tutin by infrared spectra was carried out to solve the questions raised by Slater on the previous report of this series which identified Japanese tutin with New Zealand tutin.

2) The inference that tutin is hydroxycoriamyrtin was endorsed by infrared spectra.

3) Tutin was isolated from mixed crystals extracted from leaves and stems of Coriaria japonica.

4) Pseudotutin, was newly extracted from plants and it was found that it is identical with the crystalline component of fruit juice, m.p. 184°. Its properties were investigated.

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The total synthesis of dl-sparteine (I) was reported in 1950 by Leonard and Beyler
d. They found that 1-ethoxyacarbonyl-3-(α-pyridyl)-4-oxoquinolizine (II) and diethyl 2,4-di-(α-pyridyl)-glutarate (III), both of which Clemo, et al., used as the intermediate in their synthesis of oxosparteine (VI), could be converted to dl-sparteine and dl-α-isosparteine in one step by their hydrogenation in dioxane solution over copper chromite catalyst at 250° and at 350°, atmospheric pressure. Galinovsky and Kainz found that on catalytic reduction followed by cyclization, (II) was converted to dioxosparteine (V), and this is readily reduced to oxosparteine (VI). From (III), by the same method, Clemo, et al., gained dioxosparteine, m.p. 113°.

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3) G. R. Clemo, R. Raper, W. S. Short: Ibid., 1949, 663.
4) F. Galinovsky, G. Kainz: Monatsh., 77, 137 (1949).
Sorm and Keil\textsuperscript{5,6} synthesized dioxosparteine by the same method as that of Galinovsky, and isolated two kinds of dioxosparteine by chromatography. One of the dioxosparteine, m.p. 172\textdegree, was reduced electrolytically to a base, C\textsubscript{13}H\textsubscript{14}N\textsubscript{3}, which formed a dipicrate of m.p. 222\textdegree. The other dioxosparteine, m.p. 135\textdegree, after reduction yielded two dipicrates; m.p. 205\textdegree and m.p. 190\textdegree. It appears likely that the dipicrate, m.p. 222\textdegree, is that of \textit{dl}-\textit{\alpha}-isosparteine and the dipicrate, m.p. 205\textdegree, is that of \textit{dl}-sparteine.

In the present series of experiments, dioxosparteine was prepared according to the method of Galinovsky. (II) was catalytically reduced over platinum oxide in glacial acetic acid to 1-ethoxycarbonyl-3-(\textit{\alpha}-piperidyl)-4-oxoquinolizidine (IV), which was cyclized on being heated for 3 hrs. at 200\textdegree in \textit{vacuo}. The product was chromatographed through alumina as a benzene solution and isolated into three isomeric dioxosparteines; (A) m.p. 135\textdegree to 137\textdegree, (B) m.p. 159\textdegree to 160\textdegree, and (C) m.p. 182\textdegree to 184\textdegree. The infrared spectra of these are shown in Fig. 1.

![Infrared Spectra of C\textsubscript{13}H\textsubscript{14}O\textsubscript{2}N\textsubscript{3} in Chloroform](image)

Fig. 1. Infrared Spectra of C\textsubscript{13}H\textsubscript{14}O\textsubscript{2}N\textsubscript{3} in Chloroform
I : m.p. 137\textdegree, II : m.p. 160\textdegree, III : m.p. 184\textdegree

Marion and Leonard\textsuperscript{7} discussed the stereochemistry of C\textsubscript{15}-lupin alkaloids. Sparteine has three racemates according to whether the hydrogen atoms in C\textsubscript{8} and C\textsubscript{11} are in \textit{cis} or trans to the methylene bridge at C\textsubscript{9}; (1) both cis, (2) cis and trans, and (3) both trans. Sparteine has a cis-trans configuration, and the \textit{\alpha}-isosparteine cis-cis configuration. The third racemate of both trans configuration, not yet found in nature, is called \textit{\beta}-isosparteine. In the same manner dioxosparteine comes in three racemates.

