Secondly, elution with benzene–$CHCl_3$ (5:1) gave a syrup, which was triturated with acetone to give crystals. Recrystallization from $CHCl_3$–ether afforded 250 mg of the base (A), namely, VIa as colorless needles, mp 253—255°. NMR τ ($CDCl_3$): 2.05—3.50 (10H, aromatic protons), 6.16, 6.17 (12H, two singlets, $4\times OC\underline{H}_3$), 7.57 (6H, singlet, $2\times NC\underline{H}_3$). *Anal.* Calcd. for $C_{44}H_{54}O_6N_2\cdot 1/2H_2O$[6]: C, 73.82; H, 7.74; N, 3.91. Found: C, 73.93; 73.67; H, 7.94; 7.75; N, 3.64. Mass (*m/e*): 706 (M^+) (40%), 691 (M^+–15) (42%), 676 (M^+–30) (37%), 661 (M^+-45) (17%), 646 (M^+-60) (6%), 352 (M-2)$^{++}$ (100%), 338 (M^+-140) (12%), 324 (M^+-372) (47%), 310 (M^+-396) (26%), 296 (M^+-410) (28%). The filtrate, from which the base (A) was removed by filtration, was chromatographed on 20 g of Al_2O_3 and removal of the benzene–$CHCl_3$ (10:1) gave 200 mg of the base (B), namely, VIb, as a pale yellow syrup. NMR τ ($CDCl_3$): 2.05—3.70 (10H, aromatic protons), 6.17, 6.12 (12H, two singlets, $4\times OC\underline{H}_3$), 7.59 (6H, singlets, $2\times NC\underline{H}_3$). Recrystallization of the perchlorate of VIb from acetone–ether afforded colorless needles, mp 280—282°. *Anal.* Calcd. for $C_{44}H_{54}O_6N_2\cdot 2HClO_4\cdot 2H_2O$[6]: C, 55.99; H, 6.41. Found: C, 56.08; H, 6.51. The fragmentation patterns in the mass spectrum of Vb was identical with that of Va.

Acknowledgement We are grateful to President Dr. M. Terasaka of Tokyo College of Pharmacy for his encouragement. We also thank Analytical Center of Tokyo College of Pharmacy for microanalysis.

[Chem. Pharm. Bull. 17(8)1733—1735(1969)]

UDC 615.322.011.5 : 547.833.9.02

Studies on Ergot Alkaloids and Related Compounds. XVI.[1] On the So-called Bohlmann Absorption of 2,4-Disubstituted Octahydrobenzo[*f*]quinoline Derivatives[2]

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Previously, we have prepared a series of 2,4-disubstituted octahydrobenzo[*f*]quinoline derivatives, structurally related to lysergic acid and established their stereochemistries and conformations of their stereoisomers on the basis of chemical and physical evidences.[2,4]

Recently, Edwards and his coworkers[5] have suggested from study on the lupine alkaloids that in a given conformation of a heterocyclic system, at least one hydrogen antiparallel to the lone pair of nitrogen is on carbon atom attached to nitrogen, the shape and intensity of Bohlmann *trans* band[6] being proportional to the number of *trans* diaxial hydrogen. This report pushed us to write this paper based on data obtained from our compounds (I—VIII), which exhibited strong and characteristic absorptions in the Bohlmann band region, although they are not of the quinolizidine type compounds.

Infrated spectra of the previously described compounds (I—VIII, measured in chloroform) were exemplified by four typical examples as shown in Fig. 1, to which all eight compounds could be classified by the shape of their Bohlmann bands.

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3) Location: *Toneyama, Toyonaka, Osaka*; Present Address: *a*) *Osaka College of Pharmacy, Takaminosato, Matsubara, Osaka*; *b*) *Kobe Women's College of Pharmacy, Nakano, Motoyama, Higashinada, Kobe, Hyogo.*
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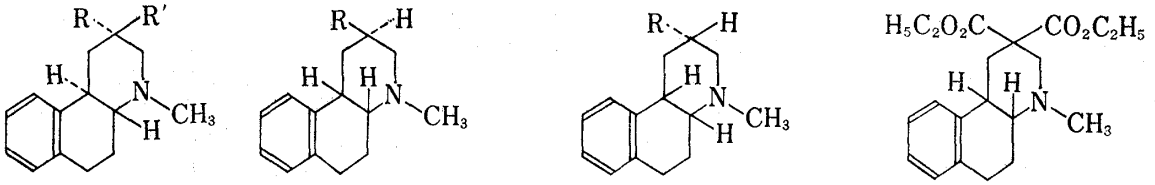

I : R=H, R'=$CO_2C_2H_5$ IV : R=$CO_2C_2H_5$ VI : R=$CO_2C_2H_5$ VIII
II : R=H, R'=CH_3 V : R=CH_3 VII : R=CH_3
III : R=CH_3, R'=H

Chart 1[7]

