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[12] Magnetization in the thermal equilibrium refers to "conventional" magnetization that is determined by the Boltzmann distribution. It differs fundamentally from the magnetization resulting from a PHIP experiment: The latter is represented by the time-averaged density matrix $\sigma_{PHIP} = I_Z I_Z$ (for the experiments described in this paper).

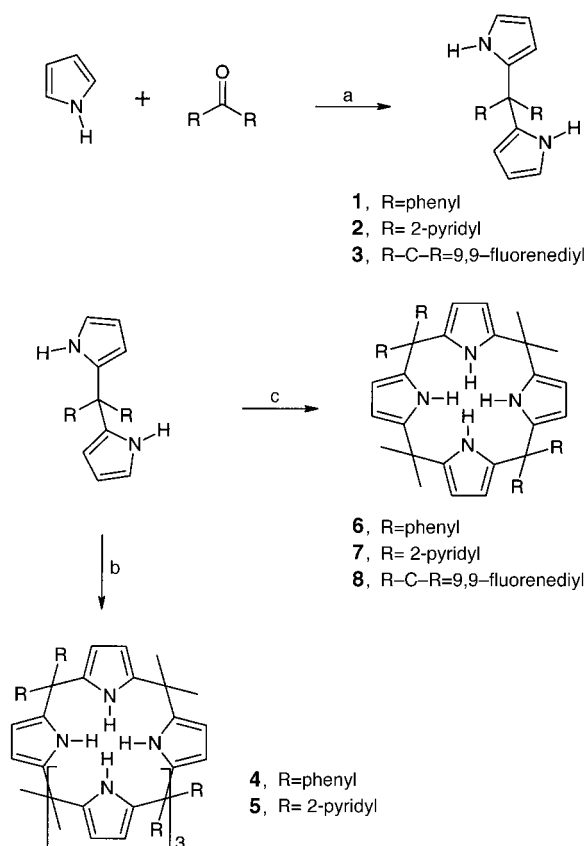# Extended Calixpyrroles: *meso*-Substituted Calix[6]pyrroles**

Boaz Turner, Mark Botoshansky, and Yoav Eichen*

Calix[*n*]pyrroles derived from pyrrole and simple ketones have recently become the subject of intensive research aimed at the development of novel ligands,[1] molecular hosts for anionic species[2–4] and for uncharged species such as simple alcohols, amines, and amides.[5] Octaalkylcalix[4]pyrroles,

[*] Dr. Y. Eichen, B. Turner, M. Botoshansky
    Department of Chemistry and Solid-State Institute
    Technion – Israel Institute of Technology
    Technion City, 32000 Haifa (Israel)
    Fax: (+972) 4-8233735
    E-mail: chryoav@techunix.technion.ac.il

which are readily accessible, are hosts for fluoride and chloride ions both in solution and in the solid state. Some of these hosts exhibit a remarkable selectivity for binding fluorides rather than other halides even though the guest anion is bound outside the cavity.[3]

It is anticipated that larger calix[*n*]pyrroles with larger cavities will enable selective and effective complexation of other anionic as well as uncharged species. Nevertheless, despite the rather simple synthesis of *meso*-alkylcalix[4]pyrroles, the only extended calix[*n*]pyrrole reported to date is the calix[5]pyrrole – calix[5]arene, the product of condensation of pyrrole with *p-tert*-butyl calix[5]arene pentamethyl ketone derivatives.[4] Furthermore, the only calix[4]pyrroles reported to date are products of condensation between pyrrole and simple aliphatic ketones containing acidic protons at the C_α atom. Here we report on a new, two-step synthesis for the preparation of *meso*-substituted calix[6]pyrroles and some new, dissymmetric, *meso*-substituted calix[4]pyrroles.

