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Total Syntheses of the Lycopodium Alkaloids (±)-Fawcettimine and (±)-8-Deoxyserratinine

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Total syntheses of (±)-fawcettimine (**1**) and (±)-8-deoxyserratinine (**3**) have been accomplished. Selective hydrogenation of the conjugated nitrile (**6**) over $(Ph_3P)_3RhCl$, followed by reduction with $LiAlH_4$ and treatment of the product with N_3CO_2–*tert*-Bu yielded the carbamate (**8**). Successive treatment of **8** with Na–liquid NH_3, the Jones reagent, N-hydroxysuccinimide–DCC, CF_3CO_2H, and *n*-Bu_3N in CH_3CN afforded the nine-membered lactam (**18**). Reduction of **18** with $LiBH_4$ gave the epimeric alcohols, **22** and **23**. Both **22** and **23** were converted into the same ketone (**28**) *via* the same sequence of reactions; reduction with $LiAlH_4$, acylation with $(CF_3CO)_2O$–pyridine, selective hydrolysis with 0.2 N KOH–MeOH, and Jones oxidation. Epoxidation of **28** gave the epimeric epoxides, **29** and **30**. The epoxide (**29**) was successively treated with $BF_3 \cdot Et_2O$, the Jones reagent, H_2-5% Pd/C, and 1 N KOH–MeOH to provide (±)-fawcettimine (**1**). The other epoxide (**30**) was converted into (±)-8-deoxyserratinine (**3**) by successive treatments with 1 N KOH–MeOH, the Jones reagent, and $NaBH_4$.

Keywords——lycopodium alkaloid; fawcettimine; 8-deoxyserratinine; nine-membered lactam; activated ester; intramolecular transacylation; high dilution method

In connection with synthetic studies of the 8-deoxyserratinine type alkaloids, such as fawcettimine (**1**),[2)] alopecuridine (**2**),[3)] and 8-deoxyserratinine (**3**),[4)] we have already reported that the Diels–Alder addition of butadiene to 2,5-dialkylcyclohex-2-en-1-ones in the presence of a Lewis acid takes place stereoselectively from the side opposite the C_5-substituent of the dienophile.[5)] By taking advantage of this type of Diels–Alder reaction, compound **4**, which bears three chiral centers comprising a common stereostructural feature of 8-deoxyserratinine type alkaloids, was stereoselectively synthesized. It has also been reported that treatment of the dialdehyde (**5**) obtained from **4** with excess morpholine and camphoric acid in Et_2O–HMPA, followed by treatment of the product with $(EtO)_2POCH_2CN$–NaH, gives the conjugated nitrile (**6**) regioselectively.[6)]

In a preliminary communication,[7)] we have already reported the total syntheses of (±)-fawcettimine (**1**) and (±)-8-deoxyserratinine (**3**). This paper describes the syntheses of these alkaloids starting from **6** in full detail.

Catalytic hydrogenation of **6** [a mixture of (*E*) and (*Z*) isomers due to the disubstituted double bond in 3:7 ratio] over $(Ph_3P)_3RhCl$ in benzene gave solely the nitrile (**7**) in 88% yield; its nuclear magnetic resonance (NMR) spectrum showed one olefinic proton signal at δ 5.65. Reduction of **7** with $LiAlH_4$ afforded the primary amine, which without purification was treated with N_3CO_2 *tert*-Bu to give the carbamate (**8**) in 84% yield.

1) Location: *Yoshida-Shimoadachi-cho, Sakyo-ku, Kyoto.*
2) Y. Inubushi, H. Ishii, T. Harayama, R.H. Burnell, W.A. Ayer, and B. Altenkirk, *Tetrahedron Lett.*, **1967**, 1069.
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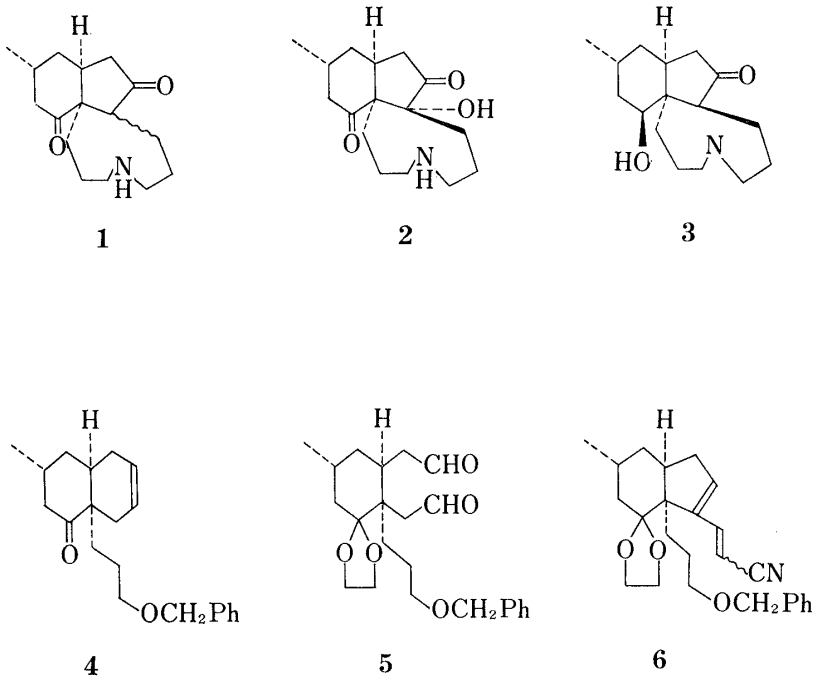
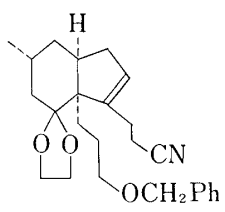


Chart 1

Next, construction of the nitrogen-containing nine-membered ring was examined. The first attempt to obtain the nine-membered lactam (**9**) as the key intermediate for the synthesis of alopecuridine (**3**) was made by intramolecular transacylation of the lactone amine (**10**). Thus, the carbamate (**8**) was oxidized with OsO_4 in pyridine to afford a sole diol (**11**) in 84% yield. This was acetylated with Ac_2O in pyridine to give the monoacetate (**12**) in 98% yield. Hydrogenolysis of the benzyl group of **12** provided the diol (**13**), which was oxidized with the Jones reagent to afford the lactone (**14**) in 81% yield from **12**. The fact that the lactone (**14**) was formed readily suggests a *cis* relationship of the tertiary hydroxy group with the angular side chain. Treatment of **14** with CF_3CO_2H afforded the lactone amine (**10**) which was heated under reflux in a sealed tube with *n*-Bu_3N in dioxane to give the desired lactam (**9**) and the N-acetylamide (**15**) in 3% and 6% yields, respectively. In order to avoid the formation of **15**, intramolecular transacylation was investigated using the alcohol (**16**) obtained in 90% yield by hydrolysis of **14** with 2% KOH–MeOH. In this case, however, dehydration occurred simultaneously with the transacylation to give the compound (**17**) in only a very low yield. These routes for construction of the nine-membered lactam, therefore, were unsuitable for the present synthesis.

