Syntheses of Substituted Furo- and Pyrano-[2,3-*a*]carbazoles from 2-Cinnamoyl-1-hydroxycarbazoles

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Reaction of 2-cinnamoyl-1-hydroxycarbazoles **2a – d**, with phenacyl bromide, mercuric acetate and H_2O_2/NaOH under different reaction conditions yielded 2-benzoyl-3-styryl-furo[2,3-*a*]carbazoles **3a – d**, 2-benzylidene-furo[2,3-*a*]carbazol-3(10*H*)-ones **4a – d** and 3-hydroxy-2-phenylpyrano-[2,3-*a*]carbazol-4(11*H*)-ones **5a – d**, respectively.

Key words: 1-Hydroxycarbazoles, Furo- and Pyranocarbazoles

Introduction

Carbazole alkaloids have been isolated from the taxonomically related higher plants of the genus Murraya, Glycosmis and Clausena from the family Rutaceae [1 – 3]. The 1-oxygenated carbazole alkaloids like clausine E, mukonine and koenoline belong to this family, and these classes of compounds are rich in their cytotoxic activity [4, 5]. The broad range of useful biological activities exhibited by many carbazole alkaloids promoted several research groups to develop synthetic strategies such as Fischer indolization, oxidative cyclization of diarylamines, transition metal-mediated and catalyzed processes for the total syntheses of carbazole compounds [6 – 8]. The total syntheses of this class of compounds led to many interesting aspects and to the discovery of many furo- and pyranocarbazole alkaloids [9 – 13]. Based on the interesting features of these 1-oxygenated compounds it was felt necessary to devise a simple synthetic method with a view to the future isolation of these biogenetically possible compounds from natural sources. Recently we reported the synthesis of some substituted pyranocarbazoles in which 2-cinnamoyl-1-hydroxycarbazoles are used as precursors [14 – 17], hence an attempt has been made to synthesize some furo- and pyranocarbazole analogs from the above mentioned precursor.

Results and Discussion

For the synthesis of furocarbazole derivatives, we treated 2-cinnamoyl-6-methyl-1-hydroxycarbazole **2a** with phenacyl bromide in the presence of ignited potassium carbonate in dry acetone and obtained product **3a**. Its IR spectrum showed absorptions at 3349 and 1695 cm^{-1} due to the presence of N–H and C=O stretchings, respectively. In the proton NMR spectrum, a one-proton broad singlet at δ = 8.60 ppm accounted for the N–H proton. The resonance cluster in the region δ = 8.13 – 7.24 ppm accounted for sixteen aromatic protons including one styryl β-proton. A doublet with J = 16 Hz was due to the styryl α-H present in the system at the C-3 position. A three-proton singlet at δ = 2.61 ppm was due to 7-CH_3. The ^{13}C NMR spectra of **3a** accounts for the presence of 30 carbons in the molecule. The molecular ion peak appeared at m/z = 427 with 81 % relative abundance. The elemental analysis supported the molecular formula $C_{30}H_{21}NO_2$. A similar series of compounds were derived from **2b – d** to yield **3b – d** (Scheme 1).

Because of the biological importance of furocarbazoles, a similar type of reaction was carried out in which we treated **2a** with mercuric acetate, which is well known for highly regioselective and stereospecific oxymercuration of olefins [18], in the presence of dimethylsulfoxide to yield a yellow product. The IR spectrum showed N–H stretching at 3414 cm^{-1} and carbonyl stretching at 1688 cm^{-1}. The ^{1}H NMR spectrum showed a broad singlet at δ = 8.56 ppm for the N–H proton. Ten aromatic protons appeared as a multiplet in the region δ = 7.97 – 7.06 ppm. Two singlets at δ = 6.49 and 2.55 ppm accounted for olefinic and 7-CH_3 protons, respectively. The presence of 22 carbons was inferred from the ^{13}C NMR spectra. The elemental analysis and the molecular ion peak at m/z =