Acid-catalyzed condensation of pyrrole with aromatic ketones such as benzophenone, di-(2-pyridyl) ketone and 9-fluorenone results in formation of the corresponding diaryl-di-(2-pyrrolyl)methanes **1 – 3** in moderate to good yields (reaction a in Scheme 1). The diaryldi-(2-pyrrolyl)methane products failed to react further with the corresponding aromatic ketones to form linear polymers or cyclic products even after prolonged reaction times or at elevated temper-

Scheme 1. Synthesis of the *meso*-substituted calix[4]- and calix[6]pyrroles. a) Ketone/pyrrole = 1:2, BF₃·OEt₂, ethanol, room temperature, 7 days; b) pyrrole derivatives from reaction a) in ethanol/acetone (1/1), trifluoroacetic acid, room temperature, 7 days; c) pyrrole derivatives from reaction a) in ethanol/acetone (1/1), BF₃·OEt₂, room temperature, 7 days.

atures, in contrast to the reaction of pyrrole and pyrrole derivatives with most aliphatic ketones.[6] Curiously, pyrrole failed to react with aromatic ketones bearing electron-donating or electron-withdrawing groups in the *para* position (e.g. 4,4'-dichloro-, 4,4'-dimethoxy-, or 2,7-dinitro-9-fluorenone). Table 1 summarizes some experimental results for the acid-catalyzed reaction of diaryl ketones with pyrroles.

Although diaryldi-(2-pyrrolyl)methanes fail to react further with aromatic ketones, they react readily with simple aliphatic ketones, such as acetone, in the presence of catalytic amounts of trifluoroacetic acid (reaction b in Scheme 1) to yield the corresponding *meso*-1,1,3,3,5,5-hexaaryl-*meso*-2,2,4,4,6,6-hexamethylcalix[6]pyrroles **4** and **5**. The corresponding *meso*-1,1,3,3-tetraaryl-*meso*-2,2,4,4-tetramethylcalix[4]pyrroles **6–8** were isolated as the main products when BF$_3$·OEt or methanesulfonic acid were used as the acid catalyst (reaction c in Scheme 1). The experimental results are summarized in Table 1.

Crystals of *meso*-1,1,3,3,5,5-hexamethyl-*meso*-2,2,4,4,6,6-hexaphenylcalix[6]pyrrole (**4**) suitable for an X-ray structure determination were obtained in the form **4**·3 acetone·H$_2$O·CHCl$_3$ by slow evaporation of a chloroform/acetone solution (1:1 *v/v*). The macrocycle **4** forms an asymmetric, conelike structure in which all three diphenylmethylene units are situated on one side of the macrocycle, while the dimethylmethylene groups are situated on the other side (Figure 1 a). One phenyl ring of each diphenylmethylene unit points perpendicular to the macrocycle plane, while the other points towards the cavity of the macrocycle. The pyrrole rings in **4** adopt a 1,3,5-*alternate* conformation, in contrast to the more abundant *cone* conformation found in calix[6]arenes[7] or the less abundant 1,2,3-*alternate* conformation.[8] The N–H groups of the 1,3,5 pyrrole rings point towards the side of the *meso*-dimethylene groups and are almost perpendicular to the macrocycle plane. The N–H groups of the other three pyrrole rings point towards the center of the cavity. The
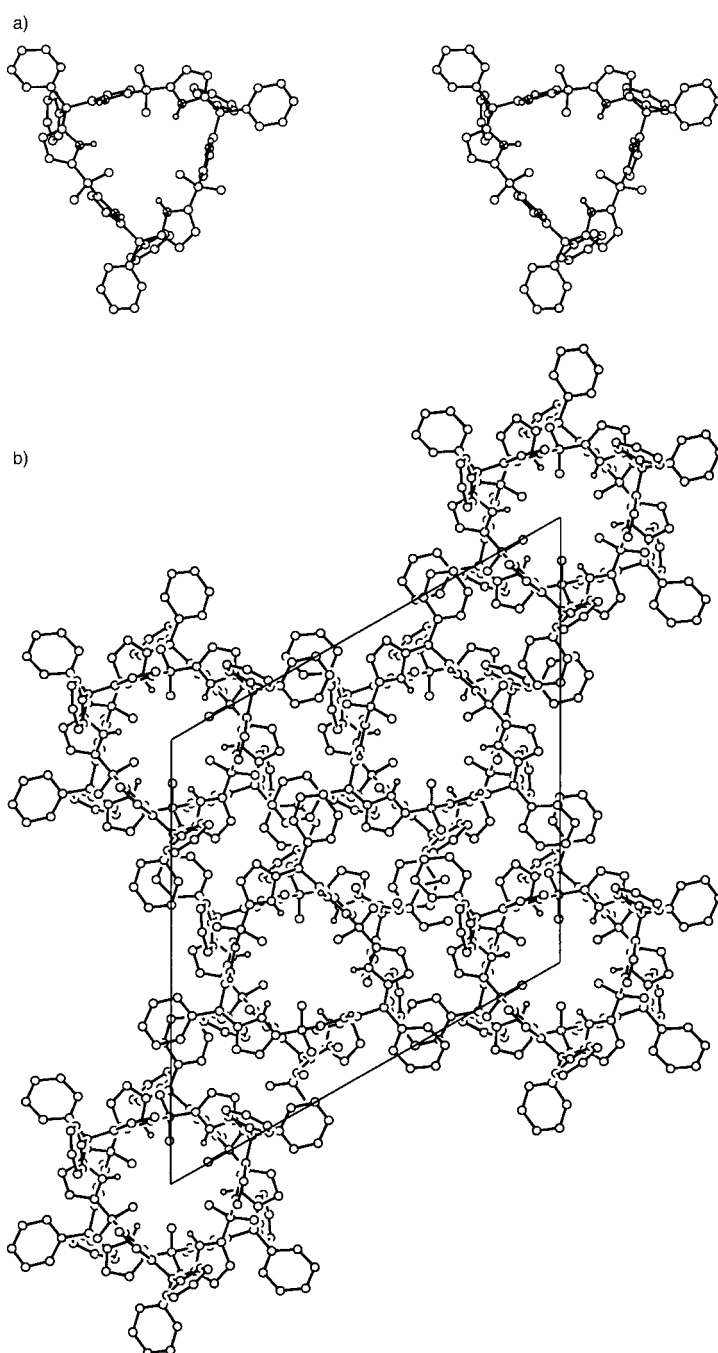