Next, an attempt was made to obtain the nine-membered lactam (**18**) directly from the activated ester amine (**19**). Thus, removal of the benzyl group of **8** with Na in liquid NH_3 gave the alcohol (**20**) in 98% yield. Successive treatments of **20** with the Jones reagent, N-hydroxysuccinimide–DCC, and CF_3CO_2H provided the trifluoroacetate salt of the activated ester amine (**19**). This salt was heated with *n*-Bu_3N in dry CH_3CN by the high dilution method to give the desired nine-membered lactam (**18**) in 42% yield from **20**. The infrared (IR) spectrum of **18** showed a band due to a six-membered ketone at 1693 cm^{-1} and a band due to a lactam at 1650 cm^{-1}. The mass spectrum of **18** showed a molecular ion peak at *m/e* 261, and no molecular ion peak corresponding to the dimeric product was detected. The acetal group of **20** might be removed during the course of treatment with the Jones reagent and/or trifluoroacetic acid.

Next, reduction of the lactam carbonyl group of **18** was examined. Acetalization of **18** was unsuccessful, and reduction of the thioamide of **18** obtained by treatment of **18**



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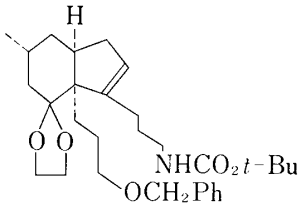

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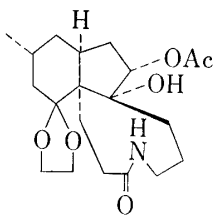

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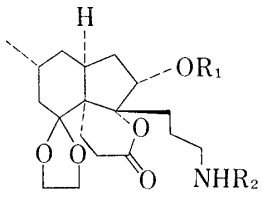

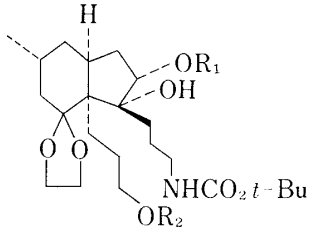

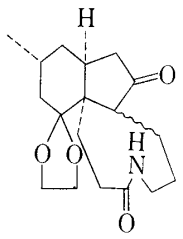

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10 : R_1=Ac, R_2=H
14 : R_1=Ac, R_2=CO_2t-Bu
15 : R_1=H , R_2=Ac
16 : R_1=H , R_2=CO_2t-Bu

11 : R_1=H, R_2=CH_2Ph
12 : R_1=Ac, R_2=CH_2Ph
13 : R_1=Ac, R_2=H

Chart 2

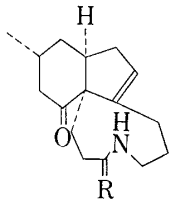
with P_2S_5 in benzene on Raney Ni gave the desired amine (**21**) in only a very low yield. Consequently, we tried to reduce the lactam carbonyl group after conversion of the ketone group of **18** to a hydroxy group. Thus, reduction of the lactam (**18**) was investigated with various kinds of reducing agent, and reduction with $LiBH_4$ gave the alcohols (**22** and **23**) quantitatively in a 3.6—4.2: 1 ratio, as shown in Table I. The configuration of the hydroxy group of **22** and **23** was deduced on the basis of the assumption that the hydride would preferentially attack the carbonyl group from the convex face of **18**, and also on the basis of the NMR coupling patterns of a proton geminal to the trifluoroacetoxy group of the N,O-bis-trifluoroacetates (**24** and **25**), as described later.

Table I

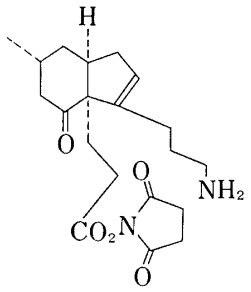
Reagent	Ratio of **22**/**23**	Total yield (%)
$NaBH_4$	2.2/1	97
$LiBH_4$	3.6—4.2/1	100
$NaBH_3CN$	3.6—4.0/1	100
$LiAlH(tert\text{-}BuO)_3$	2.8/1	100
Iso-Bu_2AlH	4.0/1	62

In order to carry out reduction of the lactam and introduction of an oxygen function on the five-membered ring at the same time, reactions of **22** and **23** with B_2H_6 were examined but no desirable product was obtained. Thus, the alcohols (**22** and **23**) were independently reduced with $LiAlH_4$ and subsequent treatment of each product without separation with $(CF_3CO)_2O$ in pyridine afforded the N,O-bis-trifluoroacetates (**24** and **25**) in 67% yields. The IR spectrum of **24** showed a trifluoroacetate band at 1780 cm^{-1} and a trifluoroacetamide band at 1689 cm^{-1}, while the NMR spectrum showed a signal due to a proton geminal to a trifluoroacetoxy group at δ 4.93 (1H, dd, J=12, 4.5 Hz), indicating the equatorial conformation

of the trifluoroacetoxy group. The compound (**25**) showed a trifluoroacetate band at 1778 cm^{-1} and a trifluoroacetamide band at 1690 cm^{-1} in the IR spectrum, and a signal due to a proton geminal to a trifluoroacetoxy group at δ 4.94 (1H, m, $W_{1/2}$=8 Hz) in the NMR spectrum, indicating the axial conformation of the trifluoroacetoxy group. Hydrolysis of **24** with 0.2 N KOH–MeOH provided the alcohol (**26**), which was oxidized with the Jones reagent to give the ketone (**28**) in 91% yield from **24**. Using the same sequence of reactions, compound (**25**) was also converted into **28** *via* the alcohol (**27**) in 84% yield.



18 : R=O
21 : R=H_2



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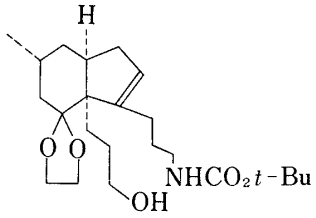

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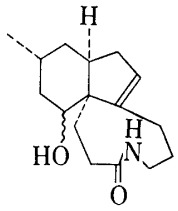
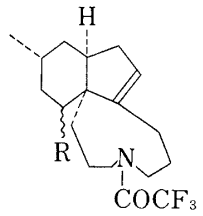
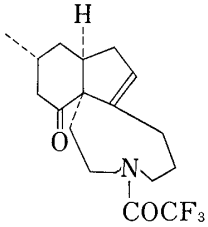


22 : β-OH
23 : α-OH



24 : R=β-$OCOCF_3$
25 : R=α-$OCOCF_3$
26 : R=β-OH
27 : R=α-OH



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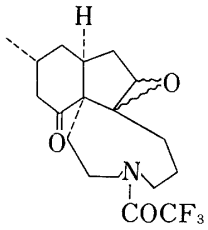
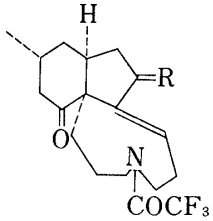
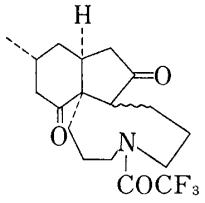


