

ALTERNATIVE STRUCTURES FOR PROPOSED DIMETHYLAMINOMETHANOL

ESTER-ALKALOIDS FROM *ERYTHROPHLEUM IVORENSE*

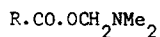
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The toxic alkaloids of *Erythrophleum* species have attracted the attention of chemists since 1876. In general, these compounds proved to be esters or amides of N-methylated ethanolamines with diterpene or cinnamic acids.^{1,2,3} A preliminary communication⁴ on new alkaloids from *E. ivorense* is of considerable interest because the proposed structures (1 and 2) are esters of the much less stable N,N-dimethylaminomethanol. It seems unlikely that alkaloids

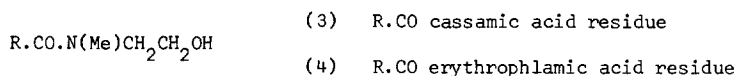


1. R.CO cassamic acid residue
2. R.CO erythrophlamic acid residue

with such structures would survive normal isolation procedures as simpler esters of N,N-dimethylaminomethanol are rapidly hydrolysed in cold water. Much of the evidence for the structures comes from a comparison of physical measurements with those of N,N-dimethylaminomethyl acetate. We therefore repeated the preparation of this ester by a method in the literature,⁵ but found its properties differ from those reported by Schultz and Hoenicke.⁴ They quote an ester carbonyl frequency of 1610 cm^{-1} and two dimethylamino signals in the p.m.r. spectrum at δ 3.00 p.p.m.; figures which are consistent with an amide structure and suggest that by some mischance their synthetic product was N,N-dimethylacetamide. Authentic N,N-dimethylaminomethyl acetate has a normal carbonyl band at 1710 cm^{-1} and the dimethylamino group signal is a six-proton singlet at δ 2.45. In addition there is a two-proton singlet at δ 4.97 due to the methylene group, apparently not observed for the natural alkaloids. These figures are at complete variance with data for the natural alkaloids and make structures 1 and 2 untenable.

We suggest that alkaloids a and b are amides of N-methylethanolamine and are

the known² compounds cassamide (3) and erythroplamide (4), respectively. In keeping with this,



the molecular formulae remain unchanged and the evidence for the diterpenoid portion of the molecules still holds. The carbonyl bands at 1610 cm^{-1} agree with the value for erythroplamide (4) measured in chloroform solution. The p.m.r. spectra of amides of N-methylethanolamine lack the two two-proton triplets at δ 2.56 and 4.18 observed in esters of N,N-dimethylethanolamine and exhibit a broad four-proton multiplet at δ 3.5 - 3.9. The six-proton signal of N,N-dimethylethanolamine esters at δ 2.25 is replaced by the amide N-methyl signals centred at δ 3.07 and other overlapping peaks including those from the hydroxyl protons. And we find that erythroplamide (4) and other amides of N-methylethanolamine have M-74 and M-75 peaks in their mass spectra corresponding to those from alkaloids a and b.

Recently cassamide and erythroplamide have been isolated from *E. ivorensis*². Erythroplamide has also been obtained from the bark of *E. chlorostachys*⁶; however, we have argued elsewhere³ that these amides are probably artefacts. We find that fresh extracts of *E. chlorostachys*, before treatment with alkali, contain only the corresponding amines. Amides, if present, are in such low concentrations as to be undetectable by p.m.r. spectroscopy.

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