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

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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: herpetriol (**3**)

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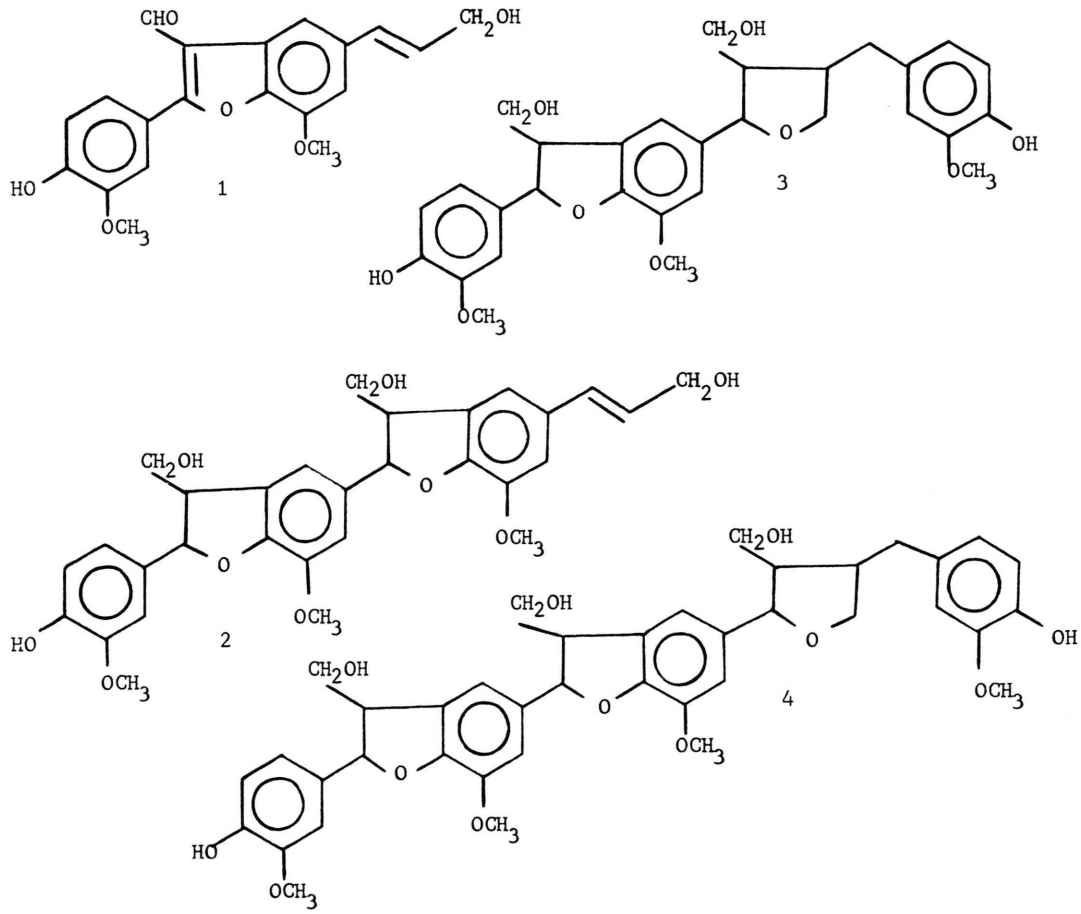


and herpetetrol (**4**) respectively generated by trimerisation and tetramerisation of coniferyl alcohol units.

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**)

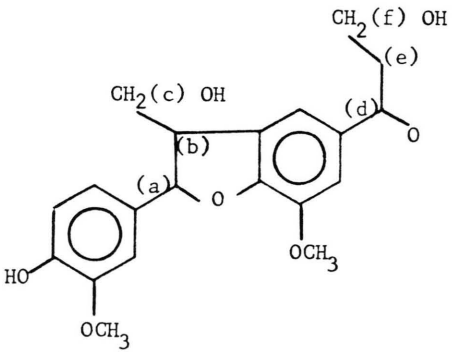
This compound is given molecular formula $C_{27}H_{21}O_2(OCH_3)_3(OH)_4$ *m/e* 538 by the exact mass determination. It effectively leads to a tetra-TMSi derivative and its PMR spectrum shows 3 OCH_3 at δ 3.61, 3.70 and 3.81 ppm; decoupling experiment indicates furthermore:

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_2(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:

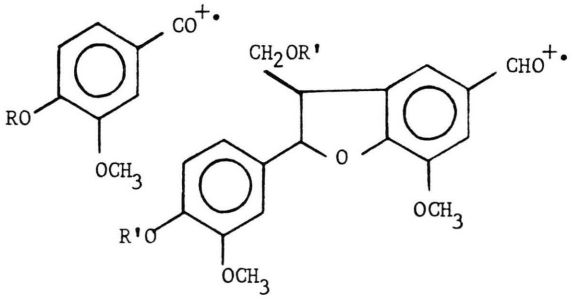


* Signals belong to a part of the curve which has been impossible to analyse at first order; however the couplings have been determined by irradiating.

