

SPECIALIA

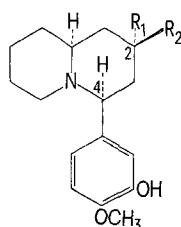
Les auteurs sont seuls responsables des opinions exprimées dans ces brèves communications. – Für die Kurzmitteilungen ist ausschliesslich der Autor verantwortlich. – Per le brevi comunicazioni è responsabile solo l'autore. – The editors do not hold themselves responsible for the opinions expressed in the authors' brief reports. – Ответственность за короткие сообщения несёт исключительно автор. – El responsable de los informes reducidos, está el autor.

A New Phenylquinolizidol of *Heimia salicifolia*

In continuing our studies on the alkaloids of *Heimia salicifolia* Link and Otto we have established the presence of 2-hydroxy(a)-4-(3-hydroxy-4-methoxyphenyl) (e)-*trans*-quinolizidine (I) in extracts of young seedlings of *H. salicifolia*. A phenolic 4-phenylquinolizidine derivative such as I has been postulated as an intermediate in the biosynthesis of the lactonic lythraceous alkaloids¹⁻⁴. Such an uncoupled and nonesterified phenylquinolizidol has not been previously identified in this or related species.

During investigations of the sequential appearance of the alkaloids of *H. salicifolia* the presence of two unknown alkaloids in 7-day-old seedlings was observed⁵. We continued with these studies and have determined that one of the compounds is the phenylquinolizidol I by direct comparison with a synthetic sample. We found that I accumulates only in relatively young seedlings. It could not be found in the seeds, in 2-week-old seedlings⁵, in 5-6-month-old plantlets, or in mature plants.

Seedlings (5-day-old) and some ungerminated seeds were dried (6.7 g), and extracted (blender) with acetate buffer at pH 5. Undesirable material was eliminated from this solution with CHCl_3 . CHCl_3 -MeOH (4:1) extraction at pH 8.5-9, gave the desired alkaloids (25.7 mg).



I, $R_1 = \text{OH}$, $R_2 = \text{H}$
 II, $R_1 = \text{H}$, $R_2 = \text{OH}$
 III, $R_1, R_2 = 0$

Compound I, (0.6 mg) was obtained by preparative TLC [$\text{Al}_2\text{O}_3\text{GF}_{254}$; NH_3 saturated benzene-MeOH (190:10), double development, followed by NH_3 saturated EtOAc-EtOH (210:2.5)]. That the natural compound was identical with the synthetic compound was verified by TLC (3 alumina and 7 silica gel systems) and by mass spectrometry.

I possesses the same stereochemistry (C-2 oxygen axial, phenyl ring equatorial, nitrogen spin pair axial) as all the *Heimia* alkaloids. We have not detected the equatorial alcohol in any plant material analyzed.

Condensation of pelletierine with isovanillin^{6,7} gave 2-keto-4-(3-hydroxy-4-methoxyphenyl)(e)-*trans* quinolizidine (III); mp 136-138° (MeOH or MeOH-acetone), reported 162-163°⁷ and mp 139-140° (Et₂O); γ - KBr_{max} cm^{-1} 2780 (*trans* quinolizidine), 1730 (CO); NMR (CDCl_3) δ 7.02 (s; 1H), 6.85 (s; 2H), 5.75 (s; 1H exchangeable with D_2O), 3.92 (s; 3H), 3.24 (q, $J = 12$ and 3 Hz; 1H), 1-2.90 (m; 13H); mass spectrum M^+ 275.1519, calcd for $\text{C}_{16}\text{H}_{21}\text{O}_3\text{N}$ 275.1516. Benzoylation gave 2-keto-4-(3-benzyloxy-4-methoxyphenyl)(e)-*trans*-quinolizidine, mp, NMR and IR as reported⁸.

