Herpetriol and Herpetetrol,
New Lignoids Isolated from *Herpetospermum caudigerum* Wall

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*Herpetospermum caudigerum*, Cucurbitaceae, Seeds, Herpetriol, Herpetetrol

Two new compounds derived from coniferyl alcohol have been isolated from *Herpetospermum caudigerum* Wall. Their structures have been established by spectral analysis (UV, PMR, CMR and MS).

Introduction

*Herpetospermum caudigerum* Wall. seeds endemic in Nepal, contain different new phenolic compounds derived from condensation of several coniferyl units. In preceding papers [1, 2], we reported structural determination of herpetal (1) and herpetotriol (2).

Keeping on our investigation, we have isolated and characterized two new compounds: herpetiol (3)

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and herpetetrol (4) respectively generated by trimerisation and tetramerisation of coniferyl alcohol units.

Results and Discussion

The UV spectra data of 3 and 4 are almost identical and suggest unconjugated and substituted aromatic rings frequently observed in lignoids. The mass spectra indicate a supplementary coniferyl unit in 4.

**Herpetriol (3)**

This compound is given molecular formula C_{27}H_{21}O_2(OCH_3)_3(OH), m/e 538 by the exact mass determination. It effectively leads to a tetra-TMSi derivative and its PMR spectrum shows 3 OCH_3 at δ 3.61, 3.70 and 3.81 ppm; decoupling experiment indicates furthermore:

1 chain: Ar - CH(a) - CH(b) - CH_2(c) OH
   CH(a): δ 6.10 ppm - J 7.5 Hz - d
   CH(b): δ ca. 4 ppm - m *
   CH_2(c): δ 4.28 ppm - m *

1 chain: Ar - CH(d) - CH(e) - CH_2(f) OH
   CH(d): δ 5.34 ppm - J 7 Hz - d
   CH(e): δ 2.80 ppm - m *
   CH_2(f): δ ca. 4.20 ppm - m *

1 chain: Ar - CH(g) - CH(h) - CH_2(i) O
   CH_2(g1): δ 3.32 ppm - J 14 and 4 Hz - dd (g2): δ 2.81 ppm - m *
   CH(h): δ 3.08 ppm - m *
   CH_2(i): δ ca. 4.20 ppm - m *

Chemical shift values of protons in this compound, compared with those of 2 [2] in the same conditions, allow to draw the following partial structure:

![Chemical structure of Herpetriol](image)

This result is also corroborated by analysing mass spectra of compounds 2, 3 and their derivatives: abundant fragment ions, typical of this kind of molecules can be observed as following [3]:

<table>
<thead>
<tr>
<th>R or R'</th>
<th>m/e</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>151</td>
</tr>
<tr>
<td>CH_3</td>
<td>165</td>
</tr>
<tr>
<td>TMSi</td>
<td>223</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R''</th>
<th>m/e</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>330</td>
</tr>
<tr>
<td>TMSi</td>
<td>446</td>
</tr>
</tbody>
</table>

Shielding of H(d) and H(e), in comparison with H(a) and H(b), indicates that they are not included like previously in a benzo[1,3]dioxole ring but in a furanocyclic one ** with H(h) and H(i). Between the two possibilities of substitution relative to this ring by benzyl radical, the one defined in 5 has to be eliminated on purpose of shift values of CH_2(i) and CH(h).

Benzyl disubstituted radical is characterised in mass spectra by the presence of important and significant ions:

<table>
<thead>
<tr>
<th>R''''</th>
<th>m/e</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>137</td>
</tr>
<tr>
<td>CH_3</td>
<td>151</td>
</tr>
<tr>
<td>TMSi</td>
<td>209</td>
</tr>
</tbody>
</table>

** Analysis of aromatic protons, possible by using MeOH, confirms that they are 8 and excludes the existence of a second benzo[1,3]dioxole ring.
In fact, the differences in condensation of coniferyl units in 2 and 3 deduced from PMR spectra are completely supported by CMR analysis (see Table); for the compound 3, one notice effectively: endocyclic O-bound \( \text{CH}_2 \) at 60.4 ppm, \( \text{CH}(h) \) at 43.9 ppm and \( \text{CH}_2(g) \) at 33.9 ppm.

**Herpetetrol (4)**

As for the establishment of 3, formula 4: \( \text{C}_{36}\text{H}_{27}\text{O}_3(\text{OCH}_3)_4(\text{OH})_5 \) is deduced both from measurements by mass spectrometry in the high resolution mode of penta-TMSi and pentamethylated derivatives and from PMR spectrum of the natural product showing 4 \( \text{OCH}_3 \) at \( \delta \) 3.63 (6 H) and 3.81 ppm (6 H). Furthermore, analysis of this last spectrum indicates 10 aromatic protons in the range 6.7 — 6.95 ppm * and:

2 chains: Ar — \( \text{CH}(a) \) — \( \text{CH}(b) \) — \( \text{CH}_2(c) \) OH

\( \text{CH}(a) \): \( \delta \) 6.09 and 6.11 ppm — \( J \) 6.5 Hz — \( d \)
\( \text{CH}(b) \): \( \delta \) ca. 4.00 ppm — \( m \)*
\( \text{CH}_2(c) \): \( \delta \) ca.4.26 ppm — \( m \)*

1 chain: Ar — \( \text{CH}(d) \) — \( \text{CH}(e) \) — \( \text{CH}_2(f) \) OH

\( \text{CH}(d) \): \( \delta \) 5.34 ppm — \( J \) 7 Hz — \( d \)
\( \text{CH}(e) \): \( \delta \) 2.82 ppm — \( m \)*
\( \text{CH}_2(f) \): \( \delta \) ca. 4.20 ppm — \( m \)*

1 chain: Ar — \( \text{CH}_2(g) \) — \( \text{CH}(h) \) — \( \text{CH}_2(i) \) O

\( \text{CH}_2(g) \): \( \delta \) 3.30 ppm — \( J \) 14 and 4 Hz — \( d \)
\( \text{CH}(h) \): \( \delta \) 3.08 ppm — \( m \)*
\( \text{CH}_2(i) \): \( \delta \) ca. 4.20 ppm — \( m \)*

* The study of aromatic protons has been realised, as for 3, in using MeOH.