The three kinds of dioxosparteine separated in the present experiments were reduced in 5\% hydrochloric acid over platinum oxide to different products. (A) yielded a base, C\textsubscript{13}H\textsubscript{15}N\textsubscript{3}O, m.p. 110\textdegree, from which \textit{d}-tartrate was separated and this was identical to that of \textit{l}-oxosparteine, the oxidation product of \textit{l}-sparteine by K\textsubscript{3}Fe(CN)\textsubscript{6}. Since both sparteine and oxosparteine possess a cis-trans configuration, (A) also has a cis-trans configuration. (B) yielded a base, C\textsubscript{13}H\textsubscript{15}N\textsubscript{3}, which formed a dipicrate melting at 219\textdegree. This must be the dipicrate of \textit{\alpha}-isosparteine, and (B) has a cis-cis configuration. (C) was not affected by the conditions in which (A) and (B) were reduced, but was reduced at 80\textdegree to 90\textdegree to a base, C\textsubscript{13}H\textsubscript{15}N\textsubscript{3}, the dipicrate of which melted at 244\textdegree to 246\textdegree. This must be the isomeric

\textsuperscript{6} Ibid., 12, 655 (1947).
racemate of sparteine, dl-β-isosparteine, and (C) has a trans-trans configuration. The infrared spectra of three kinds of dipicrate, l-sparteine dipicrate, and dipicrate of m.p. 219° and of m.p. 246°, are shown in Fig. 2.

Experimental

Hydrogenation of 1-Ethoxycarbonyl-3-(α-pyridyl)-4-oxoquinolizine (II)—A solution of 10 g. of (II) in 100 cc. glacial AcOH was shaken for 36 hrs. with 0.5 g. PbO in H₂ at room temperature. The yellow fluorescent solution became colorless after absorption of 5500 cc. H₂ (theoretical amount for hydrogenation of seven double bonds, 5330 cc.). After the catalyst was filtered off, AcOH was removed on a water bath under reduced pressure and a brown oil remained.

Ring Closure to Dioxosparteine and its Separation by Chromatography—The above oil was heated in vacuo for 3 hrs. in a metal bath at 200°. The product was brownish gum (8.5 g.), which was dissolved in 100 cc. benzene and chromatographed on 400 g. alumina. Every 100 cc. of the effluent was fractionally collected. Fraction 1–21 yielded 1.15 g. of crystals (A); Fr. 22–40, 0.46 g. (B); Fr. 41–50 (developed with CHCl₃), 2.41 g. (C); Fr. 51–55 (developed with ether), 0; Fr. 56–60 (developed with ether containing 3% EtOH), 0.61 g. (D).

The recrystallization of crystals (A) from ether yielded colorless needles, m.p. 135°–137°. Anal. Calcd. for C₉H₆N₂O₄: C, 68.7; H, 8.4; N, 10.70. Found: C, 68.97; H, 8.08; N, 10.98. d-Tartrate crystallized from MeOH, m.p. 174°–175°. Anal. Calcd. for C₉H₆O₄N₂·C₄H₆O₄: C, 55.5; H, 6.79; N, 6.8. Found: C, 55.31; H, 6.63; N, 7.11. The recrystallization of the crystals (C) from EtOAc yielded colorless needles, m.p. 159°–160°. Anal. Calcd. for C₉H₆O₂N₂: C, 68.7; H, 8.4; N, 10.70. Found: C, 68.27; H, 8.39; N, 10.62. d-Tartrate, m.p. 210°–211°. Anal. Calcd. for C₉H₆O₂N₂·C₄H₆O₄: C, 55.5; H, 6.79; N, 6.8. Found: C, 55.33; H, 6.56; N, 7.12. The recrystallization of the crystals (D) from EtOAc–ether mixture yielded colorless small needles, m.p. 182°–184°. Anal. Calcd. for C₈H₆O₂N₂: C, 68.7; H, 8.4; N, 10.70. Found: C, 68.33; H, 7.92; N, 10.77. d-Tartrate, m.p. 167°–168°. Anal. Calcd. for 2C₇H₆O₂N₂·C₄H₆O₄: N, 8.31. Found: N, 8.35. The crystals (B) was separated into two kinds of crystals, m.p. 135°–137° and m.p. 160°, respectively identical with (A) and (C), by fractional recrystallization from ether and EtOAc.

