the A/B rings are intact. The diene readily formed an adduct with maleic anhydride, m.p. 221-23^{o}, $(\alpha)_D$ +25^{o} (chf). Its UV spectrum showed only end absorption and the R-band of the C_1-ketone at λ_{max} 290 mμ. Its PMR spectrum showed methyl signals at τ 8.74, 8.68, 8.65 (C_8, C_{10} and C_4 methyls) 8.15 (C_{13}-vinyl methyl), 7.95, 7.86 (C_6-, C_7-α-acetate methyls), 6.3 (6H, the two carbomethoxy groups) and signals for the C_7-H at τ 5.02 ($J \sim 3$ cps), C_6-H at τ 4.73 ($J \sim$ 3 and 12 cps) and no signal for any vinyl proton. These, and its IR spectrum are consistent with structure (III) or (IV) for the adduct.

C_{15}, C_{17}. The protons at these positions can exist in four different combinations viz. two *cis* forms with either α-H or β-H at both C_{15} and C_{17} and two *trans* forms, C_{15} α-H, $C_{17}\beta$-H or $C_{15}\beta$-H, C_{17} α-H. The C_{15}-H, as has been indicated before[1], is coupled with the vicinal C_{16}-CH_2 to a triplet ($J \sim 7$ cps) which is broadened by biallylic coupling[4,5] with the C_{13}-methyl and the C_{17}-H. Decoupling experiments on pyronimbic acid mesylate m.p. 200^{o} (chars), $(\alpha)_D$ +180^{o} (prepared by mesylating pyronimbic acid[1]), on a 100 Mc/s NMR Spectrometer show that the C_{17}-H is coupled with the two protons at C_{16} with $J \sim$ 7.5 and 1 cps. Models indicate that if the two protons at C_{15} and C_{17} are either α- or β-*cis*, the C_{17}-H would not make with either of the protons at C_{16} any dihedral angle which would justify a coupling constant of 1 cps (angle, around 90^{o}). The *cis* structures are therefore untenable. For the two possible *trans*-structures, the approximate dihedral angles measured on Dreiding models as well as the observed (by decoupling experiments) and calculated (according to the revised Karplus curve[6]) J values are given in Table I.

TABLE I

		J calc.	J obs.
15α-H/17β-H			
✗ 15α/16α	18°	~9	~7
15α/16β	138°	~9	~7
17β/16α	102°	~1	~1
17β/16β	18°	~9	~7.5
15β-H/17α-H			
✗ 15β/16α	150°	~12	~7
15β/16β	30°	~7	~7
17α/16α	18°	~9	~7.5
17α/16β	102°	~1	~1

Comparing the two possibilities it is fairly obvious that the first one, viz 15α-H/17β-H represents the correct stereochemistry, since only under such conditions the C_{15}-H can give rise to a triplet. (Since the calculated J values are based[6] on a cyclohexane system, smaller coupling constants have to be expected[7] in our cyclopentene system due to large C-C-H angles).

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