

STEREOCHEMISTRY OF MALKANGUNIOL AND STEREOSTRUCTURES OF SOME  
OTHER RELATED POLYALCOHOLS FROM CELASTRUS PANICULATUS WILLD.

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In our previous communication<sup>1)</sup>, we reported that several sesquiterpene polyalcohols are present in the saponified 80% MeOH extract of the seed oil of Celastrus paniculatus Willd. and described the gross structure of one of the major constituents - malkanguniol. A recent paper<sup>2)</sup> describing the structures of three sesquiterpenoid esters isolated from the same oil, prompts us to place on record our recent findings on the stereochemistry of malkanguniol and stereostructures of four related polyalcohols.

Five alcohols have so far been isolated from the saponified 80% MeOH extract of the seed oil, by column chromatography, followed by preparative chromatography/fractional crystallization. Table 1 gives the physical constants of these alcohols, which are originally esterified with one or more of the following acids: acetic acid, benzoic acid,  $\beta$ -furanic acid and  $\beta$ -nicotinic acid

Table 1. Polyalcohols from Celastrus paniculatus Willd.

N <sup>o</sup> .	Trivial name	Structure	Mol. formula	(M <sup>+</sup> )	m.p.	$[\alpha]_D^{25}$ (MeOH)	R <sub>f</sub> *
1.	Polyalcohol-A	II	C <sub>15</sub> H <sub>26</sub> O <sub>6</sub>	(302)	185-186.5 <sup>o</sup>	-16.0 <sup>o</sup>	0.48
2.	Polyalcohol-B	III	C <sub>15</sub> H <sub>26</sub> O <sub>5</sub>	(286)	236-239 <sup>o</sup>	-30.2 <sup>o</sup>	0.43
3.	Malkanguniol	I <sup>a</sup>	C <sub>15</sub> H <sub>26</sub> O <sub>5</sub>	(286)	171-172 <sup>o</sup>	-20.0 <sup>o</sup>	0.40
4.	Polyalcohol-C	IV <sup>a</sup>	C <sub>15</sub> H <sub>26</sub> O <sub>6</sub>	(302)	205-207 <sup>o</sup>	-28.9 <sup>o</sup>	0.32
5.	Polyalcohol-D	V	C <sub>15</sub> H <sub>26</sub> O <sub>5</sub>	(286)	243-245 <sup>o</sup>	-46.6 <sup>o</sup>	0.27

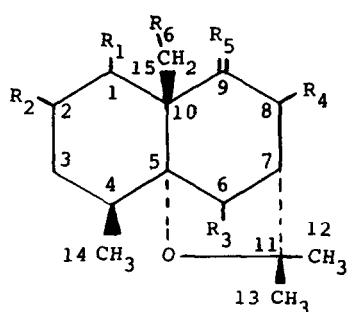
\* T.L.C.: silicagel Merck PF<sub>254</sub>, thickness 0.25 mm; solvent, 5% MeOH in EtOAc. These values have relative significance only.

Malkanguniol (I<sup>a</sup>)

In our previous paper, the stereochemistry of the C<sub>4</sub>-Me as well as the ring-fusion of the two six-membered rings in malkanguniol, remained to be determined. It has now been possible to establish the stereochemistry of I<sup>a</sup> on the base of

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X-ray analysis, the details of which will be published separately<sup>3)</sup>.



	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>
I <sup>a</sup>	β-OH	H	H	α-OH	H, α-OH	OH
I <sup>b</sup>	β-OAc	H	H	α-OAc	H, α-OH	OAc
I <sup>c</sup>	β-OAc	H	H	α-OAc	H, -OAc	OAc
I <sup>d</sup>	β-OH	H	H	α-OH	O	OH
I <sup>e</sup>	β-OAc	H	H	α-OAc	O	OAc
II	β-OH	H	α-OH	β-OH	H, α-OH	OH
III	β-OH	H	α-OH	α-OH	H, β-OH	H
IV <sup>a</sup>	β-OH	H	α-OH	α-OH	H, α-OH	OH
IV <sup>b</sup>	β-OAc	H	α-OAc	α-OAc	H, α-OH	OAc
V	β-OH	α-OH	H	β-OH	H, α-OH	H

### Structures of other polyalcohols

By a careful comparison of the p.m.r. and c.m.r. spectroscopic measurements of these polyalcohols and their suitable derivatives with those of malkanguniol (and derivatives), it has been possible to assign structures (vide supra) to these compounds. The relevant p.m.r. and c.m.r. data are listed in Tables 2 and 3. The assignments of the  $\delta_C$  values are based on spectra taken with noise- and off-resonance decoupling (at 25.2 Mhz on a Varian XL-100 n.m.r. spectrometer) thereby using the chemical shift changes expected upon acetylation and introduction of a keto group (I<sup>d</sup>, I<sup>e</sup>)<sup>4)</sup>. The relative stereochemistry of the relevant hydroxyls was established by suitable decoupling and N.O.E. experiments; these are described below.

