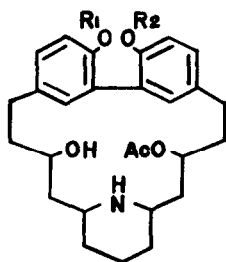


FURTHER EVIDENCE FOR THE NEW SKELETON OF  
LYTHRUM ALKALOIDS

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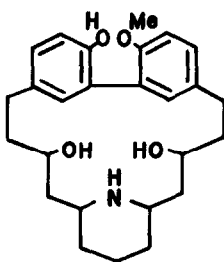
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In the previous communication<sup>2</sup>, we proposed the structures of lythranine (I), lythranidine(II), and lythramine(III) isolated from Lythrum anceps Makino. Now, we present unambiguous evidence for the new skeleton of these alkaloids.

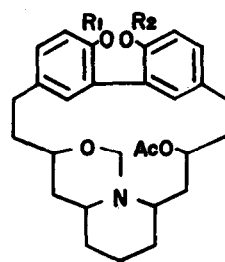


Lythranine I

$R_1=H, R_2=CH_3$  or  
 $R_1=CH_3, R_2=H$



Lythranidine II

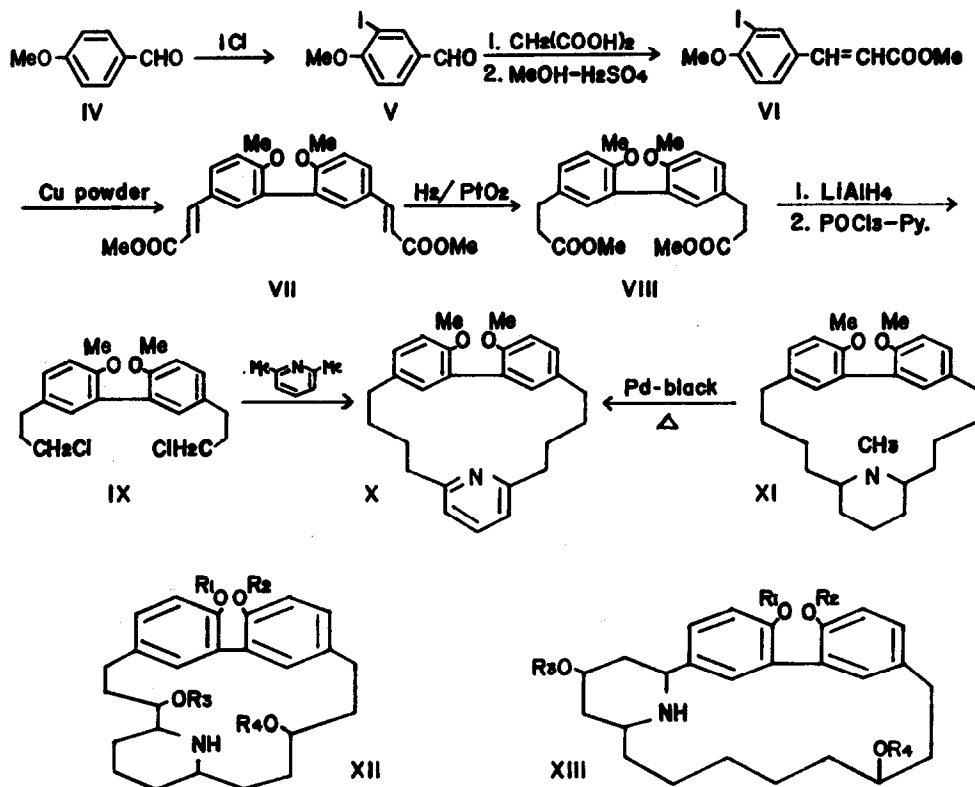


Lythramine III

$R_1=H, R_2=CH_3$  or  
 $R_1=CH_3, R_2=H$

O-Iodoanisaldehyde, m.p. 104-6°, prepared by iodination of anisaldehyde (IV) with iodine monochloride in acetic acid, was subjected to Perkin reaction with malonic acid followed by methylation with methanol and sulfuric acid to give only a trans isomer VI, m.p. 135-8°. Ullmann condensation of VI with copper powder afforded a biphenyl VII, m.p. 156-8°, in 60-70% yield. On catalytic hydrogenation in ethyl acetate under 20 atm. at 120°, VII gave VIII, m.p. 50.5-3°, which was converted into an oily dichloride IX by reduction with  $LiAlH_4$  in tetrahydrofuran followed by chlorination with phosphorus oxychloride and pyridine in 41% overall yield from VIII to IX. Compound IX was allowed to

react with 2,6-lutidine in liquid ammonia in the presence of potassium amide to give X, m.p. 154.5-6.5°.



On the other hand, bisdeoxy-O,N-dimethyllythranidine **XI**<sup>2</sup> derived from natural source, on dehydrogenation with Pd-black at 300°, yielded a pyridine derivative which was identified with the synthesized specimen X. Thus, the possibility of XII- or XIII-type structure for lythranine and lythranidine was completely excluded.

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#### REFERENCES

- <sup>1</sup> To whom correspondence should be addressed.
- <sup>2</sup> E. Fujita, K. Fuji, K. Bessho, A. Sumi, and S. Nakamura, Tetrahedron Letters, 4595 (1967).