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## Lythraceous Alkaloids. X.1) Alkaloids of Lagerstroemia subcostata and L. favriei: A Contribution to the Chemotaxonomy

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The basic components of Lagerstroemia subcostata collected on Amami-ohshima Island and two slightly different types of Lagerstroemia fauriei collected on Tanegashima Island were investigated. We distinguished the two types by calling them L. fauriei and L. fauriei (Tanegashima-type). Four new alkaloids, lasubine-I (12), -II (14), subcosine-I (15), and -II (16), all of which belong to type E, were isolated from the former. From the latter two, however, lythrine (3), cryogenine (17), and lythridine (18), all of which belong to type C, were isolated.

L. fauriei has been classified as L. subcostata var. fauriei by S. Hatusima, but from the chemotaxonomical aspect, it shows prominent differences from L. subcostata. Thus their classification under species would be more appropriate.

Keywords—alkaloid; structure elucidation; phenyl quinolizidine; chemotaxonomy; Lythraceae; Lagerstroemia subcostata; Lagerstroemia fauriei

Lagerstroemia subcostata Koehne (Japanese name: Shima-sarusuberi) is widely distributed in the Amami Islands,<sup>3,4)</sup> Taiwan,<sup>5,6)</sup> and the central region of China<sup>7)</sup> (Kwangtung, Honan, Anhwei, Kiangsi, and Chekiang). On the other hand, L. fauriei Koehne (Syn.=L. subcostata Koehne var. fauriei (Koehne) Hatusma) (Japanese name: Yakushima-sarusuberi) is endemic in islands of Yakushima and Tanegashima.<sup>3,4,8)</sup>

The Lagerstroemia plants we collected on Tanegashima Island in June, 1975 consisted of a species (A) which was identified with L. fauriei and another species (B), the leaves of which were slightly different in the character from A but very different from L. subcostata Koehne collected on Amami-ohshima Island in June, 1976. Since the perfect samples of flowers and fruit of the latter (B) have not been available, the determination of the species is not possible. On the basis of the form of the leaves and our findings on the alkaloid components which are described below, however, this plant is represented as L. fauriei (Tanegashima Type) in this paper. Hatusima, who specializes on the plants in Yakushima, Tanegashima and the Ryukyu Islands, named it L. subcostata var. fauriei, but it would be more rational to name it as the independent species because of the chemotaxonomical evidence shown in this paper.

<sup>1)</sup> Part IX: E. Fujita and Y. Saeki, J. C. S. Perkin I, 1973, 306.

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<sup>3)</sup> S. Hatusima, "Flora of the Ryukyu," Okinawa Seibutsu Kyoiku Kenkyu Kai, Naha 1975, p. 427.

<sup>4)</sup> S. Hatusima, "Woody Plants in Japan," Kodan-sha, Tokyo, 1976, p. 508.

<sup>5)</sup> Tseng-Chieng Huang, "Flora of Taiwan," Vol. 3, Epoch Publishing Co., Ltd., Taipei, Taiwan, 1977, pp. 817—819.

<sup>6)</sup> Hui-Lin Li, "Woody Flora of Taiwan," Livingston Publishing Co., Narberth, Pennsylvania, U.S.A., 1963, pp. 626—628.

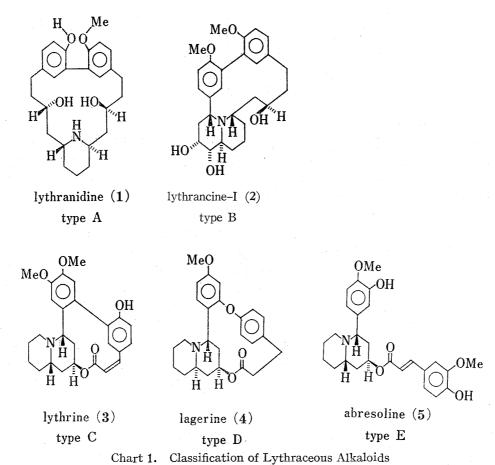
<sup>7) &</sup>quot;Iconographia Cormophytorum Sinicorum," Vol. 2, ed. by Instituti Botanici Academiae Sinicae, Hua Hsuae Shu Pan She, Peking China, 1972, p. 973.