**Polyalcohol-A (II).** This compound, like malkanguniol has a 15-CH<sub>2</sub>OH group, but displays an axial 8-OH and a fifth, equatorial OH at C<sub>6</sub>. Irradiation of 7-H shows a sharpening of the broad 6-H singlet ( $\delta$  4.51) and a collapse of the small 8-H doublet ( $\delta$  4.18, J = 3Hz) into a broad singlet (due to the small e,e coupling with the equatorial 9-H). The double doublet pattern of 1-H is partly covered by the low field part of the 15-CH<sub>2</sub>OH group AB quartet and the 8-H doublet.

Table 2. P.M.R. spectral characteristics ( $\delta$ , multiplicity, J)

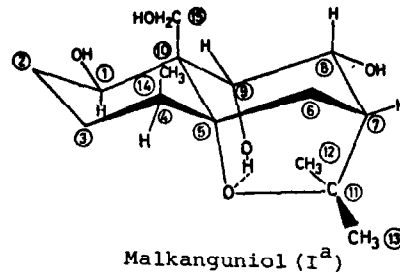
	H-1	H-2	H-3	H-4	H-6	H-7	H-8	H-9	3H-12	3H-13	3H-14	H-15
I <sup>b</sup>	5.37 dd 4.5 12.0	1.3- 2.2	1.3- 2.2	1.3- 2.2	1.3- 2.2	2.27 br.tr	5.23 dd 3.3 5.2	3.91 dd 5.2 11.8	1.60 s	1.20 s	1.03 d 7.5	4.39 4.53 AB q 12.0
II	4.0 - 4.3	1.2- 2.0	1.2- 2.0	1.2- 2.0	4.51 br.s	2.07 br.d 3	4.18 d 3	4.10 s	1.47 s	1.43 s	1.09 d 7.0	3.68 4.22 AB q 12
III	3.82 dd 4 10	1.1- 2.1	1.1- 2.1	1.93 <sup>*</sup>	4.06 br.s	2.08 br.d 3 10	3.51 dd 3 10	3.98 d 10	1.40 <sup>**</sup> br.s	1.40 <sup>**</sup> br.s	1.05 d 7.5	0.90 s
IV <sup>b</sup>	5.42 dd 4 10	1.2- 2.2	1.2- 2.2	2.14 <sup>*</sup>	5.71 br.s	2.46 d 3 5	5.28 dd 3 5	3.91 dd 5 10	1.59 s	1.36 s	0.93 d 7.5	4.30 4.52 AB q 12
V	3.84 d 10	3.66 dd 10 4	1.3- 1.9	1.70 <sup>*</sup>	1.68 2.32 AB q 12	2.02 tr 3	4.08 br.d 3	3.36 br.s	1.41 s	1.07 s	1.01 d 7.5	1.04 s

\* determined by double resonance

\*\* interchangeable

Table 3. C.M.R. spectral characteristics

	I <sup>a</sup>	I <sup>b</sup>	I <sup>c</sup>	I <sup>d</sup>	I <sup>e</sup>	II	III	IV <sup>a*</sup>	IV <sup>b</sup>	V
1	69.7	71.8	71.8	71.6	71.2	71.0	76.8	69.7	71.8	80.0
2	25.7	22.2	22.6	23.5	22.4	26.0	25.3	26.0	22.6	73.5
3	27.4	26.7	26.5	26.6	25.8	27.6	27.2	27.6	26.6	36.3
4	40.0	39.3	39.6	39.4	39.4	33.5	33.7	33.6	33.6	40.9
5	87.4	88.6	86.3	89.4	89.0	91.3	92.0	91.3	90.8	88.0
6	35.6	36.1	36.4	36.6	37.2	74.8	74.6	74.1	76.1	30.3
7	50.5	48.2	48.1	50.4	48.7	58.1	56.4	57.8	53.5	51.1
8	71.7	74.6	72.2	77.5	77.1	74.8	73.2	71.4	73.5	73.0
9	69.8	69.0	68.2		199.8	71.4	79.3	70.0	69.5	66.1
10	51.9	51.1	50.9	64.3	60.9	53.1	45.7	52.8	51.9	47.9
11	80.9	82.9	81.9	83.4	83.7	80.2	81.5	80.9	83.2	80.1
12	25.7	24.9	24.5	24.9	24.7	26.4	26.1	26.0	26.6	24.5
13	31.8	30.4	31.2	30.4	30.0	31.5	31.8	31.9	30.9	30.8
14	17.2	16.7	17.1	15.0	15.0	17.6	17.5	17.4	16.4	17.8
15	61.3	63.2	63.7	62.3	61.5	62.9	10.9	63.8	63.8	18.6



\* after subtraction of the spectrum of compound I<sup>a</sup>, which occurs as a small contamination in the polyalcohol-C (IV<sup>a</sup>)

\*\* interchangeable

All spectra were recorded in DMSO-d<sub>6</sub> as a solvent, except I<sup>b</sup> and IV<sup>b</sup>, which were recorded in CDCl<sub>3</sub>. Proton and carbon shifts are in p.p.m. downfield from T.M.S.

