hr). Removal of the catalyst and solvent left a residue, tetrahydrowisanidine (400 mg), which was crystallised from hexane–Et_2O mp 58–60°, ν_{max}^{KBr} cm^{-1} 2960, 2940, 1635, 1500, 1470, 1430, 1295, 1212, 1180, 1150, 1075, 1030, 990, 920, 855, NMR: δ 1.63 (4H, *m*), 2.28 (2H, *t*), 2.56 (2H, *t*), 3.44 (4H, *t*), 3.73 (3H, *s*), 5.87 (2H, *s*), 651 (1H, *s*), MS M^+ 305, 274, 175, 165, 135 (Found C, 66.71, H 7.45, N 4.52, $C_{17}H_{23}NO_4$ requires C, 66.89; H, 7.54; N, 4.59).

Reduction of **1** *with Zn–Cu couple.* Preparation of the Zn–Cu couple [6, 7]. Zn powder (35 g) was washed (4 × 20 ml) with dilute HCl (3%) each washing taking 5 min. The mixture was stirred during each washing and the acid removed by decantation. The Zn was then washed with water 3 × to eliminate traces of acid and (4 × 20 ml) with 2% $CuSO_4$. The couple was finally washed (3 × 20 ml) with the solvent, MeOH and rapidly poured into the reaction vessel. Alkaloid **1** (1.00 g) in MeOH–H_2O (3:1) was refluxed with the couple prepared above for 52.5 hr. The reaction mixture was taken up in more MeOH (50 ml) and filtered. The filtrate was evaporated to dryness under reduced pressure and the residue crystallised from Et_2O–hexane (1:1) mp 58–69°. This product was identical (IR, UV, NMR, MS, mp, mmp) with tetrahydrowisanidine.

Dehydrogenation of **1** *with DDQ.* A mixture of alkaloid **1** (1.420 g) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (1.40 g) in dry C_6H_6 (100 ml) was refluxed for 5 hr after which the mixture was chromatographed over neutral alumina eluting with hexane–C_6H_6. A yellow solid was obtained (500 mg) which was recrystallised from Me_2CO mp 170°. This compound was identical (IR, UV, NMR, MS, mp, mmp) with wisanidine.

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NUPHAROPUMILINE, A NEW QUINOLIZINE ALKALOID FROM *NUPHAR PUMILA*

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Key Word Index—*Nuphar pumila*; Nymphaeaceae; quinolizine alkaloids; (+)-nupharopumiline.

Abstract—A new quinolizine alkaloid, (+)-nupharopumiline, has been isolated from the rhizomes of *Nuphar pumila*. It has been shown by spectroscopic and chemical methods to possess the stereostructure **6** (1R, 4S, 7S).

INTRODUCTION

Several *Nuphar* species produce alkaloids having a furyl group attached to a quinolizine or piperidine ring system [1–3]. Similar compounds have been isolated from the scent gland of the Canadian beaver [4].

In connection with our investigation of the alkaloid contents of *Nuphar pumila* (Timm.) DC. (Nymphaeaceae), a perennial rhizomatous herb with a wide distribution in the temperate zone of the northern hemisphere [5–7], we isolated several basic compounds (total alkaloids obtained represent about 0.5% of the air dry material). In addition to the earlier known [1–3] (−)-deoxynupharidine **1**, (−)-7-*epi*-deoxynupharidine **2**, (+)-nupharidine **3**, and (+)-7-*epi*-nupharidine **4**, a new unstable base, for which the name (+)-nupharopumiline is proposed, was isolated in low yield.

RESULTS

(+)-Nupharopumiline, $[\alpha]_D^{20}$ + 27° ($CHCl_3$), mn 195–197° (CCl_4), represents about 0.15% of the total alkaloids of *Nuphar pumila* (*vide supra*), from which it was separated by column and preparative layer chromatography (*vide infra*). The ^1H NMR spectrum ($CDCl_3$) of nupharopumiline reveals the presence of two methyl groups (δ 0.93, 3H, *d*, 6 Hz: δ 1.03, 3H, *d*, 6 Hz), a vinyl proton (δ 4.48§, 1H, *dd*, 12 Hz, 4 Hz), and a furyl group (δ 6.60, 1H, *m*: δ 7.45, 1H, *m*: δ 7.64, 1H, *m*).