<sup>8)</sup> S. Kitamura and G. Murata, "Coloured Illustrations of Woody Plants of Japan," Vol. 1, Hoiku-sha, Tokyo, 1971, p. 208.

<sup>9)</sup> We reported orally this plant regarding as *L. subcostata* on 31st October 1976 at the 26th annual meeting of the Kinki Branch of the Pharmaceutical Society, but now we revise it as described here.

Many botanists<sup>10–13)</sup> describe the distribution of L. subcostata (Shima-sarusuberi) and the non-distribution of L. fauriei (Yakushima-sarusuberi) on Tanegashima Island. On the other hand, Hatusima<sup>4)</sup> describes the distribution of only the latter in Tanegashima Island, and Kitamura<sup>6)</sup> does the presence of both of the species there. We were not able to find L. subcostata in Tanegashima Island, and furthermore two species collected on Tanegashima Island were found to be very similar in their alkaloid components as mentioned below. Thus, the botanical description of "the natural growth of L. subcostata on Tanegashima Island" needs to be reinvestigated.

In the last decade a number of alkaloids have been isolated from the Lythraceous plants and their structures determined by X-ray analyses and/or chemical degradations.<sup>14)</sup> Those alkaloids are classified based on their structures into five groups, *i. e.* types A—E. The representative alkaloid of each type is shown in Chart 1. The alkaloids of types A and B had been isolated only from *Lythrum anceps* Makino by our group,<sup>1,15)</sup> and they had occupied a unique position in the Lythraceous alkaloids. Recently, however, lythrumine (6) and acetyllythrumine (7) of type B were isolated together with decinine (8) of type C from *Lythrum lanceolatum* by Ferris' school,<sup>16)</sup> and taxonomical grouping of *Lythrum* together with *Decodon*,



10) J. Ohwi, "Flora of Japan," Shibun-do, Tokyo, 1972, p. 938.

13) T. Makino and K. Nemoto, "Flora of Japan," Shunyo-do, Tokyo, 1931, p. 792.

16) H. Wright, J. Clardy, and J.P. Ferris, J. Am. Chem. Soc., 95, 6467 (1973).

<sup>11)</sup> S. Okamoto, "Coloured Illustrations of Trees and Shrubs of Japan," Hoiku-sha, Tokyo, 1959, p. 618.

<sup>12)</sup> T. Terasaki, "Terasaki's Illustrated Flora of Japan," Kodan-sha, Tokyo, 1977, p. 517.

<sup>14)</sup> For a recent review, see E. Fujita, and K. Fuji, "International Review of Science, Organic Chemistry Series Two," Vol. 9, ed. by K. Wiesner, Butterworths, London, 1976, pp. 119—159.

<sup>15)</sup> E. Fujita and K. Fuji, J. Chem. Soc. (C), 1971, 1651; E. Fujita, K. Bessho, Y. Saeki, M. Ochiai, and K. Fuji, Lloydia, 34, 306 (1971); E. Fujita and Y. Saeki, J. C. S. Perkin I, 1972, 2141; 1973, 297; E. Fujita, Farumashia, 9, 599 (1973).

$$\begin{array}{c} \text{MeO} \\ \text{HO} \\ \text{HO} \\ \text{RO} \\ \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \\ \text{OMe} \\ \text{OMe} \\ \text{OH} \\ \text{OH} \\ \text{H} \\ \text{H} \\ \text{OH} \\ \text{OH} \\ \text{H} \\ \text{H} \\ \text{OH} \\ \text{OH$$

Heimia, and Lagerstroemia was supported. Furthermore, it was suggested that all of these structural types of Lythraceous alkaloids have a common biosynthesis. Lagerstroemia indica L. is only one species in the genus Lagerstroemia which has been investigated on alkaloids. It has been reported to contain only alkaloids of types C and D. Now, we wish to report the new results which were obtained in the investigation on Lagerstroemia species growing on Amami-ohshima and Tanegashima Islands.