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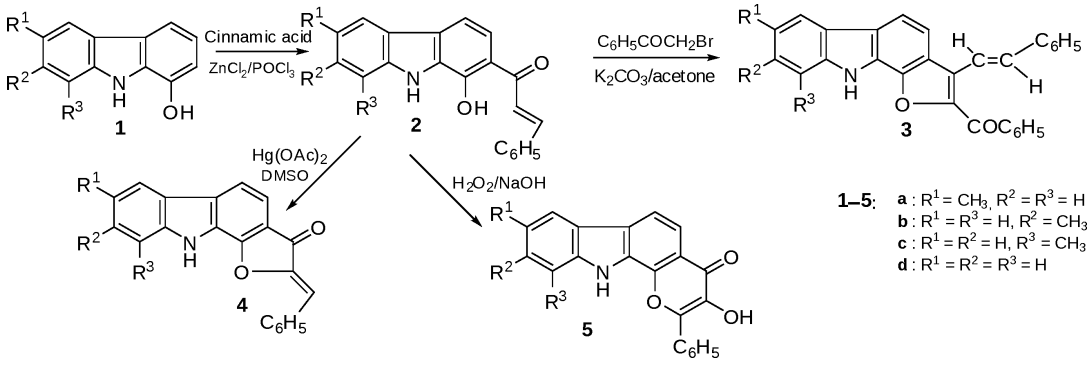

Scheme 1.

325 agreed well with the molecular formula $C_{22}H_{15}NO_2$. Based on all the data it was concluded that the product formed was 2-benzylidene-7-methylfuro[2,3-*a*]carbazol-3(10*H*)-one (**4a**). The generality of this reaction was tested with other carbazole derivatives (Scheme 1).

In order to obtain the biogenetically possible pyranocarbazoles, we treated **2a** in alkaline hydrogen peroxide to obtain a yellow product which was identified as 3-hydroxy-8-methyl-2-phenylpyrano[2,3-*a*]carbazol-4(11*H*)-one (**5a**). Its IR spectrum showed absorptions at 3425, 3200, and 1618 cm^{-1} due the presence of N–H, OH and C=O groups, respectively. The carbonyl absorption was at low wavenumbers due the presence of a hydroxy group adjacent to the carbonyl group. The proton NMR spectrum showed two broad singlets at δ = 11.92 and 9.60 ppm due to the presence of OH and N–H protons. Ten aromatic protons appeared as a multiplet at δ = 8.53 – 7.20 ppm, and a singlet at δ = 2.48 ppm due to 8-CH_3. The mass spectra and the elemental analysis supported the molecular formula $C_{22}H_{15}NO_3$. A similar series of compounds **5b – d** were realized from **2b**, **2c** and **2d**, respectively (Scheme 1).

In conclusion, some biogenetically possible furo- and pyranocarbazoles were synthesized using a simple synthetic pathway. These heterocyclic analogs may possess an important application towards biologically active natural products as well as in pharmaceuticals.

Experimental Section

Melting points were determined using a Mettler FP 51 apparatus (Mettler Instruments, Switzerland) and are uncorrected. IR spectra were recorded using KBr pellets on a Shimadzu FTIR-8201PC spectrophotometer. NMR spectra were recorded in $CDCl_3$ on a Varian AMX 400 FT-NMR instrument using TMS as internal standard. Mass spectra were recorded on a Jeol-D-300 mass spectrometer. Microanalyses were obtained with a Vario EL III model CHNS analyzer. The purity of the products was tested by TLC using plates coated with silica gel G and petroleum ether and ethyl / acetate (85 : 15) as the eluents.

