of an α-ketol9) (Ⅵ), derived from securinine, or application of the octant rule10) predicts that an absolute configuration of norsecurinine at C_{9b} should be S-configuration.

Norsecurinine is, therefore, represented by either Ⅰa or Ⅰb and dihydronorsecurinine by either Ⅱa or Ⅱb. The stereochemistry at C_{9a} will be discussed in a subsequent paper.

Osaka research Laboratory,
Tanabe Seiyaku Co., Ltd.,
Kajima-cho Higashiyodogawa-ku,
Osaka

Seiichi Saito (斎藤清一)
Tadasu Tanaka (田中　雅)
Keishi Kotera (小寺啓司)
Hideo Nakai (仲井英雄)
Norio Sugimoto (杉本典夫)

Faculty of Pharmaceutical Sciences,
Osaka University,
Toneyama, Toyonaka,
Osaka-fu

Zen-ichi Horii (堀井善一)
Masazumi Ikeda (池田正澄)
Yasumitsu Tamura (田村恭光)

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On the Structure of Pergularin

The isolation of sarcostin (Ⅰ), metaplexigenin (Ⅱ), benzoylramanone (Ⅲ), deacylcynanchogenin (Ⅳ), utendin (Ⅴ), pergularin (Ⅵ), and two other aglycones from *Metaplexis joponica* Makino has been reported previously.1~5) In this communication, the experimental result leading the structure of pergularin (Ⅵ) is described. Pergularin (Ⅵ), m.p. 220~234°, $C_{21}H_{32}O_5 \cdot \frac{1}{2}H_2O$ (*Anal.* Calcd. : C, 67.55; H, 8.85. Found : C, 67.65; H, 9.32). $[\alpha]^{19}_{589}$ $-33°$ (c=0.1, MeOH, from ORD measurement). IR $\nu^{\text{Nujol}}_{\text{max}}$ cm^{-1} : 3550, 3450, 1720, 1690. Although Ⅵ showed two bands in the carbonyl region of the infrared spectrum,[*1] it gave only a monooxime (Ⅶ) which revealed no carbonyl absorption. Therefore, Ⅵ possesses only one carbonyl group. Very similar facts were reported in the case of deacylmetaplexigenin (Ⅱa).2,3) Acetylation of Ⅵ with acetic anhydride-pyridine afforded a diacetate (Ⅷ), m.p. 130~137°, $C_{25}H_{36}O_7$ (*Anal.* Calcd. : C, 66.94; H, 8.09. Found : C, 66.97; H, 8.46). The nuclear magnetic resonance spectrum of pergularin (Ⅵ) showed three singlet at 8.96 ($18\text{-}CH_3$), 8.29 ($19\text{-}CH_3$), 7.43 ($17\text{-}COCH_3$) τ in pyridine.[*3] The optical rotatory dispersion curves of pergularin (Ⅵ), and its acetate (Ⅷ), in methanol showed negative Cotton effect.

[*1] Pergularin (Ⅵ) is practically insoluble to CCl_4 and $CHCl_3$.
[*2] *Pergularia japonica* Thunb. is the synonym of *Metaplexis japonica* Makino.
[*3] In this paper, 10 p.p.m. value (from tetramethylsilane, used as internal standard) is used as τ.
1) H. Mitsuhashi, T. Nomura, Y. Shimizu, I. Takemori, E. Yamada : This Bulletin, **10**, 811 (1962). In the report, pergularin was expressed as crystal 3, and utendin as crystal 4.
2) H. Mitsuhashi, T. Nomura : *Ibid.*, **11**, 1333 (1963).
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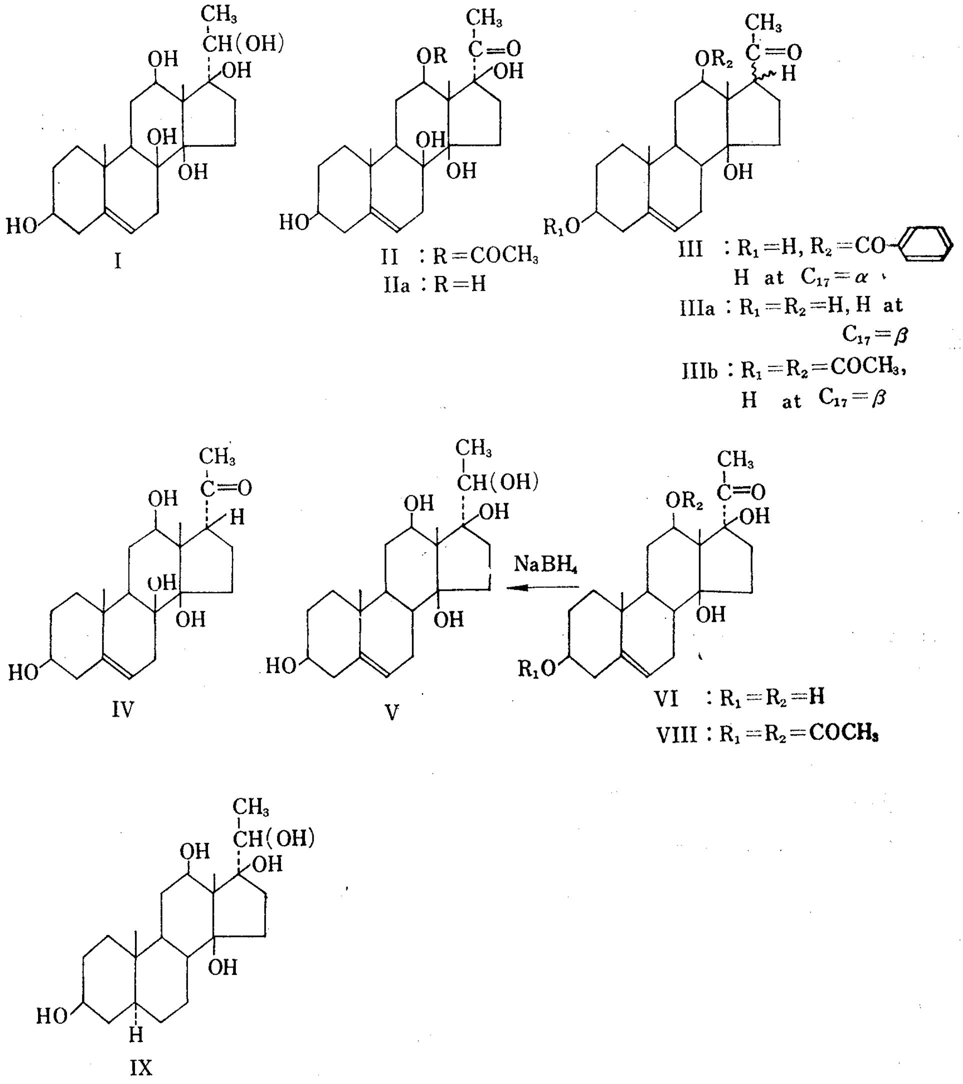
These curves were shifted about 10 mμ to longer wave length in comparison with those of ramanone (IIIa), and its acetate (IIIb),[2,5,6] suggesting the presence of a α-ketol system.[6,7]