From the methanol extract of the leaves of L. subcostata collected before flowering on Amami-ohshima Island, four new alkaloids, lasubine-I, -II, subcosine-I and -II were isolated. All alkaloids except lasubine-I were oily. Lasubine-I,  $C_{17}H_{25}NO_3$ , mp 120.5—122°,  $[\alpha]_{23}^{25}-8.8$ °, was suggested to have the hydroxyl groups and an aromatic ring in the molecule by spectroscopic investigation. Its mass spectrum showed a strong fragment ion at m/e 136 which was attributed to ion 9. Thus the presence of a quinolizine ring was assumed. The proton nuclear magnetic resonance (NMR) spectrum supported two methoxyl groups on an aromatic ring (Table I). Lasubine-I was thus regarded as a phenylquinolizidine derivative. The <sup>13</sup>C NMR spectrum clarified the substitution pattern of the methoxyl groups on the benzene ring. The comparisons of the observed chemical shift data for lasubine-I with

Table I. NMR Spectra of the Alkaloids Isolated from L. subcostata

		Chemica	al shift (ppm fr	om TMS)	
Alkaloid	-OCH <sub>3</sub>	C-4-H	C-2-H	Aromatic	H > C = C < H
Lasubine-I (12)	3.88(3H, s) 3.87(3H, s)	4.10(m)a)	4.10(m)b)	6.86(2H, s) 6.83(1H, s)	
Lasubine-II (14)	3.88(3H, s)	3.33 (dd, $J=5.6$ , 9.5 Hz)	4.14(m) W1/2=8 Hz	6.92(1H, s)	
Subcosine-I (15)	3.91(6H, s)			7.27—6.78	7.62(d, $J = 16 \text{ Hz}$ ) 6.31(d, $J = 16 \text{ Hz}$ )
Subcosine-II (16)	3.95(3H, s) 3.92(3H, s) 3.89(3H, s) 3.86(3H, s)	3.22(m) $W1/2 = 24$ Hz	5.21(m) $W1/2 = 12 Hz$		7.68(d, $J = 15.9 \text{ Hz}$ 6.40(d, $J = 15.9 \text{ Hz}$
Abresoline (5)¢)	3.95(3H, s)	3.22 (dd, $J=10$ , 1 Hz)	5.18(m) W1/2=8 Hz	7.02(6H, m)	7.63(d, $J = 18 \text{ Hz})$ 6.36(d, $J = 18 \text{ Hz})$

a) Unresolved from C-2-H.

b) Unresolved from C-4-H.

c) From reference 20.

<sup>17)</sup> J.P. Ferris, R.C. Briner, and C.B. Boyce, *J. Am. Chem. Soc.*, 93, 2958 (1971); M. Hanaoka, H. Sassa, N. Ogawa, Y. Arata, and J.P. Ferris, *Tetrahedron Lett.*, 1974, 2533.

the data calculated for the possible six substitution patterns of dimethoxybenzylamine using parameters for benzylamine<sup>18)</sup> and dimethoxybenzenes<sup>19)</sup> led to a good coincidence between the alkaloid and 3,4-dimethoxybenzylamine as shown in Table II. In the proton NMR spectrum of lasubine-I, a proton signal appeared at  $\delta$  4.10, which was assigned to a hydrogen on a carbon atom between the aromatic ring and the nitrogen atom. Hence, the aromatic ring must be on the 4-carbon atom of the quinolizine ring. On the basis of the known structures for Lythraceous alkaloids, the hydroxyl group was reasonably attached to the 2-carbon atom. Thus, the structure (10)(2-hydroxy-4-3',4'-dimethoxyphenylquinolizidine)was assigned to lasubine-I.

Table II. 13C NMR Data of Aromatic Carbons of Lasubine-I

Compound	Chemical shift (ppm from TMS)			
Compound	$(\underline{C}-OMe) \times 2$ $\underline{C}-CH-N$		(C-H) × 3	
Lasubine-I (12) MeO	148.6, 147.7	135.5	120.5, 111.8, 110.6	
$MeO CH_2NH_2$ (Calcd.)	149.0, 147.2	135.8	119.3, 111.4, 110.0	

