Disclosing Biosynthetic Connections and Function of Atypical Angucyclinones with Fragmented C-Ring

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Supporting information

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Structure corrections

The entire primary NMR data for all the compounds, [1–21] which are presented on Figure 2 in the main manuscript, were analyzed to exclude misinterpretation and/or in search for possible match of the spectral data and thus ambiguous assignment. Mostly the performed analysis has confirmed the correct assignment. Nearly all the structures were found consistent with the NMR data presented in the literature.

The only exception of misinterpretation was Elmenol H,[21] which structural formula was originally established to be identical to pratensilin A[8] (**36**, herein and later on the numbering is identical with those in the main text) but the NMR spectra were different. Further study has revealed that spectra of Elmenol H are in perfect agreement with those for pratensilin B[8] (**38**) – an isomer of pratensilin A with alternative position of methoxy group. Both structures of pratensilin A **36** and pratensilin B **38** were unambiguously established by X-Ray crystallography.

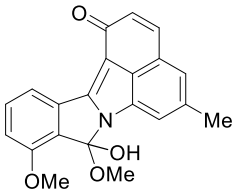
Structures for the compounds **33**, **37** and **40**[3] were ambiguous in both terms of chemical logic and unambiguous NMR assignment. In the publication compound **33** was assigned as a hemiacetal of amide, compound **40** – as hemiaminal and compound **37** as positively charged secondary amide hemiaminal.

For the compound **40** basing on match of its spectral data with those for pratensilin A **36** the structure was reassigned.

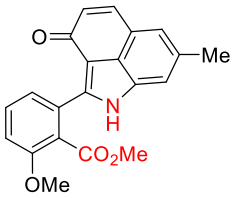
Compound **33**, as we believe, is a normal ester, since it has signal with the usual chemical shift of ester group and does not look to form amide hemiacetal structure. HMBC correlations also do not support the original structure.

Finally, for the compound **37** a non-charged structure was required. Based on ^{1}H, ^{13}C and HMBC data (+HRMS) we have decided that the compound **37** should have very similar structure to pratensilin A **36**.

Below follows the details on such interpretations. Problematic fragments in the original structures and structure corrections are marked with color. To help the analysis the chemical shifts and the other experimental data are replicated from the primary publications.[3,8,21]

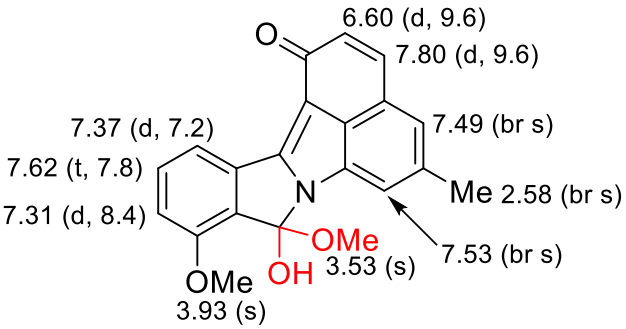


33 (original structure)

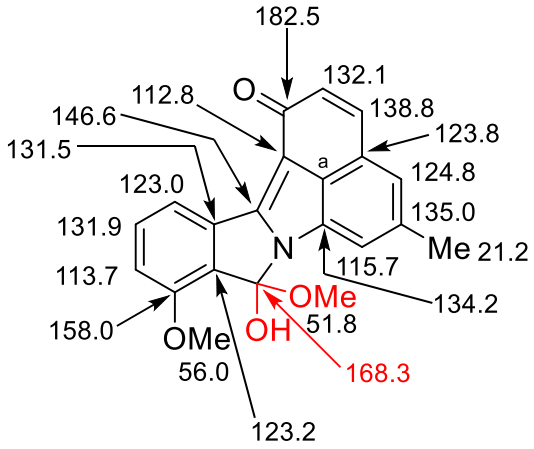


33 (corrected structure)

^{1}H NMR (600 MHz, CD_3OD):[3]

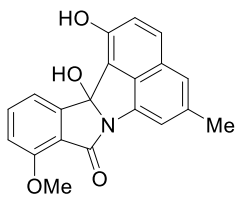


^{13}C NMR (600 MHz, CD_3OD):

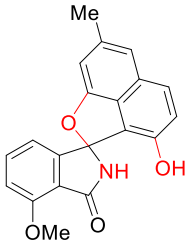


[a]124.8

HRMS $[M + H]^+$ at *m/z* 348.1255
$C_{21}H_{17}NO_4$ (calc'd for 347.1158).

