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DEHYDRODIHYDROROTENONE AND FLEMICHAPPARIN-B IN *TEPHROSIA CANDIDA*

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Key Word Index—*Tephrosia candida*; leguminosae; stems and leaves; dehydrodihydrorotenone; flemichapparin-B.

Abstract—Dehydrodihydrorotenone and flemichapparin-B (dehydropterocarpin) have been isolated and identified from the stems and leaves of *Tephrosia candida*

INTRODUCTION

In an earlier communication [1] we reported the isolation of a new prenylated flavanone, candidone from the petrol extract of the stems and leaves of *T. candida*. A preliminary entomological screening of the petrol extract and benzene soluble fraction of the alcoholic extract of *T. candida* revealed that these two extracts possessed significant insecticidal and antifeeding properties against some insects. These results prompted us to reinvestigate the stems and leaves of *T. candida* in search of biologically active compounds. We report the isolation and identification of a new naturally occurring rotenoid, dehydrodihydrorotenone (**1**) and flemichapparin-B (dehydropterocarpin) (**5**).

RESULTS AND DISCUSSION

Dehydrodihydrorotenone (**1**), analysed for $C_{23}H_{22}O_6$ (*m/z* 394 $[M]^+$), mp 214°. The mass spectrum showed peaks at *m/z* 394 $[M]^+$, 379, 351 and 347, each of which was only two mass units higher than the corresponding fragments obtainable from dehydrorotenone (**2**) [2]. The mass fragmentation pattern, especially the appearance of two peaks at *m/z* 190 $[M - 204]^+$ and 161 $[204 - C_3H_7]^+$, was found to be consistent with the presence of an isopropyl side chain instead of an isopropylidene in the E ring of dehydrorotenone. Although most of the NMR spectral data were similar to those reported for dehydrorotenone [3–5] (**2**), there appeared a broad 6H-singlet at δ1.52 which could be attributed to the two methyl groups of the isopropyl side chain. On the basis of the spectral evidence, the compound appeared to be dehydrodihydrorotenone (**1**).

Confirmation of structure **1** was achieved by its partial synthesis from rotenone (**3**). Reduction of **3** with 10% Pd/charcoal in anhydrous chloroform afforded dihydrorotenone (**4**) which on dehydrogenation [6] gave dehydrodihydrorotenone (**1**), mp 214°. The latter was found to be identical with the natural one in all respects (mmp, co-TLC, UV and IR).

Flemichapparin-B (**5**) analysed for $C_{17}H_{12}O_5$ (*m/z* 296 $[M]^+$), mp 178–179°. Its mass spectrum showed a prominent peak only at *m/z* 281. The presence of a modified isoflavonoid skeleton as in the pterocarpinoids [7] was indicated by the high stability of this compound in the mass spectrometer. Its UV spectrum (λ_{max}^{EtOH} 241, 265, 254, 299 nm) also suggested it to be a pterocarpinoid [8]. The spectral data (UV, IR, MS, ^{1}H NMR) showed resemblance with those reported for flemichapparin-B (dehydropterocarpin) isolated from *Flemingia chappar* [9]. Its identity was confirmed by direct comparison with an authentic sample (co-TLC and superimposable IR).

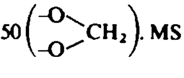
EXPERIMENTAL

MPs uncorr. UV spectra were recorded in EtOH. For CC silica gel (BDH, 60–120 mesh) was used. NMR spectra were determined in $CDCl_3$ with TMS as int. standard. The *T. candida* material was provided by United Chemicals and Allied Products, 10 Clive Row, Calcutta 1, where a voucher specimen is preserved.