Catalytic Hydrogenation of Dioxosparteine—i) The dioxosparteine, m.p. 135° (500 mg.), was hydrogenated in 5% HCl (20 cc.) over PbO (300 mg.) at a room temperature. During 7 hrs., 176 cc. H₂ was absorbed (theoretical amount, 146 cc.). The catalyst was filtered off, the solution was made alkaline with 10% NaOH, and extracted with ether. The ethereal residue was recrystallized from petroleum ether and yielded colorless plates, m.p. 109°–111°. Yield, 220 mg. Anal. Calcd. for C₉H₆O₂N₂ (Oxosparteine): C, 72.6; H, 9.7; N, 11.29. Found: C, 73.21; H, 9.32; N, 11.39.

To the solution of dl-oxosparteine (200 mg.) in 1.5 cc. MeOH was added a solution of d-tartaric acid (121 mg.) in 2 cc. MeOH. The mixture was cooled in an ice box, and the tartrate crystallized out. Recrystallization from MeOH yielded colorless small needles, m.p. 235° (decomp.). This substance showed no depression of the melting point when fused with the d-tartrate of the oxidation product of
natural l-sparteine. *Anal.* Calcd. for C_{18}H_{20}O_{7}N_{2} (oxosparteine tartrate): N, 7.03. Found: N, 6.85.

i) Dioxosparteine, m.p. 160°, was reduced in 5% HCl solution at a room temperature over PtO_{2} as in the foregoing. The product was derived to the dipicrate, m.p. 219° (from EtOH-dioxane). *Anal.* Calcd. for C_{15}H_{18}N_{2}·2C_{8}H_{4}O_{7}N_{2} (α-isosparteine dipicrate): C, 46.82; H, 4.66; N, 16.28. Found: C, 46.58; H, 4.74; N, 15.85.

ii) Dioxosparteine, m.p. 184°, was reduced in 5% HCl solution at 80~90° over PtO_{2} as before. The product formed a dipicrate, m.p. 244~246° (from EtOH). *Anal.* Calcd. for C_{15}H_{20}N_{2}·2C_{8}H_{4}O_{7}N_{2}: C, 46.82; H, 4.66; N, 16.28. Found: C, 46.52; H, 5.26; N, 15.87.

**Summary**

Dioxosparteine, obtained from 1-ethoxycarbonyl-3-(α-pyridyl)-4-oxoquinolizine, was chromatographically separated into three isomers: (A) m.p. 135~137°, (B) m.p. 159~160°, and (C) m.p. 182~184°. They were respectively reduced to oxosparteine, α-isosparteine, and a new isomer of sparteine.

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44. Shigehiko Sugasawa and Takashi Tatsuno: Oxidation of N-(β-3',4'-Methylenedioxyphenethyl)-3-ethylpyridinium Salt and the Constitution of the Resultant Pyridone.

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The course of the oxidation of 3-substituted pyridinium salts (I) is governed only by the nature of R', whereas R seems to have hardly any influence. The results hitherto obtained in our laboratories are as follows:

When R' is carboxyl(1), N-methylpyrrolidyl-2(2), phenyl(3), or α-ethylenedioxyethyl(3), pyridone-6 (III) type of derivatives are the main, if not the sole, products, while N-methyl-3-ethylpyridinium salt gave only N-methyl-3-ethylpyridone-2 in a good yield(4). In these cases, the constitution of pyridones were proved by chemical method, but in some cases this method of confirmation is not always an easy task to do.

One of us (T. T.) proposed to make use of the dipole moment data in such cases to deduce the constitution and his attempts along this line have achieved substantial results. The present paper adds another successful example of his method of deduction.

When N-β-3',4'-methylenedioxyphenethyl-3-ethylpyridinium bromide was subjected to alkaline ferricyanide oxidation, there was obtained a single pyridone derivative in a good yield. By measuring the dipole moment of this pyridone Tatsuno attributed N-(β-3',4'-methylenedioxyphenethyl)-3-ethylpyridone-2 (IIb) to this substance, which was proved to be correct by an independent synthesis.

Ethyl α-carbethoxy-γ-cyanobutyrate (IV) was prepared from acrylonitrile and diethyl malonate and this was then reduced to furnish ethyl 2-ketonepicotate (V), followed by ethylation (VI). After hydrolysis the latter was subjected to decarboxylation, yielding (VII), N-potassio derivative of which was then condensed with β-3,4-methylenedioxyphene-