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5*H*-Isoindolo[1,2-*b*][3]benzazepines IX.* The ¹H and ¹³C NMR Spectra of 5*H*-Isoindolo- [1,2-*b*][3]benzazepin-5-ones

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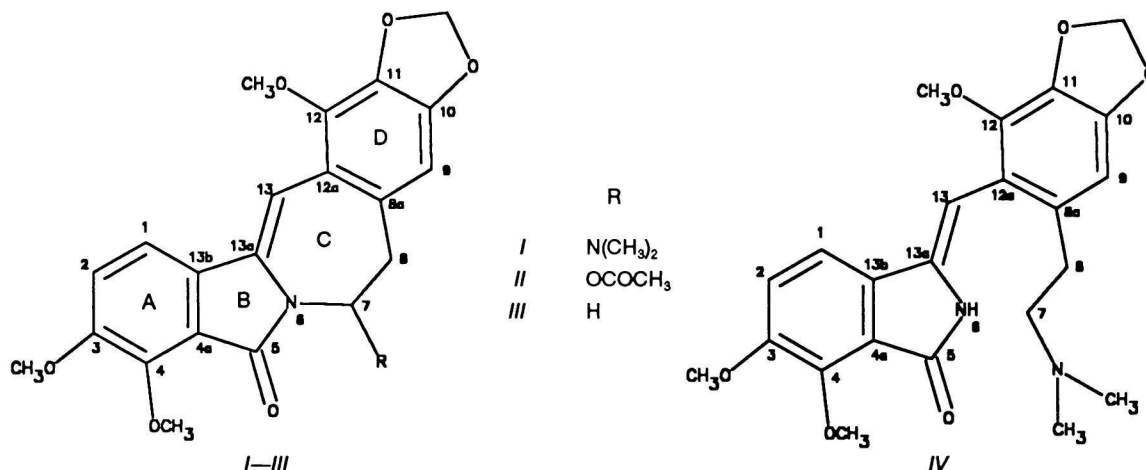
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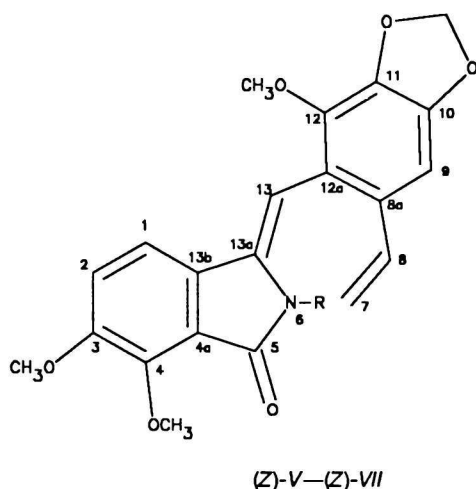
One- and two-dimensional NMR methods were employed for constitutional studies of 7,8-dihydro-5*H*-isoindolo[1,2-*b*][3]benzazepin-5-one derivatives synthesized from the unnatural alkaloid narceine imide. Their chemical shifts were compared with those of geometric isomers of substituted 1-benzylideneisoindolin-3-ones — synthetic precursors of the above-mentioned group of compounds.

Chilenine and lennoxamine, plant metabolites with an isoindolo[1,2-*b*][3]benzazepine ring system, isolated from species of the *Berberidaceae* family, constitute a new group of alkaloids [1]. Several synthetic procedures were developed for their preparation [2–4]; the secophthalideisoquinoline

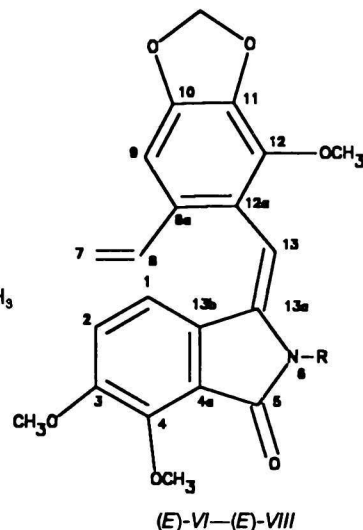
alkaloid narceine imide was the starting material for preparation of a series of derivatives and analogues of lennoxamine [5–7]. This paper presents the NMR study of 7,8-dihydro-5*H*-isoindolo[1,2-*b*][3]benzazepin-5-ones *I–III*, their model substances and their isomers *IV–VIII*.