*Preparation of 2-benzoyl-3-styryl-furo[2,3-a]carbazole (**3**); general procedure*

A mixture of the respective 2-cinnamoyl-1-hydroxycarbazole (**2**, 0.001 mol), phenacyl bromide (200 mg, 0.001 mol) and ignited potassium carbonate (276 mg, 0.002 mol) in dry acetone (15 mL) was refluxed in a steam bath for 4 h. The reaction was monitored by TLC. After the completion of the reaction the excess solvent was removed, and the reaction mixture was poured onto ice water. The solid was filtered, dried, and purified by column chromatography over silica gel using petroleum ether ethyl / acetate (95 : 5) as eluant to get the respective 2-benzoyl-3-styryl-furo[2,3-*a*]carbazole **3**. The compound thus obtained was recrystallized from ethanol.

*2-Benzoyl-3-styryl-7-methylfuro[2,3-a]carbazole (**3a**)*

M. p. 217 – 219 °C. – Yield: 0.31 g (72 %). – IR (KBr): ν = 3349, 2925, 1695, 1626, 1570, 1449, 737 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (b s, 1 H, N-10-H), 8.13 – 7.24 (m, 16 H, 4-H, 5-H, 6-H, 7-H, 8-H, styryl β-H, C-2 {2′-H, 3′-H, 4′-H, 5′-H, 6′-H}, C-3 {2′-H, 3′-H, 4′-H, 5′-H, 6′-H}), 6.62 (d, 1 H, styryl α-H, J = 16 Hz), 2.61 (s, 3 H, 7-CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.41 (2-C=O), 170.73 (C-1a), 145.32 (C-2), 139.13 (C^2-C1′), 136.48 (C^3-C1′), 134.27 (C^3-β-C), 133.08 (C-3), 133.11 (C^2-C4′), 130.53 (C^3-C4′), 129.61 (C^3-α-C), 128.80 (C^2-C2′ and C^2-C6′), 128.72 (C^2-C3′ and C^2-C5′), 128.64 (C^3-C2′ and C^3-C6′), 126.17 (C^3-C3′ and C^3-C5′), 125.15 (C-10a), 123.87 (C-3a), 122.48 (C-5), 121.21 (C-4), 119.98 (C-5a), 117.55 (C-7), 117.13 (C-8), 113.09 (C-6), 116.44 (C-9), 111.35 (C-9a), 109.91 (C-5b), 27.45 (7-CH_3). – MS (EI, 70 eV): *m/z* (%) = 427 (81) $[M]^+$. – $C_{30}H_{21}NO_2$ (427.49): calcd. C 84.29, H 4.95, N 3.28; found C 84.09, H 4.82, N 3.32.

*2-Benzoyl-3-styryl-8-methylfuro[2,3-a]carbazole (**3b**)*

M. p. 234 – 239 °C. – Yield: 0.34 g (80 %). – IR (KBr): ν = 3327, 2923, 1689, 1632, 1564, 1454, 748 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 8.71 (b s, 1 H, N-10-H), 8.26 – 7.49 (m, 16 H, 4-H, 5-H, 6-H, 7-H, 9-H, styryl β-H, C-2 {2′-H, 3′-H, 4′-H, 5′-H, 6′-H}, C-3 {2′-H, 3′-H, 4′-H, 5′-H, 6′-H}), 6.67 (d, 1 H, styryl α-H, J = 15.60 Hz), 2.49 (s, 3 H, 8-CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.12 (2-C=O), 175.72 (C-1a), 144.53 (C-2), 140.37 (C^2-C1′), 137.51 (C^3-C1′), 136.75 (C^3-β-C), 134.62 (C-3), 133.70 (C^2-C4′), 132.64 (C^3-C4′), 132.61 (C^3-α-C), 129.61 (C^2-C2′ and C^2-C6′), 129.56 (C^2-C3′ and C^2-C5′), 128.53 (C^3-C2′ and C^3-C6′), 125.65 (C^3-C3′ and C^3-C5′), 123.38 (C-10a), 122.12 (C-3a), 120.48 (C-5), 119.22 (C-4), 117.20 (C-5a), 116.31 (C-6), 115.76 (C-7), 113.95 (C-8), 113.82 (C-9), 112.44 (C-9a), 111.81 (C-5b), 25.58 (8-CH_3). – MS (EI, 70 eV): *m/z* (%) = 427 (67) $[M]^+$. – $C_{30}H_{21}NO_2$ (427.49): calcd. C 84.29, H 4.95, N 3.28; found C 84.04, H 4.79, N 3.22.

