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Identification of Phenyl Naphtho Furans and Phenyl Ethenyl Naphthol in Commercial 2-Naphthol

Jiří Čermák,[a] Josef Jirman,[a]* Jiří Kulhánek[b] & Jaroslav Toman[c]

[a]Research Institute of Organic Syntheses, 53218, Pardubice-Rybitví, Czech Republic
[b]University of Pardubice, 53210, Pardubice, Czech Republic
[c]Synthesia, 53217, Pardubice-Rybitví, Czech Republic

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ABSTRACT

3-phenyl naphtho[2,1-b]furan (1), 1-(1-phenylethenyl)-2-naphthol (2) and 2-phenyl naphtho[2,1-b]furan (3) were identified in technical 2-naphthol and distillation pitches from its production. Their structures have been derived from mass spectral analyses and NMR spectra. The identification was verified by comparison with mass spectra, retention data and ^1H and ^{13}C NMR data of authentic compounds synthesised for this purpose. © 1997 Elsevier Science Ltd

Keywords: 2-naphthol, impurities, GC–MS, NMR.

INTRODUCTION

2-Naphthol is among the most important naphthalene intermediates in dye production. It finds application, for example, in the production of tar dyes and azo dyes [1] and serves as starting raw material in the preparation of artificial tanning materials and other organic substances used in the perfumery, pharmaceutical and pesticide industry. The production of 2-naphthol, however, burdens the environment considerably by emissions. The substance is manufactured by the process [2] of discontinuous sulfonation of naphthalene with sulphuric acid. The sulfonation mixture is subjected to hydrolysis and treatment by salting-out to isolate sodium 2-naphthalenesulfonate. The salt is then added portionwise to sodium hydroxide and converted to sodium

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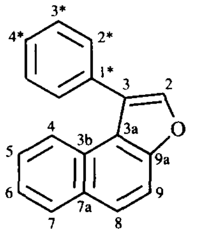
*Corresponding author.

2-napththolate by alkali fusion at 280–335°C. The product is obtained by acidification, isolation and refining.

In previous papers [3–5] we have discussed the use of capillary column gas chromatography (GC–MS) for the identification of some impurities in gaseous releases and distillation residues from the production of 2-naphthol. The present work was aimed at the unambiguous identification of some higher molecular impurities which had been previously detected in technical 2-naphthol, but without structure elucidation [3]. In this present work, reference GC–MS and NMR analyses of authentic compounds were used for the unambiguous identification of 3-phenyl naphtho[2,1-b]furan (**1**), 1-(1-phenylethenyl)-2-naphthol (**2**) and 2-phenyl naphtho[2,1-b]furan (**3**), not only in the product, but also in the distillation residues from 2-naphthol production.



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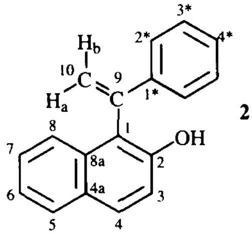

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Only limited data concerning the identification of impurities in 2-naphthol have been reported in the literature [6]. These authors applied mass spectrometry data, together with IR and TLC results, for the identification of naphthylnaphthol and binaphthol derivatives originating from the condensation reactions. No references about the presence of compounds **1** and **2** in 2-naphthol samples and their analytical data (MS, NMR spectra) have been published to date.

EXPERIMENTAL

Sample preparation

Samples to be analysed (2-naphthol pitches and technical product of 2-naphthol production) were taken from the manufacture of 2-naphthol at Synthesia in Pardubice, Czech Republic.

(1) The solid sample of 2-naphthol residue from vacuum distillation was dissolved in methanol before GC–MS analysis.