* For Part VIII see *Chem. Papers* 45, 567 (1991).



- V H
 VI CH₂CH(OH)CH₃
 VII CH₂C₆H₅
 VIII CH₂COCH₃



The H-1 and H-2 protons of all compounds under study appeared in their NMR spectra as AB quartets (Tables 1–4). The chemical shift of H-1 was determined unambiguously by the H,H-NOESY experiment [8] showing its interaction with the H-13 proton; the H-2 proton displayed a spatial interaction with protons resonating at $\delta = 3.93$ ascribed to C-3—OCH₃ grouping. The chemical shift of protons belonging to the adjacent methoxyl group at C-4 ($\delta = 4.11$) was only sparingly dependent on the structural differences in the remaining part of the molecule of compounds I–VIII. A small upfield move of the ¹H chemical shift was observed with *E* isomers ((*E*-VI, (*E*-VIII) only.

Signals of the third methoxyl group at C-12 of the tetracyclic compounds I–III appeared at $\delta = 4.10$, whilst those of *seco* derivatives IV–VIII were upfield shifted to $\delta = 3.93$ – 3.96 for derivatives *Z*, or to $\delta = 3.86$ for *E* ones.

An analogous change in chemical shift was also observed with the H-13 proton signal of compounds I–III appearing in the resonance region of aromatic protons ($\delta = 6.9$), but in the spectra of compounds IV–VIII these signals were shifted to the polyene region ($\delta = 6.2$) and even to $\delta = 5.77$ in case of (*E*-VIII). It could be assumed that this change was subject to the twist of coplanarity of the molecule, and consequently, to the change in conjugation of

Table 1. ¹H Chemical Shifts (δ) of Compounds I–V

Proton	I	II	III	IV	V
H-1	7.53 d (8.4)	7.54 d (8.4)	7.50 d (8.4)	7.44 d (8.4)	7.47 d (8.4)
H-2	7.16 d (8.4)	7.18 d (8.4)	7.12 d (8.4)	7.15 d (8.4)	7.17 d (8.4)
H-7	5.03 dd (5.8; 1.1)	7.18 d (6.5)	4.11 m	2.47 m	5.60 dd (17.4; 1.1)
	–	–	–	–	5.18 dd (10.9; 1.1)
H-8	3.27 dd (15.4; 5.8)	3.61 dd (14.9; 6.5)	3.00 m	2.75 m	6.74 dd (10.9; 17.4)
	2.88 dd (15.4; 0.4)	2.99 d (14.9)	–	–	–
H-9	6.47 d (0.44)	6.36 s	6.42 s	6.53 s	6.81 s
H-13	6.94 s	6.97 s	6.83 s	6.24 s	6.30 s
C-3—OCH ₃	3.93 s	3.93 s	3.93 s	3.93 s	3.93 s
C-4—OCH ₃	4.11 s	4.11 s	4.11 s	4.12 s	4.11 s
C-12—OCH ₃	4.11 s	4.11 s	4.08 s	3.93 s	3.96 s
OCH ₂ O	5.95 ABq (1.5)	5.95 ABq (1.5)	5.95 s	5.98 s	5.95 s
N(CH ₃) ₂	2.19 s	–	–	2.24 s	–
COCH ₃	–	1.85 s	–	–	–