29 : α-epoxide
30 : β-epoxide



31 : R=
32 : R=O



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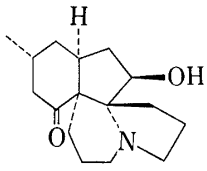

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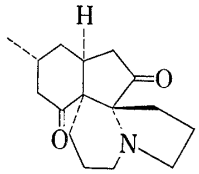

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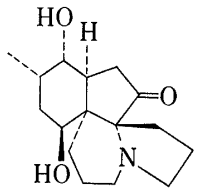

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Chart 3

Oxidation of **28** with *m*-chloroperbenzoic acid afforded two epimeric epoxides (**29** and **30**), in 58% and 40% yields, respectively. Since the reagent seems to attack the double bond of **28** preferentially from the convex face, the structure of the main product should correspond to **29** and that of the minor product to **30**. More conclusive evidence for these assignments was obtained by the conversion of **30** to (±)-8-deoxyserratinine (**3**), as described later. Treatment of **29** with $BF_3 \cdot Et_2O$ in CH_2Cl_2 gave the allyl alcohol (**31**) in 77% yield and this was oxidized with the Jones reagent to afford the enone (**32**) in 75% yield. The enone (**32**) showed bands due to a conjugated ketone at 1723, 1650 cm^{-1}, a saturated ketone band at 1703 cm^{-1}

and a trifluoroacetamide band at 1690 cm^{-1} in the IR spectrum, and a signal attributable to an olefinic proton at δ 6.98 (1H, dd, J=11, 8 Hz) in the NMR spectrum. Hydrogenation of **32** on 5% Pd–C gave the diketone (**33**) in 99% yield. Finally, the diketone (**33**) was hydrolyzed with 1 N KOH–MeOH to afford (±)-fawcettimine in 61% yield, a sample of which was identical with an authentic sample in terms of the IR (in CCl_4 and $CHCl_3$) spectrum and TLC behavior.

On the other hand, the epoxide (**30**) was treated with $BF_3 \cdot Et_2O$ in CH_2Cl_2 to give an unidentified complex mixture. Treatment of **30** with 1 N KOH–MeOH, however, caused simultaneous removal of the N-protective group and ring closure to yield the alcohol (**34**) quantitatively. The IR spectrum of **34** showed hydroxy bands at 3665, 3425 cm^{-1} and a band due to a six-membered ketone at 1692 cm^{-1}. Oxidation of **34** with the Jones reagent gave the diketone (**35**) in 64% yield, a sample of which was identical with an authentic sample of 8-deoxy-13-dehydroserratinine derived from natural serratinine (**36**). Finally, reduction of **35** with $NaBH_4$ afforded (±)-8-deoxyserratinine (**3**) in 85% yield. A synthetic sample of (±)-8-deoxyserratinine was identical with an authentic specimen of natural 8-deoxyserratinine except in its specific rotation.

Experimental

All melting points were taken on a microscopic hot stage (Yanagimoto melting point apparatus) and are uncorrected. All NMR spectra were obtained in $CDCl_3$ solution with tetramethylsilane as an internal standard on a Varian A-60 spectrometer, and IR spectra were recorded on a Shimadzu IR 400 spectrometer in $CHCl_3$. Low-resolution and high-resolution mass spectra were taken with a Hitachi RMU-6C spectrometer using a heated direct inlet system, and with a JEOL JMS-01SG-2 spectrometer, respectively. Column chromatography was performed on basic alumina (Merck, aluminium oxide 90, activity II—III) (A) or silica gel (Mallinckrodt silicic acid, 100 mesh) (B). Preparative TLC was performed on silica gel (Merck, silicic acid PF-254 containing $CaSO_4$) or alumina (Merck, aluminium oxide PF-254).

The Nitrile (**7**)——A mixture of a solution of 1.20 g (3.05 mmol) of the conjugated nitrile (**6**) in 100 ml of dry benzene and 1.05 g of tris(triphenylphosphine)chlororhodium was stirred under a hydrogen atmosphere at room temperature for 4 days. The solvent was removed under reduced pressure to leave the residue. The residue in *n*-hexane–ether–benzene was chromatographed on basic alumina (A), and elution with 20% ether in *n*-hexane afforded 1.06 g (88%) of the nitrile (**7**) as an oil. IR cm^{-1}: $\nu_{C\equiv N}$ 2251. NMR δ: 0.89 (3H, d, J=6 Hz, >CH–C$\underline{H}_3$), 3.47 (2H, t, J=6 Hz, –C$\underline{H}_2$–OBzl), 3.82 (4H, m, –OC$\underline{H}_2$C$\underline{H}_2$O–), 4.50 (2H, s, –OC$\underline{H}_2$–Ph), 5.65 (1H, m, olefinic proton), 7.31 (5H, s, aromatic protons). MS *m/e*: 395 (M^+).

The Carbamate (**8**)——A solution of 1.63 g (4.13 mmol) of the nitrile (**7**) in 60 ml of anhyd. THF was added to a suspension of 0.33 g (8.68 mmol) of $LiAlH_4$ in 100 ml of freshly distilled THF at 0° under stirring. The mixture was refluxed for 2 hr and excess reagent was then decomposed with ether and water. The organic layer was decanted, dried over K_2CO_3 and concentrated to leave the residue. A solution of the residue in 60 ml of AcOEt was treated with 2.40 g (16.78 mmol) of *t*-BuOCON$_3$. The mixture was stirred at room temperature under an argon atmosphere for 24 hr, diluted with 5% citric acid solution and extracted with AcOEt. The extract was successively washed with water and 5% $NaHCO_3$ solution, then dried over $MgSO_4$ and concentrated. The residue in ether–*n*-hexane was chromatographed on basic alumina (A) and elution with 50% ether in *n*-hexane gave 1.68 g (84%) of the carbamate (**8**). IR cm^{-1}: ν_{N-H} 3451, $\nu_{C=O}$ 1705. NMR δ: 0.88 (3H, d, J=6.5 Hz, >CH–C$\underline{H}_3$), 1.43 (9H, s, –C(C$\underline{H}_3$)$_3$), 3.12 (2H, m, –C$\underline{H}_2$–N), 3.47 (2H, m, –C$\underline{H}_2$OBzl), 3.80 (4H, m, –OC$\underline{H}_2$C$\underline{H}_2$O–), 4.51 (2H, s, –OC$\underline{H}_2$Ph), 5.57 (1H, m, olefinic proton), 7.31 (5H, s, aromatic protons). MS *m/e*: 499 (M^+).