*2-Benzoyl-3-styryl-9-methylfuro[2,3-a]carbazole (**3c**)*

M. p. 209 – 211°C. – Yield: 0.29 g (69 %). – IR (KBr): ν = 3342, 2924, 1692, 1580, 1460, 757 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 8.69 (b s, 1H, N-10-H), 8.05 – 7.32 (m, 16 H, 4-H, 5-H, 6-H, 7-H, 8-H, styryl β-H, C-2 {2′-H, 3′-H, 4′-H, 5′-H, 6′-H}, C-3 {C'_2-H, 3′-H, 4′-H, 5′-H, 6′-H}), 6.61 (d, 1 H, styryl α-H, J = 14.80 Hz), 2.52 (s, 3 H, 9-CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.21 (2-C=O), 165.73 (C-1a), 147.43 (C^2-C1′), 144.37 (C^3-C1′), 139.45 (C^3-β-C), 138.15 (C-3), 137.97 (C^2-C4′), 136.18 (C^3-C4′), 135.17 (C^3-α-C), 134.45 (C^2-C2′ and C^2-C6′), 129.50 (C^2-C3′ and C^2-C5′), 129.21 (C^3-C2′ and C^3-C6′), 125.61 (C^3-C3′ and C^3-C5′), 124.69 (C-10a), 123.45 (C-3a), 122.04 (C-5), 121.65 (C-4), 120.24 (C-5a), 119.36 (C-8), 119.09 (C-7), 116.24 (C-6), 115.19 (C-9), 113.80 (C-9a), 113.50 (C-5b), 22.19 (9-CH_3). – MS (EI, 70 eV): *m/z* (%) = 427 (69) $[M]^+$. – $C_{30}H_{21}NO_2$ (427.49): calcd. C 84.29, H 4.95, N 3.28; found C 84.44, H 4.81, N 3.39.

*2-Benzoyl-3-styryl-furo[2,3-a]carbazole (**3d**)*

M. p. 246 – 248 °C. – Yield: 0.26 g (64 %). – IR (KBr): ν = 3402, 2926, 1659, 1641, 1572, 1471, 786 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 8.54 (b s, 1 H, N-10-H), 8.10 – 7.22 (m, 17 H, 4-H, 5-H, 6-H, 7-H, 8-H, styryl β-H, C-2 {2′-H, 3′-H, 4′-H, 5′-H, 6′-H}, C-3 {2′-H, 3′-H, 4′-H, 5′-H, 6′-H}), 6.60 (d, 1 H, styryl α-H, J = 16.20 Hz). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.11 (2-C=O), 166.17 (C-1a), 161.64 (C-2), 147.15 (C^2-C1′), 146.28 (C^3-C1′), 144.15 (C^3-β-C), 139.61 (C-3), 138.19 (C^2-C4′), 138.05 (C^3-C4′), 137.14 (C^3-α-C), 129.95 (C^2-C2′ and C^2-C6′), 129.58 (C^2-C3′ and C^2-C5′), 128.76 (C^3-C2′ and C^3-C6′), 127.83 (C^3-C3′ and C^3-C5′), 126.91 (C-10a), 121.09 (C-3a), 121.25 (C-5), 120.97 (C-4), 120.22 (C-5a), 119.97 (C-8), 118.07 (C-7), 117.65 (C-6), 115.41 (C-9), 115.39 (C-9a), 109.17, (C-5b). – MS (EI, 70 eV): *m/z* (%) = 413 (49) $[M]^+$. – $C_{29}H_{19}NO_2$ (413.14): calcd. C 84.24, H 4.63, N 3.39; found C 84.14, H 4.70, N 3.46.