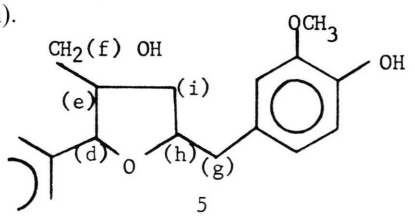
This result is also corroborated by analysing mass spectra of compounds **2, 3** and their derivatives: abundant fragment ions, typical of this kind of molecules can be observed as following [3]:

R or R′	*m/e*
H	151
CH_3	165
TMSi	223

H	330
TMSi	446
	(474 – 28)



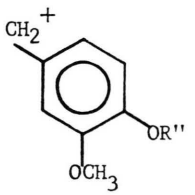
Shielding of H(d) and H(e), in comparison with H(a) and H(b), indicates that they are not included like previously in a benzofuranic ring but in a furanic one ** with H(h) and H(i). Between the two possibilities of substitution relative to this ring by benzyl radical, the one definited in **5** has to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



5

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

R″	*m/e*
H	137
CH_3	151
TMSi	209



** Analysis of aromatic protons, possible by using MeOH, confirms that they are *s* and excludes the existence of a second benzofuranic ring.

Table. CMR spectra (methanol-D_4; δ ppm/TMS)

	Herpetriol	Herpetetrol
Quatern.	6 at $145 < \delta < 150$	149.2 – 149.2 – 148.6 – 148.3
O-bound C		148.2 – 147.5 – 145.1 – 145.1
Quatern. C	135.6 – 135.3 – 134.5 – 130	137.7 – 135.3 – 133.8 – 133.7 130 – 130
Arom. CH	119.6 – 119.6 – 118 – 116 116 – 114 – 110.4 – 110.4	119.7 – 119.7 – 118.1 – 116.3 – 116.3 115.7 – 114.2 – 111.7 – 110.5 – 110.5
OCH	88.9 – 83.9	89.2 – 89.1 – 84.2
OCH_2	73.4 – 64.8 – 60.4	73.5 – 64.8 – 64.8 – 60.5
OCH_3	56.5 – 56.3 – 56.3	56.7 – 56.7 – 56.3 – 56.3
CH	55.3 – 54 – 43.9	55.2 – 55.2 – 54 – 43.9
CH_2	33.9	33.9

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 CH_2(i) at 60.4 ppm, CH(h) at 43.9 ppm and CH_2(g) at 33.9 ppm.

Herpetetrol (**4**)

As for the establishment of **3**, formula **4**: $C_{36}H_{27}O_3(OCH_3)_4(OH)_5$ 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 OCH_3 at δ 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 – CH(a) – CH(b) – CH_2(c) OH
CH(a): δ 6.09 and 6.11 ppm – J 6.5 Hz – d
CH(b): δ ca. 4.00 ppm – m *
CH_2(c): δ ca.4.26 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 2.82 ppm – m *
CH_2(f): δ ca. 4.20 ppm – m *

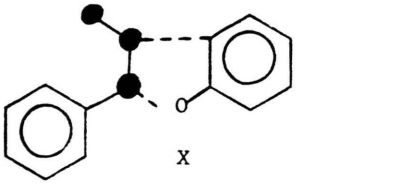
1 chain: Ar – CH_2(g) – CH(h) – CH_2(i) O
CH_2(g1): δ 3.30 ppm – J 14 and 4 Hz – dd
(g2): δ 2.82 ppm – m *
CH(h): δ 3.08 ppm – m *
CH_2(i): δ ca. 4.20 ppm – m *

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

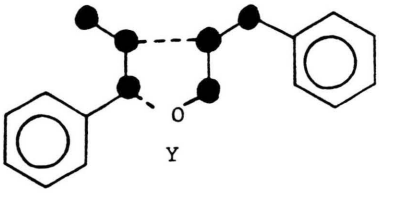
The presence in CMR spectrum of 10 CH, 6 quaternary C and 8 O-bound C in the range 110 – 150 ppm confirms the existence of 4 aromatic rings how the PMR spectrum suggested; this result allow to keep from hypothesis of a multiple substitution of one or several aromatic rings by a C_3 chain. Chemical shifts (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-



X



Y

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 λ_{max} nm (ε): 214, 230, 278 (11 000) and 285 sh. $\alpha_D^{20} = +72°$, (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 ($M-H_2O$; 28%; 520.208; $C_{30}H_{32}O_8$: 520.2097), 508 (M−MeOH; 42%; 508.205; $C_{29}H_{30}O_8$: 508.2097), 490 ($M-H_2O$−MeOH; 58%), 478 (100%; 478.118; $C_{28}H_{30}O_7$: 478.1191), 330 (11%), 298 (58%; 298.1203; $C_{18}H_{18}O_4$: 298.1205), 297 (75%; 297.1126; $C_{18}H_{17}O_4$: 297.1127), 285 (75%; 285.1123; $C_{17}H_{17}O_4$: 285.1127), 205 (66%), 151 (84%; 151.0757 (30%) $C_9H_{11}O_2$: 151.0757; 151.0399 (70%) $C_7H_7O_3$: 151.0395), 137 (100%; 137.0602; $C_8H_9O_2$: 137.0603).

Permethylated derivative: MS (70 eV): *m/e* 594 (M^+; 98%; 594.281; $C_{34}H_{42}O_9$ 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 λ_{max} nm (ε): 214, 235 sh., 281 (12 400) and 285 sh. $\alpha_D^{20} = +56°$, (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 recordered 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.

Acknowledgements

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[3] V. Kovacik and J. Skamla, Chem. Ber. **102,** 3623 (1969); V. Kovacik, J. Skamla, D. Joniak, and B. Kosokova, Chem. Ber. **102,** 1513 (1969).