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Isolation of Alkaloids from *Vinca* (*Lochnera*) *rosea* L. REICHB.

Since the isolation of reserpine from *Rauwolfia serpentina*, studies of alkaloidal constituents of various Apocynaceae plants have been carried out all over the world. Our investigations on the alkaloids of a Japanese ornamental plant, *Vinca rosea* (or *Lochnera rosea*) have led to the isolation of δ-yohimbine, tetrahydroalstonine, and serpentine. At the same time the presence of alstonine was also presumed.

From the weakly basic alkaloidal fraction, obtained from the dried roots of *Vinca rosea*, two crystalline alkaloids were isolated by chromatography with aluminum oxide. The first eluted alkaloid, crystallizing from methanol into plates, was proved to be identical with tetrahydroalstonine, which had been found in *Rauwolfia sellowii*,[1] m.p. 225~227°, $[\alpha]_D^{21}$: −86°(pyridine) (*Anal.* Calcd. for $C_{21}H_{24}O_3N_2$: C, 71.57; H, 6.87; N, 7.95. Found : C, 71.35; H, 6.72; N, 7.77). This alkaloid produced brownish violet color in the Keller reaction. U.V. λ_{max}^{EtOH} mμ(log ε) : 226(4.54), 280(3.84), λ_{min}^{EtOH} mμ(log ε) : 265(3.80); I.R. λ_{max}^{Nujol} μ : 2.94, 5.89, 6.17, 9.19, 13.33. The hydrochloride crystallized from methanol and melted at 277~280°(decomp.), which showed no depression on admixture with an authentic specimen.*

The second eluted alkaloid crystallized from methanol into prisms, m.p. 253~255°, $[\alpha]_D^{23}$: −54°(pyridine), and was found to be identical with δ-yohimbine, which had been found in Rauwolfia[2] and also in *Vinca rosea.*[3] (*Anal.* Calcd. for $C_{21}H_{24}O_3N_2$: C, 71.57; H, 6.87; N, 7.95. Found : C, 71.29; H, 6.65, N, 7.86). Keller reaction showed a brownish violet color. U.V. λ_{max}^{EtOH} mμ(log ε) : 228(4.34), 280(3.65); λ_{min}^{EtOH} mμ(log ε) : 261(3.49); I.R. λ_{max}^{Nujol} μ : 2.96, 5.93, 6.27, 9.03, 13.55. The hydrochloride, crystallized from methanol, had m.p. 272~275°(decomp.). A mixture of authentic δ-yohimbine** and the free base showed no depression of the melting point.

On the other hand, a colored alkaloid was obtained from the strongly basic fraction by chromatography of reineckate, which formed yellow crystalline nitrate of m.p. 190~200°(decomp.). *Anal.* Calcd. for $C_{21}H_{20}O_3N_2HNO_3 \cdot 1.5H_2O$: C, 57.53; H, 5.52; N, 9.59. Found : C, 57.46; H, 5.69; N, 9.79 U.V. λ_{max}^{EtOH} mμ(log ε) : 250(4.48), 305(4.30), 365(3.63). The ultraviolet spectrum of this alkaloid was typical of those found in anhydronium base in indole alkaloids. The ultraviolet spectrum of this alkaloid was compared with that of the pure serpentine obtained by Pd-maleic acid dehydrogenation from δ-yohimbine and were found to be almost identical. In addition, the reduction of this base by $NaBH_4$ in methanol gave a good yield of δ-yohimbine (ca. 90%) which showed no depression in mixed fusion. Therefore, it is highly probable that above nitrate is an almost pure serpentine nitrate. Serpentine was originally found in the root of *Rauwolfia serpentina*[4] and later in *Vinca rosea.*[3]

A strongly basic crude fraction similarly obtained in another batch was reduced by $NaBH_4$ in methanol and gave tetrahydroalstonine and δ-yohimbine in the ratio of about 2 to 3, and the presence of alstonine in the strongly basic alkaloids was presumed.

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1) S.C. Pakrashi, C. Djerassi, R. Wasicky, N. Neuss : J. Am. Chem. Soc., **77**, 6687(1955).
2) A. Hofmann : Helv. Chim. Acta, **37**, 849(1954).
3) C. Djerassi, *et al.* : Chem. & Ind. (London), **1956**, 173.
4) E. Schlittler, H. Schwarz : Helv. Chim. Acta, **33**, 1463(1950); F. Bader, H. Schwarz : *Ibid.*, **35**, 1594(1952).

