Phenalenones from *Strelitzia reginae*

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Phytochemical analysis of rhizomes of *Strelitzia reginae* resulted in the isolation and identification of an unusual new (**1**) and four known phenalenone-type compounds, which were identified using MS and NMR spectroscopic techniques. The occurrence of phenalenones in Strelitziaceae, which has been established for the first time, is of chemotaxonomic interest.

Strelitzia species, originally treated as members of a tribe of Musaceae,[1,2] later were classified as a separate family, Strelitziaceae.[3,4] To our knowledge, no attempts have been undertaken to clarify the relationships of Strelitziaceae in terms of chemotaxonomy. Moreover, only limited phytochemical information on *Strelitzia* species is available in the literature. Investigations on the occurrence of oxypipecolinic acids in the leaves of *S. reginae*,[5] the carotenoid composition of the sepals,[6,7] the proanthocyanidin pattern of the leaves,[8] the sugar composition of the nectar,[9] and the chemistry of epicuticular wax crystalloids[10] have been published. The close relationship to Musaceae[11] and other families such as Haemodoraceae[12] and Pontederiaceae,[13] containing phenalenone-type compounds, encouraged us to study the occurrence of phenalenones in the "bird of paradise" plant, *S. reginae* (Banks).

Rhizomes of *S. reginae* were extracted with EtOH, and the extract was partitioned between *n*-hexane−H_2O and $CHCl_3$−H_2O. The organic extracts were separated by preparative TLC on Si gel, and finally purified by reversed-phase HPLC.

2-Hydroxy-9-phenylphenalenone (anigorufone), which is a known compound of *Anigozanthos rufus*,[14] *Anigozanthos preissii*,[15] *Musa acuminata*,[16] and *Ensete ventricosum*,[17] was isolated from the *n*-hexane fraction. The $CHCl_3$ extract contained 2-hydroxy-9-(4-hydroxyphenyl)phenalen-1-one (hydroxyanigorufone) as the major compound of that type. Hydroxyanigorufone was first isolated from *A. rufus*[14] and has been detected also in *A. preissii*,[15] *M. acuminata*,[18] and *E. ventricosum*.[17] The majority of known phenylphenalenones carry a phenyl substituent at C-9. However, the phenyl ring is often attached to other positions of the phenalenone nucleus. Thus, 8-hydroxy-7-methoxy-6-phenylphenalen-1-one recently has been described as a constituent of *E. ventricosum*,[17] and 5-hydroxy-6-methoxy-7-phenylphenalen-1-one was first isolated from *A. preissii*.[15] These two compounds were found in the $CHCl_3$ extract of *S. reginae* in the present study. Analytical data of the four known compounds from *S. reginae* exactly matched those of the reference compounds previously isolated from *A. preissii*[15] and *E. ventricosum*,[17] respectively.

A novel compound, 4-hydroxy-2-methoxyphenalen-1-one (**1**), was also found in the $CHCl_3$ extract. The ^1H NMR and ^1H−^1H COSY spectra of **1** exhibited resonances of three adjacent aromatic protons (δ 8.56, 8.18, and 7.65), two doublets of an AB spin systems (δ 7.93, 7.27), a single aromatic proton (δ 7.60), and a methoxyl signal (δ 3.93). This pattern, together with MS data, suggested a phenalenone molecule without a phenyl ring. The most downfield signal in the ^1H NMR spectrum (δ 8.56) belonging to the ABX spin system was assigned to H-9. This assignment was based on the *peri* position of this proton relative to the carbonyl group. The multiplicity of the double doublet at δ 7.65 and cross-peaks in the COSY spectrum readily assigned this signal to H-8. The signal of H-7 (δ 8.18), completing the ABX spin system, showed a NOE with the doublet at δ 7.93, which therefore must be H-6. The COSY correlation between H-6 and the doublet at δ 7.27 indicated the latter to be H-5. The singlet at δ 7.60 (H-3) exhibited HMBC connectivities through three bonds with the C-1 carbonyl (δ 186.2) and through two bonds with C-2 (δ 152.3). The position of the methoxyl group (δ 55.2) at C-2 was established by the HMBC cross-peak of its ^1H signal with this carbon. A correlation in the 2D NOESY spectrum between the methoxyl resonance and H-3 singlet confirmed the spatial proximity of the corresponding protons. H-3, H-6, H-7, and H-9 exhibited HMBC cross signals with the carbon atom at δ 126.8, which therefore was attributed to C-9b. Another HMBC connectivity between H-6 and the quaternary carbon at δ 160.5 indicated the latter signal to be C-4. The chemical shift of C-4 indicated a hydroxyl function attached to this carbon. Further HMBC connectivities, for example, between H-6/C-7 and H-7/C-6, and a complete set of HMQC cross signals were also in agreement with the suggested structure of this new compound as 4-hydroxy-2-methoxyphenalen-1-one (**1**), representing the first phenalenone lacking a phenyl substituent from plants.

