nylthiomethyl)lithium, 13307-75-0; bis(phenylthio)methyllithium, 13307-76-1.

Supplementary Material Available: Preparative, spectroscopic, and analytical data on compounds **3**, **6–13**, **15**, **18**, **20**, **24**, and **27–30** (6 pages). Ordering information is given on any current masthead page.

Synthesis of 1,3-Diketones Using α-Diazo Ketones and Aldehydes in the Presence of Tin(II) Chloride

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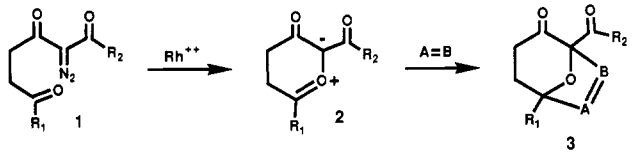
Recent publications from our laboratory have introduced a new general strategy for oxapolycyclic ring synthesis in which a rhodium(II)-catalyzed tandem cyclization–cycloaddition reaction represents the central element.[1] For ongoing studies to further implement and develop this strategy, we required a general route to α-diazo 1,3-diketones, which serve as the precursors for carbonyl ylide dipoles of type **2**. Highly stabilized β-dicarbonyl enolates



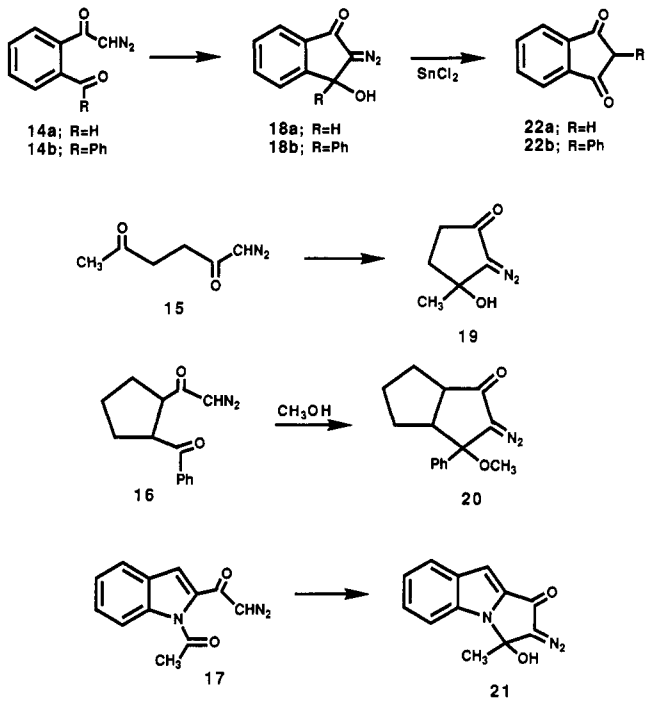
1 2 3

are known to readily react with sulfonyl azide reagents to give the desired diazo compounds in good yield.[2-6] Thus, for the subsequent development of our fundamental strategy, we needed an efficient method to prepare 1,3-diketones. A wide variety of procedures have been described in the literature for the synthesis of β-dicarbonyl compounds, including the reaction of metal enolates with acid chlorides[7] and acyl cyanides,[8] the acylation of enamines,[9] the direct acid-catalyzed acylation of ketones with acid anhydrides,[10] and the acylation of ketone silyl enol ethers.[11] A two-step method for the conversion of aldehydes into 1,3-diketones has also been reported, which involves the reaction with 1-diazo-1-lithioacetone followed by an acid-induced rearrangement of the initially formed α-diazo β-hydroxy keto derivative.[12-14] However, under these conditions the α-diazo alcohol also undergoes a retro-aldol reaction, leading to variable amounts of the starting aldehyde and diazo ketone. This approach is unsuitable for 1,3-diketones that have acid-labile groups incorporated into the side chain. Herein we report that the reaction of α-diazo ketones with aldehydes in the presence of Lewis acids is an effective method for the synthesis of a variety of 1,3-diketones.[15]