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A New Triterpenoid Alcohol, 24-Methylenecycloartanol, as its Ferulate, from Rice Bran Oil

Recent reports[1] from this laboratory described the isolation of three phenolic substances, oryzanol-A, -B, and -C, from rice bran oil and the structure of oryzanol-A was determined as cycloartenyl ferulate. The structure of oryzanol-C has now been elucidated as 24-methylenecycloartanyl ferulate by the following experiments.

From the most insoluble fraction of oryzanol acetate mixtures, oryzanol-C acetate, m.p. 216~218°, $[\alpha]_D$ +39°[2] (*Anal.* Calcd. for $C_{43}H_{62}O_5$: C, 78.38; H, 9.48. Found : C, 78.18; H, 9.20), was obtained and deacetylated under weakly alkaline conditions to oryzanol-C, m.p. 162~164/193~194°, $[\alpha]_D$ +36°. U.V. : λ_{max}^{EtOH} 322 mμ (log ε 4.29) (*Anal.* Calcd. for $C_{41}H_{60}O_4$: C, 79.82; H, 9.80. Found : C, 79.59; H, 10.07). Drastic saponification of oryzanol-C gave ferulic acid and a new triterpenoid alcohol (I), m.p. 121~122°, $[\alpha]_D$ +43° (*Anal.* Calcd. for $C_{31}H_{52}O$: C, 84.48; H, 11.89. Found : C, 84.30; H, 11.66), characterised as its acetate (II), m.p. 116~117°, $[\alpha]_D$ +54° (*Anal.* Calcd. for $C_{33}H_{54}O_2$: C, 82.09; H, 11.27. Found : C, 82.48; 11.06), and its benzoate, m.p. 156~157°, $[\alpha]_D$ +62° (*Anal.* Calcd. for $C_{38}H_{56}O_2$: C, 83.77; H, 10.36. Found : C, 83.79; H, 10.49). Oppenauer oxidation of (I) afforded a ketone, m.p. 111~112°, $[\alpha]_D$ +20° (*Anal.* Calcd. for $C_{31}H_{50}O$: C, 84.86; H, 11.49. Found : C, 84.40; H, 11.66); oxime, m.p. 189~190°. (I) contains one double bond which was determined by oxidation of (II) with perbenzoic acid, and catalytic hydrogenation of (I) with platinum catalyst gave a dihydric alcohol, m.p. 135.5~136.5°, $[\alpha]_D$ +46.5°; acetate, m.p. 123~124°, $[\alpha]_D$ +54.5° (*Anal.* Calcd. for $C_{33}H_{56}O_2$: C, 81.75; H, 11.64. Found : C, 81.60; H, 11.64).

The infrared spectrum of (I) exhibits absorptions at 1045, 1020, 1005, and 988 cm^{-1} (in CS_2), and the acetate (II) at 1242, 1039, 1022, and 978 cm^{-1} (in CS_2), which can be interpreted as indicatiag the presence of cycloartane-type ring system.[3] Absorptions at 1639 and 887 cm^{-1} in the spectrum of (I) or (II) also suggest the presence of a vinylidene group, and the fact was confirmed by the formation of formaldehyde on ozonolysis of (II). The other product obtained by ozonolysis is an acetoxy-demethyl-oxo compound (III), m.p. 121~123°, $[\alpha]_D$ +52°; I.R. $\nu_{C=O}$ 1710 cm^{-1} (Nujol) (*Anal.* Calcd. for $C_{32}H_{52}O_3$: C, 79.28; H, 10.81. Found : C, 79.17; H, 10.63); oxime, m.p. 192~194°, $[\alpha]$, +50°. (III) was not isomerised on treating with alkali, apart from hydrolysis of the acetoxyl group, and the fact, contrary to the case of oxonorcyclolaudanyl acetate,[4] shows the absence of

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1) M. Shimizu, *et al.* : This Bulletin, **5**, 36, 40(1957).
2) Optical rotations were taken in $CHCl_3$ unless otherwise stated.
3) cf. I.L. Allsop, *et al.* : J. Chem. Soc., **1956**, 4868.
4) cf. J.A. Henry, *et al.* : *Ibid.*, **1955**, 1607.