Methylation of compound **1** (diazomethane) yielded a mixture containing approximately 50% 2,4-dimethoxyphenalen-1-one (**2**) and 50% 7,8-dimethoxyphenalen-1-one (**3**). Only compound **3** could be isolated by reversed-phase HPLC, as compound **2** was not stable. To assign the NMR signals of **3**, a strategy similar to that used for the parent compound **1** was employed. The ^1H NMR data of **2** were obtained from a mixture of **2** and **3**, obtained immediately after methylation. The occurrence of two methyl derivatives indicated that compound **1** very likely occurred in two tautomeric forms, **1** and **1a**. Alternatively, the electron-rich carbonyl of **1** might get methylated first with simul-

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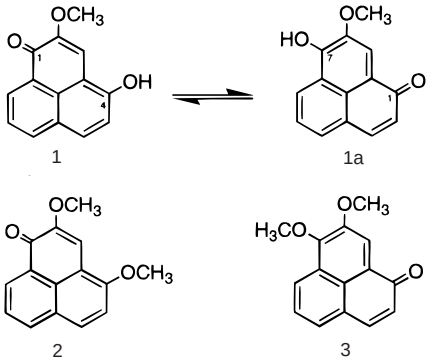
taneous or subsequent loss of the hydroxyl proton to give **3**.



This study reports the occurrence of phenylphenalenones in *Strelitzia reginae*. Four of these compounds were previously found in Musaceae[16−18] and related monocots.[14,15] Thus, from a chemotaxonomic point of view, it may not be appropriate to separate Musaceae and Strelitziaceae into different plant families. However, phylogenetic analyses provide strong arguments for classifying Strelitziaceae into a separate family.[19]

Experimental Section

General Experimental Procedures. NMR spectra were recorded on a Bruker DRX 500 spectrometer at 500.13 MHz (^{1}H) and 125.75 MHz (^{13}C), respectively, using standard Bruker software. TMS was used as internal standard. ^{1}H NMR, ^{1}H−^{1}H COSY, 2D NOESY, HMBC, and HMQC experiments were recorded in a 2.5-mm inverse detection microprobe head. Broadband decoupled ^{13}C spectra were run using a 2.5-mm broadband microprobe head. Mass spectra were recorded on a Micromass MasSpec sector mass spectrometer (70 eV). Reversed-phase HPLC was conducted on a Merck Hitachi LiChrograph chromatography system (L-6200A pump, L-4250 UV−vis detector, D-2500 integrator). A Nucleosil 7 C_{18} column (250 × 20 mm, i.d.) was used for semipreparative separation. Analytical HPLC was carried out on a LiChrospher 100 RP_{18} column (250 × 4 mm, i.d.; 5 μm). TLC was performed on Si gel 60 F_{254}, using precoated plates and toluene−acetone 4:1 (v:v) and 2:1 (v:v), respectively, as eluents. Compounds on TLC plates were detected from their UV absorbance at 254 nm.

Plant Material. *S. reginae* (Banks) plants were obtained from the Botanical Gardens in Berlin and Düsseldorf, Germany, where this species is under permanent maintenance. Rhizomes of freshly harvested plants were used for extraction.

Isolation and Purification. Rhizomes (11 kg fresh wt) were chopped and exhaustively extracted with EtOH at room temperature. The EtOH extract was evaporated (<40 °C) and partitioned between *n*-hexane−H_2O and $CHCl_3$−H_2O. The *n*-hexane and $CHCl_3$ fractions were subjected to TLC. Final separation of TLC zones was carried out by semipreparative reversed-phase HPLC. Isocratic elution with 85% MeCN−15% H_2O was used (flow rate 10 mL min^{-1}; UV detection at 254 nm). Analytical reversed-phase HPLC runs were used for purity check. A linear gradient profile of MeCN−H_2O containing 0.1% TFA as a mobile phase was used as follows: 0 min: 50% MeCN; 20 min: 80% MeCN; 25 min: 90% MeCN (flow rate 0.8 mL min^{-1}; UV detection at 254 nm). This yielded anigorufone (2.0 mg), hydroxyanigorufone (1.5 mg), 8-hydroxy-7-methoxy-6-phenylphenalen-1-one (1.0 mg), 5-hydroxy-6-methoxy-7-phenylphenalen-1-one (0.9 mg), and **1** (1.1 mg).