The Diol (**11**)——A solution of 556 mg (1.11 mmol) of the carbamate (**8**) in 36 ml of dry pyridine was mixed with a solution of 368 mg (1.45 mmol) of OsO_4 in 4 ml of dry pyridine. The mixture was stirred for 28 hr under an argon atmosphere at room temperature in the dark. A solution of 6.6 g of $NaHSO_3$ in 20 ml of water was then added to the mixture with stirring. After 2 hr, 10.5 g of magnesium silicate was added to the mixture and vigorous stirring was continued for a further 30 min. The precipitates were filtered off and the filtrate was extracted with AcOEt. The extract was dried over $MgSO_4$ and concentrated to leave the residue. The residue in ether–*n*-hexane was chromatographed on basic alumina (A), and elution with 20% MeOH in $CHCl_3$ afforded a solid mass. Recrystallization from *n*-hexane–ether gave 499 mg (84%) of the diol (**11**), as colorless needles, mp 110—111°. IR cm^{-1}: $\nu_{OH,NH}$ 3150—3750, $\nu_{C=O}$ 1705. NMR δ 0.85 (3H, d, J=6 Hz, >CH–C$\underline{H}_3$), 1.44 (9H, s, –C(C$\underline{H}_3$)$_3$), 3.02 (2H, m, –C$\underline{H}_2$–N), 3.50 (2H, m, –C$\underline{H}_2$OBzl), 3.90 (4H, m, –OC$\underline{H}_2$C$\underline{H}_2$O–), 4.08 (1H, m, >C$\underline{H}$–OH), 4.52 (2H, s, –C$\underline{H}_2$Ph), 7.34 (5H, s, aromatic protons). MS *m/e*: 533 (M^+).

The Monoacetate (**12**)——A solution of 237 mg (0.45 mmol) of the diol (**11**) in 11 ml of dry pyridine was

treated with 267 mg (2.62 mmol) of Ac_2O. The mixture was stirred for 6 days at room temperature under an argon atmosphere. The reaction mixture was diluted with 3% $NaHCO_3$ solution and extracted with AcOEt. The extract was washed with water, dried over $MgSO_4$ and concentrated to leave the residue. Purification of the residue by preparative TLC gave a solid mass, and recrystallization from *n*-hexane–ether provided 250 mg (98%) of the monoacetate (**12**), as colorless needles, mp 99—100°. IR cm^{-1}: ν_{O-H} 3580, ν_{N-H} 3460, $\nu_{C=O}$ 1729, 1710, ν_{C-O} 1200—1290. NMR δ 0.85 (3H, d, J=6 Hz, >CH–C$\underline{H}_3$), 1.42 (9H, s, –C(C$\underline{H}_3$)$_3$), 2.06 (3H, s, COC$\underline{H}_3$), 3.06 (2H, m, –C$\underline{H}_2$–N), 3.48 (2H, m, –C$\underline{H}_2$OBzl), 3.89 (4H, m, –OC$\underline{H}_2$C$\underline{H}_2$O–), 4.52 (2H, s, –OC$\underline{H}_2$Ph), 5.14 (1H, m, >C$\underline{H}$–OAc), 7.35 (5H, m, aromatic protons). MS *m/e*: 575 (M^+).

The Diol (**13**)——A mixture of a solution of 393 mg (0.68 mmol) of the monoacetate (**12**) in 80 ml of 99% EtOH and 0.8 g of 10% Pd–C was stirred under a hydrogen atmosphere at room temperature. When the absorption of hydrogen had ceased, the catalyst was filtered off and the filtrate was evaporated down to leave the residue. Purification of the residue by preparative TLC on silica gel afforded 310 mg (94%) of the diol (**13**) as an oil. IR cm^{-1}: ν_{O-H} 3575, ν_{N-H} 3450, $\nu_{C=O}$ 1729, 1710, ν_{C-O} 1200—1285. NMR δ: 0.86 (3H, d, J=6 Hz, >CH–C$\underline{H}_3$), 1.43 (9H, s, –C(C$\underline{H}_3$)$_3$), 2.06 (3H, s, COC$\underline{H}_3$), 3.06 (2H, m, –C$\underline{H}_2$–N), 3.62 (2H, m, –C$\underline{H}_2$–OH), 3.91 (4H, m, –OC$\underline{H}_2$C$\underline{H}_2$O–), 5.12 (1H, m, >C$\underline{H}$–OAc). MS *m/e*: 485 (M^+).

The Lactone (**14**)——A solution of 320 mg (0.66 mmol) of the diol (**13**) in 40 ml of acetone was treated dropwise with 0.63 ml (1.70 mmol) of the Jones reagent at 0° under stirring. The mixture was stirred for 15 min at room temperature. Excess reagent was decomposed with MeOH and the mixture was diluted with water, then extracted with AcOEt. The extract was washed with water, dried over $MgSO_4$ and concentrated to leave the residue. Purification of the residue by preparative TLC on silica gel gave 274 mg (86%) of the lactone (**14**) as an oil. IR cm^{-1}: ν_{N-H} 3450, $\nu_{C=O}$ 1720, ν_{C-O} 1200—1290. NMR δ: 0.88 (3H, d, J=6 Hz, >CH–C$\underline{H}_3$), 1.42 (9H, s, –C(C$\underline{H}_3$)$_3$), 2.08 (3H, s, COC$\underline{H}_3$), 3.09 (2H, m, –C$\underline{H}_2$–N), 3.95 (4H, m, –OC$\underline{H}_2$C$\underline{H}_2$O–), 5.37 (1H, dd, J=9.5, 4 Hz, >C$\underline{H}$–OAc). MS *m/e*: 481 (M^+).

The Lactone Amine (**10**)——A solution of 74 mg (0.15 mmol) of the lactone (**14**) in 3 ml of CF_3CO_2H was stirred for 1.5 hr at 0°. CF_3CO_2H was then removed under reduced pressure to leave the residue. The residue was diluted with 28% ammonia solution and extracted with CH_2Cl_2. The extract was dried over K_2CO_3 and concentrated to afford 56 mg (96%) of the lactone amine (**10**). IR cm^{-1}: ν_{N-H} 3100—3610, $\nu_{C=O}$ 1720. NMR δ: 0.88 (3H, d, J=6 Hz, >CH–C$\underline{H}_3$), 2.09 (3H, s, COC$\underline{H}_3$), 3.96 (4H, m, –OC$\underline{H}_2$C$\underline{H}_2$O–), 5.38 (1H, m, >C$\underline{H}$–OAc).

