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(+)-MITORUBRIN DERIVATIVES FROM *HYPOXYLON FRAGIFORME**

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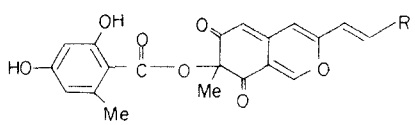
The hemispherical fruiting bodies of *Hypoxylon fragiforme* (Pers. ex Fr.) Kickx are common on dead trunks and branches of beech in autumn and winter. The stroma is covered with a brown-red layer, the pigment of which is easily soluble in acetone. We chromatographed the crude extract on silica gel and obtained the following pure compounds.

(+)-Mitorubrin **1**, yield 0·43%, yellow microcrystals from $CHCl_3$ or EtOAc, m.p. 213–214° (decomp.), $[\alpha]_D^{25}$ 586° (*c*, 0·5 in dioxane), UV (MeOH) λ_{max} 346 (ε 16 100), 292 (10 700), 266 (18 200), 216 nm (17 600), IR (KBr) 3430, 1720, 1630 cm^{-1}, MS *m/e* 382 (18%) [M^+, $C_{21}H_{18}O_7$], 233 (5·5%), 232 (7·5%) [$C_{13}H_{12}O_4$], 216 (12%), 215 (5%), 190 (9%) [$C_{11}H_{10}O_3$], 189 (8·5%), 187 (6%); 151 (100%) [$C_8H_7O_3$], 150 (14%), 129 (5%), 124 (6%), 123 (5%), 122 (6%), 116 (5%), 115 (5%); NMR ([$^2H_6$]acetone), δ 1·64 (*s*) [3]; 1·92 (*dd*, J_1 6 Hz, J_2 1·2 Hz) [3]; 2·61 (*s*) [3], 5·59 (*d*, *J* 1·2 Hz) [1], 6·22 (*dq*, J_1 16 Hz, J_2 1·2 Hz) [1], 6·23 (*d*, *J* 2 Hz) [1], 6·33 (*dq*, J_1 2 Hz, J_2 0·6 Hz) [1], 6·45 (*s*) [1], 6·58 (*dq*, J_1 16 Hz, J_2 6 Hz) [1], 8·05 (*d*, *J* 1·5 Hz) [1]; 9·06 (*s*, OH) [1], 10·70 (*s*, OH) [1]. (Found: C, 65·44; H, 5·27. Required for $C_{21}H_{18}O_7$: C, 65·97, H, 4·75). The spectroscopic data are in accord with those reported by Büchi *et al.*[1] for (−)-mitorubrin.

(+)-Mitorubrinol **2**, yield 0·12%, yellow microcrystals from EtOAc/Et_2O or acetone/hexane, m.p. 211–212° (decomp.), $[\alpha]_D^{25}$ 548° (*c*, 0·6 in dioxane). Identical in IR, MS and R_f-values with an authentic sample of (−)-mitorubrinol, kindly provided by Prof. G. Büchi, Cambridge, U.S.A.



1, R = Me

2, R = CH_2OH

3, R = CH_2OCOMe

4, R = CO_2H

(+)-Mitorubrinol acetate **3**, yield 0·23%, glittering orange-yellow platelets from EtOH, m.p. 212–214° (decomp.), $[\alpha]_D^{25}$ 525° (*c*, 0·5 in dioxane). Same UV as **1**; IR (KBr): 3430, 1745, 1720, 1630 cm^{-1}; MS *m/e* 440 (100%) [M^+, $C_{23}H_{20}O_9$], 398 (1%); 396 (1%), 382 (2%), 274 (8%), 248 (2%), 203 (10%), 168 (8%), 153 (5%), 152 (8%), 151 (60%), 150 (12%). NMR ([$^2H_6$]-acetone): δ 1·56 (*s*) [3], 2·10 (*s*) [3], 2·47 (*s*) [3]; 4·75 (*dt*, J_1 3 Hz, J_2 1 Hz) [2], 5·66 (*d*, *J* 1 Hz) [1]; 6·16 (*d*, *J* 2 Hz) [1], 6·25 (*d*, *J* 2 Hz) [1], 6·42 (*dt*, J_1 17 Hz, J_2

* Part XX in the series. For Part XIX see: STEGLICH, W., BUSS, H. and ZIPSER, K. (1974) *J. Naturforsch.* **29b**, 96 (1974).

