THE STRUCTURE OF EUCLANONE, A DIMERIC NAPHTHOQUINONE OF EUCLEA NATALENSIS

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Key Word Index: Euclea natalensis, Ebenaceae, euclanone, dimeric napthquinone.

Abstract: Euclanone, a constituent of Euclea natalensis A.D. C., was shown to be the 2,7'-linked dimer of 7-methyljuglone and 2-methylnaphthazarin; it predominates as tautomer IIa in solution.

Euclanone (5, 5', 8'-trihydroxy-7,2'-dimethyl-2,7'-binaphtho-1,4;1', 4'-diquinone) was shown to be a dimer of 7-methyljuglone and 2-methylnaphthazarin and its partial structure was assumed to be (Ia, Ib) on the basis of its spectral characteristics (1).

Re-examination of its $^1$H NMR spectrum at 100 MHz has shown that the signal for the olefinic proton at $\delta$ 6.96 (see Table) is a quartet, and so must be coupled with a methyl group — the only possible one being that resonating at $\delta$ 2.28, although apparently a singlet*. As the methyl group

*Doublet in the $^1$H NMR of synthetic IIa at higher resolution (see Table), similar to 2-methylnaphthazarin, which shows a singlet for the methyl group at $\delta$ 2.24, but in more expanded spectra a broad signal or doublet (unpublished data).
at δ 2.28 and the quinonoid proton at δ 6.96 in
eucalanone have practically the same chemical
shifts as the corresponding protons in 2-methyl-
naphthazarin (2), it is evident that eucalanone
exists in the tautomeric form (Ib) in solution.
However, the way the two units are linked must
still be established.

As two m-coupled aromatic protons are pre-
sent (see Table), the juglone unit must be linked
through C-2 or C-3. However, the possibility of
the juglone moiety being linked via C-3 to the
naphthazarin unit may also be excluded on the
basis of peri-OH shifts in similar dimers with a
C-2 or C-3 linked juglone moiety (3). Where the
naphthazarin is linked to the C-2 of the juglone
moiety may also be deduced from the shifts of the
two peri-OH protons in unit B (IIa). While the
signal at δ 12.34 in the eucalanone spectrum prac-
tically coincides with that of the C-5 OH proton
(δ 12.42) in 2-methylnaphthazarin (3), the other
one at δ 12.84 has a considerably higher value
than that of the C-8 OH proton (δ 12.54) in the
same monomer. This may be attributed to the
proximity of the internuclear bond, i.e. this linkage
must be localized at C-7’ (IIa).

One of us (4) has calculated the peri-hydrox-
ical shifts for the biogenetically possible
trihydr-in-bijuglones from substituent increment
values obtained in a manner similar to that of
Lillie and Musgrave (3), but by computation of
about 400 juglone spectra and also including the
direction of dimerization and steric hindrance.
As can be seen in the Table, the chemical shifts
calculated for IIa in this way correspond very well
to the experimental data and clearly exclude the
3,6'-isomer. The correctness of this structure has
been confirmed by the synthesis of IIa and some
of its isomers (5).

TABLE. 100 MHz ¹H NMR signals for natural and synthetic eucalanone (IIa) in CDCl₃
(TMS as internal standard)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Unit</th>
<th>Observed values (CDCl₃)</th>
<th>Calculated (4) for IIb</th>
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<tbody>
<tr>
<td>Natural sample</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>H-3</td>
<td>7.06, s</td>
<td>5-OH</td>
</tr>
<tr>
<td></td>
<td>H-6</td>
<td>7.12, d</td>
<td>2.7'-dimer</td>
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<td></td>
<td>H-8</td>
<td>7.50, d</td>
<td>3.6'-dimer</td>
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<tr>
<td></td>
<td>7-CH₃</td>
<td>2.45, s</td>
<td>11.81, s</td>
</tr>
<tr>
<td></td>
<td>5-OH</td>
<td>11.81, s</td>
<td>11.92</td>
</tr>
<tr>
<td>Synthetic sample</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>J=2</td>
<td>2.7'-dimer</td>
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</tr>
<tr>
<td></td>
<td>J=2</td>
<td>3.6'-dimer</td>
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</tr>
<tr>
<td></td>
<td>H-3'</td>
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<td></td>
<td>H-6'</td>
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<td></td>
<td>2'-CH₃</td>
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<td>5'-OH</td>
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<tr>
<td></td>
<td>B</td>
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</tr>
<tr>
<td></td>
<td>5'-OH</td>
<td>11.83</td>
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<td></td>
<td>8'-OH</td>
<td>11.92</td>
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<tr>
<td></td>
<td>Synthetic sample</td>
<td>6.96, q</td>
<td>2.28, s</td>
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<td>7.24, s</td>
<td>12.84</td>
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<td>J=1.5</td>
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REFERENCES