The Lactam (**9**) **and N-Acetylamide** (**15**)——*n*-Bu_3N [32 mg (0.17 mmol)] was added to a solution of 64 mg (0.17 mmol) of the lactone amine (**10**) in 10 ml of freshly distilled dioxane. The mixture was refluxed for 7 days in a sealed tube. The reaction mixture was concentrated under reduced pressure. The concentrated solution was made acidic with 5% HCl solution and extracted with AcOEt. The extract was dried over $MgSO_4$ and evaporated down to leave the residue. Separation of the residue by preparative TLC on silica gel gave 4 mg (6%) of the N-acetylamide (**15**) from the less polar zone and 2 mg (3%) of the lactam (**9**) from the more polar zone. **9**: IR cm^{-1}: $\nu_{OH,NH}$ 3150—3650, $\nu_{C=O}$ 1722, 1660. NMR δ: 0.92 (3H, m, >CH–C$\underline{H}_3$), 2.10 (3H, s, COC$\underline{H}_3$), 3.96 (4H, m, –OC$\underline{H}_2$C$\underline{H}_2$O–), 5.31 (1H, m, >C$\underline{H}$–OAc). High-resolution MS: Calcd for $C_{20}H_{31}NO_6$: 381.215. Found: 381.209. **15**: IR cm^{-1}: ν_{O-H} 3560, ν_{N-H} 3450, $\nu_{C=O}$ 1729, 1669. NMR (100 MHz) δ: 0.88 (3H, d, J=6.5 Hz, >CH–C$\underline{H}_3$), 1.95 (3H, s, –NCOC$\underline{H}_3$), 3.96 (4H, m, –OC$\underline{H}_2$C$\underline{H}_2$O–), 4.32 (1H, m, >C$\underline{H}$–OH). MS *m/e*: 381 (M^+).

The Alcohol (**16**)——KOH (2% solution, 1 ml) was added to a solution of 125 mg (0.26 mmol) of the lactone (**14**) in 30 ml of MeOH. The mixture was stirred for 4 hr at room temperature under an argon atmosphere. The reaction mixture was diluted with water and extracted with AcOEt. The extract was washed with water, dried over $MgSO_4$ and concentrated. Purification of the residue by preparative TLC on silica gel gave 103 mg (90%) of the alcohol (**16**) as an oil. IR cm^{-1}: ν_{O-H} 3560, ν_{N-H} 3450, $\nu_{C=O}$ 1722, 1705. NMR δ: 0.88 (3H, d, J=6 Hz, >CH–C$\underline{H}_3$), 1.43 (9H, s, –C(C$\underline{H}_3$)$_3$), 3.06 (2H, m, –C$\underline{H}_2$N), 3.96 (4H, m, –OC$\underline{H}_2$-C$\underline{H}_2$O–), 4.30 (1H, m, >C$\underline{H}$–OH). MS *m/e*: 439 (M^+).

The Compound (**17**)——A solution of 72 mg (0.16 mmol) of the alcohol (**16**) in 3 ml of CF_3CO_2H was stirred for 1.5 hr at 0°. The mixture was concentrated under reduced pressure and remaining CF_3CO_2H was removed by co-evaporation with benzene to leave the residue. *n*-Bu_3N [45 mg (0.24 mmol)] was added to a solution of the residue in 10 ml of freshly distilled dioxane. The mixture was heated under reflux for 3 days in a sealed tube. The reaction mixture was concentrated and purification of the residue by preparative TLC on alumina gave 4 mg (8%) of the compound (**17**). IR cm^{-1}: ν_{N-H} 3400, $\nu_{C=O}$ 1730, 1650. High-resolution MS: Calcd for $C_{18}H_{27}NO_4$: 321.194. Found: 321.191.

The Alcohol (**20**)——A solution of 1.23 g (2.46 mmol) of the carbamate (**8**) in 30 ml of dry ether and 70 ml of liquid ammonia was treated with 0.36 g (15.65 mmol) of Na at −75°. The mixture was stirred for 20 min, then NH_4Cl was added. NH_3 was removed at room temperature and the residue was diluted with water and extracted with ether. The extract was washed with water, dried over $MgSO_4$ and concentrated. The residue in ether–*n*-hexane was chromatographed on basic alumina (A), and elution with CH_2Cl_2 gave 0.99 g (98%) of the alcohol (**20**). IR cm^{-1}: $\nu_{NH,OH}$ 3452, $\nu_{C=O}$ 1705. NMR δ: 0.88 (3H, d, J=6.5 Hz, >CH–C$\underline{H}_3$), 1.43 (9H, s, –C(C$\underline{H}_3$)$_3$), 3.18 (2H, t, J=6.5 Hz, –C$\underline{H}_2$N), 3.63 (2H, t, J=5.5 Hz, –C$\underline{H}_2$OH), 3.81 (4H, m, –OC$\underline{H}_2$C$\underline{H}_2$O–), 5.57 (1H, m, olefinic proton). MS *m/e*: 409 (M^+).

The Lactam (**18**)——A solution of 1.006 g (2.46 mmol) of the alcohol (**20**) in 40 ml of acetone was treated

with 2.93 ml (7.81 mmol) of the Jones reagent under ice-cooling. The mixture was stirred at 0° for 25 min. Excess reagent was decomposed with iso-PrOH and the mixture was diluted with water, then extracted with AcOEt. The extract was washed with water, dried over $MgSO_4$ and concentrated. To a solution of the residue in 70 ml of anhyd. CH_2Cl_2 and 70 ml of AcOEt, 0.452 g (3.93 mmol) of N-hydroxysuccinimide and 0.810 g (3.93 mmol) of dicyclohexylcarbodiimide were added. The mixture was stirred at room temperature for 3 hr under an argon atmosphere. The precipitates were filtered off and the filtrate was evaporated down to leave the residue. The residue was dissolved in 35 ml of CF_3CO_2H and the solution was stirred at 0° for 1 hr. CF_3CO_2H was removed under reduced pressure and a small amount of benzene was added to the residue in order to remove remaining CF_3CO_2H by co-evaporation providing the crude salt of the activated ester-amine (**19**) as an oil. A solution of the crude salt of **19** in 100 ml of dry CH_3CN was added dropwise to a solution of 1.468 g (7.920 mmol) of *n*-Bu_3N in 1.35 l of dry CH_3CN at 75—79° over 2 hr under an argon atmosphere. The mixture was stirred for 12 hr at 70°, then refluxed for a further 30 min. The reaction mixture was concentrated, diluted with 10% HCl solution and extracted with $CHCl_3$. The extract was washed with water, dried over $MgSO_4$ and evaporated down to leave the residue. The residue in $CHCl_3$ was chromatographed on basic alumina (A), and elution with the same solvent afforded a solid mass. Recrystallization from AcOEt–ether gave 0.267 g (42%) of the lactam (**18**) as colorless needles, mp 196.5—197.5°. IR cm^{-1}: ν_{N-H} 3400, $\nu_{C=O}$ 1693, 1650. NMR δ: 1.02 (3H, m, >CH–C<u>H</u>$_3$), 2.96—3.68 (2H, m, –C<u>H</u>$_2$–N), 5.71 (1H, m, olefinic proton). *Anal.* Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87. Found: C, 73.69; H, 8.98. MS *m/e*: 261 (M^+).