(2) The sample of 2-naphthol was processed for GC–MS and especially NMR analysis in the following way: the solid sample (800 g) was twice extracted with a boiling mixture of benzene (600 ml) and *n*-heptane (1960 ml). The filtrate was concentrated and cooled to 20°C; crystalline 2-naphthol was then separated by filtration. The filtrate was evaporated to dryness under vacuum evaporator. The residual 2-naphthol was removed from this residue by preparative liquid chromatography using a Waters Prep 4000 System preparative liquid chromatograph, equipped with a preparative column (50×250 mm, Biospher Si C_{18}, 10 μm). The sample was injected as a methanol solution (3%, w/v) and eluted by 90% methanol. The impurities under study were detected as the main components in the fractions A and B.

Preparation of standard substances

3-Phenylnaphtho[2,1-b]furane [7] (1)

A mixture of 12 g (0.046 mol) 2-(2-naphthoxy)-1-phenylethanone, [8] 250 ml benzene and 72 g phosphoric anhydride was refluxed on a water bath for 18 h. The mixture was cooled and poured onto crushed ice; the benzene layer was separated and dried ($MgSO_4$). Benzene was removed under the vacuum and 3-phenyl-naphtho[2,1-b]furane (5.2 g, 46.5%) was thus obtained as a viscous oil which distilled at 215–216°C/8 mm (lit. [7] 200°C/2 mm).

1-(1-Phenylethenyl)-2-naphthol (2)

A solution of Grignard reagent was prepared from methyliodide (34 g), magnesium (10 g) and dry diethylether (170 ml). Into this reagent was then dropped a solution of 1-benzoyl-2-naphthol [9] (10 g, 0.04 mol) in ether (235 ml). The mixture was stirred for 3.5 h at room temperature and then refluxed for 30 min. Then reaction mixture was poured onto ice and acidified with conc. hydrochloric acid. The ethereal layer was separated and the aqueous phase was extracted with ether (2×200 ml). The combined organic extracts were dried ($CaCl_2$) and ether was removed. The tertiary alcohol was dehydrated by distillation with 2 drops of conc. sulphuric acid. The viscous product, fraction 255–265°C (2.9 g, 29.3%), was crystallised from dichloromethane, to yield colourless crystals, m.p. = 105–112°C (in lit. [10] 117–119°C).

2-Phenylnaphtho[2,1-b]furane [7] (3)

2-(2-naphthoxy)-1-phenylethanone [8] (4.7 g, 0.018 mol) was added to polyphosphoric acid, obtained from 45 g of phosphoric anhydride and 23 ml of phosphoric acid (85%). The mixture was heated with stirring for 7 h at 150°C, cooled, cautiously poured onto ice and extracted with ether. The ethereal layer was dried ($MgSO_4$) and ether removed. Product (2.1 g, 48.0%) was crystallised from acetic acid m.p. = 137–140°C (in lit. [7] 140°C).

Apparatus and measurement conditions

MS 25 RFA mass spectrometer (Kratos) was used. Electron impact (EI) spectra were recorded at 70 eV and an ionisation current of 100 μA under low resolution conditions R = 600 (10% valley). The mass spectra were measured also with resolution $R_{10\%} = 3000$ and provided information about the elemental composition of molecular ions and some fragments of unknown compounds. The ion source temperature was 250°C. The calibration region for routine measurements was 28–480 daltons.

The mass spectrometer was directly interfaced to a HP 5890 gas chromatograph (Hewlett Packard) equipped with capillary column and working in the splitless mode. The capillary column used was a HP Ultra-2 (25 m 0.20 mm i.d.; 0.11 μm film thickness, fused-silica, 5% phenylmethylsilicone) and was directly introduced into MS ion source. The temperature program was as follows: 40°C for 2 min, 5°C min^{-1} rise up to 280°C, then isothermally, injector temperature 250°C. Helium served as carrier gas. The interface line between the GC system and MS ion source was held at 220°C.

^1H and ^{13}C NMR spectra were measured in deuteriochloroform at 23°C on an AMX 360 (Bruker) instrument at 360.13 and 90.57 MHz, respectively, using a tuneable 5 mm probe. For the ^1H measurement, hexamethyldisiloxane ($\delta(^1H) = 0.05$) was used as internal standard, ^{13}C chemical shifts were referenced to the solvent signal ($\delta(^{13}C) = 77.00$).