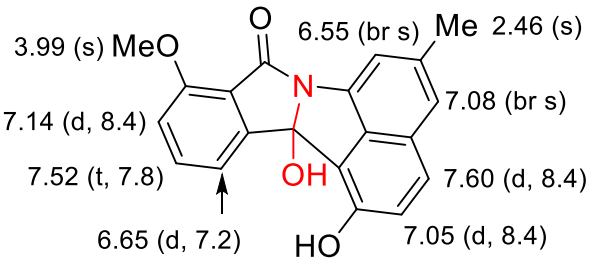


40 (original structure)

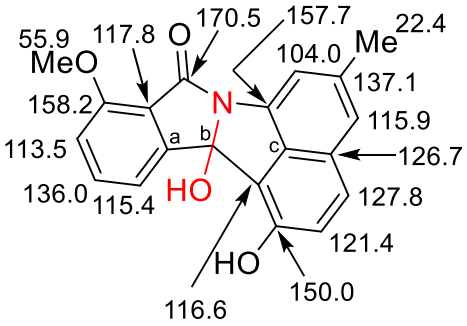


(corrected structure)
match with Pratensilin A **36**

^{1}H NMR (600 MHz, CD_3OD):[3]



^{13}C NMR (600 MHz, CD_3OD):



[a]148.8, [b]102.1, [c]129.3

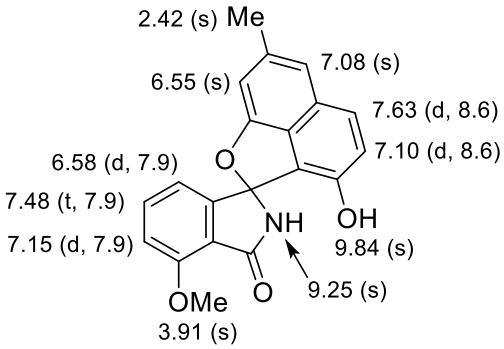
(+)-HRMS $[M+H]^+$ at *m/z* 334.1109

(+)-HRMS $[M+Na]^+$ at *m/z* 356.0895.

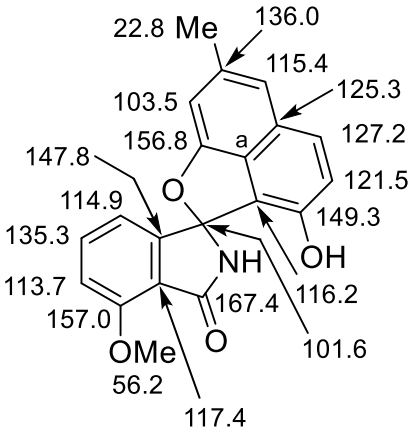
$[\alpha]_D$ not given

Pratensilin A:

^{1}H NMR (500 MHz, DMSO-d_6):[8]



^{13}C NMR (125 MHz, DMSO-d_6):



[a]128.5

(+)-Pratensilin A:

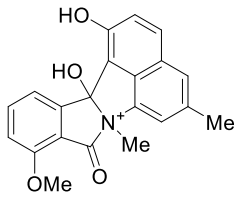
HRMS $[M + Na]^+$ at *m/z* 356.0895 (Δ –0.4 ppm)

$[\alpha]^{25}_D$ +7.3 (*c* 0.11, acetone);

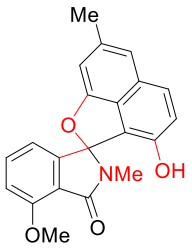
(–)-Pratensilin A:

X-RAY: CCDC 1474259

HRMS $[M + Na]^+$ at *m/z* 356.0895 (Δ –0.4 ppm)
$[\alpha]^{25}_D$ –34.6 (*c* 0.04, acetone)

