

conjugates added to pregnancy urine were gel-filtered on Sephadex G-25, and peaks I and II were collected separately and evaporated to dryness *in vacuo*. The dry residues were taken up in 3 ml of the eluting solvent and chromatographed in the systems designed for peak I and II conjugates. The presence of urinary peak I and II contents in the samples did not alter the elution pattern of the labeled reference compounds.

Application. In chromatographic experiments on Sephadex LH-20 the elution pattern of labeled estriol glucuronides and estriol sulfate closely resembled that of the neutral steroid glucuronides and monosulfates. In addition, the estriol double conjugate (E₃-3S,16Gl) was strongly retarded in the column, as is the case with the neutral steroid disulfates.^{11,15} This seems to confirm earlier studies,^{8,9} which suggested that it is the mode of conjugation, rather than the steroid nucleus, which determines the elution behaviour of conjugated steroids on lipophilic Sephadex. Experiments with labeled estriol conjugates indicate that by chromatography on Sephadex LH-20 a convenient group separation of estrogen conjugates may be achieved, where at least glucuronides, sulfates, and sulfo-glucuronides can be separated from each other. In addition, gel filtration on Sephadex G-25 can be used in the separation of estrogen 3-glucuronides from estrogen 16-glucuronides. Thus it can be concluded that gel chromatography on Sephadex LH-20 in combination with gel filtration on Sephadex G-25 provides a useful means for group separation of urinary estrogen conjugates.

Acknowledgements. We are indebted to Mrs. Diana Godenhjelm and Mr. Henrik Brunholm for skilful technical assistance.

The expenses of this investigation were defrayed by grants from the *Population Council, New York* (Nos. M69.7 and M70.10C) and from the *Nordisk Insulinfond*.

One of us (M.J.T.) is a research fellow of the *National Research Council for Medical Sciences* in Finland.

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Received November 13, 1970.

Studies on Orchidaceae Alkaloids

XX.* The Constitution and Relative Configuration of Crepidine, an Alkaloid from *Dendrobium crepidatum* Lindl.

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Five closely related crystalline alkaloids have been isolated from *Dendrobium crepidatum* Lindl.² One of the bases (C₂₁H₂₉NO₃), named crepidine (I), crystal-

* No. XIX of this series, see Ref. 1.

signals at τ 9.10 (d, 3 H, $J=6$ Hz, CHCH_3), τ 8.33 (s, 3 H, $\text{CH}_3\text{COCH}_2-$), τ 7.82 (s, 3 H, NCH_3 or $\text{CH}_3\text{CO}-$), τ 7.77 (s, 3 H, NCH_3 or $\text{CH}_3\text{CO}-$), τ 7.55 (d, 2 H, $J=5$ Hz, $-\text{COCH}_2\text{CH}-$), τ 6.48 (t, 1 H, $J=5$ Hz, $-\text{COCH}_2\text{CHN}$), τ 5.38 (s, 1 H, OH, concentration dependent) and τ 2.2–2.9 (m, 5 H, phenyl group). Two olefinic protons exhibits an ABX₂ pattern with τ_A 3.82 and τ_B 3.14 ($J_{AB}=16$ Hz, $J_{AX_2}=1.1$ Hz, $J_{BX_2}=6$ Hz) indicating the $-\text{CH}_2-\text{CH}_B=\text{CH}_A-\text{CO}-$ system. The large AB coupling implies a *trans* configuration for these protons.

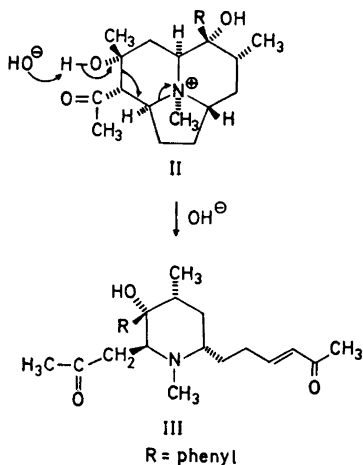


Fig. 3. Alkaline degradation of crepidine methiodide (II).

A full report on the isolation and structural determination of the alkaloids found in *D. crepidatum* will be published later.

Acknowledgements. We are indebted to Dr. Björn Luning for his interest in this work. A fellowship from *Stiftelsen Bengt Lundqvists Minne* to one of us (K.L.) is gratefully acknowledged. This work was supported by the *Tri-Centennial Fund of the Bank of Sweden* and the *Swedish Natural Science Research Council*.

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- Received november 17, 1970.

Acta Chem. Scand. **24** (1970) No. 10

Solute Alignment in the Nematic Mesophase

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The anisotropy in the solute-solvent intermolecular potential results in the partial alignment of non-spherical solutes by nematogenic solvents. The nature of the anisotropic potential is conveniently studied by measuring the ordering matrix ϕ which describes the solute alignment.^{1,2} The elements of the matrix are defined by

$$\phi_{ij} = \frac{3\bar{l}_i l_j - \delta_{ij}}{2}$$

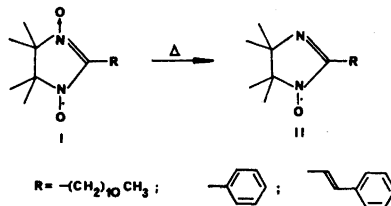
where the bar denotes an ensemble average and l_i is the direction cosine between the i th molecular axis and the optic axis of the mesophase.³ When the solute is paramagnetic the ordering matrix may be determined from the electron resonance spectra of the solute, both above and below the nematic-isotropic transition point.⁴ The resulting shifts in the g factor and coupling constants are directly related to the elements of the ordering matrix by

$$\delta g = \sum_{i,j} g'_{ij} \phi_{ij}$$

and

$$\delta a = \sum_{i,j} A'_{ij} \phi_{ij}$$

where g' and A' are the anisotropic g and hyperfine tensors.⁴ In this communication we report such measurements for 2-substituted 4,4,5,5-tetramethyl-1,3-dioxymidazolines (I) which were prepared by employing the synthesis described by Osiecki and Ullman.⁵



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