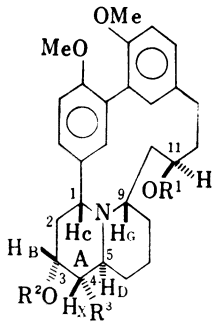
[Chem. Pharm. Bull. 19(7)1515—1516(1971)] UDC 547.94.02 : 581.192

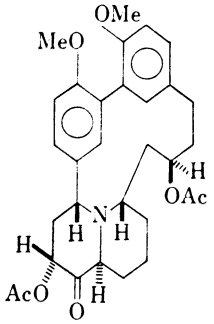
Absolute Configuration of Lythrancine-I, -II, -III, -IV, Lythrancepine-I, -II, and -III

Recently, seven new alkaloids shown in the title were isolated from *Lythrum anceps* MAKINO, and their structures were elucidated.[1] Now, their absolute configuration is discussed.

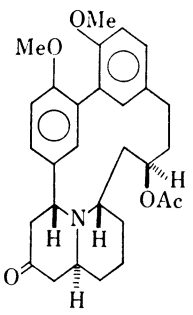
First of all, attention was paid to the nuclear magnetic resonance (NMR) spectrum of lythrancine-IV (IV), because of an effectiveness for the discussion of the stereochemistry of three (C-1, C-3, and C-4) of six asymmetric centers. The chemical shift of the proton Hc (δ 4.17) indicates that the quinolizidine ring junction is *cis* rather than *trans*.[2] The fact that



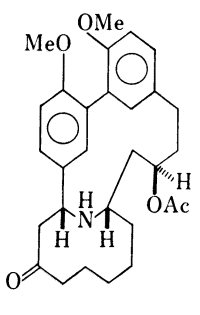
lythrancine-I (I) : R^1=H, R^2=H, R^3=OH
lythrancine-II (II) : R^1=Ac, R^2=H, R^3=OH
lythrancine-III (III) : R^1=Ac, R^2=Ac, R^3=OH
lythrancine-IV (IV) : R^1=Ac, R^2=Ac, R^3=OAc
lythrancepine-I (V) : R^1=H, R^2=H, R^3=H
lythrancepine-II (VI) : R^1=Ac, R^2=H, R^3=H
lythrancepine-III (VII) : R^1=Ac, R^2=Ac, R^3=H



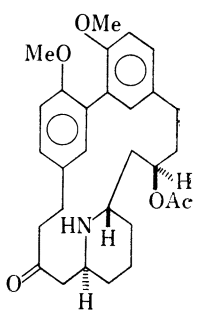
VIII



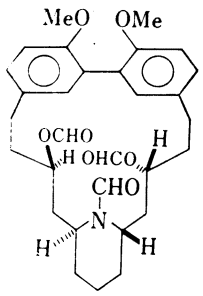
IX



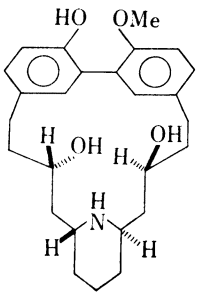
X



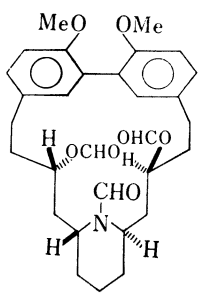
XI



XII



XIII



XIV

1) E. Fujita and Y. Saeki, *Chem. Commun.*, **1971**, 368.
2) F. Bohlmann, D. Shumann, and C. Arndt, *Tetrahedron Letters*, **1965**, 2705; J.P. Ferris, C.B. Boyce, and R.C. Briner, *ibid.*, **1966**, 3641.

the Bohlmann absorption band[3] was absent in its infrared (IR) spectrum also supported it. Under expectation that the *cis*-quinolizidine moiety exists in a chair-chair conformation in the molecule, the splitting with 11 and 4 H_Z of the H_C signal represents that it has an axial orientation. Moreover, an octet (J 3, 6, and 11.5 H_Z) at δ 5.15 (H_B) and a narrow triplet (J 3 H_Z) at δ 4.91 (H_X) show that these two hydrogens should have an axial and an equatorial orientation, respectively. This indicates a *cis*-relationship of two acetoxy groups on C-3 and C-4, and is consistent with the chemical evidence.[1]

Subsequently, an optical rotatory dispersion (ORD) spectrum of dehydrolythrancine-III (VIII)[1] was taken. It showed a negative Cotton effect at 312 mμ, which indicated the S configuration of C-5 *i.e.* α-H_D (equatorial C-H_D to the ring A) in the formula shown.

A *trans*-relationship between H_D and H_G is clear, since *trans*-2-carboxy-6-carboxymethyl hexahydropyridine[1] has been afforded on oxidation of lythrancine-II.

Consequently, the absolute configurations of five asymmetric centers were clarified; C-1: *R*, C-3: *R*, C-4: *S*, C-5: *S*, and C-9: *S* in lythrancine-I—-IV, and all the same except C-4 in lythrancepine-I—-III. The determination of the absolute configuration of the remaining asymmetric center C-11 and the final confirmation of the foregoing assignment was achieved by the following chemical conversions.

Jones' oxidation of lythrancepine-II (VI) gave an oxoproduct IX, mp 219—220°, $C_{29}H_{35}O_5N$, which was treated with silica gel, then was subjected to catalytic hydrogenation to give a mixture of products, from which the ketone X, mp 81—82°, $C_{29}H_{37}O_5N$ (NMR δ 3.80, dd, J 8 and 4 H_Z, C-1-H) and the desired ketone XI, mp 89—90°, $C_{29}H_{37}O_5N$, were isolated. The $LiAlH_4$ reduction of XI and subsequent formylation with acetic anhydride and formic acid afforded an O,O,N-triformate XII, mp 211—212°, $C_{30}H_{37}O_7N$, $[\alpha]_D$ +82°. This proved to be the antipode of compound XIV, mp 214—216°, $C_{30}H_{37}O_7N$, $[\alpha]_D$ −80°, derived from lythranidine (XIII), whose absolute configuration had been clarified.[4] Thus, the absolute stereochemistry of the seven bases was established as shown.

Institute for Chemical Research,
Kyoto University
Uji, Kyoto-fu, 611, Japan

EIICHI FUJITA
YUKIKAZU SAEKI

Received March 19, 1971

3) F. Bohlmann, *Chem. Ber.*, **91**, 2157 (1958).
4) E. Fujita and K. Fuji, *J. Chem. Soc.* (*C*), **1971**, 1651.

[Chem. Pharm. Bull. 19(7)1516—1518(1971)]

UDC 547.269.3.09 : 615.35.076.7

Mechanism of Utilization of Pantetheine-S-Sulfonic Acid by *Bifidobacterium bifidum*

4′-Phosphopantetheine-S-sulfonic acid (P-PaSSO_3H) and 3′-dephospho-coenzyme A-S-sulfonic acid (DP-Co$ASSO_3H$) were isolated from carrot root as growth factors for *Bifidobacterium bifidum* N4 by Yoshioka, *et al.*[1,2] They described that these new type of compounds

1) M. Yoshioka and Z. Tamura, *Chem. Pharm. Bull.* (Tokyo), **19**, 178 (1971).
2) M. Yoshioka and Z. Tamura, *Chem. Pharm. Bull.* (Tokyo), **19**, 186 (1971).