Table I

diazo ketone R_1COCHN_2, R_1 =	aldehyde R_2CHO, R_2 =	diketone (% yield) $R_1COCH_2COR_2$
Ph	C_2H_5	**4** (88)
Ph	$PhCH_2$	**5** (90)
Ph	C_4H_9	**6** (73)
$CH_3COCH_2CH_2$	C_2H_5	**7** (83)
$PhCH_2CH_2$	C_4H_9	**8** (80)
$PhCH_2CH_2$	$PhCH_2$	**9** (90)
$PhCOCH_2CH_2$	$CH_2=CH(CH_2)_2$	**10** (42)
$PhCOCH_2CH_2$	$CH_2=CH(CH_2)_3$	**11** (49)

Scheme I



A series of unsymmetrical 1,3-diketones were readily prepared by treating various α-diazo ketones with the appropriate aldehyde in the presence of a Lewis acid using methylene chloride as the solvent (Table I). The reaction is catalyzed by several different Lewis acids but the best results were obtained with $SnCl_2$ or BF_3. Methylene chloride was the solvent of choice since it gave the highest yields and was the easiest to remove. No reaction occurred in the absence of a catalyst and the formation of product appears to be relatively insensitive to the atmosphere.

The mild conditions of this reaction are illustrated by the facility with which 4-pentenal and 5-hexenal react with 1-diazo-5-phenyl-2,5-pentanedione to give the labile triones **10** (42%) and **11** (49%). Other aspects of the reaction were briefly probed. Yields and relative rate of reaction were

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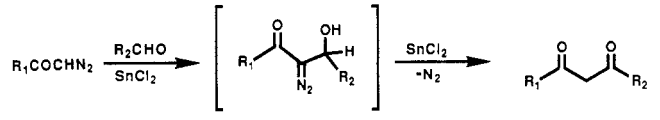
(15) While our work was in progress, Holmquist and Roskamp reported that aldehydes are efficiently converted into β-keto esters by reaction with ethyl diazoacetate in the presence of tin(II) chloride, see: Holmquist, C. R.; Roskamp, E. J. *J. Org. Chem.* **1989**, *54*, 3258.

0022-3263/90/1955-5297$02.50/0

found to be significantly lower when aromatic aldehydes were used. In fact, treatment of 1-diazo-4-phenylbutan-2-one (**12**) with benzaldehyde in the presence of $SnCl_2$ afforded only 1-chloro-4-phenylbutan-2-one (**13**) with no detectable signs of the 1,3-diketone. Treatment of the diazo ketones with tin(II) chloride in the absence of an aliphatic aldehyde also afforded the chloro ketones in good yield (60–85%).

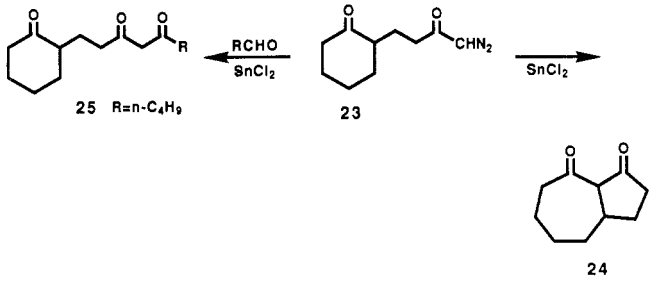
$$\underset{\mathbf{12}}{PhCH_2CH_2COCHN_2} + PhCHO \xrightarrow[SnCl_2]{} \underset{\mathbf{13}}{PhCH_2CH_2COCH_2Cl}$$

We speculate that formation of the 1,3-diketone proceeds via an α-diazo β-hydroxy keto derivative, which readily loses nitrogen under the reaction conditions, and this is followed by a 1,2-hydrogen shift to give the observed dicarbonyl compound. In certain cases it was possible to



actually isolate the suspected intermediate if the diazo keto carbon and the carbonyl group were located close in space. For example, treatment of diazo ketones **14–17** with mild base afforded **18–21** in high yield. When diazo keto alcohol **18** was allowed to stir with $SnCl_2$, a near quantitative yield of dione **22** was obtained (Scheme I).