*Preparation of 2-benzylidene-7-furo[2,3-a]carbazol-3(10H)-one (**4**); general procedure*

The respective 2-cinnamoyl-1-hydroxycarbazole (**2**, 0.001 mol) was dissolved in dimethylsulfoxide (6 mL), and after adding mercuric acetate (0.0015 mol) the mixture was refluxed for 6 h. The reaction was monitored by TLC. After completion, the mixture was poured into ice-cold water. A yellow solid was separated, which was filtered, washed with water, dried and recrystallized from methanol to yield the corresponding 2-benzylidene-7-furo[2,3-*a*]carbazol--3(10*H*)-one **4** as yellow prisms.

*2-Benzylidene-7-methylfuro[2,3-a]carbazol-3(10H)-one (**4a**)*

M. p. 284 – 286 °C. – Yield: 0.26 g (80 %). – IR (KBr): ν = 3414, 2922, 1688, 1446, 1300, 1122, 768 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 8.56 (b s, 1 H, N-10-H), 7.97 – 7.06 (m, 10 H, 4-H, 5-H, 6-H, 8-H, 9-H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H), 6.49 (s, 1 H, 2-olefinic-H), 2.55 (s, 3 H, 7-CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.12 (3-C=O), 147.37 (C-2), 132.65 (C-1a), 130.71 (C^2-C1′), 129.74 (C^2-C3′ and C^2-C5′), 128.82 (C^2-C4′), 128.40 (C^2-C2′ and C^2-C6′), 125.16 (C-10a), 122.97 (C-3a), 120.19 (C-4), 118.76 (C-5a), 115.08 (C-5), 114.28 (C-6), 112.66 (C-8), 116.15 (C-9), 115.39 (C-7), 114.22 (C-9a), 110.33 (C-5b). 109.81 (2-olefinic C), 29.67 (7-CH_3). – MS (EI, 70 eV): *m/z* (%) = 329 (54) $[M]^+$. – $C_{22}H_{15}NO_2$ (325.36): calcd. C 81.21, H 4.65, N 4.30; found C 81.11, H 4.72, N 4.41.

*2-Benzylidene-8-methylfuro[2,3-a]carbazol-3(10H)-one (**4b**)*

M. p. 295 – 297 °C. – Yield: 0.24 g (74 %). – IR (KBr): ν = 3439, 2930, 1691, 1451, 1308, 1118, 773 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 8.69 (b s, 1 H, N-10-H), 8.04 – 7.36 (m, 10 H, 4-H, 5-H, 6-H, 7-H, 9-H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H), 6.53 (s, 1 H, 2-olefinic H), 2.44 (s, 3 H, 8-CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.19 (3-C=O), 147.21 (C-2), 133.37 (C-1a), 129.39 (C^2-C1′), 129.04 (C^2-C3′ and C^2-C5′), 128.59 (C^2-C4′), 128.19 (C^2-C6′ and C^2-C2′), 127.94 (C-10a), 127.07 (C-3a), 122.18 (C-4), 120.77 (C-5a), 116.18 (C-5), 115.48 (C-6), 113.63 (C-7), 113.91 (C-8), 112.94 (C-9), 110.58 (C-9a), 107.69 (2-olefinic C), 106.46 (C-5b). 27.43 (8-CH_3). – MS (EI, 70 eV): *m/z* (%) = 329 (67) $[M]^+$. – $C_{22}H_{15}NO_2$ (325.36): calcd. C 81.21, H 4.65, N 4.30; found C 81.44, H 4.77, N 4.46.