Figure 1. a) Molecular structure of **4** (stereoview). b) Axial projection of the packing of molecules of **4** in the crystal. In both figures solvent molecules and nonacidic hydrogen atoms have been omitted for clarity.

distance d(H···H) between the protons of the latter three pyrrole rings is 4.93 Å and the cross section of the cavity measures about 60 Å^2. The macrocycle is composed of three different regions: a) An aromatic part formed by three phenyl rings of the *meso*-diphenylmethylene moieties. b) A central part containing three acidic protons of three pyrrole rings pointing towards the center of the cavity. c) An aliphatic part composed of three methyl groups from the *meso*-dimethylmethylene moieties with three N–H groups of three pyrrole rings pointing out of the cavity. All the solvent molecules in the crystal are situated outside the cavity, probably due to a

Table 1. Condensation reactions between ketones and pyrroles.

Ketone	Pyrrole	Product	Yield [%]	M.p. [°C]
benzophenone	pyrrole	**1**	22[a], 39[b]	263–264
		–	–[c, d]	
4,4'-dimethoxybenzophenone	pyrrole	–	–[a, b, c, d]	
4,4'-dichlorobenzophenone	pyrrole	–	–[a, b, c, d]	
9-fluorenone	pyrrole	**3**	58[a]	238–239
		–	–[b, c, d]	
2,7-dinitro-9-fluorenone	pyrrole	–	–[a, b, c, d]	
di-(2-pyridyl) ketone	pyrrole	**2**	25[a], 35[b]	165–166
		–	–[c, d]	
dibenzosuberone	pyrrole	–	–[a, b, c, d]	
acetone	**1**	**6**	20,[a] 56[b], 25[c]	243–244
		4	9,[b] 25[c]	247–248
acetone	**2**	–	–[a]	
		7	20,[b] 9[c]	302–303
		5	2[c]	307–308
acetone	**3**	**8**	38[a]	302–303
		–	–[b]	

[a] Methanesulfonic acid as catalyst. [b] BF$_3$·Et$_2$O as catalyst. [c] Trifluoroacetic acid as catalyst. [d] No reaction under the given conditions.

mismatch between their size and the size of the cavity. Figure 1b depicts the packing of the macrocycle molecules in the crystal.