Table 2. ^{13}C Chemical Shifts (δ) of Compounds *I*–*V*

Carbon	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>
C-1	114.7	114.8	114.6	114.9	115.2
C-2	117.2	117.6	116.4	116.9	117.0
C-3	152.7	152.9	152.8	153.1	153.4
C-4	147.1	147.5	146.8	147.1	147.2
C-4a	119.3	119.2	120.3	121.4	121.3
C-5	164.6	163.2	163.6	166.5	166.7
C-7	70.1	74.8	42.0	60.5	115.2
C-8	39.6	38.0	35.8	32.3	134.8
C-8a	131.5	128.9	135.1	134.0	131.6
C-9	105.4	105.5	104.4	104.7	100.7
C-10	148.6	148.9	148.4	148.8	149.3
C-11	135.1	135.4	135.3	135.6	136.5
C-12	140.8	140.8	141.2	140.6	140.5
C-12a	120.8	120.2	120.1	119.2	119.6
C-13	99.4	99.7	98.6	97.9	97.9
C-13a	132.1	131.4	133.1	133.6	133.8
C-13b	132.1	132.1	131.6	132.2	131.8
C-3—OCH ₃	56.9	56.9	56.8	56.8	56.9
C-4—OCH ₃	62.4	62.5	62.4	62.4	62.4
C-12—OCH ₃	59.8	60.0	60.0	60.0	60.0
OCH ₂ O	101.1	101.2	101.1	101.2	101.3
N(CH ₃) ₂	42.4	—	—	45.7	—
COCH ₃	—	169.4	—	—	—
	—	20.7	—	—	—

double bonds, which is higher with cyclic structures of *I*–*III* than with seco derivatives *IV*–*VIII*. The H-13 proton in compound *I* is located in the plane of the benzene ring D and shielded by this ring and therefore, its signal was observed more downfield. On the other hand, the benzene ring D in compound *IV* is partly deviated from the plane

intersecting rings A, B and the C-13—C-13a double bond due to a rotation around the C-12a—C-13 bond; as a result, the proton H-13 appeared in the shielding sphere of π -electrons of the benzene ring D.

The change in the chemical shift of signal belonging to C-12—OCH₃ can be rationalized in the same way; nevertheless, here the shielding was caused by the ring A and possibly by the double bond in conjugation with it. Change in the planarity of molecules of *I*–*III* vs. *IV*, *V* was observed in the ^{13}C NMR spectra in the shift of C-12a and C-13 signals and in the UV spectra of compounds *I*–*III* by bathochromic and hyperchromic shifts.

Conformation of the dihydroazepine ring of compounds *I*–*III* was mainly deduced from the ^1H NMR spectra. Spatial interaction recognized from the NOE difference spectrum evidenced the N(CH₃)₂ and CH₃CO groups in *I* and *II*, respectively, interacting with protons H-1, H-2, H-13 and C-12—OCH₃, to be axially bonded. The coupling constant values $^3J_{\text{H,H}}$ indicated that the equatorially bonded proton H-7 disclosed a spin-spin interaction with the proton H-8eq only and consequently, they occupied a synperiplanar orientation. Signal of the H-8eq proton is more downfield shifted than the axially oriented counterpart as a result of a deshielding effect of the benzene ring D. This arrangement of compound *I* was backed by the appearance of an interaction between H-8ax and H-9 ($^4J_{\text{H,H}}$). Absence of the substituent at C-7 in

Table 3. ^1H Chemical Shifts (δ) of Compounds *VI*–*VIII*

Hydrogen	(<i>Z</i>)- <i>VI</i> ^a	(<i>E</i>)- <i>VI</i> ^a	(<i>Z</i>)- <i>VII</i> ^a	(<i>E</i>)- <i>VIII</i>
H-1	7.45 d (8.4)	6.86 d (8.4)	7.45 d; 7.47 d (8.4)	6.88 d (8.5)
H-2	7.16 d (8.4)	6.34 d (8.4)	7.16 d (8.4)	6.60 d (8.5)
H-7a	5.59 dd; 5.58 dd (17.4; 1.0)	5.32 dd (17.5; 1.0)	5.53 dd; 5.60 dd (17.4; 1.0)	5.53 dd (17.4; 1.0)
H-7b	5.16 dd (10.9; 1.0)	4.86 dd; 4.85 dd (10.9; 1.0)	5.08 dd; 5.24 dd (10.9; 1.0)	5.05 dd (10.9; 1.0)
H-8	6.68 dd; 6.64 dd (17.4; 10.9)	6.71 dd (17.4; 10.9)	6.51 dd; 6.72 dd (17.4; 10.9)	6.69 dd (17.4; 10.9)
H-9	6.84 s; 6.82 s	6.89 s; 6.88 s	6.77 s; 6.82 d	6.87 s
H-13	6.29 s; 6.27 s	6.15 s; 6.13 s	6.21 s; 6.30 s	5.77 s
C-3—OCH ₃	3.93 s	3.83 s	3.54 s; 3.93 s*	3.83 s*
C-4—OCH ₃	4.10 s	4.05 s	4.15 s; 4.11 s	4.07 s
C-12—OCH ₃	3.98 s	3.87 s	3.94 s; 3.96 s*	3.86 s*
OCH ₂ O	5.98 s*; 5.96 ABq*	6.01 ABq	5.92 ABq; 5.97 s	5.99 ABq
CH ₂	—	—	5.04 d; 4.49 d (16.2)	4.63 s
CH	—	—	—	—
CH(OH)	—	—	—	—
CH ₃	0.80 d; 0.82 d (6.1; 5.8)	1.28 d; 1.27 d (6.3)	—	2.23 s
C ₆ H ₅	—	—	7.07 m; 6.66 m	—