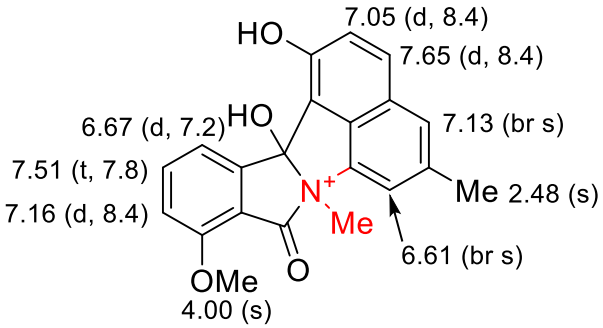


37
(proposed structure)

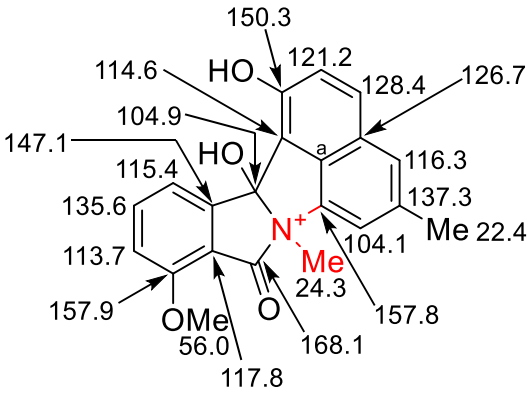


37
(corrected structure)

^{1}H NMR (600 MHz, CD_3OD):[3]



^{13}C NMR (600 MHz, CD_3OD):



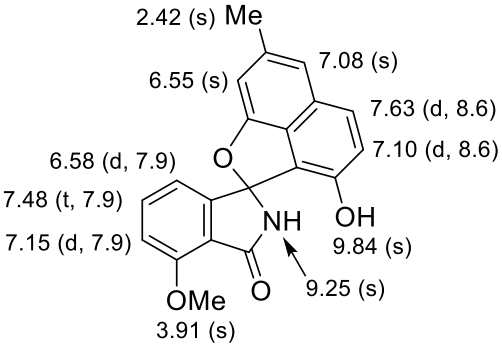
[a]129.6

HRMS $[M+H]^+$ at *m/z* 348.1239
$C_{21}H_{18}NO_4$ (calc'd for 348.1230).

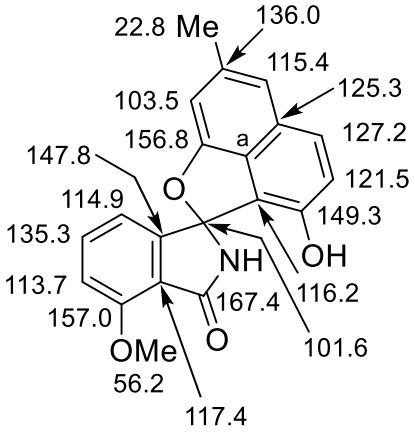
$[\alpha]_D$ <u>not given</u>

<u>Pratensilin A:</u>

^{1}H NMR (500 MHz, DMSO-d_6):[8]



^{13}C NMR (125 MHz, DMSO-d_6):



[a]128.5

<u>(+)-Pratensilin A:</u>

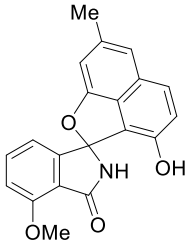
HRMS $[M + Na]^+$ at *m/z* 356.0895 (Δ –0.4 ppm)

$[\alpha]^{25}_D$ +7.3 (*c* 0.11, acetone);

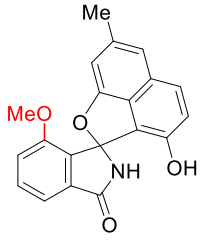
<u>(–)-Pratensilin A:</u>

X-RAY: CCDC 1474259

HRMS $[M + Na]^+$ at *m/z* 356.0895 (Δ –0.4 ppm)
$[\alpha]^{25}_D$ –34.6 (*c* 0.04, acetone)

