Naucleactonin D, an Indole Alkaloid and other Chemical Constituents from Roots and Fruits of *Mitragyna inermis*

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Phytochemical investigation of the roots and fruits of *Mitragyna inermis* (Rubiaceae) resulted in the isolation of a new indole alkaloid, named naucleactonin D (**1**), together with fourteen known compounds: nauclefiline (**2**), naucleficine (**3**), nauclefidine (**4**), angustoline (**5**), angustine (**6**), barbinervic acid (**7**), quinovic acid 3-*O*-α-L-rhamnopyranoside (**8**), betulinic acid (**9**), a mixture of ursolic (**10**) and oleanolic acid (**11**), a mixture of stigmasterol and β-sitosterol, β-sitosterol 3-*O*-β-D-glucopyranoside, and strictosamide (**12**) as the major compound. The structures of the isolated compounds were elucidated by detailed spectroscopic analysis and by comparison with published data. No ^{13}C NMR data for **2** and **3** exist in the literature and compounds **2**, **3**, **5**, **7**, and **12** are reported for the first time from the genus *Mitragyna*. The crude extract and isolated compounds were tested *in vitro* for their preliminary cytotoxicity against brine shrimps (*Artemia salina*).

Key words: *Mitragyna inermis*, Rubiaceae, Indole Alkaloids, Naucleactonin D, NMR, Cytotoxicity Activity

Introduction

Mitragyna inermis (Willd.) O. Kuntze (Rubiaceae), Synonyms: *Mitragyna africana* (Willd.) Korth.; *Nauclea africana* Willd.; *Uncaria inermis* Willd. [1], is a small tree that grows on low alluvial plains and swampy savanna in West Africa [2, 3]. In traditional medicine, this plant is used to treat diseases such as diabetes, fever, diarrhea, dysentery, cholera, malaria, rheumatism, and osteoarthritis [4 – 7]. The leaves of *M. inermis* have been used in traditional medicine in Mali for hepatic illnesses [8]. Previous phytochemical investigations of *M. inermis* revealed the presence of indole and oxindole alkaloids in the leaves [9]. In addition, several pharmacological studies reported antimicrobial, antiplasmodial, hepatic activities, and cardiovascular properties of the crude extract of this plant. Toxicity studies as for cytotoxicity and genotoxicity have also been carried out [4, 7, 10 – 12]. No phytochemical studies have been reported to date on fruits and roots of *M. inermis*. In the continuing search for bioactive or new secondary metabolites from Cameroonian medicinal plants, we have investigated solvent extracts of the fruits and roots of *M. inermis*. In this article, we report on the isolation and structure elucidation of a new indole alkaloid, named naucleactonin D (**1**), and on ^{13}C NMR assignments for nauclefiline (**2**) and naucleficine (**3**). Compound **6** has been isolated and identified previously from *Mitragyna javanica* and *Mitragyna parvifolia* [13]. The structure of compound **1** was elucidated on the basis of a detailed spectroscopic analysis, and by comparison with reported data. In addition, the known

compounds, nauclefidine (**4**), angustoline (**5**), angustine (**6**), barbinervic acid (**7**), quinovic acid glycoside (**8**), betulinic acid (**9**), a mixture of ursolic acid (**10**) and oleanolic acid (**11**), strictosamide (**12**), a mixture of β-sitosterol and stigmasterol, and β-sitosterol 3-*O*-β-D-glucopyranoside were also isolated.

Results and Discussion

The air-dried and powdered roots and fruits of *Mitragyna inermis* were extracted separately with dichloromethane/methanol (1:1). The crude extract from the roots was subjected to column chromatography and delivered ten compounds including naucleficine (**3**) and one new indole alkaloid, named naucleactonin D (**1**). The crude extract from fruits was also subjected to column chromatography with an *n*-hexane-EtOAc gradient and delivered five compounds including nauclefiline (**2**).