*2-Benzylidene-9-methylfuro[2,3-a]carbazol-3(10H)-one (**4c**)*

M. p. 269 – 271 °C. – Yield: 0.25 g (76 %). – IR (KBr): ν = 3422, 2921, 1679, 1445, 1311, 1127, 745 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 8.64 (b s, 1 H, N-10-H), 8.12 – 7.53 (m, 10 H, 4-H, 5-H, 6-H, 7-H, 8-H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H), 6.62 (s, 1 H, 2-olefinic H), 2.50 (s, 3 H, 9-CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.78 (3-C=O), 146.24 (C-2), 134.53 (C-1a), 133.15 (C^2-C1′), 130.65 (C^2-C3′ and C^2-C5′), 130.0 (C^2-C4′), 129.53 (C^2-C2′ and C^2-C6′), 128.91 (C-10a), 127.55 (C-3a), 126.15 (C-4), 122.37 (C-5), 119.13 (C-5a), 117.45 (C-6), 116.52 (C-7), 115.83 (C-8), 114.19 (C-9), 112.48 (C-9a), 110.06 (2-olefinic C), 109.59 (C-5b), 28.19 (9-CH_3). – MS (EI, 70 eV): *m/z* (%) = 329 (73) $[M]^+$. – $C_{22}H_{15}NO_2$ (325.36): calcd. C 81.21, H 4.65, N 4.30; found C 81.20, H 4.57, N 4.39.

*2-Benzylidene-furo[2,3-a]carbazol-3(10H)-one (**4d**)*

M. p. 262 – 264 °C. – Yield: 0.22 g (72 %). – IR (KBr): ν = 3414, 2918, 1684, 1431, 1309, 1128, 766 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = δ 8.51 (b s, 1 H, N-10-H), 8.22 – 7.65 (m, 11 H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H), 6.71 (s, 1 H, 2-olefinic H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.50 (3-C=O), 148.44 (C-2), 136.23 (C-1a), 131.27 (C^2-C1′), 128.91 (C^2-C3′ and C^2-C5′), 127.52 (C^2-C4′), 127.61 (C^2-C2′ and C^2-C6′), 126.13 (C-10a), 125.61 (C-3a), 125.11 (C-5), 120.61 (C-4), 120.45 (C-5a), 119.51 (C-7), 119.06 (C-8), 117.33 (C-6), 116.12 (C-9), 115.47 (C-9a), 110.79 (2-olefinic C), 105.34 (C-5b). – MS (EI, 70 eV): *m/z* (%) = 311 (59) $[M]^+$. – $C_{21}H_{13}NO_2$ (311.33): calcd. C 81.01, H 4.21, N 4.50; found C 81.14, H 4.12, N 4.56.

*Preparation of 3-hydroxy-2-phenylpyrano[2,3-a]carbazol-4(11H)-one (**5**); general procedure*

To a solution of a 2-cinnamoyl-1-hydroxycarbazole (**2**, 0.001 mol), in 20 mL of a 10 % alcoholic sodium hydroxide kept at 0 °C, hydrogen peroxide (2 mL) was added in drops, and the mixture was stirred for 5 h. The reaction was monitored by TLC. After the completion of the reaction the solvent was removed, and the residue was poured onto ice water. The separated solid was filtered, dried and purified by column chromatography over silica gel using petroleum ether ethyl / acetate (85 : 15) as eluant to get the respective 3-hydroxy-2-phenylpyrano[2,3-*a*]carbazol-4(11*H*)-one **5**. The compound thus obtained was recrystallized from ethanol to yield pale yellow crystals.

*3-Hydroxy-8-methyl-2-phenylpyrano[2,3-a]carbazol-4(11H)-one (**5a**)*

M. p. 274 – 276 °C. – Yield: 0.25 g (73 %). – IR (KBr): ν = 3425, 3200, 2921, 2855, 1618, 1569, 1465, 1329, 1097, 760 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 11.92 (b s, 1 H, 3-OH), 9.60 (b s, 1 H, N-11-H), 8.53 – 7.20 (m, 10 H, 5-H, 6-H, 7-H, 9-H, 10-H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H), 2.48 (s, 3 H, 8-CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.69 (4-C=O), 144.36 (C-2), 143.41 (C-1a), 140.17 (C-3), 139.39 (C^2-C1′), 131.93 (C-11a), 129.58 (C_2-C4′), 129.53 (C^2-C2′ and C^2-C6′), 128.34 (C^2-C3′ and C^2-C5′), 127.41 (C-8), 126.37 (C-5), 126.73 (C-6), 122.85 (C-10a), 121.96 (C-6a), 120.19 (C-4a), 119.48 (C-9), 118.71 (C-10), 117.62 (C-7), 114.20 (C-6b), 22.91 (8-CH_3). – MS (EI, 70 eV): *m/z* (%) = 341 (87) $[M]^+$. – $C_{22}H_{15}NO_3$ (341.36): calcd. C 77.41, H 4.43, N 4.10; found C 77.33, H 4.38, N 4.15.