a) Two distinct *Z* and *E* isomers were present in solution of which only some proton signals were resolved and appeared as two bands; * ambiguously assigned; m - multiplet in a broad range ($\delta = 2.8$ – 4.2).

Table 4. ^{13}C Chemical Shifts (δ) of Compounds VI—VIII

Carbon	(E)-VI ^a	(Z)-VII ^a	(E)-VIII
C-1	116.9	115.0	116.4
C-2	119.6	116.8	119.0
C-3	154.0	153.1	153.5
C-4	147.1	146.7	146.6
C-4a	122.5	120.2	121.7
C-5	166.9	166.6; 166.1	164.5
C-7	114.7	114.0; 115.2	114.1
C-8	134.6; 134.7	134.7; 134.4	134.0
C-8a	129.6	128.5	128.7
C-9	102.7; 102.6	102.7; 100.9*	101.4
C-10	150.1	149.4; 149.2	149.5
C-11	137.9	137.3	136.7
C-12	140.5	141.3	141.2
C-12a	120.6	119.5	119.6
C-13	100.0; 99.9	99.3; 99.2*	99.3
C-13a	136.8	135.0	136.2
C-13b	132.4	132.2	132.0
C-3—OCH ₃	57.1	56.8	56.4
C-4—OCH ₃	63.0	62.4	62.3
C-12—OCH ₃	60.4	58.8	59.7
OCH ₂ O	101.9	101.3	101.2
CH ₂	48.1; 48.0	43.9; 43.0	49.4
CH(OH)	68.3; 67.9	—	68.3
CH ₃	22.0; 21.8	—	26.9
C=O	—	—	203.6
C ₆ H ₅	—	126.2; 127.1; 127.8	—

a) Chemical shifts of preferred isomers only; some carbons afforded two spectral bands. Minor constituents (Z)-VI and (E)-VII are also in solution; *ambiguously assigned.

the molecule of compound III conditioned a greater conformational freedom of the C ring between C-7 and C-8 visualized by the unresolved multiplets of hydrogen signals and the equilibrated value of the dioxymethylene grouping signals appearing as a simple singlet. Signals of this grouping in more or less rigid structures of I and II occurred as a sharp AB quartet.

Opening of the C ring and introduction of a further substituent at the imino nitrogen favoured a greater flexibility of the C-12a—C-13 bond and, e.g. another Z to E ratio of isomers of compound VI. This effect was also observed with analogous compounds substituted at the imide nitrogen [7]. Compound VI, affording Z and E isomers showed, after equilibration, a preferential formation of the E isomer with a great twist of the benzylidene moiety from coplanarity, this being particularly manifested by shielding the H-1 and H-2 hydrogens by π -electrons of this ring and by a considerable upfield shift when compared with that of the Z isomer. The same effect was also encountered with signals of H-7 and H-13 protons; on the other hand, the H-8 proton and the CH₃ group protons of the substituent were partly deshielded and observed more downfield (Table 3). Replacement of hydrogen for a 2-hydroxypropyl group on the imide nitrogen of compound V was associated with origination of

a chiral centre in the 1-benzylideneisoindolin-3-one moiety. The NMR spectra of compound VI evidenced the existence of four (two Z and E each) isomers in solution, both being seen in duplication of proton signals bonded in the proximity of the chiral centre. This effect was remarkable with H-9, H-13, H-7, H-8 and in smaller extent also with the H-2 proton signals in addition to those belonging to the 2-hydroxypropyl group. The E isomer having the H-7, H-8, and H-9 protons more remote from the chiral centre displayed, in comparison with the Z one, a shorter distance between the corresponding bands. The existence of four various isomers in solution was proved by the 1D-NOE difference measurements [9, 10] as well.