Reduction of III (as the tetraphenylborate salt⁸) with sodium borohydride gave, as expected, a minor (the

axial, I) and a major (the equatorial, II) compound. The mixture was resolved using column chromatography [alumina, basic, I; CHCl_3 plus increasing amount of MeOH 2-10%] followed by preparative TLC, [$\text{Al}_2\text{O}_3\text{GF}_{254}$; NH_3 saturated CHCl_3 -EtOH (19:1.3), double development, or NH_3 saturated benzene-MeOH (19:1.2), triple development].

2-Hydroxy (e)-4-(3-hydroxy-4-methoxyphenyl) (e)-*trans* quinolizidine (II) gave mp 158-159° (MeOH-EtOAc); λ MeOH_{max} nm 282 ($\log \epsilon = 3.5$); addn of NaOH (0.5 N gave 292; γ KBr_{max} cm^{-1} 3380 (OH), 2780 (*trans* quinolizidine), NMR ($\text{CDCl}_3 + \text{d}_6$ acetone) δ 6.80 (s; 1H), 6.70 (s; 2H), 3.75 (s; 3H), 3.50 (m; 2H, one exchangeable with D_2O), 2.85 (q; $J = 11$ and 2.5 Hz; 1H), 1-2.80 (m); mass spectrum M^+ 277.1682 calcd for $\text{C}_{16}\text{H}_{23}\text{O}_3\text{N}$ 277.1672. Benzoylation gave 2-hydroxy(e)-4-(3-benzyloxy-4-methoxyphenyl)(e)-*trans* quinolizidine, IR as reported⁸.

2-Hydroxy (a)-4-(3-hydroxy-4-methoxyphenyl) (e)-*trans* quinolizidine (I) gave mp 94-95° (EtOAc); γ KBr_{max} cm^{-1} 3380 (OH), 2850, 2800 (*trans* quinolizidine); λ MeOH_{max} nm 282 ($\log \epsilon = 3.45$), addn of NaOH (0.5 N) gave 289; NMR (CDCl_3) δ 6.95 (s; 1H), 6.75 (s; 2H), 4.10 (broad t; 2H), 3.85 (s; 3H), 3.25 (m; 2H), 1-2.90 (m); mass spectrum M^+ 277.1679, calcd for $\text{C}_{16}\text{H}_{23}\text{O}_3\text{N}$ 277.1672, found for natural I 277.1680.

Studies to determine the nature of the second compound present in the seedlings and to determine the possible biosynthetic significance of I are in progress.

Zusammenfassung. 2-Hydroxy(a)-4-(3-hydroxy-4-methoxyphenyl)(e)-*trans*-chinolizidin, eine Verbindung welche die strukturellen Merkmale eines vorgeschlagenen biosynthetischen Zwischenproduktes der lactonischen Lythraceae Alkaloide besitzt, wurde in Sämlingen von *Heimia salicifolia* nachgewiesen.

A. ROTHER and A. E. SCHWARTING

School of Pharmacy, University of Connecticut, Storrs (Connecticut 06268, USA),
 31 July 1973.

- J. P. FERRIS, C. B. BOYCE and R. C. BRINER, *Tetrahedron Lett.*, 1966, 5129.
- S. H. KOO, R. N. GUPTA, I. D. SPENSER and J. T. WROBEL, *J. chem. Soc. D, Chem. Commun.* 1970, 396.
- S. H. KOO, F. COMER and I. D. SPENSER, *J. chem. Soc. D, Chem. Commun.* 1970, 897.
- A. ROTHER and A. E. SCHWARTING, *Phytochemistry* 11, 2475 (1972).
- R. H. DOBBERSTEIN, Ph. D. thesis, University of Connecticut (1973).
- T. MATSUNAGA, I. KAWASAKI and T. KANEKO, *Tetrahedron Lett.*, 1967, 2471.
- J. T. WROBEL and M. W. GOLEBIEWSKI, *Roczn. Chem.* 45, 705 (1971).
- J. P. ROSAZZA, J. M. BOBBITT and A. E. SCHWARTING, *J. org. Chem.* 35, 2564 (1970).