West African Timbers. Part XI. The Structure of Carapin, an Extractive from *Carapa procera*

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WE have isolated from *Carapa procera*[1] a substance, carapin, m.p. 175—178°, $[\alpha]_D^{25} = +64°$, which on chromatography over alumina gives compound B, now known to be (I).[2,3] Carapin and compound B are distinguished by thin-layer chromatography, and by the fact that compound B, but not carapin, gives compound C (II)[3] with methanolic sulphuric acid. On alkaline hydrolysis, both substances give compound D (III).[2,3] The structure of carapin is revealed by the n.m.r. spectrum, which shows a single proton singlet at δ 5·79, due to the α-proton on a double bond conjugated with an ester or lactone. We therefore consider carapin to be (IV), the conjugated isomer of compound B. This is

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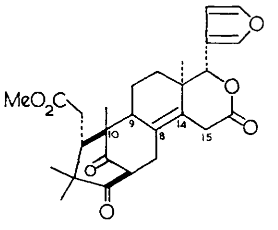
[1] C. W. L. Bevan, J. W. Powell, and D. A. H. Taylor, *J. Chem. Soc.*, 1963, 980.

[2] J. D. Conolly, R. McCrindle, and K. H. Overton, *Chem. Comm.*, 1965, 162.

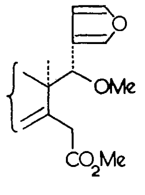
[3] C. W. L. Bevan, J. W. Powell, and D. A. H. Taylor, *Chem. Comm.*, 1965, 281.

supported by the u.v. spectrum of carapin, λ_{max} 213 mμ (ϵ16,000) [*c.f.* deoxykhivorin (V), λ_{max} 213 mμ (ϵ14,000).]

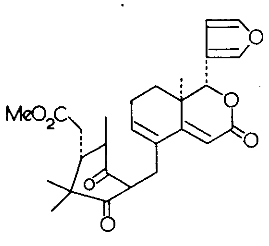
Conolly, McCrindle, and Overton[2] suggest that the first stage in the alkaline rearrangement of mexicanolide C(=Compound B, I) is isomerisation to the conjugated compound (IV), which loses a proton from C–8 giving a carbanion which rearranges to compound D. We find that the rearrangement of both compound B and carapin, followed spectrophotometrically, is bimolecular. The velocity constant for carapin agrees with that for the ionisation (or isomerisation) of a simple unsaturated ester,[4] but that for compound B is about 250 times faster.



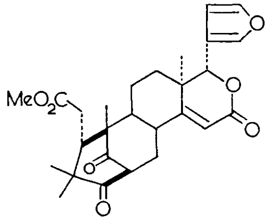
(I)



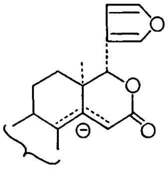
(II)



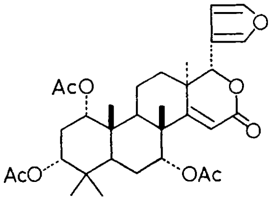
(III)



(IV)



(VI)



(V)

We would suggest that in the absence of a concerted reaction leading directly to compound D, the removal of a proton from C–8 (in IV) or C–15 (in compound B) would give the same mesomeric anion (VI) which might rearrange to compound D. The difference in rate for the enolisation of the isomers is likely to be small.[4,5] The comparatively large difference observed suggests that the fragmentation of compound B is a concerted reaction, and subject to what Grob has described as frangomeric acceleration.[6] Examination of models of both isomers of (IV) and of compound B shows that in all three the carbon chain involved in the fragmentation (C–8, 9, 10, 14, and 15) is antiperiplanar. In compound B the leaving hydrogen (at C–15) is favourably placed in the plane of the carbon chain, although *syn* and not *anti*, while in both isomers of (IV) the C–8 proton is unfavourably placed *syn* and out of the plane. We consider that the stereoelectronic configuration of compound B leads to a concerted, one-stage fragmentation to compound D, with the acceleration observed.

It remains to decide if the rearrangement of carapin proceeds by fragmentation of the ion (VI) or by isomerisation to compound B which then fragments. Compound C (II), where the lactone ring is opened, is stable to alkali. This agrees with the observation of Grob[6] that synchronous fragmentation does not occur in open chains, but only in rigid cyclic systems. Compound C will give a carbanion closely analogous to (VI), and the fact that this does not fragment shows that the rate of protonation is greater than the rate of the hypothetical fragmentation reaction. Similar considerations should apply to the ion (VI), and we therefore consider that compound B is an intermediate in the base-catalysed fragmentation of carapin.

That carapin isomerises to compound B on alumina, without further change, is due to the different mechanisms which may operate on a catalytic surface, and which are at present not well understood.

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[4] G. A. R. Kon and R. P. Linstead, *J. Chem. Soc.*, 1929, 1269.

[5] C. K. Ingold, "Structure and Mechanism in Inorganic Chemistry," Cornell University Press, 1953, p. 565.

[6] C. A. Grob and W. Schwarz, *Helv. Chim. Acta*, 1964, **47**, 1870.