The following measurement techniques were employed: H,H-homonuclear correlated spectrum [11], H,C-heteronuclear correlated spectrum with composite 180° transmitter pulse [12], H,C-heterocorrelated spectrum via long-range couplings with H–H decoupling in F1 [13] and selective INEPT via long range couplings [14].

RESULTS AND DISCUSSION

The main attention has been devoted to the separation and identification of higher boiling components detected above in the distillation pitches of the production of 2-naphthol and also in the final product. Compounds **1**, **2** and **3** were detected in the given GC–MS conditions in the range of retention times (R_t) 35:00–37:00 min and were eluted before a large group of isomeric naphthylnapthols and binaphthols (R_t = 40:00–50:00 min). Part of the GC–MS run of the methanolic solution of the distillation residues is shown in Fig. 1. The presence of the studied compounds is characterised by the chromatographic peaks no. 1: 3-phenyl naphtho[2,1-b]furan (structure **1**), and no. 2: 1-(1-phenylethenyl)-2-naphthol (structure **2**).

A sample of 2-naphthol of common quality was, before the GC–MS and NMR analysis, treated by the procedure described in the Experimental, owing to the necessity of the concentration of observed compounds. This procedure was not successful in obtaining pure components, but only fractions in which the studied compounds were always the main components.

The course of the GC–MS analysis of the fraction A is shown in Fig. 2a, representing total ion current (TIC). The main component of this fraction is a compound with molecular ion in nominal value 244 daltons (mass chromatogram of M^+ ion is in Fig. 2b) and with elementary composition $C_{18}H_{12}O$. Owing to the fact that the derivatisation reaction (silylation with agent BSTFA-N,O-bis(trimethylsilyl) trifluoracetamid) was not successful, one can assume that there is not a hydroxyl group in the molecule structure. The structure 3-phenylnaphtho[2,1-b]furan has been proposed for the main component of the fraction A.

The following reasons (A–E) lead us to propose the structure from the point of view of the NMR analysis:

A. The three carbons of 2-unsubstituted benzofurane or naphthofurane type. This implies C–H carbon with chemical shift 141.57 ppm, C–H carbon with chemical shift 112.5 ppm and C-quaternary carbon (chemical shift 153.09).

B. The two ^{13}C signals with double intensity (chemical shifts 130.01 and 128.46) correspond to the ortho and meta carbons of the free rotating phenyl group, respectively.

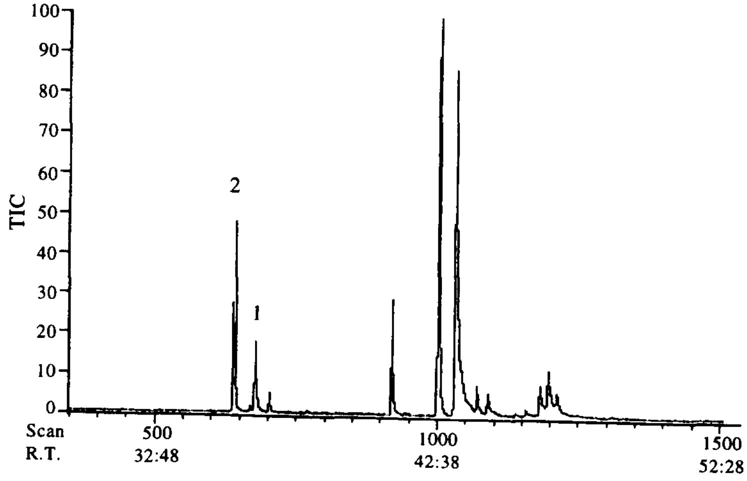

Fig. 1. GC–MS analysis of methanolic solution of distillation residues from the 2-naphthol production. (**1**) 3-phenyl naphtho[2,1-b]furan (M^+ 244); (**2**) 1-(1-phenylethenyl)-2-naphthol (M^+ 246).