Compound **1** (Fig. 1) was obtained as a yellowish powder with a yellow fluorescence (365 nm) from the dichloromethane-methanol (98:2) fraction. It reacted positively with Dragendorff's reagent giving an orange color, indicating alkaloid properties. The UV spectrum of **1** in MeOH exhibited absorption bands at $\lambda_{max} = 212$, 337 and 368 nm, which indicated the presence of a highly conjugated system, and IR bands at 1651 and 1629 cm^{-1} suggested conjugated carbonyl and amide carbonyl groups. The molecular formula, $C_{19}H_{14}N_2O_3$, implying fourteen double bond equivalents, was deduced from NMR data and negative ion-mode HRESIMS. The broadband decoupled ^{13}C NMR spectrum (Table 1) displayed 19 carbon resonances, which were sorted by DEPT and HSQC experiments into 10 quaternary carbons (including one carbonyl function at $\delta = 151.7$), 6 methines (including one aldehyde carbonyl at $\delta = 186.4$), 2 methylenes at $\delta = 19.0$ and 40.3, and a methyl group at $\delta = 12.8$. The ^1H NMR spectrum (Table 1) exhibited signals for four coupled protons of an *ortho*-disubstituted aromatic ring system at $\delta = 7.06$ (t, $J = 8.1$ Hz), 7.21 (t, $J = 8.1$ Hz), 7.41 (d, $J = 8.1$ Hz), and 7.58 (d, $J = 8.1$ Hz), another aromatic proton at $\delta = 7.39$ (s), two sets of methylene protons at $\delta = 3.07$ (t, $J = 6.6$ Hz) and $\delta = 4.40$ (t, $J = 6.6$ Hz), and one proton at $\delta = 11.82$ (s), suggesting the presence of an NH or OH group. The ^1H-^1H COSY and HMBC spectra allowed the identification of the fragment C=C–CH_2–CH_2–N. The above ^1H and ^{13}C NMR data of **1** were similar to those of naucleactonin A [14], suggesting the same indolo[2,3-*a*]quinolizine skeleton in the two compounds. The differences appeared in the substitution of the furan ring. In fact, the acetyl groups at C-20 and H-17 in naucleactonin A were replaced by methyl and formyl groups in **1**. These substituents were located on the furan ring by means of HMBC correlations (Fig. 2). Correlations from H-21 ($\delta = 2.81$, CH_3) to carbons C-18 ($\delta = 169.5$) and C-19 ($\delta = 117.6$) and from H-20 ($\delta = 10.17$, CHO) to carbons C-19 ($\delta = 117.6$) and C-15 ($\delta = 129.8$), clearly indicated that the methyl and formyl groups were fixed at C-18 and C-19, re-

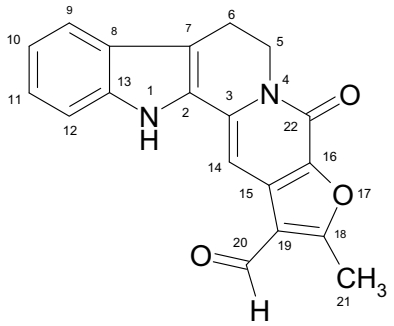


Fig. 1. Chemical structure of naucleactonin D (**1**).

Table 1. ^1H (300 MHz) and ^{13}C (125 MHz) NMR and HMBC data for naucleactonin D (**1**) in [D_6]DMSO.

Position	δ_C	δ_H (m, *J* in Hz)	HMBC
1	–	11.82	C-2, C-7, C-8, C-13
2	128.0	–	–
3	135.3	–	–
4	–	–	–
5	40.3	4.40 (2H, t, 6.6 Hz)	C-3, C-6, C-7, C-16, C-22
6	19.0	3.07 (2H, t, 6.6 Hz)	C-2, C-3, C-5, C-7, C-8
7	112.3	–	–
8	125.2	–	–
9	119.1	7.58 (1H, d, 8.1 Hz)	C-7, C-8, C-11, C-13
10	119.5	7.06 (1H, t, 8.1 Hz)	C-8, C-11, C-12
11	123.5	7.21 (1H, t, 8.1 Hz)	C-9, C-13
12	111.7	7.41 (1H, d, 8.1 Hz)	C-8, C-10
13	138.0	–	–
14	93.0	7.39 (1H, s)	C-2, C-3, C-16, C-19
15	129.8	–	–
16	140.5	–	–
17	–	–	–
18	169.5	–	–
19	117.6	–	–
20	186.4	10.17 (1H, s)	C-15, C-19
21	12.8	2.81 (3H, s)	C-15, C-18, C-19
22	151.7	–	–