The X-ray structure of crystals of the dihydrate dietherate complex of *meso*-1,1,3,3-tetramethyl-*meso*-2,2,4,4-tetraphenylcalix[4]pyrrole (**6**) is depicted in Figure 2. Crystals of **6** · 2 H_2O · 2 Et_2O were obtained by slow evaporation of a diethyl
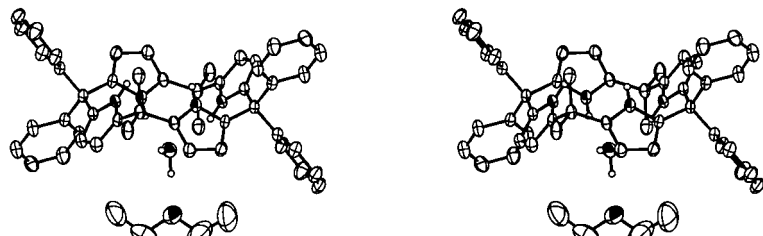

Figure 2. Molecular structure of **6** (stereoview). Nonacidic hydrogen atoms and one set of solvent molecules have been omitted for clarity.

ether/dichloromethane solution (1:1 *v/v*). Apparently, the small number of water molecules present in the crystallization solution were trapped by the macrocycle host, forming a solid-state complex. The calix[4]pyrrole receptor **6** adopts a 1,2-*alternate* conformation, the less abundant conformation of calix[4]arene[9] and calix[4]pyrrole systems.[4] The two water molecules are attached at the two sides of the macrocycle plane. The water molecules are attached to the macrocycle through two, almost equivalent, hydrogen bonds between the oxygen atom of the water molecule and two acidic N–H protons of adjacent pyrrole rings, (d(NH···O) = 2.170(5) and 2.144(4) Å, α(N–H···O) = 161.1° and 160.1°, respectively). One of the hydrogen atoms of each water molecule is bound to an oxygen atom of a diethyl ether molecule, (d(OH···OEt$_2$) = 1.753(5) Å, α(O–H···OEt$_2$) = 177.9°), while the other is "sandwiched" between two adjacent electron-rich pyrrole rings, probably due to π-H interactions (d(X···HO) = 2.84 and 2.93 Å, X = center of pyrrole ring; α(O–H···N) = 127.8° and 116.2°). The cross section of the cavity measures about 30 Å^2, and is more crowded than that of its calix[6]pyrrole analogue. The two crystalline complexes **4** and **6** are monomeric and do not form hydrogen bond networks in the crystal lattice.

Preliminary studies suggest that *meso*-aryl-substituted calix[*n*]pyrroles can act as efficient hosts for neutral and charged molecules in solution and in the solid state. The investigation of the host–guest chemistry of the new systems, such as the ditopic *meso*-tetra- and *meso*-hexapyridinecalixpyrroles is currently in progress.

Experimental Section

General: NMR spectra were recorded on a Brucker AC-200F spectrometer. Mass spectra were recorded by using a triple quadrupole TSQ-70 Spectrometer (Finnigan MAT). Melting points were recorded on a PL-DSC (Polymer Laboratories) machine. Elemental analysis were performed on a CHN Analyzer (Perkin Elmer). All reagents and solvents were used as received unless stated. Anhydrous solvents were dried before use by using standard methods. Acid catalysts and pyrrole were distilled before use.

General procedure for the preparation of diaryldi-(2-pyrrolyl)methanes: The ketone (2.5 mmol) and freshly distilled pyrrole (5 mmol) were dissolved in dry ethanol (45 mL). BF$_3$·OEt$_2$ (0.3 mL) was added to the solution, and the reaction mixture was stirred for one week at room temperature. Then solvents were removed under reduced pressure to give a

viscous residue, which was dissolved in dichloromethane and washed with aqueous ammonia solution. The aqueous phase was extracted with dichloromethane (50 mL). The organic phase was dried with anhydrous sodium sulfate, and purified by chromatography over silica (alumina for the pyridine derivatives).

General procedure for the preparation of *meso*-1,1,3,3,5,5-hexamethyl-*meso*-2,2,4,4,6,6-hexa-(2-aryl)calix[6]pyrroles and *meso*-1,1,3,3-tetramethyl-*meso*-2,2,4,4-tetraarylcalix[4]pyrroles: The di-(2-aryl)di-(2-pyrrolyl)methane (1.1 mmol) was added to a mixture of dry acetone (30 mL) and dry ethanol (30 mL). Trifluoroacetic acid (0.3 mL) (in the case of calix[6]pyrroles) or BF$_3$·OEt$_2$ (0.15 mL) (in the case of calix[4]pyrroles) were added to the solution and the reaction mixture was stirred at room temperature for one week. Solvents were removed under reduced pressure and the viscous residue was dissolved in dichloromethane and washed with aqueous ammonia solution. The aqueous phase was extracted with dichloromethane (50 mL). The organic phase was dried with anhydrous sodium sulfate and purified by chromatography over silica (alumina for the pyridine derivatives).

