Tetrahedron Letters No. 27, pp 2481 - 2482, 1973. Pergamon Press. Printed in Great Britain.

ISOLATION FROM THE HYPOBRANCHIAL GLANDS OF MARINE MOLLUSCS OF 6-BROMO-2, 2-DIMETHYLTHIOINDOLIN-3-ONE AND 6-BROMO-2-METHYLTHIOINDOLENINONE AS ALTERNATIVE PRECURSORS TO TYRIAN PURPLE.

J.T. Baker and C.C Duke

Department of Chemistry, James Cook University of North Queensland, Townsville, Queensland 4811, Australia.

(Received in UK 1 May 1973; accepted for publication 24 May 1973)

Studies on the precursors to Tyrian purple by Baker and Sutherland[1] led to the proposals[2] that during ether extraction of the hypobranchial glands of *Dicathais orbita* Gmelin and other gastropod molluscs, 6-bromo-2-methylthioindoleninone III was produced by the hydrolysis and oxidation of an absolute precursor, sodium tyrindoxyl sulphate (I). Aqueous ether extraction of fresh, frozen, or freeze-dried glands from *D.orbita* gave either a yellow or a red ether solution, from which, after passage over active or deactivated neutral alumina, followed by alumina t.l.c., III or 6-bromo-2,2-dimethylthioindolin-3-one IV were obtained as major products. T.l.c. and paper chromatography showed that these compounds were not present in an ethanol extract of the fresh, frozen, or freeze-dried glands. Alumina t.l.c. of the ether extract showed that IV was decomposing to III and that a purple-producing compound, possibly tyrindoxyl II, was being converted to IV. II was almost totally destroyed during preparative t.l.c. Using a trace of methanethiol in the thin layer chromatographic solvent prevented the formation of the red-coloured III and yields obtained for IV were increased to a level which indicated almost complete transformation of the absolute precursor to this compound.

Decomposition of IV in refluxing toluene[3] gave III plus methanethiol and reaction of III with diazomethane[4] gave spiro [6-bromo-2-methylthioindolenine]-3,2'-oxirane (55%) and 7-bromo-2-methylthio-3-methoxyquinoline (23%) as the major products. These compounds are identical with those reported by Baker and Sutherland[1] for the reaction of diazomethane with the ether extracts of *D.orbita*.

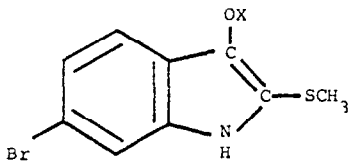
Ether extracts of the hypobranchial glands of the marine molluscs *Mancinella bufo* Lamarck, *Mancinella kenneri* Deshayes and *Mancinella distinguenda* Dunker and Zelebor were found to contain III and IV when examined by alumina t.l.c. Yellow crystals were isolated

from *M.bufo* and *M.keinerı* extracts and red crystals from *M dustınguenda* extracts by alumına t.l c. and found to have m p., t.l c and spectral behavıour ıdentıcal to IV and III respect ıvely

PHYSICAL MEASUREMENTS.

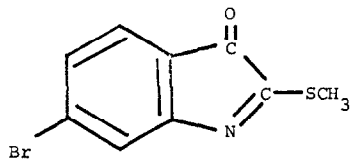
(III) C_9H_6BrNOS red needles m.p 109 5° M^+ (Br = 79) 255 p m.r. (CCl_4, δ) s, 2.60 (3H) $-SCH_3$ m. 7.3 (3H) aromatıc.

(IV) $C_{10}H_{10}BrNOS_2$. yellow needles m p. 117° M^+ (Br = 79) 303 (loses CH_3SH to $^m/_e$ 255) p.m r. ($CDCl_3$, δ) s, 2.20 [6H], $-SCH_3$ br.s. 5.45 (1H) -NH- m. 7.4 (3H) aromatıc

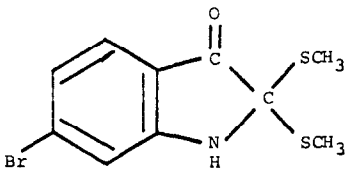


I X = $-SO_3^{\ominus}Na^{\oplus}$

II X = H



III



IV

REFERENCES

1. J.T. Baker and M.D Sutherland, Tetrahedron Letters, 1968, 43 [structure III corrected 1968 No. 26].
2. J.T. Baker, Ph.D. Thesıs, Unıversıty of Queensland, 1967
3. J T. Baker and C C. Duke, Aust. J. Chem 25, 2467, (1972).
4. J T. Baker and C C Duke, Tetrahedron Letters, 1972, 307.