electron pair of the bridgehead nitrogen and the hydroxyl group in the infrared spectra of these isomers are shown in Table I. The infrared spectrum (in carbon tetrachloride) of pyrroloisoquinoline A showed the presence of the Bohlmann's bands (2778 and 2715 cm^{-1}) and the absence of a band due to the intramolecular hydrogen bonding, whereas the spectrum of pyrroloisoquinoline B showed the absence of the former bands and the presence of the latter band (3560 cm^{-1}). Therefore, it is most reasonable to conclude that pyrroloisoquinoline A has a structure (IX), existing in a conformation (IXa), and pyrroloisoquinoline B a structure (X), in a conformation (Xa), since both compounds must be C_{6a} isomers and a *trans-syn-trans* conformer with a boat-formed piperidine ring of X is supposed to be unstable. This configurational assignment is consistent with that obtained above from the hydrogenation attitudes.

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Preparation of L-β-Ribonucleosides and L-β-Ribonucleotides

It has become amply evident that ribofuranosylnucleosides and -nucleotides obtained from naturally occurring ribonucleic acid, coenzyme, vitamin B_{12} and antibiotics (*i.e.* puromycin) possess D-ribose as their sugar components. Moreover, there are several previous investigations of the ribonucleosides and ribonucleotides which deal exclusively with the chemical and biological studies of D-compounds, although the corresponding L-derivatives of nucleoside and nucleotide prepared only by chemical methods have not been studied biologically.*1

Interest in biochemical activity of nucleoside and nucleotide analogues has led us to suggest that L-β-derivatives of the above mentioned substances would act as metabolic inhibitors, or as anticancer agents. Therefore, the synthesis of L-nucleosides and L-nucleotides seemed to be valuable and of interest.

The purpose of this communication is to report, as a continuation of our study of the synthesis of nucleotides, on the optical resolution of DL-β-nucleosides and DL-β-nucleotides using microbiological and enzymatic methods.

DL-Adenosines (IV) and DL-inosines (V) were prepared by using the chloromercuri method starting from DL-ribose,[1] according to the procedure for D-adenosine.[2]

*1 In a paper which came to hand after our manuscript had been submitted for publication, Acton, Ryan, and Goodman (J. Am. Chem. Soc., **86**, 5352 (1964) have reported for the synthesis of L-adenosine.

1) I. Iwai, T. Iwashige, M. Asai, K. Tomita, T. Hiraoka: This Bulletin, **11**, 188 (1963).

2) J. Davoll, B. A. Lowy: J. Am. Chem. Soc., **73**, 1650 (1951), wherein the chlorosugar was the triacetate.

When the chloromercuri salt of 6-benzamidopurine (II)[2,3] were allowed to react at 140° with 2,3,5-tri-O-benzoyl-DL-ribofuranosyl chloride (I), then the protecting groups removed, DL-β-adenosines (IV) were produced in 35% yield.

IV were treated with nitrous acid to afford DL-inosines (V).

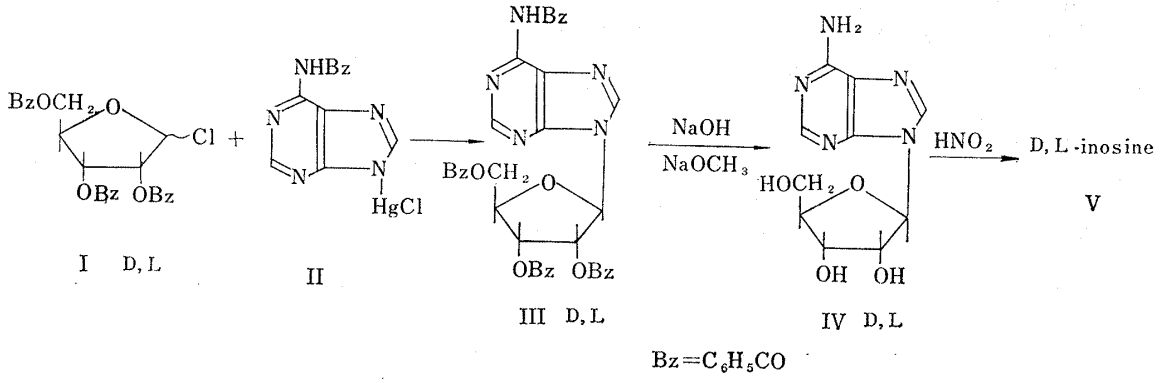

Chart 1.

Subsequently, DL-β-adenosines (IV) were phosphorylated with phenylphosphorodichloridate to afford DL-β-AMP (VI) by the known method.[4]

In a similar manner DL-β-IMP (VII) were obtained starting from DL-β-inosines (V).

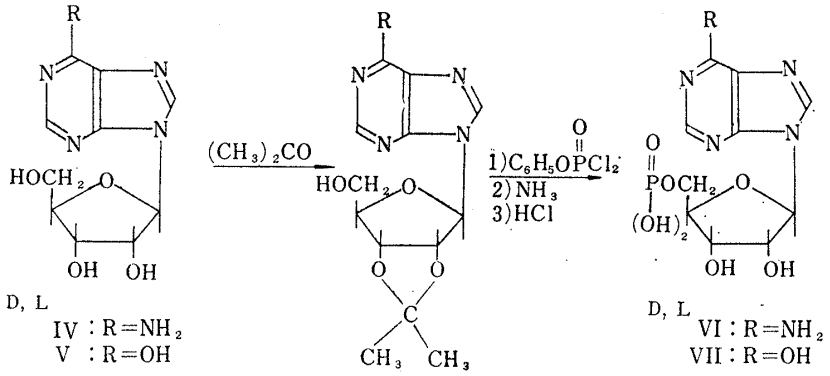

Chart 2.