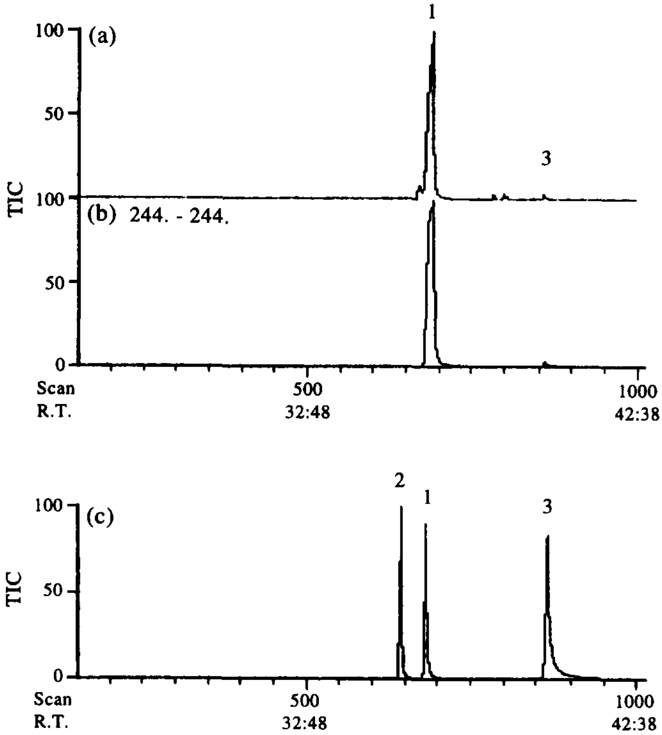

Fig. 2. Comparison of GC–MS analyses of fraction A from the sample of 2-naphthol (a, b) and a standard mixture of compounds **1**, **2** and **3** (c). Total ion current (a, c). Mass chromatogram of M^+244 (b).

C. The proton singlet at 7.42 ppm from H,C-correlated spectrum corresponds to the carbon atom with chemical shift 141.57 (probably C–O carbon).

D. The AB system of protons (7.55 and 7.51 ppm). The second one (7.51 ppm) correlates to the carbon with chemical shift 112.51 and this information excludes the possibility of the benzofurane skeleton in the molecule.

E. The sum of protons and carbons detected in the NMR spectra corresponds to the number of C and H determined by MS technique.

In fraction A the presence of a further isomeric compound 2-phenyl naphtho[2,1-b]furan (**3**) (chromatographic peak no. 3 in Fig. 2a, b and c) was also detected using the GC–MS technique.

Fraction B also obtained by preparative LC contains a number of compounds in which there is the main component with molecular ion of nominal value 246 daltons and elementary composition $C_{18}H_{14}O$. GC–MS analyses of the silylated fraction B confirmed not only the molecular weight of the