A similar behaviour revealed also compound VII bearing the CH₂C₆H₅ substituent, which equilibrated to give a greater amount of isomers seen as several series of spectral bands around the region of substituent resonance. This phenomenon prevented a more principal analysis of the spectrum. The ^1H NMR spectrum of compounds VI and VII contained signals of the dioxymethylene group as both singlet and AB quartet. Formation of a series of bands of the particular isomers was also observed in the ^{13}C NMR spectrum, but the chemical shift changes of spectral lines were less significant and therefore, Table 4 lists chemical shifts of the preferred isomer only.

The ketone VIII, obtained by oxidation of compound VI, is thermodynamically stable as an E isomer (proved by the ^1H NMR data (Table 3) and NOE experiments) characteristic of an upfield shift of H-1, H-2, and H-13 proton signals. The NOE difference spectrum showed a spatial interaction of H-13 and H-7 protons with H-8 and H-9, respectively, and concurrently an interaction of the CH₂ group protons of the substituent with H-13.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra of deuteriochloroform solutions of compounds containing tetramethylsilane as an internal reference were recorded at 25 °C with a spectrometer AM-300 (Bruker) operating at 300 and 75 MHz for ^1H and ^{13}C nuclei, respectively. Signals of the NMR spectra (Tables 1–4) were ascribed according to H,H-COSY experiments [11] (for ^1H nuclei), the protonated carbons were identified from either uncoupled ^{13}C or H,C-COSY [12] spectra, quaternary carbons from the semiselective INEPT experiment [13] optimized for the long-range interactions. The dipole—dipole interactions were investigated employing the 1D-NOE [9, 10] or 2D-NOESY [8] experiments.

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Photooxidation of Hydroxyethylcellulose Changes in Physical Properties due to Corona Discharge

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The photooxidation of hydroxyethylcellulose by the action of corona discharge in air was studied at 25 °C. The influence of exposure on physical properties of polymer film was examined. It has been found that the transport process of diffusion of the distilled water into the polymer obeys the second Fick's law in the first period of one. The measured average apparent diffusion coefficient of the studied system varies in the interval $(2.1\text{--}15.2) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and decreases with exposure in an equal manner as the activation energies of diffusion which vary in the interval $(23.3\text{--}57.5) \text{ kJ mol}^{-1}$. On the basis of limiting contact angle measurements the temperature of glass transition was determined. It has been found that the preponderance of the cross-linking process over photodestruction of the polymer is significantly influenced by the time of irradiation by low-temperature plasma of corona source.

The photodegradation of cellulose materials has been extensively investigated [1—5]. The primary process is chain scission which occurs during UV irradiation (at $\lambda = 253.7 \text{ nm}$) of cellulose yielding many different compounds, e.g. xylose, D-glucose, and cellobiose. Many volatile products such as acetaldehyde, acetone, methanol, ethanol, ethane, water vapour are formed. These compounds are the results of the secondary degradation process. The composition of the photodegradation products depends on the system used. The following mechanism for the primary process has been proposed (Scheme 1).

Formation of free radicals during irradiation of cellulose with light has been verified by EPR spectroscopy [1, 2].

As obvious, the study of both kinetics and the mechanism of photochemical reactions in polymer materials has lately made a great progress and is very important from the viewpoint of polymer application. The low-temperature plasma treatment of polymer surface has been recently studied because of the ability to modify a polymer surface without great affecting its bulk properties. It can be presumed that the high speed of plasmochemical surface reactions results from the plasma effectiveness — solid surface energy transfer by electrons, excited atoms and ions collisions. During the past few years there has been a steady growth in the use of plasma for the modification of the surface properties of various solid materials [6—9]. This interest has been motivated by the ability