Since the optical resolution of DL-adenosines could not be achieved by any of the chemical methods so far tested, a biological method using a bacterial cell suspension was applied here. The strain used was PS-264, an unidentified stock culture of our laboratories.

Appropriate amounts of DL-adenosines were incubated with the bacterial cell suspension for 2~3 days at 38°, and at pH 7.0. This treatment resulted in the complete deamination and hydrolysis of D-adenosine whereas about 50% of L-adenosine remained unattacked and the rest was deaminated to give the corresponding L-inosine.

Separation of L-adenosine and L-inosine was carried out by chromatography using ion exchange resin Dowex 1.

L-AMP and L-IMP were obtained as follows: when DL-AMP were incubated with snake venom obtained from *Trimeresurus flavoviridis* (Hallowell), only D-antipode was dephosphorylated by 5'-nucleotidase to D-adenosine and, L-AMP left unchanged. L-AMP was separated from D-adenosine by paper or ion exchange chromatography. L-IMP was also obtained from DL-IMP by the same method.

3) T. Ukita, H. Hayatsu: J. Am. Chem. Soc., 84, 1879 (1962).
4) M. Ikehara, E. Ohtsuka, F. Ishikawa: This Bulletin, 9, 173 (1961).

TABLE I. Physical Properties of the Synthetic Nucleosides and Nucleotides

Compound[a]	m.p. (°C)[b]	$[\alpha]_D^{20°}$	Rf[c]	UV λ_{max}^{pH7} mμ (H_2O)
9-β-DL-Ribofuranosyladenine	245	0	0.58	260
9-(2,3,5-Tri-O-acetyl-β-DL-ribofuranosyl)hypoxanthine	218	0		
9-β-DL-Ribofuranosylhypoxanthine	210	0	0.36	249
Barium-9-β-DL-ribofuranosyladenine-5′ phosphate	—	0	0.19	260
Barium 9-β-DL-ribofuranosylhypoxanthine-5′ phosphate	—	0	0.12	249
9-β-L-Ribofuranosyladenine	230	+59	0.58	260
9-β-L-Ribofuranosylhypoxanthine	218	+48.7	0.36	249
Barium 9-β-L-ribofuranosyladenine-5′ phosphate	—	+50[d]	0.19	260
Barium 9-β-L-ribofuranosylhypoxanthine-5′ phosphate	—	+18	0.12	249

a) Satisfactory elemental analyses (CHNP) were obtained for each compound except DL-IMP and L-IMP, which were not analyzed.
b) Melting points are uncorrected.
c) Solvent system: *t*-butanol-methylethylketone-acetic acid-water (5:5:6:4), using Toyo Roshi No. 50, ascending at 20°.
d) Free nucleotide (pH 13).

As shown in Table I, all of the nucleosides and nucleotides thus obtained showed many of the properties characteristic of the corresponding natural D-series and were identical with the latters except that the specific rotations, while of the same numerical values, were opposite in sign.

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Ableitung von *trans*-1,2,3,4,6,7,12,12*b*-Octahydroindolo-[2,3-*a*]chinolizin aus Chinolin

In der Fortsetzung der Versuche zur Ableitung von Derivaten der Indol-3-essigsäure aus Chinolin haben wir nun Chinolin nach unten mit Formeln angegebenen Reaktionsstufen in *trans*-1,2,3,4,6,7,12,12*b*-Octahydroindolo[2,3-*a*]chinolizin übergeführt.

Chinolin wurde nämlich nach Takahashi[1] über α-(2-Pyridyl)-4-chinolinacetonitril-1-oxyd in 4-Picolinoylcarbostyril (I) übergeführt. Die Druckhydrierung von I mittels Raney-Nickels in Methanol-Lösung unter Zusatz von geringer Menge konz. Ammoniak bei 150° und bei 100 kg/cm² H_2-Druck ergab zwei isomere Dekahydroderivate (II) und (II′) (II: Prismen vom Schmp. 246~248°. $C_{15}H_{20}O_2N_2$—Ber.: C, 69.20; H, 7.74; N, 10.76. Gef.: C, 69.53; H, 7.62; N, 10.65. II′: Blättchen vom Schmp. 227~228°. Gef.: C, 69.11; H, 7.56; N, 10.90) in fast gleicher Menge.

Die beiden zeigen die Diazoreaktion des aromatischen Primäramins und bilden je ein Diacetat (II-Diacetat: Nadeln vom Schmp. 179~181°. $C_{15}H_{18}O_2N_2(COCH_3)_2$—Ber.: C, 66.26; H, 7.02; N, 8.13. Gef.: C, 66.06; H, 6.67. II′-Diacetat: Blättchen vom Schmp.

1) M. Takahashi: Ann. Rept. ITSUU Lab. (Tokyo), **13**, 25 (1963).