The presence in CMR spectrum of 10 CH, 6 quaternary C and 8 O-bound C in the range 110 — 150 ppm confirms the existence of 4 aromatic rings how the PMR spectrum suggested; this result allow to keep from hypothesis of a multiple substitution of one or several aromatic rings by a C\(_3\) chain. Chemical shifts (see Table) are comparable with those relative to herpetriol (3).

Even mass spectrum of 4 in EI, CI or FD does not lead to characterize molecular ion (the highest mass observed is \( m/e \) 534 in EI), however fragments at \( m/e \) 137, 151 and 330 typical of skeleton of this kind of compounds are found again. It is only by using the technique CI/D of ionisation we can demonstrate that the molecular ion of the natural compound is quite \( m/e \) 716.

Results given by *Herpetospermum caudigerum*, up to day, show coniferyl units generally condense to form a sequence of benzofuran rings with an Ar(OH, OCH\(_3\)) in the begining. In that case, the joint of C\(_6\) — C\(_3\) links is realised between the propyl chain of a co-
niferyl unit and the aromatic ring of another coniferyl one, as shown in X. When two C$_6$ – C$_3$ units condense by their propyl chain, an “isolated” furan ring is issued from; this occurs at the distal extremity as noticed in 3, 4 and Y.

**Experimental**

**Herpetriol:** m. p. = 110 °C, UV $\lambda_{max}$ nm (e): 214, 230, 278 (11 000) and 285 sh. $\alpha_{D}^{0} = + 72 ^\circ$, (MeOH, $c = 0.38$ mg/ml). PMR and CMR: see text and table.

MS (70 eV): $m/e$ 538 ($M^{+}$; 7%; 538.218; C$_{30}$H$_{34}$O$_{9}$: 538.218), 520 (M–H$_{2}$O; 28%; 520.208; C$_{29}$H$_{32}$O$_{9}$: 520.2097), 508 (M–MeOH; 42%; 508.205; C$_{29}$H$_{30}$O$_{9}$: 508.2097), 490 (M–H$_{2}$O–MeOH; 58%), 478 (100%; 478.118; C$_{28}$H$_{34}$O$_{5}$: 478.1191), 330 (11%), 298 (58%; 298.1203; C$_{19}$H$_{20}$O$_{5}$: 298.1205), 297 (75%; 297.1127; C$_{18}$H$_{19}$O$_{5}$: 297.1127), 285 (75%; 285.1123; C$_{17}$H$_{18}$O$_{5}$: 285.1127), 205 (66%), 151 (84%; 151.0757 (30%) C$_{9}$H$_{10}$O$_{2}$: 151.0757; 151.0399 (70%) C$_{7}$H$_{7}$O$_{3}$: 151.0395), 137 (100%; 137.0602; C$_{18}$H$_{14}$O$_{4}$: 137.0603).

**Permethylated derivative:** MS (70 eV): $m/e$ 594 ($M^{+}$; 98%; 594.281; C$_{45}$H$_{54}$O$_{12}$: 594.283), 562 (100%), 532 (10%), 530 (16%), 379 (16%), 354 (7%), 338 (11%), 312 (24%), 311 (43%), 297 (21%), 219 (22%), 165 (41%), 151 (79%).

**TMSi-derivative:** MS (70 eV): $m/e$ 826 (27%), 754 (11%), 736 (54%), 664 (16%), 646 (33%), 574 (11%), 527 (8%), 502 (9%), 446 (5%), 438 (19%), 412 (38%), 396 (20%), 369 (30%), 298 (12%), 297 (24%), 277 (40%), 223 (66%), 209 (100%), 179 (42%), 151 (32%), 137 (32%).

**Herpetetrol:**

UV $\lambda_{max}$ nm (e): 214, 235 sh., 281 (12 400) and 285 sh. $\alpha_{D}^{0} = + 56 ^\circ$, (MeOH, $c = 0.624$ mg/ml). PMR and CMR: see text and table.

**Permethylated derivative:** MS (70 eV): $m/e$ 786 (M$^{+}$; 100%; 786.360; C$_{45}$H$_{54}$O$_{12}$: 786.3615), 754 (M–MeOH; 65%), 722 (M–2 MeOH; 32%), 446 (5%), 368 (20%), 311 (30%), 297 (20%), 258 (20%), 256 (20%), 236 (45%), 181 (30%), 165 (28%), 151 (70%).

**TMSi-derivative:** MS (70 eV): $m/e$ 1076 (10%), 986 (15%), 914 (10%), 896 (5%), 809 (5%), 484 (8%), 437 (10%), 369 (25%), 355 (15%), 297 (17%), 239 (100%), 223 (40%), 209 (100%).

PMR spectra were recorded on a Cameca 250, CMR on XL-100 Varian and mass spectra in CI/D on R-1010 B Ribermag in using reacted gas NH$_3$.

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