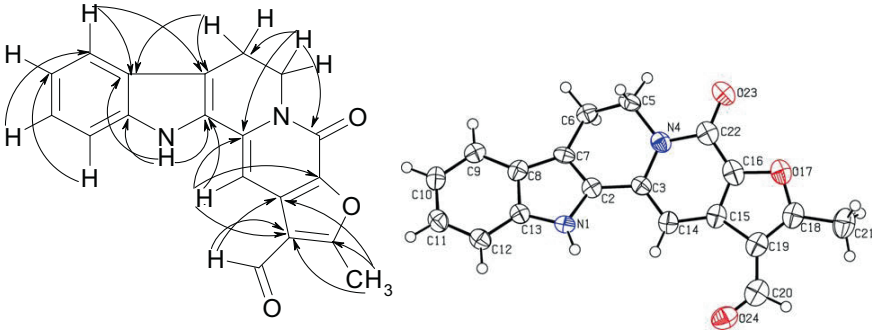


Fig. 2 (color online). Important HMBC correlations and ORTEP [38] plot based on single-crystal X-ray structure determination of naucleactonin D (**1**).

spectively. The X-ray crystallographic analysis (see Fig. 2 and Experimental Section) and NOESY correlations between the methyl and formyl groups confirmed further their positions. On the basis of the above data, the structure of naucleactonin D (**1**) was elucidated as 6,7-dihydro-2-methyl-4-oxo-12*H*-indolo[2,3-*a*]furo[2,3-*g*]quinolizine-3-carbaldehyde (Fig. 1). The HMBC correlations (Fig. 2) in **1** agreed with the structure assignment.

The known compounds nauclefiline (**2**) [15], naucleficine (**3**) [16], nauclefidine (**4**) [17], angustoline (**5**) [18], angustine (**6**) [13, 18], barbinervic acid (**7**) [19], quinovic acid 3-*O*-α-L-rhamnopyranoside (**8**) [20, 21], betulinic acid (**9**) [22], a mixture of ursolic acid (**10**) [23, 24] and oleanolic acid (**11**) [24], strictosamide (**12**) [18, 28] (Fig. 3), a mixture of stigmasterol [25] and β-sitosterol [26], and β-sitosterol 3-*O*-β-D-glucopyranoside [27] were identified by comparison of their spectral and physical (melting points and/or optical rotations) data with published values. The ^{13}C NMR assignments for compounds **2** and **3** were obtained *via* extensive analysis of their 1D and 2D NMR spectra. The spectral data as well as the occurrence of **2**, **3**, **5**, **7**, and **12** in the genus *Mitragyna* are reported here for the first time.

The crude extracts and sixteen pure compounds were tested for their cytotoxicity against *A. salina*. Only angustoline (**5**) and angustine (**6**) delivered significant biological activities revealing 40 % and 100 % mortality of the brine shrimps at 10 μg mL^{-1}, respectively (Table 2). The determination of the lethal dose resulted in a high activity for angustine (**6**) ($LD_{50} = 3.24\,\mu g\,mL^{-1}$) and moderate toxicity for angustoline (**5**) ($LD_{50} = 14.45\,\mu g\,mL^{-1}$), which is, however, still more than the value for the well-known anticancer alkaloid berberine hydrochloride ($LD_{50} = 26\,\mu g\,mL^{-1}$) [29]. It should be noted that good correlations between activities in the *Artemia salina* test and antitumor as well as antimalarial, pesticidal, antiviral, and antifilarial activities have been reported [30 – 32].

Experimental Section

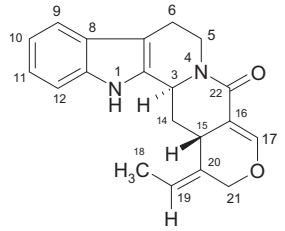
General

The ^{1}H NMR spectra were recorded on Varian Mercury-300 (300.141 MHz), Varian VNMRS-300 (300.536 MHz),

Table 2. Toxicity of angustoline (**5**), angustine (**6**), and crude extracts from fruits and roots of *Mitragyna inermis*, measured as mortality rates in percent and LD_{50} values in μg mL^{-1} of brine shrimps (*Artemia salina* nauplii) in comparison with actinomycin D and berberine hydrochloride.