Schwarting et al. have synthesized many 2-hydroxy-4-phenyl-quinolizidine derivatives, in order to clarify the structures of alkaloids 11 and  $12^{20}$ ) synthetically. In the proton NMR spectra in CDCl<sub>3</sub>, the C-4 protons in compound 11 and its derivatives, all of which had a cis-quinolizidine ring, were observed at  $\delta$  4.00—4.20. On the other hand, in the trans-quinolizidine ring system i.e. compound 13 and its derivatives, they were observed at  $\delta$  3.00—3.25.<sup>21)</sup> In lasubine-I, it appeared at  $\delta$  4.10, hence this alkaloid was assumed to have a cis-quinolizidine ring. This assumption was confirmed by its identification with the product 12 prepared from the synthetic sample 11 kindly sent from Professor Schwarting by methylation with diazomethane through the comparison of their NMR and infrared (IR) spectra (in CHCl<sub>3</sub>). Lasubine-I is thus proved to have the structure, 2-hydroxy-trans-4-3',4'-dimethoxyphenyl-cis-quinolizidine (12).

L.F. Johnson and W.C. Jankowski, "Carbon-13 NMR Spectra," John Wiley and Sons Inc. New York, N.Y. 1972, spectrum number 251.

<sup>19)</sup> Chemical shifts in CS<sub>2</sub> described in the following reference were used for *m*-dimethoxybenzene, since no solvent effect on chemical shifts of *o*- and *p*-dimethoxybenzene in CDCl<sub>3</sub> and CS<sub>2</sub> was observed. P.C. Lauterbur, J. Am. Chem. Soc., 83, 1846 (1961).

<sup>20)</sup> The stereochemistry of the structural formulae, 11—16, represents the relative one.

<sup>21)</sup> A. Rother and A.E. Schwarting, Lloydia, 38, 477 (1975).

Lasubine-II,  $[\alpha]_{\mathbf{D}}^{23}$  —34.7°, was shown to have the same molecular formula as lasubine-I  $(C_{17}H_{25}NO_3)$ , and the comparisons of their spectroscopic data with each other led to an assumption that lasubine-II may be 2-hydroxy-trans-4-3',4'-dimethoxyphenyl-trans-quinolizidine (14). The structure was confirmed to be correct by its identification with the product 14 derived from the authentic sample 13 by methylation.

Subcosine-I,  $C_{28}H_{35}NO_6$ ,  $[\alpha]_D^{22}+68.0^\circ$ , showed also a strong fragment ion at m/e 136 in its mass spectrum, which suggested the presence of a quinolizidine ring in the molecule. The proton NMR spectrum suggested four methoxyl groups on the aromatic rings. Multiplet signals at  $\delta$  4.07 and 5.30 were observed for each one proton, which suggested an esterified lasubine structure. In fact, subcosine-I on alkaline hydrolysis gave lasubine-I (12) and 3,4-dimethoxycinnamic acid, which clarified the structure of the alkaloid to be formulated as 15.

Subcosine-II,  $[\alpha]_D^{23}$  +85.3°, has the same molecular formula as subcosine-I, and the comparison of its several spectroscopic data with those of subcosine-I (15) and abresoline (5)<sup>22)</sup> led to assignment of structure 16 to this alkaloid. This structure was confirmed by the hydrolysis of the alkaloid into lasubine-II (14) and 3,4-dimethoxycinnamic acid.

Subsequently, we isolated the known lythrine  $(3)^{23}$  and cryogenine  $(17)^{24}$  from L. fauriei Koehne growing on Tanegashima Island. Furthermore, we isolated lythridne  $(18)^{22}$  in addition to these two alkaloids from L. fauriei Koehne (Tanegashima Type). Thus only type C alkaloids were found from Lagerstroemia species on Tanegashima Island.

The mass spectra of all of the alkaloids isolated this time showed such strong molecular ion peaks as possible for determination of M<sup>+</sup> even in the crude bases. Thus the types of the alkaloids (e.g. C or E) were easily known by the measurements of the mass spectra in the crude base and every step of fractionations. The detailed investigation with the mass spectrometry showed absence of type C lactonic alkaloids in L. subcostata from Amamiohshima Island and of type E alkaloids in L. fauriei from Tanegashima Island. Type E alkaloids, except for abresoline (5), have been isolated only from about 10-day-old seedlings of Heimia salicifolia, and they disappeared with their growing and instead only type C alkaloids were detected. Hence type E alkaloids have been regarded as the precursor of type C alkaloids. Oxygenation pattern of the biphenyl group and co-occurence of types C and D alkaloids in the same plant species suggested the formation of the biphenyl linkage by the oxidative coupling. Lasubine-I (12), -II (14), subcosine-I (15), and -II (16) have

<sup>22)</sup> R.B. Hörhammer, A.E. Schwarting, and J.M. Edwards, J. Org. Chem., 40, 656 (1975).

