$$S_{Day \times Diff.\ Curv.} = (Q_1^2 + {}_2Q^2 + \cdots\cdots + Q_6^2)/48 - Q_{\cdot}^2/48\times 6 \qquad (f=5)$$

cf.

$$S_{Diff.\ Curv.} = Q_{\cdot}^2/48\times 6$$

As stated above, the interaction between **B** (or *Bath*) and **P**(or Treatment) can also be analyzed into subdivided ones, if necessary.

TABLE VII Table for the Calculation of the Interaction, *Day*×*Diff*. *Curv*.

	Sum of Products
D_1	$(x_{11}+2x_{15}+x_{13})-(x_{14}+2x_{12}+x_{16})=Q_1$
D_2	$(x_{21}+2x_{25}+x_{23})-(x_{24}+2x_{22}+x_{26})=Q_2$
$\vdots$	$\vdots$
D_6	$(x_{61}+2x_{65}+x_{63})-(x_{64}+2x_{62}+x_{66})=Q_6$
Total	$Q_{\cdot}=Q_1+Q_2+\cdots\cdots+Q_6$ $=(x_{\cdot 1}+2x_{\cdot 5}+x_{\cdot 3})-(x_{\cdot 4}+2x_{\cdot 2}+x_{\cdot 6})$

Tatsuo Ohta and Toshio Miyazaki: Furoquinolines. II.[1] Catalytic Reduction of Skimmianine (Addendum).

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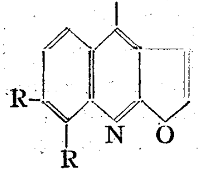
Recently, one of the authors (Ohta)[1] published that 2:3-furo-(2′:3′)-quinoline series of alkaloids, such as dictamnine (I) and skimmianine (II), are cleaved to 2-hydroxy-3-ethylquinoline compounds by catalytic hydrogenation with PtO_2 as a catalyst, and this is a new degradation procedure for the determination of chemical structures employing a small amount of sample.

In the present paper, the authors describe the demethylation of the reduction product of skimmianine, namely, 4,7,8-trimethoxy-2-hydroxy-3-ethylquinoline (III). By boiling (III) with conc. hydrochloric acid, hydrolysis of the one methoxyl group in the pyridine nucleus[2] occurred and 7,8-dimethoxy-2,4-dihydroxy-3-ethylquinoline (IV) was formed as crystals of m.p. 202°. The acetylation of (IV) with acetic anhydride containing a few drops of pyridine gave a monoacetate of m.p. 174°. It was presumed that the monoacetate thus obtained is the ester of 4-hydroxyl group, viz. 4-acetoxy-7,8-dimethoxy-2-hydroxy-3-ethylquinoline (V), as in the case of the monoacetate of 2,4-dihydroxyquinoline[3] and 2,4-dihydroxy-3-ethylquinoline[1].

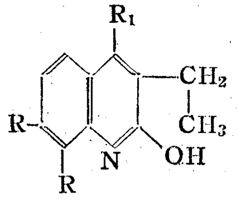
The demethylation of 4,7,8-trimethoxy-2-hydroxy-3-ethylquinoline (III) with HI gave 2,4,7,8-tetrahydroxy-3-ethylquinoline (VI), m.p. 243~244°, which forms a triacetate of m.p. 264° by means of acetic anhydride and pyridine. This acetate was considered as 4,7,8-triacetoxy-2-hydroxy-3-ethylquinoline (VII) from the case of (V).

Analyses were made by Mr. T. Kaneko to whom the authors' thanks are due.



(I) R=H

(II) R=OCH3



(III)	R=OCH_3,	R_1=OCH_3
(IV)	R=OCH_3,	R_1=OH
(V)	R=OCH_3,	R_1=$OCOCH_3$
(VI)	R=OH,	R_1=OH
(VII)	R=$OCOCH_3$,	R_1=$OCOCH_3$.

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[2] Y. Asahina, M. Inubuse: Ber., **63**, 2052 (1930).

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Experimental

Catalytic reduction of skimmianine—An absolute alcoholic solution of 3 g. of the sample was submitted to catalytic reduction with PtO_2 as a catalyst, at room temperature and under ordinary pressure. Almost 2 moles of hydrogen was absorbed quite smoothly, the violet fluorescence disappearing gradually. After removal of the catalyst by filtration, the solvent was evaporated to almost dryness, yielding colorless prisms of m.p. 183°. Yield, quantitative. When the crystals were recrystallized from alcohol, the melting point did not rise any more and showed no depression of the melting point when mixed with the reduction product of skimmianine, which was previously obtained in glacial acetic acid solution.

Demethylation of the reduction product of skimmianine with conc. HCl (Formation of 7,8-dimethoxy-2,4-dihydroxy-3-ethylquinoline (IV))—0.7 g. of the sample was dissolved in 14 cc. of conc. hydrochloric acid (d=1.183) and boiled on a wire-gauze, by which crystals began to deposit. After 1 hour, cooled reaction mixture was made alkaline with aq. potassium hydroxide solution, the minute amount of insoluble amorphous material filtered off, and the filtrate was slightly acidified with hydrochloric acid. The crystals that separated were collected, washed with water, and crystallized from alcohol to colorless prisms, m.p. 202°. Yield, 0.4 g. It gives no coloration with ferric chloride. *Anal.* Calcd. for $C_{13}H_{15}O_4N$: C, 62.65; H, 6.02; N, 5.62. Found: C, 62.59; H, 5.70; N, 5.53.

Monoacetate of (IV)—A mixture of 0.2 g. of the sample, 3 cc. of acetic anhydride, and a drop of pyridine was heated on a boiling water bath for 1 hour, cooled, poured into ice-water, and the crystalline mass was collected and washed with water. The crude crystals were recrystallized from alcohol to colorless needles, m.p. 174°. *Anal.* Calcd. for $C_{15}H_{17}O_5N$; C, 61.85; H, 5.84; N, 4.81. Found: C, 61.51; H, 5.82; N, 4.82.

Demethylation of the reduction product of skimmianine with HI (Formation of 2,4,7,8-tetrahydroxy-3-ethylquinoline (VI))—0.8 g. of the sample was boiled gently with HI (d=1.7) for 1 hour. The content, which solidified on cooling, was filtered by suction and the crude product was crystallized from 10% alcohol to colorless pillars (0.5 g.), m.p. 243~244°. It gives green coloration with ferric chloride in an alcoholic solution. *Anal.* Calcd. for $C_{11}H_{11}O_4N \cdot 1\frac{1}{2}H_2O$: C, 53.22; H, 5.64; N, 5.64; H_2O, 10.88. Found: C, 52.68; H, 5.18; N, 5.49; H_2O, 10.77.

Triacetate of (VI)—To 0.1 g. of tetrahydroxy-3-ethylquinoline were added 2 cc. of acetic anhydride and a drop of pyridine, and the mixture was heated on a water bath for 50 minutes. After decomposition of the excessive acetic anhydride with ice-water, the acetate was recrystallized from alcohol to colorless needles, m.p. 264° (softening at 261°). It gives negative color reaction with ferric chloride. *Anal.* Calcd. for $C_{17}H_{17}O_7N$: C, 58.79; H, 4.89; N, 4.03. Found: C, 59.10; H, 4.77; N, 4.01.

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