Concentration (in μg mL^{-1})	100.00	50.00	25.00	12.50	10.00	6.25	3.12	1.65	0.02	LD_{50}
Fruits, % (crude extract)	90	7	0	0	0	0	0	0	–	72.44
Roots, % (crude extract)	0	0	0	0	0	0	0	0	–	/
5, %	100	81	64	–	40	0	0	0	–	14.45
6, %	100	100	100	100	100	86	48	13	–	3.24
Actinomycin D	100	100	100	100	100	100	100	100	50	0.02
Berberine hydrochloride[a]										26.00

[a] LD_{50} value taken from ref. [29].



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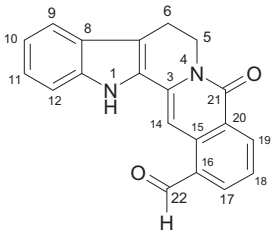

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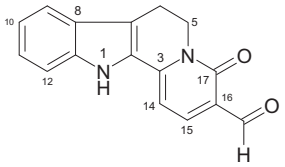

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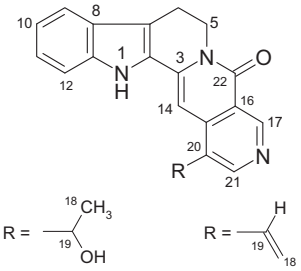
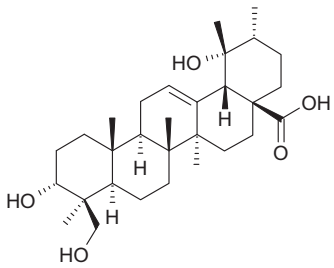


5 **6**



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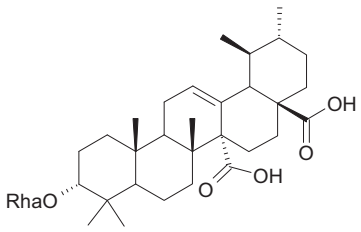

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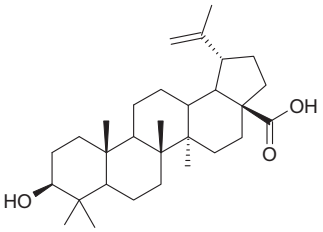

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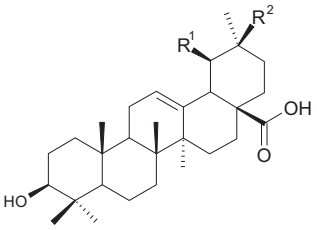

10: $R^1 = CH_3$, $R^2 = H$
11: $R^1 = H$, $R^2 = CH_3$

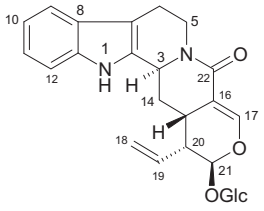

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Fig. 3. Structures of known compounds **2**–**12** isolated from *Mitragyna inermis*.

Varian Inova-500 (499.8 MHz), and Varian Inova-600 (599.743 MHz) spectrometers equipped with 3 mm probes; ^{13}C NMR spectra were measured at 75.575, 125.707 and 150.815 MHz relatively to TMS as internal standard; shifts are reported as δ values. UV/Vis spectra were recorded in MeOH on a Varian Cary 3E UV/Vis spectrophotometer. IR spectra were recorded on a Jasco FT/IR-4100 Fourier-transform infrared spectrometer type A. Electrospray-ionization mass spectrometry (ESIMS) and high-resolution mass spectra (HRESIMS) were recorded on a micrOTOF time-of-flight mass spectrometer (Bruker Daltonics, Bremen/Germany), as well as on an Apex IV 7 Tesla Fourier-transform ion cyclotron resonance mass spectrometer (Bruker Daltonics, Billerica, MA/USA). Flash and column chromatography: silica gel (230 – 400 and 70 – 230 mesh; Merck). TLC was performed on Merck precoated silica gel 60 F_{254} aluminum sheets and pre-coated silica gel sheets of Polygram SIL G/UV_{254} (Macherey-Nagel and Co., Düren/Germany), with mixtures of *n*-hexane, ethyl acetate, dichloromethane, and methanol as eluents; spots were detected using UV light (254 and 365 nm) or by spraying with 50 % H_2SO_4 followed by heating at 50 – 100 °C.