<sup>23)</sup> R.M. Blomster, A.E. Schwarting, and J.M. Bobbitt, Lloydia, 27, 15 (1964).

<sup>24)</sup> B. Douglas, J.L. Kirkpatrick, R.F. Raffauf, O. Ribeiro, and J.A. Weisbach, Lloydia, 27, 25 (1964).

<sup>25)</sup> A. Rother and A.E. Schwarting, *Experientia*, 30, 222 (1974); R.H. Dobberstein, J.M. Edwards, and A.E. Schwarting, *Phytochemistry*, 14, 1769 (1975).

<sup>26)</sup> J.P. Ferris, C.B. Boyce, and R.C. Briner, Tetrahedron Lett., 1966, 5129; A. Rother and A.E. Schwarting, Chem. Commun., 1969, 1411; S.H. Koo, F. Comer, and I.D. Spenser, Chem. Commun., 1970, 897; A. Rother and A.E. Schwarting, Phytochemistry, 11, 2475 (1972).

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all methylated O-functions on their aromatic rings and the possibility of their partial demethylation followed by oxidative coupling to give type C alkaloids seems low. They are probably the final biosynthetic products.

## Experimental

Melting points were taken on a micro hot-stage and are uncorrected. Ultraviolet (UV) spectra were run on Hitachi EPI-S<sub>2</sub> spectrophotometer and IR spectra on Hitachi EPS-3 spectrophotometer. Rotations were measured on JASCO DIP-180 automatic polarimeter. Proton and <sup>13</sup>C NMR spectra were taken with JEOL JNM-FX 100 spectrometer at 100 MHz and 25 MHz. Chemical shifts were given in  $\delta$  (ppm) scale with tetramethylsilane (TMS) as the internal standard. Mass spectra were determined on JEOL JMS-OISG double-focusing mass spectrometer. Silica gel G nach stahl (Merck) was used for both thin–layer (TLC) and column chromatography. Aluminium oxide G 150F 254 (Type E) (Merck) and aluminium oxide (Type E) (Merck) were used for TLC and column chromatography, respectively.