TABLE I.

Compound	Trough $[\varphi]_{311}$	Peak $[\varphi]_{268}$	$a \times 10^{-2}$
VI	−3878	+5086	−89.6
VIII	−5037	+4606	−96.4

After VI was treated with 3% methanolic potassium hydroxide for 24 hr. at room temperature, the resulting mixture showed only one spot which was identified as starting material (VI) on paper partition chromatogram ($CHCl_3$/formamide).[8] This results indicated that pergularin (VI) could not be isomerized under this condition, which led



I

II : R=$COCH_3$
IIa : R=H

III : R_1=H, R_2=CO–
H at $C_{17}=\alpha$
IIIa : $R_1=R_2$=H, H at $C_{17}=\beta$
IIIb : $R_1=R_2=COCH_3$, H at $C_{17}=\beta$

IV

V

VI : $R_1=R_2$=H
VIII : $R_1=R_2=COCH_3$

IX

Chart 1.

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6) H. Mitsuhashi, T. Nomura, M. Fukuoka : Steroids, **4** : 4, 483 (1964).

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8) H. Mitsuhashi, Y. Shimizu, E. Yamada, I. Takemori, T. Nomura : This Bulletin, **10**, 808 (1962).

17-H-20-one steroids to complete equilibrium mixture of the side chain in most cases.[6,11] The above facts strongly suggest that pergularin (VI) has C/D *cis* ring juncture, and 17β-OH, 17α-$COCH_3$ side chain.[6] Since sarcostin (I), and four other compounds (II, III, IV, V), which have 3β,12β,14β-OH groups, have been isolated from the same plants, biogenetic analogy would favour the structure (VI) for pergularin. This assumption was proved by the following results. Pergularin (VI) was reduced with $NaBH_4$, and the product examined by paper chromatography ($CHCl_3$/formamide),[8] giving two spots. The major spot was identical with that of utendin (V). On partition chromatography over Celite(C_6H_6+BuOH/H_2O), crystals, m.p. 240~250°, were isolated, which was identified with utendin (V) by a mixed fusion. Utendin has been isolated from *Pacycarpus lineolatus*,[10] 5α-dihydroutendin = tomentogenin (IX) from *Marsdenia tomentosa*.[11] Recently, the structures of these compounds (V, IX) were established by Reichstein's group[12] and Mitsuhashi's group,[13] independently.

Thus perugularin is represented by the structure (VI).

Faculty of Pharmaceutical Sciences,
School of Medicine,
Hokkaido University,
Sapporo, Hokkaido

Hiroshi Mitsuhashi (三橋 博)
Taro Nomura (野村太郎)

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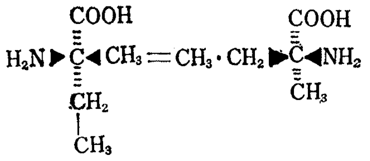
The Absolute Configuration of Optically Active Isovaline

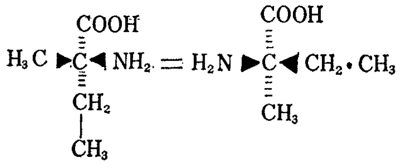
Many of the recent studies on α-alkyl-α-amino acids have revealed that some of them have physiologically very interesting properties,[1] and few were found in natural products.[2] The absolute configuration of these amino acids is either still unknown or just only suggestive.[3~5]



$$H_2N\blacktriangleright\overset{COOH}{\underset{CH_2\cdot CH_3}{C}}\blacktriangleleft CH_3 = CH_3\cdot CH_2\blacktriangleright\overset{COOH}{\underset{CH_3}{C}}\blacktriangleleft NH_2$$

$S^{a)}$- isovaline

IIa IIb



$$H_3C\blacktriangleright\overset{COOH}{\underset{CH_2\cdot CH_3}{C}}\blacktriangleleft NH_2 = H_2N\blacktriangleright\overset{COOH}{\underset{CH_3}{C}}\blacktriangleleft CH_2\cdot CH_3$$

$R^{a)}$- isovaline

IIIa IIIb

a) cf. R.S. Cahn, C.K. Ingold, V. Prelog : Experientia, **12**, 81 (1956).

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