Plant material

The roots and fruits of *M. inermis* were collected in May 2008 at Nkoteng in the Centre Region of the Republic of Cameroon and identified by Mr. V. Nana, botanist at the National Herbarium (Yaoundé, Cameroon), where a voucher specimen (no. 8886/SRF/Cam.) has been deposited.

Extraction and isolation

The dried and powdered roots (3.6 kg) and fruits (2.0 kg) of *M. inermis* were extracted separately with a CH_2Cl_2-MeOH (1:1) mixture at room temperature for 48 h. The extracts were concentrated under reduced pressure to afford 145 g (brown) and 60 g (green) extracts, respectively. A portion of 96.0 g of the roots extract was fractionated by flash chromatography over silica gel (230 – 400 mesh; Merck; $7 \times 42\ cm^2$), eluted with a CH_2Cl_2-MeOH gradient of increasing polarity [(100:0)–(0:100)]. The resulting 96 fractions of each 500 mL were combined on the basis of TLC analysis to yield five main fractions: F_1 (13 g), F_2 (14.6 g), F_3 (11.0 g), F_4 (17.0 g), and F_5 (28.0 g). Fractions F_1 (composed of subfractions 1 – 7) and F_5 (composed of subfractions 60 – 96) were complex mixtures containing mostly oils and polar compounds, respectively, and were not further studied. Fraction F_2 (composed of subfractions 8 – 25) was subjected to column chromatography over silica gel (70 – 230 mesh; Merck; $4 \times 40\ cm^2$), eluted with gradient mixtures of CH_2Cl_2-MeOH [(100:0)–(95:5)], to yield a mixture of stigmasterol and β-sitosterol (38 mg), nauclefidine (**4**, 3.4 mg), barbinervic acid (**7**, 26 mg), and naucleactonin D (**1**, 2.6 mg). Fraction F_3 (composed of subfractions 26 – 45) was further separated by column chromatography over silica gel (70 – 230 mesh; Merck; $4 \times 40\ cm^2$), eluted with gradient mixtures of CH_2Cl_2-MeOH [(98:2)–(90:10)], and afforded naucleficine (**3**, 5.6 mg), angustoline (**5**, 11 mg), angustine (**6**, 3.4 mg), and β-sitosterol 3-*O*-β-D-glucopyranoside (46 mg). Fraction F_4 (composed of subfractions 46 – 59) was separated by column chromatography over silica gel (70 – 230 mesh; Merck; $4 \times 40\ cm^2$), and eluted with gradient mixtures of CH_2Cl_2-MeOH [(95:5)–(85:15)], to yield quinovic acid 3-*O*-α-L-rhamnopyranoside (**8**, 36 mg) and strictosamide (**12**, 107 mg).

A portion of 58 g of the fruit extract was subjected to column chromatography over silica gel (70 – 230 mesh; Merck; $7 \times 42\ cm^2$), eluted with a gradient of increasing polarity of mixtures of *n*-hexane-EtOAc [(100:0) – (0:100)] and EtOAc-MeOH [(95:5) – (90:10)], resulting in the collection of 210 fractions of each 200 mL, which were combined on the basis of TLC analysis. Fractions 10 – 42 yielded betulinic acid (**9**, 128 mg), β-sitosterol (27 mg) and a mixture of ursolic acid and oleanolic acid (**10** and **11**; 69 mg). Fractions 66 – 154 were combined and subjected to column chromatography over silica gel (70 – 230 mesh; Merck; $4 \times 40\ cm^2$) and eluted with *n*-hexane-EtOAc mixtures [(50:50)–(0:100)]; nauclefiline (**2**, 47 mg), angustoline (**5**, 2 mg) and β-sitosterol 3-*O*-β-D-glucopyranoside (73 mg) were obtained.