The Amine (21)——A solution of 20 mg (0.077 mmol) of the lactam (**18**) in 15 ml of dry benzene was treated with 12 mg (0.053 mmol) of P_2S_5. The mixture was refluxed for 1 hr under an argon atmosphere. After cooling, anhyd. THF was added to the reaction mixture and the precipitates were filtered off. The filtrate was concentrated to give the thiolactam of **18**. IR cm^{-1}: ν_{N-H} 3880, $\nu_{C=O}$ 1699. MS *m/e*: 277 (M^+). A solution of the thiolactam in 10 ml of anhyd. THF was treated with a suspension of Raney Ni (W-2) in anhyd. THF. The mixture was stirred for 2.7 hr at room temperature under an argon atmosphere. The catalyst was filtered off and the filtrate was evaporated down to leave the residue. The residue in CH_2Cl_2 was chromatographed on basic alumina (A), and elution with the same solvent afforded 5 mg (26%) of the amine (**21**) as an oil. IR cm^{-1}: ν_{N-H} 3100—3600, $\nu_{C=O}$ 1693. NMR δ: 0.98 (3H, d, J=7 Hz, >CH–C<u>H</u>$_3$), 3.02 (4H, m, –C<u>H</u>$_2$–N–C<u>H</u>$_2$), 5.62 (1H, m, olefinic proton). MS *m/e*: 247 (M^+).

The Alcohol (22) and the Alcohol (23)——1) Reduction of **18** with $NaBH_4$: A solution of 120 mg (0.46 mmol) of the compound (**18**) in 30 ml of MeOH was treated with 44 mg (1.16 mmol) of $NaBH_4$. The mixture was stirred for 50 min at room temperature and concentrated under reduced pressure. The concentrated solution was diluted with water and extracted with AcOEt. The extract was dried over $MgSO_4$ and evaporated down to leave the residue. Separation of the residue by preparative TLC on silica gel provided 37 mg (31%) of the alcohol (**23**) from the less polar zone and 80 mg (66%) of the alcohol (**22**) from the more polar zone. **22**: colorless prisms ($CHCl_3$–*n*-hexane), mp 191—192°. IR cm^{-1}: ν_{O-H} 3600, 3400, $\nu_{C=O}$ 1648. NMR (in pyridine D_5) δ: 0.87 (3H, d, J=5.5 Hz, >CH–C<u>H</u>$_3$), 2.95—3.35 (2H, m, –C<u>H</u>$_2$–N), 3.58—4.02 (1H, m, >C<u>H</u>–OH), 5.58 (1H, m, olefinic proton). *Anal.* Calcd for $C_{16}H_{25}NO_2$: C, 72.96; H, 9.57. Found: C, 72.90; H, 9.73. **23**: colorless flakes (AcOEt–*n*-hexane), mp 169—171°. IR cm^{-1}: ν_{O-H} 3550, 3400, $\nu_{C=O}$ 1650. NMR (in pyridine D_5) δ: 0.89 (3H, d, J=6.5 Hz, >CH–C<u>H</u>$_3$), 3.11—3.33 (2H, m, –C<u>H</u>$_2$–N), 3.47—3.83 (1H, m, >C<u>H</u>–OH), 5.80 (1H, m, olefinic proton). *Anal.* Calcd for $C_{16}H_{25}NO_2$: C, 72.96; H, 9.57. Found: C, 73.05; H, 9.87.

2) Reduction of **18** with $LiBH_4$: $LiBH_4$ [5 mg (0.23 mmol)] was added to a solution of 20 mg (0.077 mmol) of **18** in 7 ml of freshly distilled THF. The mixture was stirred for 3 days at room temperature. The reaction mixture was diluted with water and extracted with AcOEt. The extract was dried over $MgSO_4$ and concentrated to leave the residue. Separation of the residue gave 16 mg (79%) of **22** and 4 mg (20%) of **23**.

3) Reduction of **18** with $NaBH_3CN$: A solution of 90 mg (0.35 mmol) of **18** in 20 ml of MeOH was mixed with 90 mg (1.43 mmol) of $NaBH_3CN$ and 1 ml of 10% HCl solution. The whole was stirred for 16 hr at room temperature under an argon atmosphere. The reaction mixture was then concentrated under reduced pressure. The concentrated solution was diluted with 10% $NaHCO_3$ solution and extracted with AcOEt. The extract was dried over $MgSO_4$ and evaporated down to leave the residue. Separation of the residue provided 70 mg (77%) of **22** and 20 mg (22%) of **23**.

4) Reduction of **18** with LiAlH(*tert*-BuO)$_3$: A solution of 21 mg (0.08 mmol) of **18** in 10 ml of anhyd. THF was treated with 31 mg (0.12 mmol) of LiAlH(*tert*-BuO)$_3$ under ice-cooling. The mixture was stirred for 20 hr at room temperature under an argon atmosphere and then excess reagent was decomposed with wet ether. The organic layer was decanted, dried over $MgSO_4$ and concentrated. Separation of the residue afforded 16 mg (76%) of **22** and 5 mg (24%) of **23**.

5) Reduction of **18** with Iso-Bu_2AlH: A solution of 20 mg (0.077 mmol) of **18** in 10 ml of anhyd. THF was treated with 0.115 ml (0.115 mmol) of iso-Bu_2AlH solution in *n*-hexane under ice-cooling. The mixture was stirred at 0° for 1 hr and then at room temperature for 22 hr. Excess reagent was decomposed with water under ice-cooling. The mixture was diluted with 5% HCl solution and extracted with AcOEt. The extract was dried over $MgSO_4$ and concentrated to leave the residue. Separation of the residue gave 10 mg

(50%) of **22** and 2.5 mg (12%) of **23**.

The N,O-bis-Trifluoroacetate (24)——$LiAlH_4$ [60 mg (1.58 mmol)] was added to a solution of 60 mg (0.23 mmol) of the alcohol (**22**) in 18 ml of freshly distilled THF under stirring. The mixture was refluxed for 48 hr under an argon atmosphere and then excess reagent was decomposed with wet ether and water. The organic layer was decanted, dried over K_2CO_3 and concentrated. A solution of the residue in 12 ml of pyridine was treated with excess $(CF_3CO)_2O$ under ice-cooling. The mixture was stirred for 3.5 hr at room temperature under an argon atmosphere and then evaporated to dryness under reduced pressure. The residue was made acidic with 5% HCl solution and extracted with $CHCl_3$. The extract was washed with water, dried over $MgSO_4$ and concentrated. Purification of the residue by preparative TLC on silica gel yielded 67 mg (67%) of the compound (**24**) as an oil. IR cm^{-1}: $\nu_{C=O}$ 1780, 1689, ν_{C-O} 1145—1200. NMR (100 MHz) δ: 0.97 (3H, d, J=6.5 Hz, >CH–C<u>H</u>$_3$), 4.93 (1H, dd, J=12, 4.5 Hz, >C<u>H</u>–$COCF_3$), 5.51, 5.67 (total 1H, m, olefinic proton). High-resolution MS: Calcd for $C_{20}H_{25}O_3NF_3$: 441.1738. Found: 441.1741.

