of sciadial, but also afforded the key step to convert sciadial 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 (+)-Isoalpinine and (−)-13-Alkylsubstituted Sophoramine from (+)-Matrine

Recently Sadykov showed that (+)-isosorphone, isolated from Sophora pachycarpa, is (+)-11,13-didehydrobeta-lactone (I). We previously reported the syntheses of (−)-sophocarpine (V) and (−)-sophoramine (VI) from (+)-matrine (II) as shown below.

![Chart 1.](image)

This paper deals with the syntheses of (+)-isosorphone (I) directly from dichloromatsine (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°C overnight, an aminic base was obtained in 58% yield: its analytical data (Calcd. for C_{18}H_{20}O_{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), [α]_D^25 +53.3° (c=1.005, EtOH), UV λ_{max} μ (log ε): 309 (3.88), 233.5 (3.78), IR ν_{max} cm^{-1}: 2830, 2770 (trans-quinoxaline), 1655, 1575, 1550 (α-pyridone)—are in quite good agreement with those of (+)-isosorphone (I). 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_{12}-position. Although the isomerization from VI to I did not occur by heating.

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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** and the equilibrium between I and VI should lie far to the right since I is energetically much more stable.

![Chart 2.](image)

When V was refluxed in 10% alcoholic potassium hydroxide, an aromatic base** was obtained in 13% yield: m.p. 178° (ether-petroleum ether), [α]_D^20 = -76.5° (c=0.96, EtOH), UV λ_{max} m_{μ} (log ε) = 309 (3.97), 239.5 (3.77), IR ν_{max} 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: H H doublet: J=7.2) : -\text{C} - \text{C} = \text{C} - \text{C}-. 8.87 (3 protons: triplet: J=7.5) : CH₃CH₂-aromatic ring, Anal. Calcd. for C₁₄H₂₂ON₂: 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 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.](image)

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), [α]_D^20 = -68.6° (c=0.44, EtOH), UV λ_{max} m_{μ} (log ε) = 312 (4.00), 239.5 (3.76), IR ν_{max} cm⁻¹: 2840, 2795 (trans-quinolizidine), 1645.

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

** 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.

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

1597, 1555 (α-pyridone). *Anal. Calculated for C₁₅H₁₇NO₃: 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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