Brine shrimp microwell cytotoxicity assay

The tests were performed as described previously [33, 34]. Actinomycin D as positive control showed a mortality rate of 100 % at 1.65 $\mu g\ mL^{-1}$.

*Naucleactonin D [6,7-dihydro-2-methyl-4-oxo-12H-indolo[2,3-a]furo[2,3-g]quinolizine-3-carbaldehyde] (**1**)*

Yellowish powder. – UV/Vis (MeOH): λ_{max} ($\log \varepsilon$) = 212 (3.88), 337 (3.4), 368 (3.1) nm. – ^1H NMR ([D_6]DMSO, 300 MHz) and ^{13}C NMR ([D_6]DMSO, 125 MHz) spectroscopic data, see Table 1. – MS ((–)-ESI): m/z = 317 [M–H]$^-$, 353 [M+Cl]$^-$, 635 [2M–H]$^-$, 671 [2M+Cl]$^-$. – MS ((+)-ESI): m/z = 341 [M+Na]$^+$, 289 (100) [M+Na–CHO]$^+$. – HRMS ((–)-ESI): m/z = 317.0926 (calcd. 317.0932 for $C_{19}H_{13}N_2O_3$, [M–H]$^-$).

*Nauclefiline (**2**)*

Yellowish amorphous powder. – ^1H NMR ([D_6]DMSO, 300 MHz): δ = 11.05 (s, 1H, NH), 7.40 (d, J = 7.5 Hz, 1H, 9-H), 7.36 (d, J = 7.8 Hz, 1H, 12-H), 7.34 (s, 1H, 17-H), 6.98 (t, J = 7.5 Hz, 1H, 10-H), 7.06 (t, J = 8.1 Hz, 1H, 11-H), 5.65 (q, J = 6.9 Hz, 1H, 19-H), 5.07 (d, J = 5.7 Hz, 1H, 3-H), 4.84 (dd, J = 12.3, 4.8 Hz, 1H, 5a-H), 4.34 (d,

$J = 11.7$ Hz, 1H, 21a-H), 4.24 (d, $J = 11.7$ Hz, 1H, 21b-H), 2.96 (td, $J = 12.2$, 4.4 Hz, 1H, 5b-H), 2.78 (m, 2H, 6a-H, 15-H), 2.65 (m, 2H, 14b-H, 6b-H), 2.20 (td, $J = 13.2$, 6.6 Hz, 1H, 14a-H), 1.60 (d, $J = 6.9$ Hz, 3H, CH_3). – ^{13}C NMR ([D$_6$]DMSO, 125 MHz): $\delta = 134.0$ (C_q, C-2), 53.4 (CH, C-3), 41.7 (CH_2, C-5), 20.9 (CH_2, C-6), 109.1 (C_q, C-7), 126.9 (C_q, C-8), 117.5 (CH, C-9), 118.6 (CH, C-10), 120.9 (CH, C-11), 111.2 (CH, C-12), 135.9 (C_q, C-13), 30.7 (CH_2, C-14), 28.5 (CH, C-15), 111.5 (C_q, C-16), 150.1 (CH, C-17), 12.9 (CH_3, C-18), 124.2 (CH, C-19), 132.8 (C_q, C-20), 69.5 (CH_2, C-21) and 163.7 (C_q, C-22). – HRMS ((+)-ESI): $m/z = 343.1406$ (calcd. 343.1417 for $C_{20}H_{20}N_2O_2Na$, $[M+Na]^+$), 663.2913 $[2M+Na]^+$, 983.4447 $[3M+Na]^+$. – HRMS ((–)-ESI): $m/z = 319.1447$ (calcd. 319.1452 for $C_{20}H_{19}N_2O_2$, $[M–H]^-$).