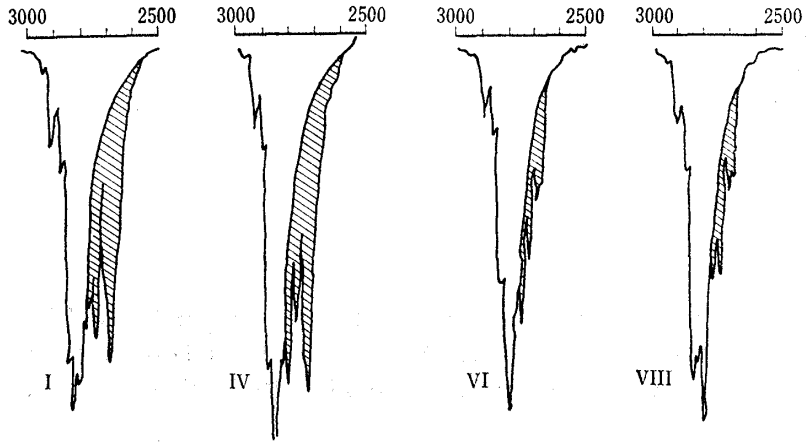

Fig. 1. Infrared Absorption Spectra of I, IV, VI and VIII in Bohlmann Band Area (cm^{-1})

When compared their *trans* band areas, shown by an oblique line in Fig. 1,[5] the compounds having the conformation A (I, II and III) and B (IV and V) exhibited very strong and characteristic band areas, whereas in the compounds having the conformation C (VI and VII) and D (VIII), these band areas were comparatively small.

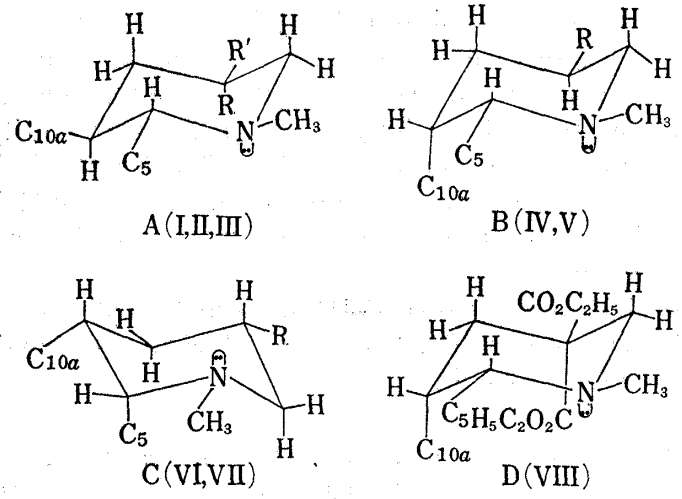

Chart 2

The relationship between the conformations of these compounds and shapes and intensities of their Bohlmann band could be explained as follows. In the partial conformation of C–ring of 2,4-disubstituted octahydrobenzo[*f*]quinolines, compounds having the conformation A (I, II and III) and B (IV and V) would have two hydrogens in antiparallel relation to the lone pair of basic nitrogen, thereby exhibiting strong band area, as shown in Chart 2.

However, in the compounds of the conformation C (VI and VII), there would exist only one hydrogen of such spatial circumstances, thereby corresponding to narrower area. And the compound VIII which have two ester groups at C–2, showed none or very narrow band area in spite of the presence of two hydrogens in anti-

7) The projections used in this paper were depicted according to the reference 4).

parallel relation to the basic nitrogen. This could be explainable by the electrostatic and the steric interferences of an ester group in 1,3-diaxial relation to the lone pair, thus causing some deformation of C-ring from taking the normal chair form.

Generally, interpretation of the absorption in the 2700—2900 cm^{-1} region in term of the Bohlmann band is said to be very careful, otherwise apt to committing misjudging the situation. Thus the application of the Bohlmann band to the ring system other than the quinolizidine system has been known very few, *i.e.*, Bohlmann bands in the oxazine system by Leonard[8] and also in the azabicycloketone system by House[9] were among rare cases reported.

Although the Bohlmann-like absorption on our compounds were obvious, further extensive and quantitative analyses are needed to draw the conclusion over the octahydrobenzo[*f*]-quinoline system.

Experimental

Infrared absorption spectra were measured in chloroform solution of the compounds previously reported[4], using NaCl cell on Hitachi Spectrophotometer EPI-G_2.

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[Chem. Pharm. Bull. 17(8)1735—1739(1969)]

UDC 581.19 : 547.918.02 : 547.92.02

Isolation and Structure of a New Tokorogenin Glycoside

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Tokorogenin which was obtained from the underground parts[2] and also from the aerial parts[3a] of *Dioscorea Tokoro* MAKINO and assigned the structure, 25D,5β-spirostane-1β,2β,3α-triol (I),[4] is the first unusual spirostanol having 3α-hydroxyl group so far found in plants. Later the analogous 2β,3α-diol (yonogenin),[3,5] 1β,2β,3α,5β-tetraol (kogagenin)[3a,6] and, quite recently, 25L,5β-spirostane-2β,3α,4β-triol (diotigenin)[3b,7] were isolated, accompanying tokorogenin, from *D. Tokoro*[3a] and *D. tenuipes* complex.[3b]

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