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77 K Luminescence of Amylobarbitone

Sir: Miles and Schenk (*1*) and Harbaugh et al. (*2*) have reported that amylobarbitone (5-ethyl-5-isoamyl barbituric acid) exhibits phosphorescence at liquid nitrogen temperatures. According to the latter group (*2*), the phosphorescence intensity of amylobarbitone is greater than that of phenobarbitone (5-ethyl-5-phenyl barbituric acid) in a range of organic solvents, whereas Miles and Schenk (*1*) found that amylobarbitone had a phosphorescence emission equivalent to only 1% of its total luminescence intensity in base at 77 K.

In a comprehensive study of the luminescence properties of oxobarbiturates, Gifford et al. (*3*) found that, in basic media, amylobarbitone exhibited only a fluorescence emission at 77 K and that the fluorescence spectrum was similar to that of other 5,5-dialkyl oxobarbiturates. Furthermore, the fluorescence intensity of amylobarbitone at 77 K was roughly equal to the phosphorescence intensity of phenobarbitone at a similar concentration. In that study (*3*), phosphoroscope-can rotation speeds of over 10,000 rpm were available and thus any species with phosphorescence lifetimes of 1.5 msec would have been readily detectable.

Since the reported phosphorescence of amylobarbitone exhibits a maximum at a wavelength similar to that of its low temperature fluorescence, a problem arises in identifying the origin of this phosphorescence. (It may be noted that the phosphorescence of phenobarbitone occurs at a shorter wavelength than its fluorescence at room temperature and, indeed, shorter than the fluorescence of corresponding 5,5-dialkyl oxobarbiturates at 77 K. However, in this case, it has been shown that the phenyl group is phosphorescent and the heterocyclic ring is fluorescent (*3*)).

To resolve the nature of amylobarbitone luminescence at 77 K, a further investigation has been made using samples of amylobarbitone from several sources (May and Baker; Smith, Kline and French; Eli Lilly). Stock solutions of the free acids were prepared in absolute ethanol and diluted before use into ethanol, chloroform, and diethyl ether, to give solutions containing ca. 50 μg/ml. Measurements were made using a Perkin-Elmer MPF-2A spectrophotofluorimeter furnished with a phosphorescence accessory. The procedure was otherwise as described earlier (*3*).

When excited in the range 250–270 nm, none of the samples of amylobarbitone showed a luminescence spectrum which was significantly different from that of the pure solvent. In all three solvents, phenobarbitone exhibited an intense phosphorescence with a characteristic fine-structure.

These results, therefore, suggest that the reported phosphorescence of amylobarbitone is probably due to a trace impurity. Although an impurity phosphorescence may be useful in identifying a particular source of this drug, it is unlikely to have any value in the analysis of amylobarbitone extracted from biological tissues.

LITERATURE CITED

(1) C. I. Miles and G. H. Schenk, *Anal. Chem.*, **45**, 130 (1973).
(2) K. F. Harbaugh, C. M. O'Donnell, and J. D. Winefordner, *Anal. Chem.*, **46**, 1206 (1974).
(3) L. A. Gifford, W. P. Hayes, L. A. King, J. N. Miller, D. T. Burns, and J. W. Bridges, *Anal. Chem.*, **46**, 94, (1974).

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