*3-Hydroxy-9-methyl-2-phenylpyrano[2,3-a]carbazol-4(11H)-one (**5b**)*

M. p. 297 – 299 °C. – Yield: 0.26 g (75 %). – IR (KBr): ν = 3422, 3196, 2924, 2841, 1612, 1559, 1464, 1318, 1089, 787 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 11.66 (b s, 1 H, 3-OH), 9.56 (b s, 1 H, N-11-H), 8.41 – 7.34 (m, 10 H, 5-H, 6-H, 7-H, 8-H, 10-H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H), 2.50 (s, 3 H, 9-CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.06 (4-C=O), 145.78 (C-2), 144.20 (C-1a), 141.82 (C-3), 139.27 (C^2-C1′), 132.54 (C-11a), 130.86 (C^2-C4′), 128.18 (C^2-C2′ and C^2-C6′), 126.69 (C^2-C3′ and C^2-C5′), 126.51 (C-8), 125.75 (C-5), 125.13 (C-6), 123.56 (C-10a), 122.19 (C-6a), 121.77 (C-4a), 119.51 (C-10), 119.93 (C-9), 118.25 (C-7), 112.92 (C-6b), 20.17 (9-CH_3). – MS (EI, 70 eV): *m/z* (%) = 341 (80) $[M]^+$. – $C_{22}H_{15}NO_3$ (341.36): calcd. C 77.41, H 4.43, N 4.10; found C 77.49, H 4.50, N 4.06.

*3-Hydroxy-10-methyl-2-phenylpyrano[2,3-a]carbazol-4(11H)-one (**5c**)*

M. p. 204 – 205 °C. – Yield: 0.27 g (80 %). – IR (KBr): ν = 3417, 3226, 2919, 2857, 1622, 1572, 1460, 1315, 1087, 764 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 11.71 (b s, 1 H, 3-OH), 9.49 (b s, 1 H, N-11-H), 8.45 – 7.29 (m, 10 H, 5-H, 6-H, 7-H, 8-H, 9-H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H), 2.47 (s, 3 H, 10-CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.10 (4-C=O), 146.12 (C-2), 145.16 (C-1a), 140.85 (C-3), 138.76 (C^2-C1′), 132.95 (C-11a), 130.28 (C^2-C4′), 129.95 (C^2-C2′ and C^2-C6′), 128.29 (C^2-C3′ and C^2-C5′), 126.13 (C-8), 126.04 (C-5), 125.39 (C-6), 125.79 (C-10a), 124.22 (C-6a), 123.43 (C-10), 121.51 (C-4a), 120.29 (C-9), 118.20 (C-7), 114.31 (C-6b), 24.14 (10-CH_3). – MS (EI, 70 eV): *m/z* (%) = 341 (49) $[M]^+$. – $C_{22}H_{15}NO_3$ (341.36): calcd. C 77.41, H 4.43, N 4.10; found C 77.33, H 4.40, N 4.12.