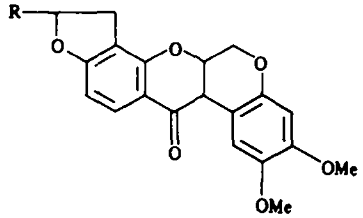
Dried stems and leaves (2 kg) were extracted with petrol (60–80°) and the concd extract chromatographed over silica gel. C_6H_6–EtOAc (9:1) eluates afforded a pale yellow dehydrodihydrorotenone (**1**), mp 214°, crystallized from EtOH, UV λ_{max}^{EtOH} nm (log ϵ): 325 nm (4.4); IR ν_{max}^{KBr} cm^{-1}: 2940, 1610, 1510, 1450, 1370, 1290, 1100, 1060, 880, 780. MS *m/z*: 394 $[M]^+$, 379 $[M - Me]^+$, 351 $[M - Me - CO]^+$, 347 $[M - Me - CH_3OH]^+$, 190 $[M - \text{RDA fragment } 204]^+$, 161 $[\text{RDA fragment } 204\text{–}C(H)Me_2]^+$. ^{1}H NMR (60 MHz, $CDCl_3$): δ8.46 (*s*, H-1), 8.07 (*d*, H-10, *J* = 6Hz), 6.95 (*d*, H-11, *J* = 6 Hz), 6.55 (*s*, H-4), 3.95 (*s*, 3H, –OMe), 3.87 (*s*, 3H, –OMe), 4.99 (*s*, 2H-6), 5.35 (*t*, H-5), 3.30 (*m*, 2H-4), 1.52 *s*, 6H, $-C(H)\underline{Me}_2$.

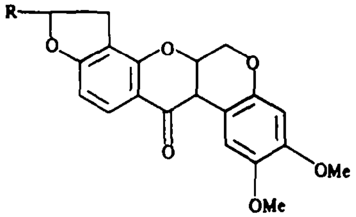
Partial synthesis of compound **1**. Dihydrorotenone (**4**) was prepared by reduction of rotenone (**3**, 200 mg) in dy $CHCl_3$ (20 ml) with 10% Pd/C for 4 hr. After usual work-up a single compound (**4**) mp 148° [10] was obtained. Compound **4** (100 mg) and CH_3CO_2K (250 mg) in EtOH (2.5 ml) was heated on a water bath. To the hot soln, an ethanolic soln of iodine (70 mg) was added and the mixture left for 24 hr. After usual workup a pale yellow solid (**1**) mp 214° was obtained (30 mg). Laforge *et al.* [6] reported the mp of **1** as 228°. The same prepared from rotenone (**3**) melted at 214°.

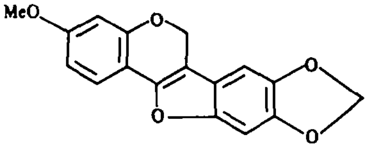
Flemichapparin. B (**5**). The benzene-soluble portion of the methanolic extract of the defatted plant material was chromatographed over silica gel. Elution with C_6H_6–petrol (1:1) furnished a white solid, mp 178–179°, crystallized from $CHCl_3$–petrol, UV λ_{max}^{EtOH} nm: 241, 254, 265, 299, 324; IR ν_{max}^{KBr} cm^{-1}: 1550 (olefinic double bond), 1610, 1230 (phenyl ether), 1080 (furan), 950



$\left(\begin{matrix}-O\\-O\end{matrix}\!\!>CH_2\right)$. MS *m/z*: 296 $[M]^+$, 281 $[M - Me]^+$ ^{1}H NMR (60 MHz, $CDCl_3$): δ3.7 (*q*, 3H, –OMe), 5.45 *s*, 2H-6), 5.90 (*s*,







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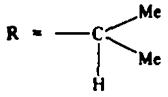
1 
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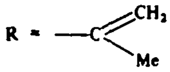
2 
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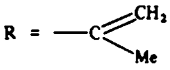
3 
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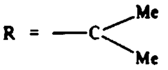
4 
$R = -\mathrm{C}{<}^{\mathrm{Me}}_{\mathrm{Me}}$

$\left.\begin{matrix}\text{C-8-O}\\ \text{C-9-O}\end{matrix}{>}\mathrm{CH_2}\right)$, 6.43 (*d*, H-2, $J = 4$Hz), 6.52 (*d*, H-4, $J = 4$Hz), 7.3 (*d*, H-1, $J = 9$Hz), 6.9 (*s*, H-10), 6.65 (*s*, H-7).

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