1: 40%; m.p. 263–264°C; ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.93 (br. s, 2H, NH), 7.25 (m, 6H, phenyl-H), 7.10 (m, 4H, phenyl-H), 6.73 (s, 2H, pyrrole-H$_\alpha$), 6.15 (m, 2H, pyrrole-H$_\beta$), 5.94 (s, 2H, pyrrole-H$_\beta$); ^{13}C NMR (50.03 MHz, CDCl$_3$): δ = 146.0, 135.4, 129.3, 127.9, 126.8, 117.4, 109.6, 108.1, 65.8; HR-MS: *m/z*: calcd for [C$_{21}$H$_{18}$N$_2$]$^+$: 298.1470; found for [*M*]$^+$ 298.1490; C,H,N analysis: calcd for C$_{21}$H$_{18}$N$_2$: C 84.53, H 6.08, N 9.39; found: C 84.32, H 6.13, N 9.34.

2: 35%; m.p. 165–166°C; ^{1}H NMR (200 MHz, CDCl$_3$): δ = 9.70 (br. s, 2H, NH), 8.53 (d, 2H, pyridine-H), 7.60 (dt, 2H, pyridine-H), 7.14 (m, 2H, pyridine-H), 6.81 (m, 2H, pyridine-H), 6.77 (s, 2H, pyrrole-H$_\alpha$), 6.18 (m, 2H, pyrrole-H$_\beta$), 5.94 (s, 2H, pyrrole-H$_\beta$); ^{13}C NMR (50.03 MHz, CDCl$_3$) δ = 165.9, 148.3, 136.7, 133.1, 123.6, 121.5, 117.6, 109.9, 107.8, 58.2; HR-MS: *m/z*: calcd for [C$_{19}$H$_{16}$N$_4$]: 300.1375; found for [*M*]$^+$: 300.1374; C,H,N analysis: calcd for C$_{19}$H$_{16}$N$_4$: C 75.98, H 5.37, N 18.65; found: C 75.63 H 5.53 N 18.48.

3: 58%; m.p. 238–239°C; ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.97 (br. s, 2H, NH), 7.74 (d, 2H, fluorene-H), 7.36 (m, 6H, fluorene-H), 6.61 (s, 2H, pyrrole-H$_\alpha$), 6.09 (m, 2H, pyrrole-H$_\beta$), 6.04 (s, 2H, pyrrole-H$_\beta$); ^{13}C NMR (50.03 MHz, CDCl$_3$): δ = 149.2, 139.6, 132.8, 128.0, 127.9, 125.3, 120.3, 117.3, 108.3, 107.2, 55.9; HR-MS: *m/z*: calcd for [C$_{21}$H$_{16}$N$_2$]$^+$: 296.1313; found for [*M*]$^+$: 296.1327; C,H,N analysis: calcd for C$_{21}$H$_{16}$N$_2$: C 85.11, H 5.44, N 9.45; found: C 84.83, H 5.48, N 9.36.

4: 25%; m.p. 247–248°C; ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.69 (br. s, 6H, NH), 7.20 (m, 18H, phenyl-H), 6.99 (m, 12H, phenyl-H), 5.71 (t, 6H, pyrrole-H$_\beta$), 5.58 (t, 6H, pyrrole-H$_\beta$), 1.46 (s, 18H, CH$_3$); ^{13}C NMR (50.03 MHz, CDCl$_3$): δ = 146.3, 138.7, 134.1, 129.0, 127.6, 126.6, 109.5, 103.4, 55.5, 35.3, 29.6; MS (CI): *m/z*: 1014.6 [*M*]$^+$; C,H,N analysis: calcd for C$_{72}$H$_{66}$N$_6$: C 85.17, H 6.55, N 8.28; found: C 85.44, H 6.66, N 8.51.

5: 2%; m.p. 307–308°C; ^{1}H NMR (200 MHz, CDCl$_3$): δ = 9.21 (br. s, 6H, NH), 8.58 (d, 6H, pyridine-H), 7.58 (m, 6H, pyridine-H), 7.21 (m, 6H, pyridine-H), 6.64 (m, 6H, pyridine-H), 5.86 (m, 6H, pyrrole-H$_\beta$), 5.06 (m, 6H, pyrrole-H$_\beta$), 1.56 (s, 18H, CH$_3$); ^{13}C NMR (50.03 MHz, CDCl$_3$): δ = 164.5, 148.4, 138.6, 136.0, 134.0, 124.1, 121.6, 107.5, 102.7, 58.2, 35.2, 28.9; MS (CI): *m/z*: 1021.7 [*M*+H]$^+$; C,H,N analysis: calcd for C$_{66}$H$_{60}$N$_{12}$·H$_2$O: C 76.28, H 6.01, N 16.17; found: C 76.56, H 6.06, N 15.71.