The intramolecular counterpart of the above reaction constitutes an easy entry into the synthesis of bicyclic diketones. Treatment of diazo ketone **23** with tin(II) chloride gave the rearranged diketone **24** in 51% yield.[16] Interestingly, the reaction of **23** with various aldehydes in the presence of $SnCl_2$ gave mainly bicyclodecanedione **24** with only 9% of the corresponding trione **25**. Apparently, internal cyclization onto the ketone is faster than bimolecular trapping with the more reactive aldehyde.



In conclusion, the reaction of α-diazo ketones with aldehydes in the presence of tin(II) chloride provides a simple one-step route to a variety of 1,3-diketones. Utilization of this method for the synthesis of α-diazo alkanediones that undergo a further rhodium(II)-induced cyclization is currently under investigation.

Experimental Section

General Procedure. A mixture containing the diazo ketone (4.0 mmol) in 10 mL of methylene chloride was added with stirring at room temperature to anhydrous tin(II) chloride (0.4 mmol). To this suspension was added the appropriate aldehyde in 5 mL of methylene chloride. After nitrogen evolution had stopped, the reaction was transferred to a separatory funnel, washed with water, and dried over sodium sulfate. Removal of the solvent left a residue, which was chromatographed on a spinning silica gel chromatron plate. The following compounds were prepared according to the above procedure.

1-Phenyl-1,3-pentanedione (4):[17] 88% yield as a colorless oil; IR (neat) 3080, 2995, 2960, 2895, 1720, 1620, 1580, 1500, 1460, 1270, 1160, 820, 770, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) enol δ 1.20 (t, 3 H, J = 7.5 Hz), 2.46 (q, 2 H, J = 7.5 Hz), 6.17 (s, 1 H), 7.4–8.0 (m, 5 H); keto form δ 1.08 (t, 3 H, J = 7.5 Hz), 2.60 (q, 2 H, J = 7.5 Hz), 4.07 (s, 2 H), 7.4–7.9 (m, 5 H).

1,4-Diphenyl-1,3-butanedione (5):[18] 90% yield as a white solid, mp 52–53 °C; IR (neat) 3090, 3060, 2930, 1725, 1610, 1580, 1500, 1460, 1280, 1190, 1909, 980, 780, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) enol δ 3.72 (s, 2 H), 6.12 (s, 1 H), 7.25–7.95 (m, 10 H); keto form δ 3.88 (s, 2 H), 4.10 (s, 2 H), 7.2–7.9 (m, 10 H).

1-Phenyl-1,3-heptanedione (6):[17] 73% yield as a colorless oil; IR (neat) 3080, 2980, 2950, 2890, 1720, 1610, 1580, 1495, 1460, 1275, 1190, 1080, 770, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) enol form δ 0.93 (t, 3 H, J = 7.5 Hz), 1.32–1.48 (m, 2 H), 1.60–1.75 (m, 2 H), 2.42 (t, 2 H, J = 7.5 Hz), 6.16 (s, 1 H), 7.4–8.0 (m, 5 H).

Nonane-2,5,7-trione (7): 83% yield as a colorless oil; IR (neat) 2990, 2970, 2920, 1715, 1620, 1410, 1370, 1170, 950, 810 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) enol form δ 1.08 (t, 3 H, J = 7.5 Hz), 2.16 (s, 3 H), 2.25 (q, 2 H, J = 7.5 Hz), 2.5–2.80 (m, 4 H), 5.52 (s, 1 H); keto form δ 1.05 (t, 3 H, J = 7.5 Hz), 2.14 (s, 3 H), 2.30 (q, 2 H, J = 7.5 Hz), 2.5–2.80 (m, 4 H), 3.60 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.80, 30.3, 32.7, 36.9, 37.8, 98.4, 191.2, 195.7, 206.8; HRMS calcd for $C_9H_{14}O_3$ 170.0943, found 170.0945.