Isolation and Characterization of Lasubine-I, Lasubine-II, Subcosine-I, and Subcosine-II-----Dried leaves (20 kg) of L. subcostata collected on Amami-ohshima Island on June 18, 1976 were repeatedly extracted with methanol. The solvent was evaporated off to leave a muddy residue (6 kg), to which 5% HCl (2 l) was added. After standing for one day, the muddy solution was filtered. The extraction of the filtered solid with 5%HCl (21) was repeated three times. The acidic solution was washed with ether, made alkaline with aq. ammonia, and extracted with dichloromethane. The extract was washed with water, dried over sodium sulfate, and concentrated to dryness to yield an amorphous solid (12 g; 0.06% yield), which, dissolved in dichloromethane, was chromatographed on a silica gel column (CH<sub>2</sub>Cl<sub>2</sub>) to separate fractions 1—30 by checking on TLC. Fractions 25-30 were combined and chromatographed on neutral alumina by eluting with chloroform. The combined fractions 3—7 (701 mg) were crystallized from ethyl acetate to give lasubine-I (12), mp 117.0—118.5° (500 mg). An analytical sample was prepared by recrystallization from ethyl acetate: mp 120.5—122.0°,  $[\alpha]_D^{22}$  -8.8° (c=0.34, methanol). IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup>: 3510, 2940, and 1517. UV  $\lambda_{\max}^{\text{methanol}}$  nm (log  $\varepsilon$ ): 279.5 (3.5). <sup>1</sup>H NMR: See Table I. <sup>13</sup>C NMR  $\delta$ : (cf. formula 10) 148.58 (s, 3'-C), 147.65 (s, 4'-C), 135.47 (s, 1'-C), 120.46 (d, 6'-C), 111.83 (d, 5'-C), 110.62 (d, 2'-C), 64.96, 62.03 (each d, 2 or 4-C), 55.89, 55.80 (each q, 10 or 11-C), 53.85 (d, 9-C), 51.17 (t, 5-C), 40.35, 40.10 (each t, 1 or 3-C), 32.50 (t, 8-C), and 24.61, 24.02 (each t, 6 or 7-C). Anal. Calcd. for  $C_{17}H_{25}NO_3$ : C, 70.07; H, 8.65; N, 4.81; M, 291.183. Found: C, 70.07; H, 8.84; N, 4.62; M+, 291.184. Fractions 12-21 of the first column chromatography were combined and chromatographed on neutral alumina (benzene-methanol, 10:1) to isolate lasubine II (14) (576 mg) and subcosine-I (15) (65 mg). Lasubine-II (14):  $[\alpha]_D^{23} - 34.7^{\circ}$  (c = 0.32, methanol). IR  $v_{\text{max}}^{\text{CHCl}_3}$  cm<sup>-1</sup>: 3510, 2930, and 1517. UV  $\lambda_{\max}^{\text{methanol}}$  nm (log  $\varepsilon$ ): 279.5 (3.6). <sup>1</sup>H NMR: See Table I. Anal. Calcd. for  $C_{17}H_{25}NO_3$ : 291.183 (M). Found: 291.179 (M<sup>+</sup>). Subcosine-I (15):  $[\alpha]_{\rm D}^{23}$  +68.0° (c=0.20, methanol). IR  $\nu_{\rm max}^{\rm cHOl_3}$  cm<sup>-1</sup>: 2930, 1705, and 1505. UV  $\lambda_{max}^{methanol}$  nm (log  $\varepsilon$ ): 232.5 (4.7), 287.5 (4.1), and 323.5 (4.2). Anal. Calcd. for C<sub>28</sub>H<sub>35</sub>NO<sub>6</sub>: 481.246 (M). Found: 481.245 (M+). Fractions 10—11 of the first column chromatography were combined and subjected to the second column chromatography on neutral alumina (eluted with benzeneethyl acetate, 10:1) to separate subcosine-II (16) (50 mg),  $[\alpha]_{\rm D}^{23}$  +85.3° (c=0.64, methanol). IR  $\nu_{\rm max}^{\rm cHGl_3}$  cm<sup>-1</sup>: 2930, 1705, and 1505. UV  $\lambda_{\max}^{\text{methanol}}$  nm (log  $\varepsilon$ ): 232.5 (4.3), 287.0 (4.1), and 323.0 (4.2). Anal. Calcd. for  $C_{28}H_{35}$ -NO<sub>6</sub>: 481.246 (M). Found: 481.245 (M<sup>+</sup>).

Methylation of Compounds 11 and 13—Compounds 11 (8 mg), dissolved in methanol (2 ml), was treated with diazomethane in ether to yield methyl ether 12 (8.3 mg), the IR (in chloroform), <sup>1</sup>H NMR, and Rf value on TLC of which were shown to be identical with those of lasubine-I. Similarly, compound 13 (14 mg) was methylated by diazomethane to give methyl ether 14 (14.5 mg), which was shown to be identical with lasubine-II.

Hydrolysis of Subcosine-I (15) to Lasubine-I (12)—To a solution of subcosine-I (15) (24 mg) in methanol (5 ml) was added aq. 2 n NaOH (5 ml). After warming at 80° for 10 minutes, the reaction mixture was acidified with 10% HCl and extracted with ethyl acetate. Evaporation of the solvent gave 3,4-dimethoxy-cinnamic acid, mp 180—182° (from benzene) (7 mg), which was proved to be identical with the authentic sample synthesized. The acidic layer was made alkaline with NH<sub>4</sub>OH and extracted with chloroform. Usual work-up gave a crystalline material, which was recrystallized from ethyl acetate to give lasubine-I, mp 120—121° (12 mg).

Hydrolysis of Subcosine-II (16) to Lasubine-II (14)—The same treatment of subcosine-II (16) (24 mg) as above yielded lasubine-II (14) (12 mg) and 3,4-dimethoxy-cinnamic acid (7 mg).