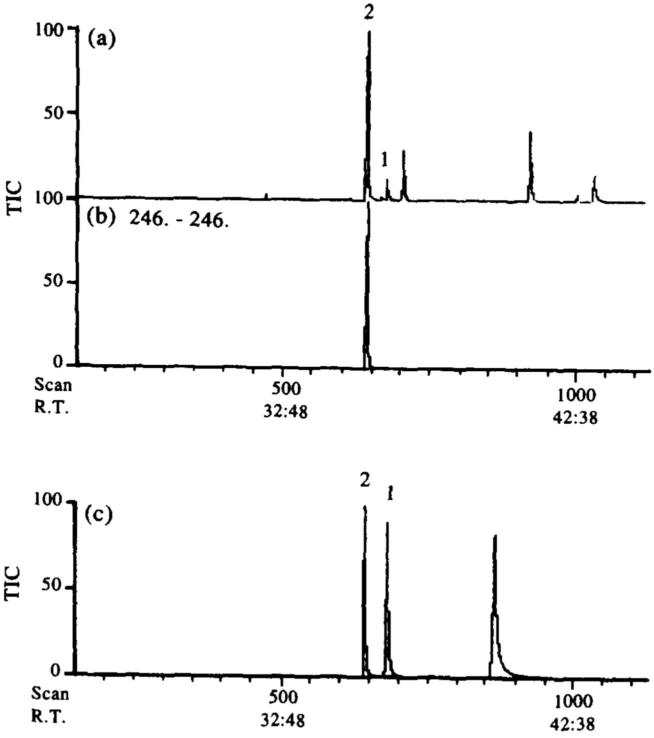

Fig. 3. Comparison of GC/MS analyses of fraction B from the sample of 2-naphthol (a, b) and a standard mixture of compounds **1**, **2** and **3** (c). Total ion current (a, c). Mass chromatogram of $M^+ 246$ (b).

main component but above all gave information about the presence of an OH group in its molecule. The course of analysis of the dichloromethane solution of the fraction B is shown in Fig. 3, whilst TIC is shown in Fig. 3a, and a mass chromatogram of M^+ 246 of the main component in Fig. 3b. We observed in the ^1H NMR spectrum of fraction B two protons with chemical shifts 5.41 and 6.21 ppm and coupling constant $^2J(H,H) = 1.33$ Hz. These signals are quite alone with nothing coinciding or overlapping, and very probably correspond to the pair of geminal protons on the double bond $C{=}CH_2$. With the combination of the results of GC–MS and NMR analyses, it is possible to propose for the studied compound the structure 1-(1-phenylethenyl)-2-naphthol (**2**).

Authentic compounds were synthesised (Preparation of Standard Substances) with respect to the given MS and NMR data. Their standard mixture was analysed under the same GC–MS conditions as fractions A and B (Fig. 2c and Fig. 3c). By comparing the mass spectra and retention data, the proposed structure for studied compounds was explicitly confirmed.

The mass spectrum of compound **1** (Fig. 4a) is characterised by an intense molecular ion as base peak. Its high stability is due to the extending the conjugation of the furan ring to the naphthofuran system. The main fragment ion is formed by elimination of the CHO group ($m/e = 215$) from the M^+, followed by elimination of acetylene, giving an ion with $m/e = 189$ in