[1] BÜCHI, G., WHITE, J. D. and WOGAN, G. N. (1965) *J. Am. Chem. Soc.* **87**, 3484.

3 Hz) [1]; 6·48 (*s*) [1]; 6·81 (*dt*, J_1 17 Hz, J_2 1 Hz) [1]; 8·28 (*d*, *J* 1 Hz) [1]; 10·27 (*s*, OH) [1], 10 34 (*s*, OH) [1]. (Found· C, 62·76; H, 4·93. Required for $C_{23}H_{20}O_9$: C, 62 72, H, 4·58).

(+)-Mitorubrinic acid **4**: yellow microcrystals, m.p. 225–227° (decomp). $[\alpha]_D^{25}$ 500° (*c*, 0·4 in dioxane). MS: *m/e* 412 (4%) [M^+]; NMR ([$^2H_6$]-acetone): δ 1·66 (*s*) [3]; 2·60 (*s*) [3]; 5·73 (*d*, *J* 1 2 Hz) [1]; 6·22 (*d*, *J* 1 Hz) [1]; 6·33 (broadened *d*, *J* 2 Hz) [1]; 6 54 (*d*, *J* 16 Hz) [1]; 7·00 (*s*) [1]; 7 29 (*d*, *J* 16 Hz) [1], 8·13 (*d*, *J* 1·2 Hz) [1]. The NMR data are in accord with lit [2], the m p. is considerably higher (lit.[2]: (−)-mitorubrinic acid, m p. 160–165°).

The production of azaphilones by *Hypoxylon* is noteworthy, because (−)-mitorubrin and (−)-mitorubinol have been isolated from cultures of *Penicillium rubrum*[1] and *P funiculosum*[2] and (−)-mitorubrinic acid from the latter fungus [2] Some of the Penicillia have perfect stages belonging to the Ascomycetes like *Hypoxylon* and a relationship between both may exist in a broad sense.[3]

EXPERIMENTAL

Fruiting bodies of *H fragiforme*[4] (100 g) were extracted with petrol (2 l, 3 days) and acetone (2 l, 14 days) at room temperature successively The acetone extract was taken to a small volume and the residue in $CHCl_3$ was chromatographed on silica gel (column 160 × 6 cm) $CHCl_3$ eluted a colourless blue fluorescent fraction, $CHCl_3$–Et_2O (8 2) after a little forerun pure **1**, followed by a mixture of **1**, **3** and two unknown yellow and red compounds $CHCl_3$–Et_2O (7 3) and (6 4) eluted the red compound and **2** successively Rechromatography with $CHCl_3$–Et_2O (8 2) yielded pure **3** **4** was isolated as a strongly yellow fluorescent fraction from a separate run by elution with acetone and a trace of HOAc after washing off the less polar pigments with EtOAc R_f-values on TLC (Silica Ready Plates Merck, C_6H_6–HCO_2Et–HCO_2H = 10·5·3): **1**, 0·38, **2**, 0·25, **3**, 0·33, **4**, 0·30

Note added on proof The m p of (−)-**4** given in ref [2] should be corrected to 227–230° (L Merlini, personal communication)

Acknowledgements—We thank the Deutsche Forschungsgemeinschaft for financial support and Prof G Buchi, Cambridge, U S A , for a generous gift of (−)-mitorubrinol

[2] LOCCI, R., MERLINI, L., NASINI, G. and ROGERS LOCCI, J. (1967) *Giorn. Microbiol.* **15**, 93

[3] BRESINSKY, A Personal communication

[4] Collected in September 1971 near Gauting, Bavaria, and kept for 2 yr in a deep freeze