The MS (70 eV: 200°) of nupharopumiline shows an

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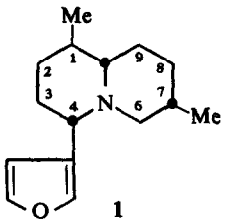
§ The corresponding signal in the ^1H NMR spectrum ($CDCl_3$) of Δ^3dehydrodeoxynupharidine **5** is claimed [8] to appear at δ 4.96.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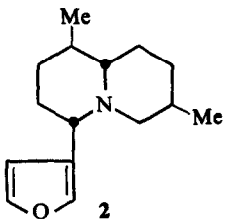
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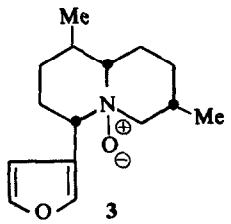
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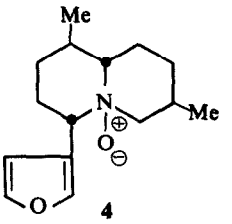
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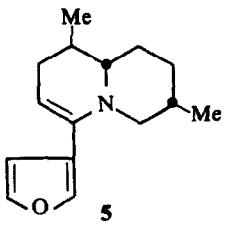
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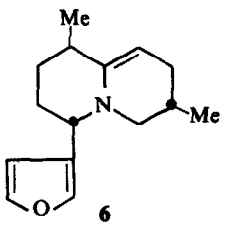
6

intense molecular ion peak at *m/e* 231 (100%) corresponding to $C_{15}H_{21}NO$. The fragmentation is relatively poor. The only ions that exceed 20% in relative intensity appear at *m/e* 216 (36%) ($M^+ - Me$), 96 (22%) ($C_6H_{10}N$), and 94 (32%) (C_6H_6O). The presence of a weak but diagnostically useful fragment ion at *m/e* 164 (6%), formed by the cleavage of the furan ring from the molecular ion‖, is noteworthy.

The IR spectrum (CCl_4 + 5% of $CDCl_3$) of nupharopumiline exhibits bands at 1670 cm^{-1} (C=C), and 1595, 1500, and 875 cm^{-1} (furan), which are in agreement with the proposed structure **6**. The absence of the so-called Bohlmann bands [11] in the 2750–2820 cm^{-1} region is noteworthy. Catalytic hydrogenation (Pd/C 10%) transforms (+)-nupharopumiline in nearly quantitative yield to (−)-deoxynupharidine **1**, the absolute configuration of which is known [12–14]. Based on the arguments presented (*vide supra*) the stereostructure **6** (1R, 4S, 7S) is proposed for (+)-nupharopumiline, which thus is the (+)-Δ^9dehydrodeoxynupharidine.

EXPERIMENTAL

Rhizomes of *Nuphar pumila* (Timm.) DC. were collected from Kyyjärvi Lake Tb, in Finland during August of 1975. Voucher specimens are deposited at the University of Helsinki, Department of Botany. Dried powdered rhizomes (400 g) were extracted with MeOH at room temp. The evaporated MeOH extract was suspended in H_2O which was then acidified with dil. HCl. After extraction with Et_2O, the aq. layer was poured into a satd Na_2CO_3 soln which was then extracted with $CHCl_3$. The $CHCl_3$ extract was washed, dried, evaporated to dryness and column chromatographed on Al_2O_3 (act. II–III). Successive elutions with *n*-hexane–Et_2O (49:1), Et_2O, and $CHCl_3$ were effectuated. After fractionation of the $CHCl_3$ eluent by PLC (Al_2O_3; $CHCl_3$–MeOH: 49:1), a solid was isolated. which upon crystallization from CCl_4 afforded 3 mg nupharopumiline as crystals mn 195–197°. The known alkaloids **1** to **4** were isolated and identified by standard procedures, including direct comparison with authentic samples.

‖ For a detailed discussion of the MS fragmentation of *Nuphar* alkaloids, see refs. [9] and [10].

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