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SHORT REPORTS

2-*N*-PHENYLAMINONAPHTHALENE FROM *LAVANDULA VERA*

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Key Word Index—*Lavandula vera*; Labiatae; 2-*N*-phenylaminonaphthalene.

Abstract—The aerial parts of *Lavandula vera* afforded a new natural aromatic substance, which was identified as 2-*N*-phenylaminonaphthalene.

From the aerial parts of racemes of *Lavandula vera*, a new compound (**1**) was isolated in addition to the known 7-methoxycoumarin [1, 2]. The structure of **1** was established by spectroscopic methods and confirmed subsequently by synthesis.

The IR spectrum exhibited intensive bands attributable to an NH group (3400, 1610 cm^{-1}), and to phenyl and naphthyl groups (1640, 1515, 1500, 1480, 878, 860, 820, 740, 690 cm^{-1}). The presence of an –NH–phenyl structural unit followed from the ^{1}H NMR signals at δ7.17, 7.32 and 6.98 (AA′BB′X system), and at 6.35 (broad singlet of an exchangeable proton). The ^{13}C NMR data (Table 1) were also in complete agreement with the above moiety. To define the sequence of the remaining seven protons, giving overlapping multiplets between δ7.2 and 7.8, a two-dimensional (2D) proton chemical shift correlated (COSY) spectrum was recorded at 200 MHz. The data inferred from the 2D spectrum, together with the results of ^{1}H–^{1}H decoupling experiments, gave the assignment of the naphthyl protons (Table 2). The site of substitution on the naphthyl ring was corroborated by the ^{13}C NMR data. The different β substituent effects on C-1 and C-3 (−16.2 and −5.8 ppm, respectively) are in accordance with those obtained for 2-methoxynaphthalene and 2-*N*-methylaminonaphthalene [3], where the differences were explained by a preferred (*Z*) orientation of the substituent.

The mass spectrum supported the proposed structure. The [M]$^{+}$ at *m/z* 219 and fragmentation ions at *m/z* 128, 116, 77, 66, 65, are consistent with the pattern shown in Scheme 1. The structure of compound **1** received further confirmation by its synthesis from β-naphthol and aniline. Isolation of an aromatic amine from the Labiatae has not been described previously.

EXPERIMENTAL

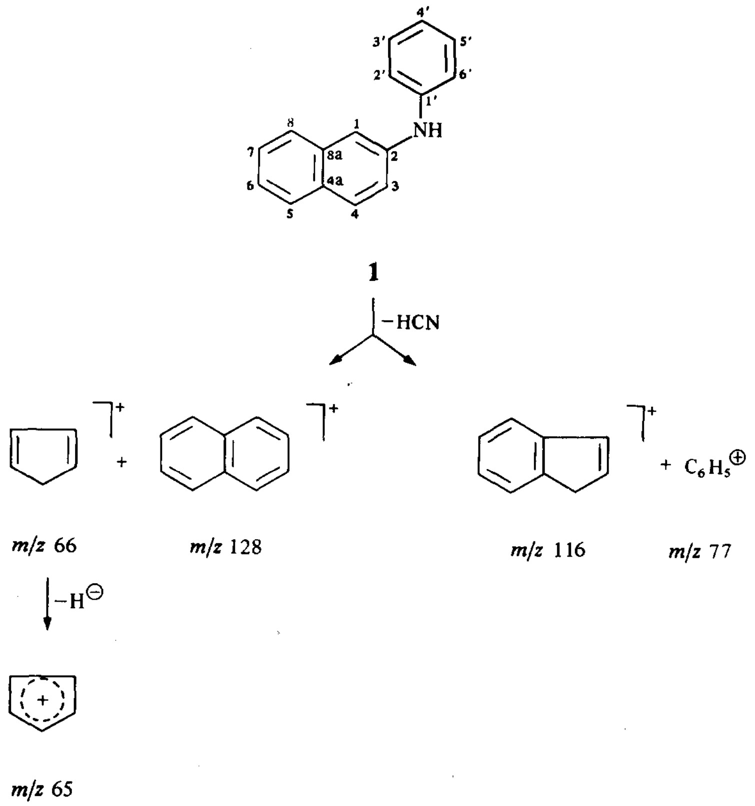
Dried lavender racemes (5 kg) were subjected to steam distillation and subsequently extracted with MeOH at 40–50°. The dried extract was re-extracted with petrol. The resulting extract (48 g) was chromatographed on a silica gel column. Elution with petrol–CH_2Cl_2 (17:3) gave crude crystals of **1**. Recrystallization from petrol–Et_2O furnished fine crystals, mp 107–108°. IR ν_{max}^{KBr} cm^{-1}: 3400 (NH), 3060, 3050, 1640, 1610, 1515, 1500, 1480, 1415, 1300, 1170, 1110, 956, 878, 860, 820, 740, 690, 490 and 480; ^{1}H and ^{13}C NMR (Tables 1 and 2); MS (70 eV) *m/z* (rel. int.): 219 [M]$^{+}$ (100), 192 (6), 193 (7), 180 (3), 166 (4), 153 (5), 127 (7), 128 (8), 115 (10), 116 (6), 77 (21), 66 (3), 65 (2), 51 (19), 39 (20), 27 (7). Further elution with petrol–CH_2Cl_2 (83:17) gave crude crystals of 7-methoxycoumarin (80 mg).

Synthesis of **1**. A mixture of freshly distilled aniline (1.86 g) and β-naphthol (1.44 g) was heated under reflux in the presence of $CaCl_2$ (1.1 g) at 280° for 8 hr. After cooling the solid product was washed with petrol. The extract was concd and separated by silica gel CC with petrol–CH_2Cl_2 eluent (49:1) to give a compound

Table 1. ^{13}C NMR data of **1** (25.16 MHz; $CDCl_3$; TMS int. standard; δ values in ppm)

C-1	111.70 *d*
C-2	140.93 *s*
C-3	120.06 *d*
C-4	129.18* *d*
C-4a	129.25 *s*
C-5	127.65* *d*
C-6	123.50 *d*
C-7	126.50† *d*
C-8	126.45† *d*
C-8a	134.68 *s*
C-1′	143.00 *s*
C-2′ C-6′	118.34 *d*
C-3′ C-5′	129.43 *d*
C-4′	121.44 *d*

*† Assignments may be interchanged.



Scheme 1. Mass spectral fragmentation of 1.

Table 2. 200 MHz ^{1}H NMR spectral data of naphthyl protons ($CDCl_3$; TMS int. standard; δ values in ppm, J values in Hz)

H-3	7.22, *dd*	$J_{3,4} = 8.5$;	$J_{1,3} = 2.2$	
H-6	7.31, *m*	$J_{5,6} = 7.5$;	$J_{6,7} = 7.5$;	$J_{6,8} = 1.5$
H-7	7.38, *m*	$J_{6,7} = 7.5$;	$J_{7,8} = 8.0$;	$J_{5,7} = 1.5$
H-1	7.44, *d*	$J_{1,3} = 2.2$		
H-8	7.65, *dd*	$J_{7,8} = 8.0$;	$J_{6,8} = 1.5$	
H-5	7.74, *dd*	$J_{5,6} = 7.5$;	$J_{5,7} = 1.5$	
H-4	7.75, *d*	$J_{3,4} = 8.5$		

(500 mg) identical in all respects (mp, mmp, IR, ^{1}H NMR and MS) to natural 2-*N*-phenylaminonaphthalene.

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