6: 56%; m.p. 243–244°C; ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.39 (br. s, 4H, NH), 7.17 (m, 12H, phenyl-H), 6.97 (m, 8H, phenyl-H), 5.89 (t, 4H, pyrrole-H$_\beta$), 5.65 (t, 4H, pyrrole-H$_\beta$), 1.63 (s, 12H, CH$_3$); ^{13}C NMR (50.03 MHz, CDCl$_3$): δ = 146.6, 139.3, 134.1, 128.9, 127.6, 126.3, 109.4, 102.9, 55.5, 35.3, 29.4; MS (CI): *m/z*: 677.0 [*M*+H]$^+$; C,H,N analysis: calcd for C$_{48}$H$_{44}$N$_4$·2H$_2$O: C 80.87, H 6.79, N 7.86; found: C 80.50, H 6.66, N 7.88.

7: 20%; m.p. 302–303°C; ^{1}H NMR (200 MHz, CDCl$_3$): δ = 9.21 (br. s, 4H, NH), 8.58 (d, 4H, pyridine-H), 7.58 (m, 4H, pyridine-H), 7.21 (m, 4H, pyridine-H), 6.64 (m, 4H, pyridine-H), 5.86 (m, 4H, pyrrole-H$_\beta$), 5.06 (m, 4H, pyrrole-H$_\beta$), 1.56 (s, 12H, CH$_3$); ^{13}C NMR (50.03 MHz, CDCl$_3$): δ = 164.5, 148.4, 138.6, 136.0, 134.0, 124.1, 121.6, 107.5, 102.7, 58.2, 35.2, 28.9; MS (CI): *m/z*: 681.1 [*M*+H]$^+$; C,H,N analysis: calcd for C$_{48}$H$_{40}$N$_8$: C 77.62, H 5.92, N 16.46; found: C 77.58, H 6.05, N 16.08.

8: 38%; m.p. 306–307°C; ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.90 (br. s, 4 H, NH), 7.73 (d, 4 H, fluorene-H), 7.38 (m, 12 H, fluorene-H), 5.89 (t, 4 H, pyrrole-H$_\beta$), 5.53 (t, 4 H, pyrrole-H$_\beta$), 1.49 (s, 12 H, CH$_3$); ^{13}C NMR (50.03 MHz, CDCl$_3$): δ = 148.4, 140.1, 139.7, 132.6, 127.8, 127.4, 124.7, 120.4, 106.3, 103.7, 55.6, 35.9, 29.8; MS (CI): m/z: 673.0 [M+H]$^+$; C,H,N analysis: calcd for C$_{48}$H$_{40}$N$_4 \cdot$ H$_2$O: C 83.45, H 6.13, N 8.11; found: C 83.56, H 6.15, N 8.0.

Crystal structure determination: Crystallographic data were collected by using a Philips PW 1100 four-circle, computer-controlled, diffractometer by using graphite crystal monochromated Mo$_{K\alpha}$ radiation (λ = 0.7107 Å) with $\omega/2\theta$ scan (scan width: 1.2°, scan rate: 3° min^{-1}). Unit cell parameters were determined by a least squares fitting of the setting angles of 25 centered reflections. The intensities of three standard reflections were measured every 120 min during the data collection. No absorption correction was performed. All non-hydrogen atoms were found by direct methods (SHELXS-86) and refined anisotropically (SHELXL-93). Hydrogen atoms were found by using a difference Fourier map and refined isotropically. The structures were solved by direct methods and refined on $|F_o|^2$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101 785 (**6**) and CCDC-101 786 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for **4**: 293 K, clear crystals, crystal dimensions 0.45 × 0.35 × 0.30 mm, trigonal, $R\bar{3}$, a = 23.75(3), b = 23.75(3), c = 24.20(3) Å, V = 11822(26) Å^3, Z = 18, ρ_{calcd} = 1.083 g cm^{-1}, μ = 0.13 mm^{-1}, $I > 2\sigma(I)$, $F(000)$ = 4092, 2θ range 4.3–24.08, 4329 reflections collected, 2718 independent, 289 refined parameters, $\Delta\rho_{max}$ = 0.205, wR = 0.1807, R_{obs} = 0.092.

