of sciadin, but also afforded the key step to convert sciadin to the above-mentioned atisine-type diterpene alkaloids (or their mirror images). The work along this line is now in progress.

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Syntheses of (+)-Isosophoramine and (−)-13-Alkylsubstituted Sophoramine from (+)-Matrine

Recently Sadykov showed that (+)-isosophoramine, isolated from *Sophora pachycarpa*, is (+)-11,13-didehydroallomatrine (I).[1] We previously reported the syntheses of (−)-sophocarpine (V) and (−)-sophoramine (VI) from (+)-matrine (II) as shown below.[2]

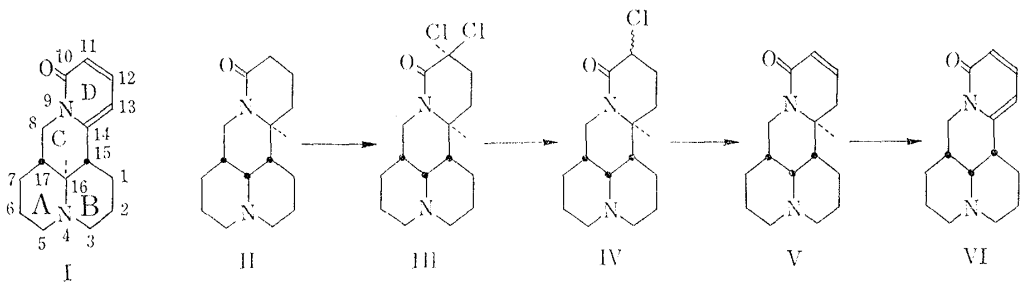

Chart 1.

This paper deals with the syntheses of (+)-isosophoramine (I) directly from dichloromatrine (III) or *via* (−)-sophoramine (VI) and also of (−)-13-alkylsubstituted sophoramines (Xa and Xb) from (−)-sophocarpine (V).

When III was heated in pyridine at 250° overnight, an aromatic base was obtained in 58% yield: its analytical data (Calcd. for $C_{15}H_{20}ON_2$: C, 73.73; H, 8.25; N, 11.47. Found.: C, 73.50; H, 8.22; N, 11.14) and physical constants—m.p. 149° (ether-petroleum ether), $[\alpha]_D^{18}$ +53.3° (c=1.005, EtOH), UV λ_{max}^{EtOH} mμ (log ε): 309 (3.88), 233.5 (3.78), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2830, 2770 (*trans*-quinolizidine), 1655, 1575, 1550 (α-pyridone)—are in quite good agreement with those of (+)-isosophoramine (I).[1] Furthermore the catalytic hydrogenation of this base offered (+)-allomatrine (VII) in a quantitative yield. Consequently, I was synthesized from III in one step, involving aromatization of ring D and inversion at the C_{16}-position.*1 Although the isomerization from VI to I did not occur by heating

*1 When the reaction temperature was ca. 200°, the mixture of I and VI was obtained.

1) A. S. Sadykov, Yu. K. Kushmuradov, Kh. A. Aslanov: Dokl. Akad. Nauk S. S. S. R., **145**, 829 (1962); C. A., **57**, 15170 (1962).
2) S. Okuda, H. Kamata, K. Tsuda, I. Murakoshi: Chem. & Ind. (London), **1962**, 1326.

in pyridine at 250°, this isomerization smoothly proceeded under the similar conditions using pyridine-hydrogen chloride. Therefore this reaction seems to involve a new type of fragmentation mechanism*2,3) and the equilibrium between I and VI should lie far to the right since I is energetically much more stable.

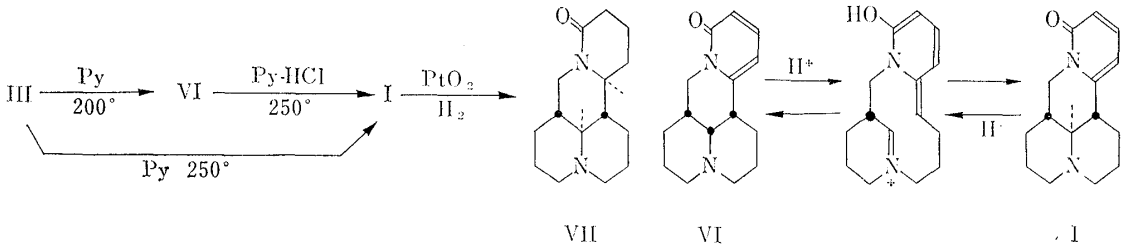

Chart 2.