4-Hydroxy-2-methoxyphenalen-1-one (1): yellow solid, UV (EtOH) λ_{max} (log ϵ) 215 (2.9), 267 (3.6), 428 (2.4); ^{1}H NMR (acetone-d_6, 500 MHz) δ 8.56 (1H, dd, J = 7.6, 1.0 Hz, H-9), 8.18 (1H, dd, J = 7.7, 1.0 Hz, H-7), 7.93 (1H, d, J = 9.0 Hz, H-6), 7.65 (1H, dd, J = 7.7, 7.6 Hz, H-8), 7.60 (1H, s, H-3), 7.27 (1H, d, J = 9.0 Hz, H-5), 3.93 (3H, s, OCH_3); ^{13}C NMR (acetone-d_6, 125 MHz) δ 186.2 (C-1), 160.5 (C-4), 152.3 (C-2), 135.0 (C-7), 133.7 (C-6), 130.4 (C-9), 128.7 (C-6a), 126.8 (C-9b), 125.1 (C-8), 121.5 (C-5), 109.0 (C-3), 55.9 (OCH_3), C-3a and C-9a not detected in the ^{13}C NMR spectrum due to long spin−lattice relaxation times (T_1),[20] EIMS *m*/*z* 226 [M]$^+$ (100), 211 (52), 197 (29); HREIMS *m*/*z* 226.0623 (calcd for $C_{14}H_{10}O_3$, 226.0630).

2,4-Dimethoxyphenalen-1-one (2) and 7,8-Dimethoxyphenalen-1-one (3). Methylation of 4-hydroxy-2-methoxyphenalen-1-one (**1**) (0.7 mg) was carried out with diazomethane in ether at room temperature. The crude reaction mixture was subjected to ^{1}H NMR measurement in acetone-d_6 immediately after evaporation of the diazomethane solution. The ^{1}H NMR data of compound **2** were obtained from the spectrum of the mixture: ^{1}H NMR (acetone-d_6, 500 MHz) δ 8.60 (1H, dd, J = 7.6, 1.0 Hz, H-9), 8.30 (1H, dd, J = 8.2, 1.0 Hz, H-7), 8.11 (1H, d, J = 9.2 Hz, H-6), 7.71 (1H, dd, J = 8.2, 7.6 Hz, H-8), 7.58 (1H, d, J = 9.2 Hz, H-5), 7.44 (s, H-3), 4.16 (3H, s, OCH_3-4), 3.90 (3H, s, OCH_3-2). A linear gradient profile of MeCN−H_2O containing 0.1% TFA as a mobile phase was used to separate compound **3** (t_R 13.6 min) on an analytical reversed-phase HPLC column: 0 min: 40% MeCN; 20 min: 80% MeCN (flow rate 1.0 mL min^{-1}; UV detection at 254 nm): ^{1}H NMR (acetone-d_6, 500 MHz) δ 8.35 (1H, dd, J = 8.5, 1.0 Hz, H-6), 8.33 (1H, s, H-9), 7.89 (1H, d, J = 9.8 Hz, H-3), 7.85 (1H, dd, J = 7.0, 1.0 Hz, H-4), 7.66 (1H, dd, J = 8.5, 7.0 Hz, H-5), 6.62 (1H, d, J = 9.8 Hz, H-2), 4.18 (3H, s, OCH_3), 4.14 (3H, s, OCH_3); ^{13}C NMR (acetone-d_6, 125 MHz) δ 184.2 (C-1), 150.7 (C-7), 150.7 (C-8), 142.2 (C-3), 131.3 (C-4), 129.5 (C-2), 128.3 (C-3a), 127.6 (C-5), 126.7 (C-6), 124.1 (C-9b), 118.1 (C-9), 62.1 (OCH_3), 57.1 (OCH_3); C-6a and C-9a not detected in the ^{13}C NMR spectrum due to long spin−lattice relaxation times (T_1),[20] EIMS *m*/*z* 240 [M]$^+$ (100), 225 (72), 210 (48), 198 (39), 197 (64).

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