1-Phenyl-3,5-nonanedione (8): 80% ad a pale yellow oil; IR (neat) 3040, 2980, 2940, 2880, 1730, 1610, 1580, 1550, 1530, 1500, 1460, 1390, 760, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.91 (t, 3 H, J = 7.5 Hz), 1.33 (m, 2 H), 1.55 (m, 2 H), 2.25 (t, 2 H, J = 7.5 Hz), 2.59 (t, 2 H, J = 7.5 Hz), 2.96 (t, 2 H, J = 7.5 Hz), 5.44 (s, 1 H), 7.1–7.3 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 22.2, 27.7, 31.4, 37.8, 40.0, 99.2, 126.0, 128.1, 128.3, 140.6, 193.3, 194.0; HRMS calcd for $C_{15}H_{20}O_2$ 232.1463, found 232.1457.

1,6-Diphenyl-2,4-hexanedione (9): 90% yield as a pale yellow oil; IR (neat) 3080, 3040, 2940, 2880, 1730, 1600, 1500, 1450, 1330, 940, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) enol δ 2.56 (t, 2 H, J = 7.5 Hz), 2.89 (t, 2 H, J = 7.5 Hz), 3.57 (s, 2 H), 5.39 (s, 1 H), 7.05–7.45 (m, 10 H); keto form δ 2.70 (t, 2 H, J = 7.5 Hz), 2.85 (t, 2 H, J = 7.5 Hz), 3.75 (s, 2 H), 4.05 (s, 2 H), 7.1–7.4 (m 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.4, 37.9, 45.0, 99.4, 126.1, 127.0, 128.2, 128.4, 128.6, 129.3, 135.0, 140.5, 192.0, 193.3; HRMS calcd for $C_{18}H_{18}O_2$ 266.1307, found 266.1309.

1-Phenyl-9-decene-1,4,6-trione (10): 42% yield as a pale yellow oil; IR (neat) 3080, 2920, 1725, 1690, 1620, 1600, 1450, 1360, 1215, 1000, 920, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) keto form δ 2.33–2.37 (m, 2 H), 2.65 (t, 2 H, J = 7.2 Hz), 2.91 (t, 2 H, J = 6.4 Hz), 3.30 (t, 2 H, J = 6.4 Hz), 3.69 (s, 2 H), 4.95–5.08 (m, 2 H), 5.74–5.84 (m, 1 H), 7.42–7.47 (m, 2 H), 7.52–7.58 (m, 1 H), 7.94–7.98 (m, 2 H); enol form δ 2.33–2.37 (m, 4 H), 2.78 (t, 2 H, J = 6.8 Hz), 3.31 (t, 2 H, J = 6.8 Hz), 4.95–5.08 (m, 2 H), 5.58 (s, 1 H), 5.74–5.84 (m, 1 H), 7.42–7.47 (m, 2 H), 7.52–7.58 (m, 1 H), 7.94–7.98 (m, 2 H); HRMS calcd for $C_{16}H_{18}O_3$ 258.1256, found 258.1262.

1-Phenyl-10-undecene-1,4,6-trione (11): 49% yield as a pale yellow oil; IR (neat) 3080, 2950, 1730, 1700, 1690, 1620, 1455, 1365, 1220, 1135, 920, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) enol form δ 1.64 (q, 2 H, J = 7.4 Hz), 2.01 (q, 2 H, J = 7.4 Hz), 2.20 (t, 2 H, J = 7.4 Hz), 2.73 (t, 2 H, J = 6.8 Hz), 3.25 (t, 2 H, J = 6.8 Hz), 4.90–4.99 (m, 2 H), 5.52 (s, 1 H), 5.66–5.76 (m, 1 H), 7.37–7.42 (m, 2 H), 7.50–7.52 (m, 1 H), 7.82–7.93 (m, 2 H); keto form δ 1.64 (q, 2 H, J = 7.4 Hz), 2.01 (q, 2 H, J = 7.4 Hz), 2.49 (t, 2 H, J = 7.4 Hz), 2.86 (t, 2 H, J = 6.4 Hz), 3.23 (t, 2 H, J = 6.4 Hz), 3.63 (s, 2 H), 4.90–4.99 (m, 2 H), 5.66–5.76 (m, 2 H), 7.37–7.42 (m, 2 H), 7.50–7.52 (m, 1 H), 7.82–7.93 (m, 2 H); HRMS calcd for $C_{17}H_{20}O_3$ 272.1412, found 272.1403.