*3-Hydroxy-2-phenylpyrano[2,3-a]carbazol-4(11H)-one (**5d**)*

M. p. 267 – 269 °C. – Yield: 0.24 g (72 %). – IR (KBr): ν = 3432, 3204, 2923, 2861, 1630, 1592, 1449, 1320, 1091,

774 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 11.31 (b s, 1 H, 3-OH), 9.30 (b s, 1 H, N-11-H), 8.55 – 7.31 (m, 11 H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.64 (4-C=O), 145.63 (C-2), 144.32 (C-1a), 141.41 (C-3), 139.53 (C^2-C1′), 131.49 (C-11a), 130.8 (C^2-C4′), 129.02 (C^2-C2′ and C^2-C6′), 128.19 (C^2-C3′ and C^2-C5′), 127.83 (C-8), 127.07 (C-5), 124.27 (C-6), 124.15 (C-10a), 123.87 (C-6a), 123.84 (C-10), 122.61 (C-4a), 121.31 (C-9), 120.49 (C-7), 118.15 (C-6b). – MS (EI, 70 eV): *m/z* (%) = 327 (73) $[M]^+$. – $C_{21}H_{13}NO_3$ (327.33): calcd. C 77.05, H 4.00, N 4.28; found C 77.13, H 3.96, N 4.18.

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[1] P. Bhattacharya, D. P. Chakraborty, in *Progress in the Chemistry of Organic Natural Products*, Vol. 52, (Eds.: W. Herz, H. Grisebach, G. W. Kirby, C. Tamm) Springer Verlag, Wien, **1987**, pp. 299 – 371.

[2] D. P. Chakraborty, S. Roy, in *Progress in the Chemistry of Organic Natural Products*, Vol. 57, (Eds.: W. Herz, H. Grisebach, G. W. Kirby, C. Tamm) Springer Verlag, Wien **1991**, pp. 71 – 110.

[3] R. S. Kapil, in *The Alkaloids*, (Ed.: R. H. F. Manske) Academic Press, New York **1971**, Vol. *13*, pp. 273.

[4] G. Bringmann, S. Tasler, H. Endress, K. Peters, E. M. Peters, *Synthesis* **1998**, 1501 – 1505.

[5] E. Brenna, C. Fuganti, S. Serra, *Tetrahedron* **1998**, *54*, 1585 – 1588.

[6] C. Ito, S. Katsuno, M. Itoigwa, N. Ruangrungsi, T. Mukainaka, M. Okuda, Y. Kitagawa, H. Tokuda, H. Nishino, H. Furukawa, *J. Nat. Prod*. **2000**, *63*, 125 – 128.

[7] M. Fiebig, J. M. Pezzuto, D. D. Soejarto, A. D. Kinghorn, *Phytochemistry* **1985**, *24*, 3041 – 3043.

[8] H. J. Knölker, K. R. Reddy, *Chem. Rev*. **2002**, *102*, 4303 – 4427, and refs. cited therein.

[9] C. Ito, H. Furukawa, *Chem. Pharm. Bull*. **1990**, *38*, 1548 – 1549.

[10] L. S. Liebeskind, R. W. Fenge, *J. Org. Chem*. **1990**, *55*, 5359 – 5364.

[11] V. Farina, *Pure Appl. Chem*. **1996**, *68*, 73 – 78.

[12] D. P. Chakraborty, S. Roy, A. K. Dutta, *J. Indian Chem. Soc*. **1985**, *62*, 673 – 678.

[13] D. P. Chakraborthy, A. Islam, P. Bhattacharya, *J. Org. Chem*. **1973**, *38*, 2728 – 2729.

[14] K. Shanmugasundaram, K. J. R. Prasad, *Heterocycles* **1999**, *51*, 2163 – 2169.

[15] C. Kavitha, K. J. R. Prasad, *J. Chem. Res*. (Synopsis) **2003**, 606 – 607; *J. Chem. Res*. (Miniprint) **2003**, 1025 – 1036.

[16] T. Vandana, K. J. R. Prasad, *J. Chem. Res*. **2004**, *11*, 717 – 721.

[17] T. Vandana, K. J. R. Prasad, *Indian J. Chem*. **2005**, *44B*, 819 – 822.

[18] M. S. Y. Khan, M. A. Mueed, *Indian J. Chem*. **2004**, *43B*, 1794 – 1797, and refs. cited therein.