The N,O-bis-Trifluoroacetate (25)——$LiAlH_4$ [59 mg (1.55 mmol)] was added to a solution of 59 mg (0.22 mmol) of the alcohol (**23**) in 15 ml of freshly distilled THF under stirring. The mixture was refluxed for 48 hr under an argon atmosphere and then excess reagent was decomposed with wet ether and water. The organic layer was decanted, dried over K_2CO_3 and concentrated. A solution of the residue in 12 ml of pyridine was treated with excess $(CF_3CO)_2O$ under ice-cooling. The mixture was stirred for 4 hr at room temperature under an argon atmosphere and then concentrated. The residue was made acidic with 5% HCl solution and extracted with $CHCl_3$. The extract was washed with water, dried over $MgSO_4$ and concentrated. Purification of the residue by preparative TLC on silica gel gave a solid mass, and recrystallization from *n*-pentane-ether yielded 66 mg (67%) of the compound (**25**), as colorless pillars, mp 119—120°. IR cm^{-1}: $\nu_{C=O}$ 1778, 1690, ν_{C-O} 1145—1195. NMR (100 MHz) δ: 0.93 (3H, d, J=6.5 Hz, >CH–C<u>H</u>$_3$), 4.94 (1H, m, $W_{1/2}$=8 Hz, >C<u>H</u>–$COCF_3$), 5.65, 5.79 (total 1H, m, olefinic proton). *Anal.* Calcd for $C_{20}H_{25}F_6NO_3$: C, 54.40; H, 5.71. Found: C, 54.37; H, 5.85.

The Alcohol (26)——A solution of 80 mg (0.181 mmol) of **24** in 15 ml of MeOH was treated with 0.9 ml of 0.2 N KOH solution. The mixture was stirred for 1.5 hr at room temperature under an argon atmosphere and concentrated under reduced pressure. The concentrated solution was diluted with water and extracted with $CHCl_3$. The extract was washed with water, dried over $MgSO_4$ and concentrated. The residue in $CHCl_3$ was chromatographed on silica gel (B), and elution with the same solvent gave 62 mg (99%) of the alcohol (**26**) as an oil. IR cm^{-1}: ν_{O-H} 3610, 3480, $\nu_{C=O}$ 1686, ν_{C-O} 1148—1195. NMR δ: 0.94 (3H, d, J=6 Hz, >CH–C<u>H</u>$_3$), 5.44, 5.58 (total 1H, m, olefinic proton). High-resolution MS: Calcd for $C_{18}H_{26}F_3NO_2$: 345.1915. Found: 345.1912.

The Alcohol (27)——A solution of 67 mg (0.152 mmol) of **25** in 12 ml of MeOH was treated with 0.8 ml of 0.2 N KOH solution. The mixture was stirred for 1 hr at room temperature under an argon atmosphere and concentrated under reduced pressure. The concentrated solution was diluted with water, dried over $MgSO_4$ and evaporated down tc leave the residue. The residue in $CHCl_3$ was chromatographed on silica gel (B), and elution with the same solvent gave a solid mass. Recrystallization from *n*-pentane-ether provided 52 mg (99%) of the alcohol (**27**), as colorless prisms, mp 109.5—110°. IR cm^{-1}: ν_{O-H} 3550, $\nu_{C=O}$ 1689, ν_{C-O} 1147—1193. NMR δ: 0.90 (3H, d, J=6.3 Hz, >CH–C<u>H</u>$_3$), 5.83, 5.98 (total 1H, m, olefinic proton). *Anal.* Calcd for $C_{18}H_{26}F_3NO_2$: C,62.57; H, 7.59. Found:C, 62. 27; H, 7.75.

The Ketone (28) from the Alcohol (26)——A solution of 68 mg (0.197 mmol) of the alcohol (**26**) in 16 ml of acetone was treated dropwise with 0.06 ml (0.162 mmol) of the Jones reagent under ice-cooling. The mixture was stirred at 0° for 10 min. Excess reagent was decomposed with iso-PrOH and the mixture was diluted with water, then extracted with $CHCl_3$. The extract was washed with water, dried over $MgSO_4$ and concentrated. Purification of the residue by preparative TLC on silica gel afforded 62 mg (92%) of the ketone (**28**) as an oil. IR cm^{-1}: $\nu_{C=O}$ 1688, ν_{C-O} 1145—1189. NMR δ: 0.97 (3H, d, J=6 Hz, >CH–C<u>H</u>$_3$), 3.18—3.80 (4H, m, –C<u>H</u>$_2$–N–C<u>H</u>$_2$), 5.73 (1H, m, olefinic proton). High-resolution MS: Calcd for $C_{18}H_{24}F_3NO_2$: 343.1759. Found: 343.1759.

The Ketone (28) from the Alcohol (27)——A solution of 51 mg (0.148 mmol) of the alcohol (**27**) in 10 ml of acetone was treated dropwise with 0.04 ml (0.108 mmol) of the Jones reagent under ice-cooling. The mixture was stirred at 0° for 10 min, then excess reagent was decomposed with iso-PrOH. The mixture was diluted with water and extracted with $CHCl_3$. The extract was washed with water, dried over $MgSO_4$ and concentrated. Purification of the residue by preparative TLC on silica gel gave 43 mg (85%) of the ketone (**28**), which was identical with an authentic sample.

The Epoxide (29 and 30)——A solution of 43 mg (0.125 mmol) of the ketone (**28**) in 12 ml of dry CH_2Cl_2 was treated with 43 mg (0.199 mmol) of 80% *m*-chloroperbenzoic acid under ice-cooling. The mixture was stirred for 23 hr at room temperature under an argon atmosphere. The reaction mixture was diluted with 1% sodium thiosulfate solution and 1% $NaHCO_3$ solution, then extracted with CH_2Cl_2. The extract was washed with water, dried over $MgSO_4$ and concentrated. Separation of the residue by preparative TLC on silica gel afforded 26 mg (58%) of the epoxide (**29**) from the less polar zone and 18 mg (40%) of the epoxide (**30**) from the more polar zone. **29**: colorless prisms (*n*-pentane–ether), mp 95—96°. IR cm^{-1}: $\nu_{C=O}$ 1690, ν_{C-O} 1146—1195. NMR δ: 1.00 (3H, d, J=5.0 Hz, >CH–C<u>H</u>$_3$),! 3.08, 3.22 (total 1H, each s, >C<u>H</u>–O), 3.28—3.93 (4H, m, –C<u>H</u>$_2$NC<u>H</u>$_2$–). High-resolution MS: Calcd for $C_{18}H_{24}F_3NO_3$: 359.1708. Found: 359.1708.

30: colorless pillars (*n*-pentane–CH_2Cl_2), mp 145—146°. IR cm^{-1}: $\nu_{C=O}$ 1690, ν_{C-O} 1147—1193. NMR δ: 0.92 (3H, d, $J=7$ Hz, >CH–C<u>H</u>$_3$), 3.50, 3.63 (total 1H, each s, >C<u>H</u>–O), 3.27—3.98 (4H, m, –C<u>H</u>$_2$NC<u>H</u>$_2$–). *Anal.* Calcd for $C_{18}H_{24}F_3NO_3$: C, 60.14; H, 6.73. Found: C, 60.41; H, 6.86.