1-Chloro-4-phenyl-2-butanone (13):[19] 83% yield as a colorless oil; IR (neat) 3080, 3040, 2950, 2870, 1740, 1600, 1500, 1460, 1400, 1100, 790, 760, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.85–3.00 (m, 4 H), 4.03 (s, 2 H), 7.15–7.35 (m, 5 H).

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2-Diazo-3-hydroxy-1-indanone (18a): 69% yield; clear oil; IR (neat) 3440 (br), 2105, 1690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.25 (bd, 1 H, J = 8.1 Hz), 5.98 (d, 1 H, J = 8.1 Hz), 7.46–7.72 (m, 4 H).

2-Diazo-3-hydroxy-3-phenyl-1-indanone (18b) 85% yield, mp 170–171 °C; IR (KBr) 3036, 2100, 1660, 1605, 1350, 1330, 1175, 1040, 780, 765, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.70 (s, 1 H), 7.26–7.61 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) 81.0, 122.3, 124.5, 125.5, 128.2, 128.8, 129.8, 134.4, 134.7, 140.2, 151.5, 186.3. Anal. Calcd for $C_{15}H_{10}O_2N_2$: C, 71.99; H, 4.03; N, 11.19. Found: C, 71.84; H, 4.04; N, 11.10.

2-Diazo-3-hydroxy-3-methyl-1-cyclopentanone (19): IR (neat) 3410, 2100, 1660, 1385, 1330, 1190, 1090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.65 (s, 3 H), 2.10–2.25 (m, 2 H), 2.34 (dd, 1 H, J = 17.6, 8.7, and 4.2 Hz), 2.67 (ddd, 1 H, J = 17.6, 8.8, and 8.6 Hz), 4.18 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.3, 35.3. 36.9, 68.6, 77.6, 197.3.

Octahydro-2-diazo-3-methoxy-3-phenylpentalen-1-one (20): 80% as a clear oil; IR (neat) 2960, 2890, 1800, 1775, 1455, 1265, 1175, 960, 770, 710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.12–1.43 (m, 3 H), 1.80–2.02 (m, 3 H), 3.13 (dt, 1 H, J = 7.4 and 7.2 Hz), 3.32 (dt, 1 H, J = 8.4 and 3.3 Hz), 3.50 (s, 3 H), 7.22–7.40 (m, 5 H).

2-Diazo-2,3-dihydro-3-hydroxy-3-methyl-1*H*-pyrrolo[1,2-*a*]indol-1-one (21): 64% yield; mp 130–131 °C; IR (KBr) 3270 (br), 2140, 1645, 1630, 1520, 1390, 1370, 1340, 1320, 1290, 1245 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.64 (s, 3 H), 7.10 (d, 1 H, J = 1.6 Hz), 7.17 (dd, 1 H, J = 8.5 and 6.6 Hz), 7.36 (dd, 1 H, J = 8.1 and 6.6 Hz), 7.45 (d, 1 H, J = 8.5 Hz), 7.70 (d, 1 H, J = 8.1 Hz), 9.84 (bs, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.8, 107.4, 111.6, 120.8, 122.4, 126.0, 126.7, 132.2, 136.3, 173.3, 189.9. Anal. Calcd for $C_{12}H_9N_3O_2$: C, 64.43; H, 3.99; N, 18.49. Found: C, 63.32; H, 3.94; N, 18.42.

Bicyclo[5.3.0]decane-2,10-dione (24):[16] 51% yield as a colorless oil; IR (neat) 2930, 2860, 1660, 1615, 1450, 1390, 1320, 1230, 1190, 910, 880 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.35–1.50 (m, 4 H), 1.80–2.0 (m, 4 H), 2.05–2.20 (m, 4 H), 2.05–2.20 (m, 1 H), 2.34–2.50 (m, 4 H), 2.75–2.85 (m, 1 H).

1-(1′-Oxocyclohex-2′-yl)-3,5-nonadiene (25): 9% yield as a colorless oil; IR (neat) 3500, 2960, 2880, 1720, 1700, 1620, 1460, 1410, 1360, 1270, 1060, 980, 810 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, 3 H, J = 7.5 Hz), 1.20–1.80 (m, 14 H), 1.80–2.06 (m, 1 H), 2.20–2.60 (m, 4 H), 3.53 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.8, 20.5, 22.1, 24.8, 25.6, 27.4, 28.8, 37.4, 41.7, 43.5, 46.1, 69.4, 202.8, 207.3, 212.6; HRMS calcd for $C_{15}H_{22}O_2$ ($M^+ - H_2O$) 234.1619, found 234.1617.

