acetylation, the diol (Ⅸ) yielded, together with its diacetate, 3β-acetoxy-cyper-11-en-4-ol (Ⅺ) (49% yield), IR bands (liquid) at 3521 (hydroxyl), 1730 cm^{-1} (acetoxyl), NMR peaks at 8.61, 6.35 (doublet and quartet, J=7 c.p.s., $C\underline{H}_3$-$C\underline{H}$(OH)-C$\lessdot$), 4.45 τ (quartet, J_1=7, J_2=9 c.p.s., $\underline{H}$-C$\lessdot$OCOCH$_3$), which was oxidized with chromic acid to 3β-acetoxy-cyper-11-en-4-one (Ⅻ) (88% yield), $[\alpha]_D$ +62.1°, IR bands (liquid) at 1742 (acetoxyl), 1701 cm^{-1} (acetyl), NMR peak at 7.96 τ ($C\underline{H}_3$-CO-), identified as cyperolone acetate. Although cyperolone, a β-ketol, is sensitive to alkali, hydrolysis of the ketol acetate (Ⅻ) using 1 mole of sodium hydroxide in ethanol furnished synthetic cyperolone (I) (91% yield), m.p. 40~41° (monohydrate), identical in every respect with the natural substance.[1]

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Structure of Innovanamine

A new glycoside, innovanamine, was isolated from the fallen leaves of *Evodiopanax innovans* NAKAI. The methanol extract of powdered leaves (17 kg.) was concentrated, equivolume of water was added, and the resinous substance was removed. The aqueous solution was saturated with basic lead acetate, the precipitate formed was filtered off, excess of ammonia was added, and the solution filtered. The final aqueous solution was concentrated *in vacuo* to 3 L. after removing lead ion with hydrogen sulfide and standing over night. The crystalline precipitate was collected (386 g.) and recrystallised from hot water to colorless prisms, m.p. 116~118°, $[\alpha]_D^{25}$ −61.6° (c=10, H_2O); NMR (p.p.m.), (D_2O): 2.47 (singlet) CH_3, 3.51, 3.85, 4.82 (multiplets), sugar hydrogen, 6.58, 7.74 (doublets, J=7 c.p.s.) aromatic hydrogen (physical constants were determined with the hydrated substance). *Anal.* Calcd. for $C_{12}H_{17}O_7N \cdot 2H_2O$: C, 44.58; H, 6.59. Found: C, 44.67; H, 6.96. for $C_{12}H_{17}O_7N$: N, 4.88; O, 38.99; mol. wt., 287. Found: N, 4.85; O, 39.11; mol. wt., 310.

Four g. of innovanamine was dissolved in 8% hydrochloric acid in methanol and heated on steam bath for 3 hours. The solution was concentrated *in vacuo*. When cooled, colorless prisms were obtained, which were recrystallised from a mixture of ethyl acetate and methanol, m.p. 185°. *Anal.* Calcd. for $C_6H_7O_2N \cdot HCl$ (Ⅱ): Cl, 21.94. Found: Cl, 21.37. The free base was recrystallised from hot water, m.p. 293~294°. *Anal.* Calcd. for $C_6H_7O_2N$: C, 57.59; H, 5.64; N, 11.20. Found: C, 58.01; H, 5.74; N, 10.97. The latter was identical with synthesized 2-methyl-3-hydroxy-4(1*H*)pyridone (Ⅲ).[1] The mother liquor was concentrated to dryness *in vacuo*, carbohydrate components were examined by paper chromatography, and glucose was detected. Thus, the structure of innovanamine must be 2-methyl-3-glucosyloxy-4(1*H*)pyridone (I). The glycoside linkage is β, because I was hydrolysed easily with emulsin.

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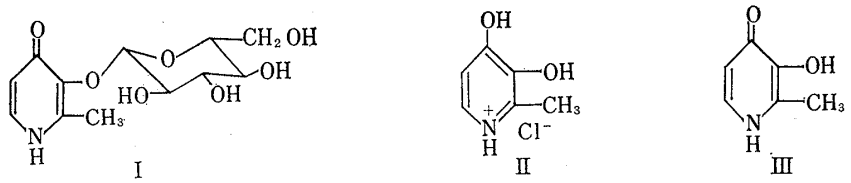

Chart 1.

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Hydrolytic Cleavage of Thiamine in Mammalian Animals

The metabolic fate of thiamine has been studied in various species of animals, but relatively little is known of how it is metabolized in the mammalian body. Verrett, *et al.*[1] reported that oral and parenteral routes of administration did not make great differences in the metabolic pattern of ^{35}S-thiamine in rabbits.

The results of the present study showed that the metabolic pattern of ^{35}S-thiamine in rats was remarkably different between oral and parenteral routes of administration. Female Wister rats weighing 150~200 g. were used. They were housed in cages constructed to permit the separate collection of urine and feces. ^{35}S-Thiamine with a specific activity of 25 μc./mg., was prepared from $C^{35}S_2$ according to the procedure of Matsukawa.[2] A dose of 0.2 mg. of ^{35}S-thiamine was administered orally and intravenously. Twenty-four-hour urine specimens were collected in glass bottles. For separation of the urinary metabolites, paper chromatography was employed. A part of the pooled urine was spotted on Toyo filter paper No. 51 and developed with *n*-butanol-acetic acid-water(4:1:5, v/v). Radioactive scanning of paper chromatograms was accomplished by dividing the chromatograms in 10 mm. segments, extracting each segment with distilled water and counting ^{35}S radioactivity of each extract in a windowless gas-flow counter. No attempt was made to correct for recovery of the radioactivity from chromatograms and sample absorption in extracts. Scintillation counting was used to determine the recovery of the administered radioactivity from the urine. The percentages of ^{35}S radioactivity in urine represented by radioactive metabolites of ^{35}S-thiamine are indicated in Table I.

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