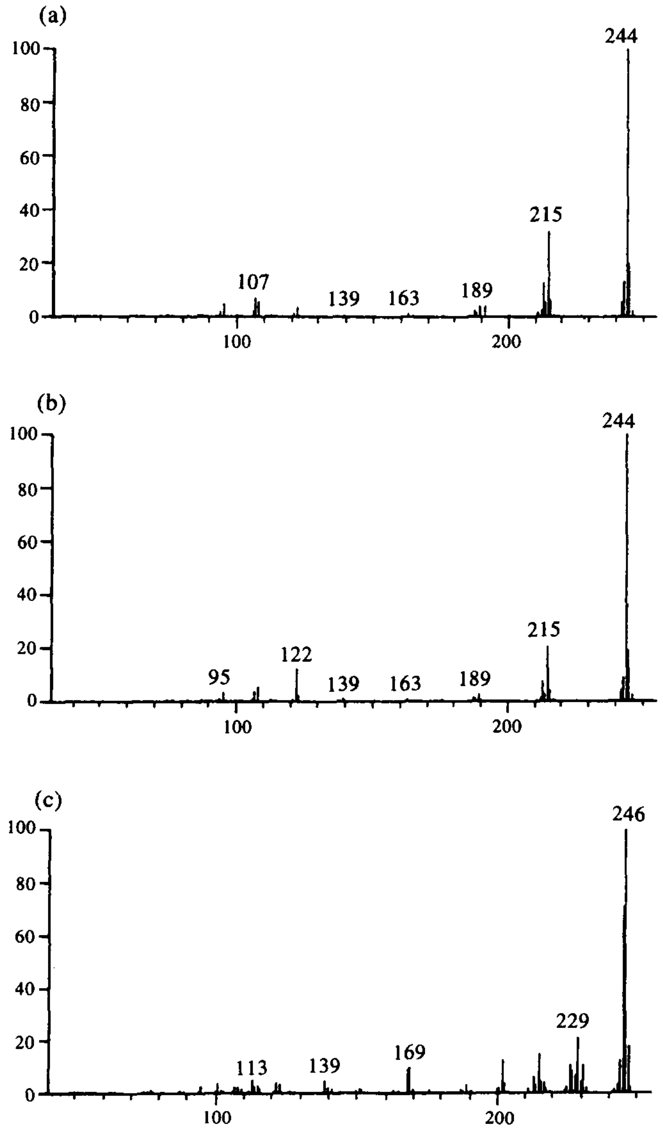

Fig. 4. Mass spectrum (EI, 70 eV): (a) 3-phenyl naphtho[2,1-b]furan; (b) 2-phenyl naphtho[2,1-b]furan (c) 1-(1-phenylethenyl)-2-naphthol.

very low abundance. The presence of double charged ions, for example (M^{2+}) and $(M\text{-}29)^{2+}$, gives the evidence of the high stability of the molecule. The mass spectrum of 2-phenylnaphtho[2,1-b]furan (**3**) (Fig. 4b) is practically identical with mass spectrum of compound **1**.

Compound **2** shows its mass spectrum in Fig. 4c; a very stable molecular ion, and the dominant fragmentation ion arises from a splitting of a hydrogen atom. Further, the presence of the $(M\text{-}17)^{+}$ ion was detected, which characterises the OH group in the molecule. The presence of an ion with $m/e = 169$ is interesting from a constitutional analysis point of view, because this corresponds to the elimination of a phenyl group from M^{+} ion.

The synthesised standards **1** and **2** were measured by NMR methods. All chemical shifts of signals were assigned to the corresponding protons and carbons and are summarised in Table 1. Techniques reported in the experimental part were used for the assignment of the signals. By comparing the ^{1}H NMR spectra of pure compounds **1** and **2** with their spectra in authentic samples, we recognised relative big differences in the chemical shifts (order up to 0.1 ppm). These differences can change the pattern of the spectra and are caused by solvation and concentration effects. Identity of the compounds with the standards was proved by comparing the ^{13}C NMR spectra. In the carbon spectra, there are no concentration and solvation effects. Another identification was proved by the method of standard addition to the sample.

TABLE 1

^{1}H and ^{13}C NMR Chemical Shifts (δ Value) of Compounds **1** and **2**

H/C No.	*$\delta^{1}H$ (1)*	*$\delta^{13}C$ (1)*	*$\delta^{1}H$ (2)*	*$\delta^{13}C$ (2)*
1	—	—	—	120.02
2	7.42	141.57	5.61 (OH)	150.34
3	—	120.62	7.21	117.30
3a	—	124.35	—	—
3b		128.28	—	—
4	7.96	123.28	7.71	129.59
4a	—	—	—	128.88
5	7.20	125.88	7.21	126.50
6	7.22	124.25	7.71	128.00
7	7.74	128.85	7.21	123.27
7a	—	130.76	—	—
8	7.55	125.88	7.48	124.85
8a	—	—	—	132.74
9	7.51	112.51	—	142.42
9a	—	153.09	—	—
10	—	—	5.41 (Ha)	118.85
10	—	—	6.21 (Hb)	—
1*	—	133.02	—	138.68
2*	7.43	130.01	7.29	126.23
3*	7.30	128.46	7.18	128.67
4*	7.29	127.73	7.18	128.48

The conformation of compound **2** in solution in deuteriochloroform is expressed in the given formula, where the double bond of ethenyl is distorted out of the 2-naphthol oxygen. The difference ^{1}H NMR spectra using nuclear Overhauser effect (NOE) give the following results: the signal of proton H-8 appears by irradiating proton H-10a, and the signal of the phenyl ortho protons appears by irradiating proton H-10b. The existence of NOE thus indicates two protons being close together in space.

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