Acknowledgment. This work was supported by the National Cancer Institute (CA26751). Use of the high-field NMR spectrometers used in these studies was made possible through equipment grants from the National Science Foundation and the National Institute of Health.

Supplementary Material Available: ^1H NMR (300 MHz) and ^{13}C NMR spectra (75 MHz) for all new compounds (9 pages). Ordering information is given on any current masthead page.

Aflavazole: A New Antiinsectan Carbazole Metabolite from the Sclerotia of *Aspergillus flavus*

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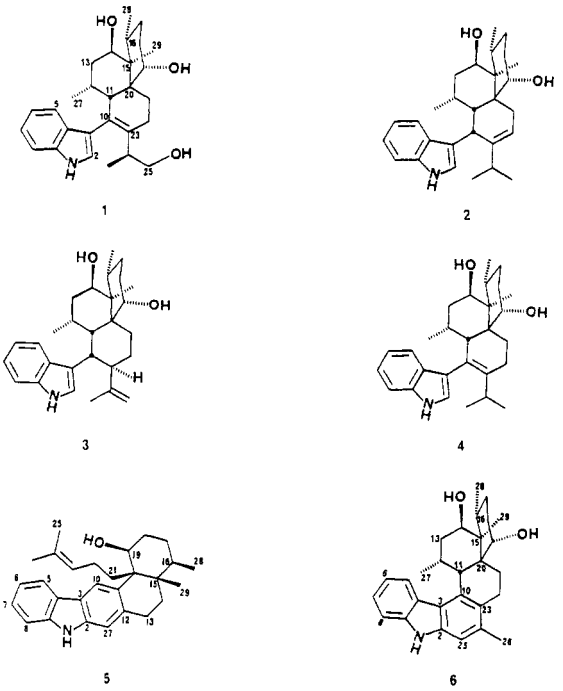
Received May 1, 1990

Extracts of the sclerotia of the common mold *Aspergillus flavus* deter feeding by the fungivorous insect *Carpophilus hemipterus*.[1,2] Our initial studies of this phenomenon led to the isolation and structure determination of four aflavinine derivatives (1–4) (Chart I) responsible for most of the antifeedant activity. One additional major antiinsectan indole metabolite was present in the chloroform extract of *A. flavus* sclerotia,[3] but its spectral data were significantly different from those of 1–4. Recently, studies of another *Aspergillus* sp. (*A. tubingensis*) have led us to isolate representatives of a new class of biologically active indole diterpene-derived metabolites containing a carbazole moiety (e.g., 5).[4] Examination of the spectral data for the remaining *A. flavus* metabolite and comparison with the data for 5 have permitted us to assign the structure of this new compound as 6. This metabolite, which we have named aflavazole, appears to be ubiquitous in sclerotial extracts of various strains of *A. flavus* and *A. parasiticus* and incorporates another previously unreported carbazole-containing ring system. Details of the isolation, structure elucidation, and biological activity of 6 are reported here.

Chart I



Sclerotia of *A. flavus* were produced by solid substrate fermentation on corn kernels.[2] The chloroform extract of the sclerotia exhibited insect antifeedant activity and was fractionated by reversed phase flash chromatography, followed by HPLC (C_{18}) to afford aflavazole (6), as well as the aflavinine derivatives 1–4. The molecular formula of 6 was established as $C_{28}H_{35}NO_2$ (12 unsaturations) on the basis of HREIMS and ^{13}C NMR data. Although 6 possessed many spectral similarities with 1–4, it was clear that 6 was not a simple aflavinine derivative. Key differences included the relatively low intensity of the quinolinium ion at m/z 130 in the mass spectrum, and the UV spectrum, which was characteristic of a carbazole unit.[5] The ^{13}C NMR spectrum of 6 indicated the presence of the

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