Crystal data for **6**: 298 K, clear crystals, crystal dimensions 0.30 × 0.22 × 0.15 mm, monoclinic, $P2_1/n$ (No. 14), a = 12.080(4), b = 14.320(4), c = 14.690(4) Å, β = 102.51(3)°, V = 2480.8(13) Å^3, Z = 4, ρ_{calcd} = 1.153 g cm^{-1}, μ = 0.072 mm^{-1}, $I > 2\sigma(I)$, $F(000)$ = 928, 2θ range 4.0–48.0, 3898 reflections collected, 3258 independent, 402 refined parameters, $\Delta\rho_{max}$ = 0.243, wR = 0.1912, R_{obs} = 0.068.

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Mevalonate-Independent Biosynthesis of Terpenoid Volatiles in Plants: Induced and Constitutive Emission of Volatiles**

Jörn Piel, Jens Donath, Katja Bandemer, and Wilhelm Boland*

Dedicated to Professor Lothar Jaenicke on the occasion of his 75th birthday

Plants utilize volatiles to overcome constraints that result from their stationary way of life. Volatiles may serve as attractants for pollinators[1, 2] or may attract prey to carnivorous plants[3] over long distances. Herbivore-induced plant volatiles can even serve as cues to direct predators into the vicinity of their prey;[4,5] this signaling of the plant to the third trophic level is frequently interpreted as "a plant's cry for help".[6] Emission of volatiles such as ethylene, methyl jasmonate, or methyl salicylate by plants under attack may even induce defense and resistance genes in undamaged neighboring plants.[7–9] For example, in the dicotyledonous lima bean (*Phaseolus lunatus*) volatile emission can be induced by treatment with jasmonic acid or spider mite infestation.[5, 10, 11] As shown in Figure 1, a large proportion of
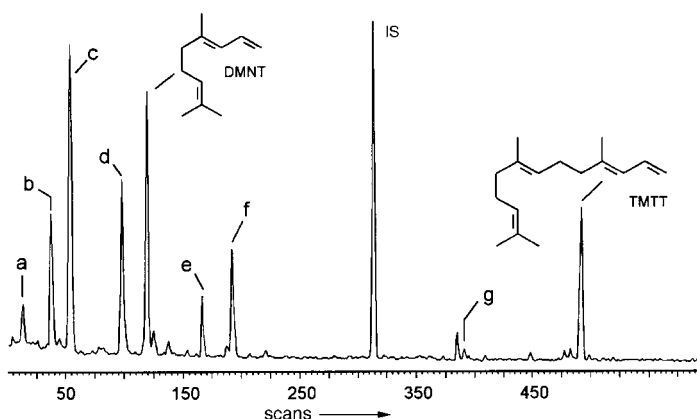

Figure 1. Profile of volatiles emitted from leaves of lima beans (*Phaseolus lunatus*) after infestation with spider mites (for details see Experimental Section). Identified compounds: a: (*Z*)-hex-3-enyl acetate; b: 2-ethylhexanol (contamination); c: ocimene; d: linalool; e: methyl salicylate; f: C$_{10}$H$_{14}$O; g: geranylacetone; DMNT, TMTT, IS: (1-bromodecane) as internal standard. After induction of lima beans with jasmonic acid (JA) a comparable blend of volatiles is released with exception of TMTT.[10]

the emitted volatiles are terpenoids. Particularly noteworthy are the two homoterpenes 4,8-dimethylnona-1,3,7-triene (DMNT) and 4,8,12-trimethyltrideca-1,3,7,11-triene (TMTT) emitted by many higher plants in response to herbivore attack[12, 13] and which are known to attract insectivores.[4, 5] Both homoterpenes are synthesized de novo: mass spectro-

[*] Prof. Dr. W. Boland, Dipl.-Chem. J. Piel, Dr. J. Donath, K. Bandemer
Max-Planck-Institut für Chemische Ökologie
Tatzendpromenade 1 a, D-07745 Jena (Germany)
Fax: (+49) 3641-643670
E-mail: Boland@ice.mpg.de