**Polyalcohol-B (III).** It shows an angular 15-Me ( $\delta$  0.90), which upon irradiation gives a N.O.E. on 6-H ( $\delta$  4.06) and 8-H ( $\delta$  3.51) of 15% and 19% respectively; this establishes the axial positions of these protons and consequently equatorial placement of C<sub>6</sub> and C<sub>8</sub> hydroxyls. Similarly, an increase in the intensity of the 9-H is observed upon irradiation of the 12-Me group at  $\delta$  1.40. C<sub>8</sub> proton occurs as a nicely resolved double doublet at  $\delta$  3.51 ( $J_1 = 3$  Hz,  $J_2 = 10$  Hz); it collapses into a doublet with  $J = 10$  Hz (a, a coupling of 8-H and 9-H) upon irradiation of the 7-H signal at  $\delta$  2.08.

**Polyalcohol-C (IV<sup>a</sup>).** This polyalcohol was readily recognised as 6 $\alpha$ -hydroxy-malkanguniol after comparison of the p.m.r. spectrum of its monohydroxytetraacetate (IV<sup>b</sup>; obtained after acetylation in the cold, m.p. 217-219°C) with that of the monohydroxytriacetate of malkanguniol (I<sup>b</sup>)<sup>1</sup>. Both compounds display the same spectral features on D<sub>2</sub>O-exchange and double resonance experiments. Upon D<sub>2</sub>O-exchange the 9-OH signal at  $\delta$  2.39 (d,  $J = 10$  Hz) disappears and the 9-H double doublet ( $\delta$  3.91,  $J_1 = 5$  Hz,  $J_2 = 10$  Hz) collapses into a doublet with  $J = 5$  Hz. Irradiation of 7-H causes a collapse of the 8-H double doublet ( $\delta$  5.28,  $J_1 = 3$  Hz,  $J_2 = 5$  Hz) into a doublet with  $J = 5$  Hz) and also causes a sharpening of the 6-H signal at  $\delta$  5.71.

**Polyalcohol-D (V).** This also shows an angular 15-Me group ( $\delta$  1.04), irradiation of which resulted in increased intensities of the 2-H ( $\delta$  3.66) and 9-H ( $\delta$  3.36) signals by 25% and 20% respectively, indicating axial 2-H and equatorial 9-H<sup>5</sup>.

Irradiation of one of the Me groups on C<sub>11</sub> ( $\delta$  1.41) gave a N.O.E. of 22% on 8-H, showing that 8-H must be equatorial and that the 12-Me group absorbs at  $\delta$  1.41. Irradiation at  $\delta$  1.70 causes collapse of the double doublet of 2-H ( $\delta$  3.66,  $J_1 = 10$  Hz,  $J_2 = 4$  Hz) into a doublet with  $J = 10$  Hz (a, a coupling 2-H and 1-H) and a collapse of the 14-Me doublet ( $\delta$  1.01) into a singlet, indicating that both the C<sub>3</sub> and C<sub>4</sub> protons must absorb around  $\delta$  1.7.

It may also be pointed out that, as expected, compound V displays in its mass spectrum the ion m/e 137 (80%) (cf. mass spectrum of malkanguniol<sup>1)</sup>), which is absent to any significant degree in the mass spectra of II, III and IV.

Work on the characterization of esters corresponding to the alcohols described above, is in progress.

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#### References:

- 1) H.J. den Hertog Jr, J.Th. Hackmann, D.D. Nanavati and Sukh Dev, Tetrahedron Letters, 1973, 845.
- 2) H. Wagner, E. Heckel and J. Sonnenbichler, Tetrahedron Letters, 1974, 213.
- 3) A.B. van Egmond, S. Harkema and T.C. van Soest, to be published.
- 4) See e.g. J.B. Stothers, Carbon-13 N.M.R. Spectroscopy. Academic Press, New York (1972).
- 5) A similar N.O.E. was found for an equatorial-H upon irradiation of an axial-Me on an adjacent C: Y. Shizuri, H. Wada, K. Sugiura, K. Yamada and Y. Hirata, Tetrahedron, 29, 1788 (1973) and references cited therein.