The Allyl Alcohol (**31**)——A solution of 17 mg (0.047 mmol) of the epoxide (**29**) in 6 ml of dry CH_2Cl_2 was treated with 0.4 mg of $BF_3 \cdot Et_2O$ under ice-cooling. The mixture was stirred for 1 hr at 0° under an argon atmosphere, then diluted with 1% $NaHCO_3$ solution and extracted with $CHCl_3$. The extract was washed with water, dried over $MgSO_4$ and concentrated. Purification of the residue by preparative TLC on silica gel gave a solid mass and recrystallization from *n*-pentane–CH_2Cl_2 afforded 13 mg (77%) of the allyl alcohol (**31**), as colorless prisms, mp 172—173°. IR cm^{-1}: ν_{O-H} 3600, 3445, $\nu_{C=O}$ 1685, ν_{C-O} 1146—1180. NMR δ: 1.02 (3H, m, >CH–C<u>H</u>$_3$), 4.41 (1H, m, >C<u>H</u>–OH), 5.98 (1H, m, olefinic proton). *Anal.* Calcd for $C_{18}H_{24}F_3NO_3$: C, 60.14; H, 6.73. Found: C, 60.13; H, 6.99.

The Enone (**32**)——A solution of 20 mg (0.056 mmol) of the allyl alcohol (**31**) in 3 ml of acetone was treated dropwise with 0.03 ml (0.081 mmol) of the Jones reagent under ice-cooling. The mixture was stirred at 0° for 30 min, then excess reagent was decomposed with iso-PrOH. The mixture was diluted with water and extracted with $CHCl_3$. The extract was washed with water, dried over $MgSO_4$ and concentrated to leave the residue. Purification of the residue by preparative TLC on silica gel gave a solid mass and recrystallization from acetone–ether provided 15 mg (75%) of the enone (**32**), as colorless plates, mp 158—158.5°. IR cm^{-1}: $\nu_{C=O}$ 1723, 1703, 1690, $\delta_{C=C}$ 1650, ν_{C-O} 1146—1181. NMR δ: 1.08 (3H, m, >CH–C<u>H</u>$_3$), 3.23—4.12 (4H, m, –C<u>H</u>$_2$NC<u>H</u>$_2$–), 6.98 (1H, dd, $J=11$, 8 Hz, olefinic proton). High-resolution MS: Calcd for $C_{18}H_{23}F_3NO_3$: 357.1552. Found: 357.1550.

The Diketone (**33**)——A mixture of a solution of 11 mg (0.031 mmol) of the enone (**32**) in 6 ml of freshly distilled AcOEt and 100 mg of 5% Pd–C was stirred under a hydrogen atmosphere at room temperature. When the absorption of hydrogen had ceased, the catalyst was filtered off and the filtrate was evaporated down to leave the residue. Purification of the residue by preparative TLC on silica gel gave a solid mass, and recrystallization from *n*-pentane–CH_2Cl_2 afforded 11 mg (99%) of the diketone (**33**) as colorless needles, mp 145—146°. IR cm^{-1}: $\nu_{C=O}$ 1745, 1690, ν_{C-O} 1110—1180. High-resolution MS: Calcd for $C_{18}H_{24}F_3NO_3$: 359.1708. Found: 359.1708.

(±)-Fawcettimine (**1**)——KOH (1 N solution, 0.1 ml) was added to a solution of 9 mg (0.025 mmol) of the diketone (**33**) in 3 ml of MeOH. The mixture was refluxed for 8 hr under an argon atmosphere. After cooling, the reaction mixture was concentrated under reduced pressure. The concentrated solution was diluted with 28% ammonia solution, then extracted with $CHCl_3$. The extract was washed with water, dried over K_2CO_3 and evaporated down to leave the residue. The residue in ether was chromatographed on basic alumina (A), and elution with 2% MeOH in $CHCl_3$ gave 4 mg (61%) of (±)-fawcettimine (**1**) as an oil. A sample was identical with an authentic sample of natural fawcettimine on the basis of IR ($CHCl_3$ and CCl_4) spectra and TLC behavior.

The Alcohol (**34**)——A solution of 26 mg (0.072 mmol) of the epoxide (**30**) in 10 ml of MeOH was treated with 0.2 ml of 1 N KOH solution. The mixture was refluxed for 25 hr under an argon atmosphere. After cooling, the reaction mixture was concentrated under reduced pressure. The concentrated solution was diluted with 28% ammonia solution, then extracted with $CHCl_3$. The extract was washed with water, dried over K_2CO_3 and evaporated down to leave the residue. The residue in $CHCl_3$ was chromatographed on basic alumina (A), and elution with the same solvent gave a solid mass. Recrystallization from *n*-hexane provided 19 mg (99.8%) of the alcohol (**34**), as colorless flakes, mp 91—92°. IR cm^{-1}: ν_{O-H} 3665, 3425, $\nu_{C=O}$ 1692. NMR δ: 1.01 (3H, d, $J=6$ Hz, >CH–C<u>H</u>$_3$), 3.82 (1H, m, >C<u>H</u>–OH).

The Diketone (**35**)——A solution of 11 mg (0.042 mmol) of the alcohol (**34**) in 2 ml of acetone was treated dropwise with 0.01 ml (0.027 mmol) of the Jones reagent under ice-cooling. The mixture was stirred at 0° for 15 min, then excess reagent was decomposed with iso-PrOH. The mixture was made alkaline with 28% ammonia solution and extracted with $CHCl_3$. The extract was washed with water, dried over K_2CO_3 and concentrated. The residue was solidified, and recrystallization from *n*-hexane gave 7 mg (64%) of the diketone (**35**), as colorless pillars, mp 153—154°. A sample was identical with an authentic specimen of 13-dehydro-8-deoxyserratinine derived from natural serratinine (**36**) on the basis of IR ($CHCl_3$) spectra and TLC behavior.

(±)-8-Deoxyserratinine (**3**)——A solution of 7 mg (0.027 mmol) of the diketone (**35**) in 4 ml of 99% EtOH was treated with 2 mg (0.053 mmol) of $NaBH_4$ under ice-cooling. The mixture was stirred for 3 hr at room temperature and then excess reagent was decomposed with acetone. The reaction mixture was concentrated under reduced pressure and the concentrated solution was diluted with 28% ammonia solution, then extracted with $CHCl_3$. The extract was washed with water, dried over K_2CO_3 and evaporated down to leave the residue. The residue was solidified, and recrystallization from acetone provided 6 mg (85%) of (±)-8-deoxyserratinine (**3**), as colorless pillars, mp 217—218°. A sample was identical with an authentic sample of natural 8-deoxyserratinine on the basis of IR ($CHCl_3$) spectra and TLC behavior.

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