When V was refluxed in 10% alcoholic potassium hydroxide, an aromatic base*3 was obtained in 13% yield: m.p. 178° (ether-petroleum ether), $[\alpha]_D^{22}$ −76.5° (c=0.96, EtOH), UV λ_{max}^{EtOH} mμ (log ε): 309 (3.97), 239.5 (3.77), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2840, 2790 (*trans*-quinolizidine), 1642, 1595, 1552 cm^{-1} (α-pyridone), NMR: 2.88 τ (1 proton: doublet: J=7.2), 3.87 (1 proton: doublet: J=7.2): $-\overset{H}{\underset{|}{C}}-\overset{H}{\underset{|}{C}}=\overset{|}{C}-\overset{|}{C}-$. 8.87 (3 protons: triplet: J=7.5): $\underline{CH_3}CH_2$-aromatic ring. *Anal.* Calcd. for $C_{17}H_{24}ON_2$: C, 74.96; H, 8.88; N, 10.29. Found: C, 75.28; H, 8.89; N, 10.28. Its empirical formula and spectral data clearly showed that this compound is 11- or 13-ethylsophoramine. In this case this base has most probably resulted from the aldol condensation of α,β-unsaturated lactam moiety of V and acetaldehyde from the air oxidation of alcohol, followed by dehydration and aromatization by migration of the double bond, as shown below. When V was refluxed in *t*-butanol*4 with meta-acetaldehyde and potassium *t*-butoxide, the same compound was obtained in a reasonable yield as expected. Therefore the compound in question is most probably 13-ethylsophoramine (Xa).

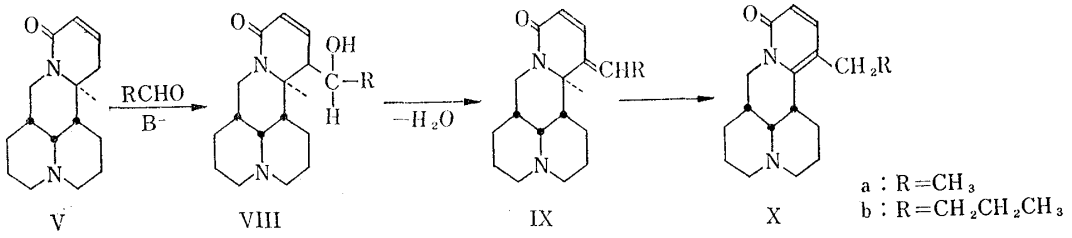

Chart 3.

In order to determine whether this type reaction is general, V was heated in 10% butanolic potassium hydroxide. In this case 13-butylsophoramine (Xb) was also obtained in 28% yield: m.p. 138° (ether-petroleum ether), $[\alpha]_D^{22}$ −68.6° (c=0.44, EtOH), UV λ_{max}^{EtOH} mμ (log ε): 312 (4.00), 239.5 (3.76). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2840, 2795 (*trans*-quinolizidine), 1645,

*2 This new fragmentation reaction is now under investigation using the other compounds such as (−)-anagyrine.

*3 This was first isolated from the nonsaponifiable base of the alkaloidal mixture of *Sophora flavescens*; Y. Kashida, *et al.*, Kanto local meeting of Pharm. Soc. Japan, Nov., 1957.

*4 To avoid the formation of an aldehyde by air oxidation, *t*-butanol was employed.

3) C. A. Grob: p. 114, Theoretical Organic Chemistry, Papers presented to the Kekule Symposium, London, September, 1958, Butterworths Science Publications, London, 1959. H. P. Fischer, C. A. Grob, E. Renk: Helv. Chim. Acta., **45**, 2539 (1962).

1597, 1555 (α-pyridone). *Anal.* Calcd. for $C_{19}H_{28}ON_2$: C, 75.95; H, 9.33; N, 9.33. Found: C, 75.58; H, 9.32; N, 9.42. For the purpose of evaluating the utility of this reaction, the precise mechanism is now under investigation using model compounds.

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