Tetrahedron Letters No.55, pp. 4763-4764, 1970. Pergamon Press. Printed in Great Britain.

THE n → π* CD OF α-CAMPHOLIDE

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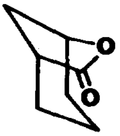
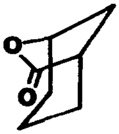
(Received in UK 19 October 1970; accepted for publication 28 October 1970)

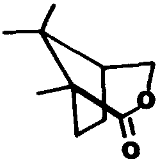
The correlation between the sign of the n → π* Cotton effect near 220 nm (1) and the chirality of the ring system incorporating the chromophore has been demonstrated for several lactone types (2,3) including the enantiomeric bridged-ring structures, I and II. No more than one CD band in this region for any lactone had been reported until the recent publication (4) of CD data from α-campholide, III, reproduced in Fig. 1. Our results for this compound are also shown in Fig. 1. We found that the ratio $\left|\frac{\Delta\varepsilon}{\varepsilon}\right|$, 0.017 in hexane, 0.010 in trifluoroethanol, taking account of the shift in position between UV and CD maxima, was constant in each solvent over a range of 20 nm through the CD peak. This is consistent with the CD and UV bands being manifestations of the same single electronic transition. The CD and UV behaviour of III is, thus, that of a normal lactone and we believe the results reported (4) to be in error.



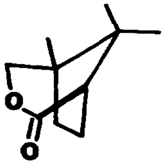
I -ve



II +ve



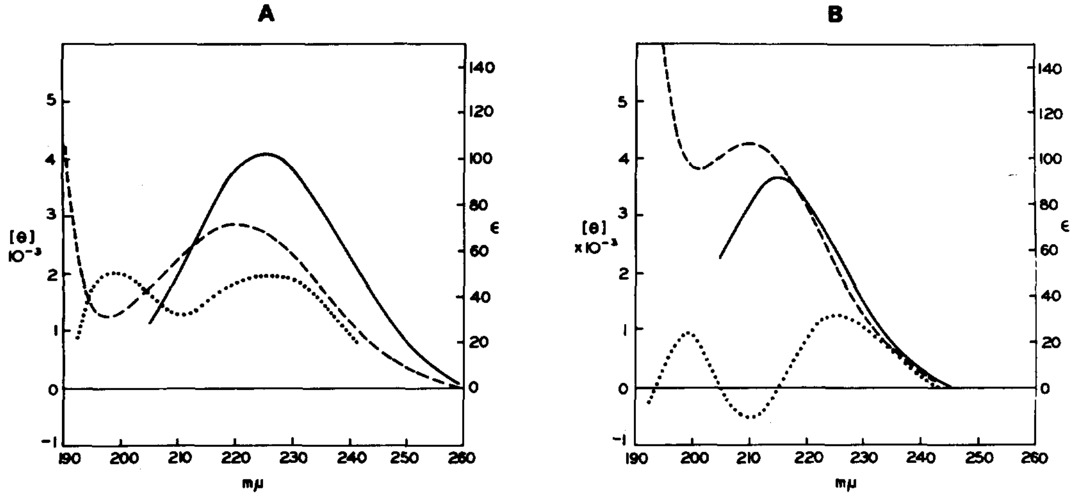
III



IV

III was prepared from (+)-camphor as previously described (5). The sample of ref. (4) was obtained from camphoric anhydride by a procedure (6) likely to produce both III and IV. The CD observed (4) could result from a mixture of two lactones of opposite chiralities (cf. a discussion of 6,8-thioctic acid) (7).

Figure 1



The CD of α-Campholide; A, in hexane; B, in TFE:

—— 0.01M, ---- UV, ···· CD from (4),

The absolute configuration of (+)-camphor and thus of III is known from X-ray studies (8). III would seem to be more closely analogous to I than to II but, since the n → π* CD of III is positive, it is evident that the analogy should not be drawn. We are currently engaged in an X-ray structure analysis of III in an attempt to define its exact molecular geometry.

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