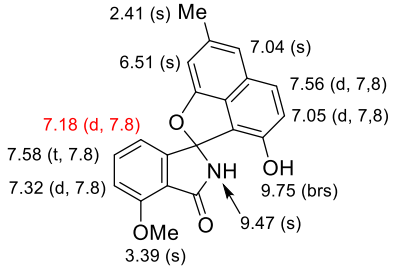


Elmenol H
(proposed structure)
NMR do not match with
Pratensilin A **36**

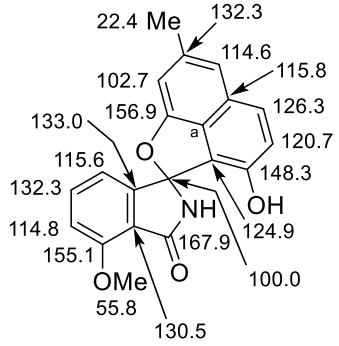


(reestablished structure)
match with Pratensilin B **38**

^{1}H NMR (500 MHz, acetone-d_6):[21]



^{13}C NMR (125 MHz, acetone-d_6):



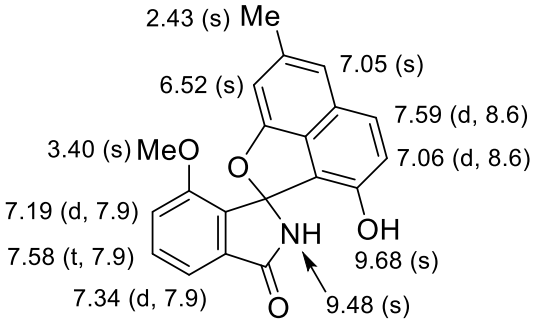
[a]128.4

(–)-HRESIMS [M - H]$^-$ at *m/z* 332.0942 $C_{20}H_{14}NO_4$ (calc'd for 332.0923).

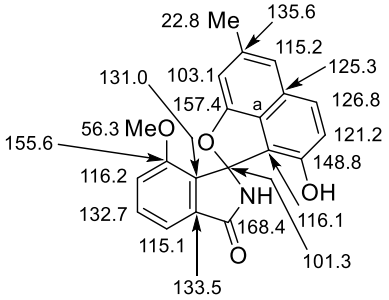
$[\alpha]^{20}_D$ +80.7 (*c* 0.06, CH_3OH);

(+)-Pratensilin B:

^{1}H NMR (500 MHz, DMSO-d_6):[8]



^{13}C NMR (125 MHz, DMSO-d_6):



[a]128.8

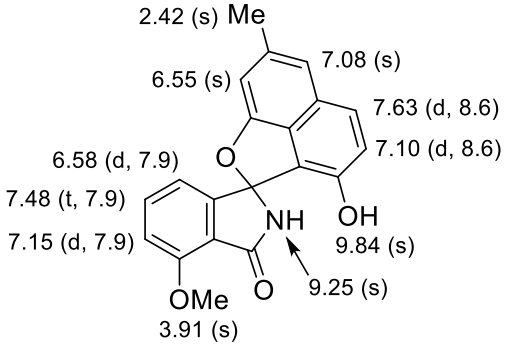
(+)-Pratensilin B:

HRESIMS [M + H]$^+$ at *m/z* 334.1075 (Δ 1.3 ppm)
$[\alpha]^{25}_D$ +13.3 (*c* 0.11, acetone);

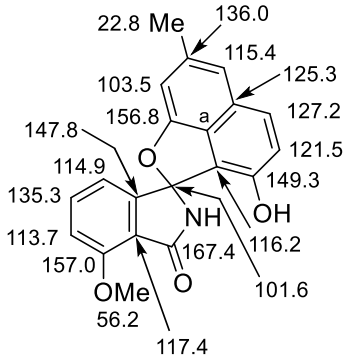
X-RAY: CCDC 1557858

Pratensilin A:

^{1}H NMR (500 MHz, DMSO-d_6):[8]



^{13}C NMR (125 MHz, DMSO-d_6):



[a]128.5

HRMS [M + Na]$^+$ at *m/z* 356.0895 (Δ –0.4 ppm)

$[\alpha]^{25}_D$ +7.3 (*c* 0.11, acetone);

X-RAY: CCDC 1474259 (–)-Pratensilin A

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