Isolation of Lythrine and Cryogenine from Lagerstroemia fauriei—Dried leaves (7 kg) of L. fauriei collected on Tanegashima Island on June 15, 1975 were extracted with methanol. The extract gave a crude alkaloid mixture (7.2 g, 0.10% yield) through the similar procedure as described above. The crude alkaloid mixture was crystallized as pale yellow substance (1.3 g) from chloroform. This crystalline material was recrystallized from chloroform to give cryogenine (17), mp  $240-250^{\circ}$  (927 mg). An analytical sample, mp  $250-252^{\circ}$ , (lit.24) mp  $250-251^{\circ}$ ) was prepared by further recrystallization from methanol. IR  $v_{\rm max}^{\rm KBT}$  cm<sup>-1</sup>: 3500 and 1720. UV  $\lambda_{\rm max}^{\rm methanol}$  nm (log  $\varepsilon$ ): 260.0 (4.1) and 285.0 (4.2). Anal. Calcd. for  $C_{26}H_{29}NO_5$ : C,

71.70; H, 6.71; N, 3.22; M, 435.205. Found: C, 71.60; H, 6.98; N, 3.23; M<sup>+</sup>, 435.205. Its identity with the authentic sample was confirmed by their direct comparison.

The filtrate from the foregoing pale yellow substance was evaporated to leave a residue (5.9 g), which was chromatographed on silica gel under elution with dichloromethane to give a pale yellow crystalline material (1.9 g). Its recrystallization from methanol gave lythrine (3), mp 240—242°. An analytical sample prepared by recrystallization from methanol gave mp 243—245°, (lit.<sup>23</sup>) mp 241—243°). IR  $r_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>: 3450 and 1680. UV  $\lambda_{\text{max}}^{\text{methanol}}$  nm (log  $\varepsilon$ ): 261.0 (4.1) and 284.0 (4.2). Anal. Calcd. for  $C_{2\varepsilon}H_{29}NO_5$ : C, 71.70; H, 6.71; N, 3.22; M, 435.205. Found: C, 71.01; H, 6.91; N, 3.21; M<sup>+</sup>, 435.205. Its identity with the authentic sample was confirmed by their direct comparison.

Isolation of Lythrine, Cryogenine, and Lythridine from Lagerstroemia fauriei (Tanegashima type)——Dried leaves (2.4 kg) of L. fauriei (Tanegashima type) collected on Tanegashima Island on June 15, 1975 were extracted with methanol. The extract on similar treatment as above gave a crude crystalline alkaloid mixture (23 g, 1.0% yield). Recrystallization from dichloromethane gave pale yellow crystals (9.7 g), which were purified by the successive recrystallization from chloroform and methanol to afford pure cryogenine (17), mp 251—253°. The alkaloid and its O-methyl ether, mp 225—228°, prepared by diazomethane were shown to be identical with the authentic samples by their direct comparisons. The filtrate from the foregoing pale yellow crystals was evaporated to leave a crystalline residue (5.1 g), which was purified to yield pure lythrine (3), mp 243—245°. The alkaloid and its O-methyl ether, mp 240—242°, were shown to be identical with their authentic samples by their direct comparisons.

The mother liquor from recrystallization of crude cryogenine from chloroform on evaporation left a crystalline residue (15.28 g), which was subjected to chromatography on silica gel column under elution with dichloromethane to give lythridine (18), mp 210—215° (from ethyl acetate) (1.03 g). An analytical sample, mp 217—218° (lit.²³) mp 217.5—219°) was prepared by further recrystallization from ethyl acetate. IR  $r_{\rm max}^{\rm RBr}$  cm<sup>-1</sup>: 3500 and 1705. UV  $\lambda_{\rm max}^{\rm methanol}$  nm (log  $\varepsilon$ ): 292.0 (3.9). Anal. Calcd. for  $C_{26}H_{31}NO_6$ : C, 68.55; H, 7.30; N, 3.08; M, 453.215. Found: C, 68.44; H, 7.52; N, 3.07; M<sup>+</sup>, 453.219. The alkaloid was shown to be identical with the authentic sample of lythridine by their direct comparison.

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