*Naucleficine (**3**)*

Orange amorphous powder. – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): $\delta = 11.76$ (s, 1H, NH), 10.43 (s, 1H, CHO), 8.53 (d, $J = 7.5$ Hz, 1H, 19-H), 8.24 (d, $J = 7.5$ Hz, 1H, 17-H), 8.11 (s, 1H, 14-H), 7.62 (t, $J = 7.2$ Hz, 1H, 18-H), 7.60 (d, $J = 7.2$ Hz, 1H, 9-H), 7.48 (d, $J = 8.1$ Hz, 1H, 12-H), 7.24 (t, $J = 7.7$ Hz, 1H, 11-H), 7.08 (t, $J = 7.8$ Hz, 1H, 10-H), 4.42 (t, $J = 6.6$ Hz, 2H, 5-H), 3.12 (t, $J = 6.6$ Hz, 2H, 6-H). – ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 127.8$ (C_q, C-2), 135.0 (C_q, C-3), 40.4 (CH_2, C-5), 19.1 (CH_2, C-6), 114.0 (C_q, C-7), 125.4 (C_q, C-8), 119.3 (CH, C-9), 119.6 (CH, C-10), 124.0 (CH, C-11), 111.9 (CH, C-12), 138.5 (C_q, C-13), 94.8 (CH, C-14), 129.5 (C_q, C-15), 135.5 (C_q, C-16), 138.4 (CH, C-17), 125.3 (CH, C-18), 133.6 (CH, C-19), 125.5 (C_q, C-20), 160.7 (C_q, C-21) and 192.6 (CH, C-22). – HRMS ((+)-ESI): m/z 337.0936 (calcd. 337.0947 for $C_{20}H_{14}N_2O_2Na$, $[M+Na]^+$), 651.1991 $[2M+Na]^+$, 965.3040 $[3M+Na]^+$. – HRMS ((–)-ESI): m/z 313.0984 (calcd. 313.0983 for $C_{20}H_{13}N_2O_2$, $[M–H]^-$).

Crystal structure determination

The structure of **1** was determined by single-crystal X-ray diffraction. Naucleactonin D, $C_{19}H_{14}N_2O_3$, co-crystallized with a DMSO solvent molecule in the monoclinic crystal system in the centrosymmetric space group $P2_1/c$ with $Z = 4$. Crystal data: $C_{19}H_{14}N_2O_3 \cdot C_2H_6OS$ (396.45); yellow plates, $0.012 \times 0.010 \times 0.002$ mm^3. Lattice parameters: $a = 12.0814(13)$, $b = 6.9510(8)$, $c = 22.213(3)$ Å, $\beta = 98.603(7)^\circ$; $D_{calcd.} = 1.428$ Mg m^{-3}, $F(000) = 832$. Data collection: a total of 24 970 diffraction intensities in the θ-range of 3.7 to 58.9° were collected, giving 2627 unique and 1982 observed [$I > 2\,\sigma(I)$] reflections; *hkl* ranges of the merged dataset of $h = -13{:}13$, $k = 0{:}7$, $l = 0{:}24$; $T = 100(2)$ K; Bruker SMART 6000 diffractometer with area detection. Empirical absorption correction (SADABS [35]); transmission (min. / max.): 0.539 / 0.753, $\mu(\mathrm{Cu}\,K_\alpha) = 1.8$ mm^{-1}. Crystallographic data were of low quality due to the fact that only a single and very small crystal specimen could be obtained from the limited amount of starting material. Despite the use of intense X-rays from a 5 kW Cu K_α rotating anode focused with INCOATEC mirror optics, and despite long exposure times using ω- and ϕ-scans very few reflections were obtained above a resolution better than 0.9 Å (> 0.56 Å^{-1} in $\sin\theta/\lambda$), so that the data were cut at this resolution. Structure solution and refinement: the structure was solved with Direct Methods using SHELXS [36]. Least-squares refinement of positions and anisotropic displacement parameters of all 28 non-H atoms with the program SHELXL [37] therefore required the use of 251 restraints. H atom positions were calculated and constrained to their parent-atom site. Despite the resolution cutoff the *R* factor (11.3 %) and the internal *R* factor (10.7 %) as well as the residual electron density ($+0.96/-0.5$ e Å^{-3}) remain high. Nevertheless, the structure elucidation allows the unambiguous determination of the atom connectivity, and there is no doubt about the correctness of space group assignment and the absence of twinning: when the diffraction data are cut to lower resolutions, the *R* factor improves considerably. Full crystallographic information can be retrieved from the CIF file.

CCDC 876431 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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