

## NEMOROSONOL B, A POLYISOPRENYLATED ALKYL-ARYL KETONE FROM *CLUSIA NEMOROSA*\*

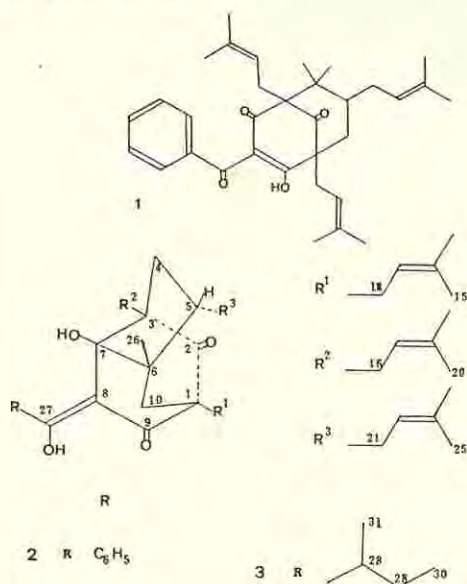
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**ABSTRACT.** The structure of nemorosonol B has been determined as a derivative of tricyclo-[4.3.1.0<sup>3,7</sup>]-decane. It represents the first modified polyisoprenylated alkyl-aryl ketone found in nature.

### INTRODUCTION

Polyisoprenylated benzophenones are secondary metabolites of Guttiferae (1,2) in which the acetate derived benzene ring has been modified to a bicyclo-[3.3.1]-nonane skeleton by the attack of four or more isoprenyl units and successive cyclization. A representative of this rare class of natural products is clusianone, 1 (3). Recently we reported on the structural determination of nemorosonol, 2 isolated from the fruits of *Clusia nemorosa* (4). Its novelty consists in the manner of cyclization which leads to a tricyclo-[4.3.1.0<sup>3,7</sup>]-decane derivative. This paper deals on the isolation from the same plant of a closely related compound, named nemorosonol B.



### EXPERIMENTAL

Purification (silica gel; benzene/n-hexane, (2:3)) of the pooled fractions N1

\* Part 4 in the series "Chemistry of *Clusia* Genus". For Part 3, see Ref. 4.

and N2a (500 mg) from the benzene extract of the fresh fruits (4) gave chromatographically pure nemorosonol B (185 mg). Nemorosonol B: colourless crystals (mp 103-5°C from n-hexane), which became yellow on exposure to light;  $[\alpha]_D^{25} + 192$  (c=0.6, CHCl<sub>3</sub>); UV  $\lambda_{max}$  (MeOH) nm: 297 (log  $\epsilon$  3.92) IR  $\nu_{max}$  (CCl<sub>4</sub>) cm<sup>-1</sup>: 3500, 1720, 1610 sh, 1580; EIMS in Table 1; <sup>1</sup>H NMR (CCl<sub>4</sub>, 60MHz)  $\delta$  15.50 (s, OH-27), 5.30-4.90 (m, H-12, H-17, H-22), 2.55-0.90 (remaining protons); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) see Table 2.

## RESULTS AND DISCUSSION

Nemorosonol B, C<sub>31</sub>H<sub>46</sub>O<sub>4</sub>, shows IR and UV data similar to those of nemorosonol (2), C<sub>33</sub>H<sub>42</sub>O<sub>4</sub>. The <sup>1</sup>H NMR spectrum of nemorosonol B lacks the signals for the unsubstituted phenyl ring exhibited by nemorosonol. This agrees with the absence of ions at m/z 105 and m/z 77 in the MS (Table 1). In the latter all the ions are displaced at 20 a.m.u. less with respect to those of nemorosonol. On the other hand, the <sup>13</sup>C NMR data (Table 2) suggests that the tricyclic ring and the three prenyl chains are still present and the main difference is found for the carbon 27 (177 vs 187).

Table 1. Main ions in the MS<sup>+</sup> of 2 and 3.

Nemorosonol (2) C <sub>33</sub> H <sub>42</sub> O <sub>4</sub>		Nemorosonol B (3) C <sub>31</sub> H <sub>46</sub> O <sub>4</sub>	
502(42)		482(56)	[M] <sup>+</sup>
433(28)	(a)	413(32)	[M-C <sub>5</sub> H <sub>9</sub> ] <sup>+</sup>
368(11)		346(13)	[M-C <sub>10</sub> H <sub>16</sub> ] <sup>+</sup>
311(100)	(b)	291(100)	[a-C <sub>9</sub> H <sub>14</sub> ] <sup>+</sup>
309(44)		289(49)	[a-C <sub>9</sub> H <sub>16</sub> ] <sup>+</sup>
255(26)		235(11)	[b-C <sub>5</sub> H <sub>9</sub> ] <sup>+</sup>
123(7)		123(7)	[C <sub>9</sub> H <sub>15</sub> ] <sup>+</sup>
121(6)		121(6)	[C <sub>9</sub> H <sub>13</sub> ] <sup>+</sup>
105(100)		-	[C <sub>6</sub> H <sub>5</sub> -C≡O] <sup>+</sup>
77(36)		-	[C <sub>6</sub> H <sub>5</sub> ] <sup>+</sup>

+ m/z (rel. int.)

Table 2. <sup>13</sup>C NMR Chemical shifts ( $\delta$ , ppm) of 2 and 3 (75 MHz, CDCl<sub>3</sub>)<sup>a</sup>.

Carbon <sup>b</sup>	Nemorosonol (2)	Mult.	Nemorosonol B (3)
1	63.4	s	62.6
2	210.6	s	211.1
3	62.7	s	62.2
4	40.2	t	38.6
5	48.6	d	48.1
6	47.4	s	47.8
7	83.7	s	85.3
8	109.7	s	107.6
9	199.0	s	197.1
10	46.5	t	46.9
26	19.4	q	18.6
27	177.0	s	187.0
28	c	d	37.5
29	c	t	26.9
30	c	q	12.2
31	c	q	18.5

<sup>a</sup> s=singlet, d=doublet, t=triplet, q=quartet

<sup>b</sup> The signals due to the prenyl chains of 3:  $\delta$  134.8 (C-13), 133.6 (C-18), 132.5 (C-23), 123.2 (C-22), 119.7, 119.6 (C-17, C-12), 33.5 (C-21), 29.2 (C-16), 26.1, 26.0, 25.8 (C-14, C-19, C-24), 25.1 (C-11), 18.1, 18.0, 17.9 (C-15, C-20, C-25).

<sup>c</sup> The signals for the aromatic ring and the prenyl chains of 2 are not reported.

On the basis of the above findings nemorosonol B shall contain a  $C_4H_9$  unit instead of the unsubstituted phenyl ring. The presence of the appropriate signals in the  $^{13}C$  NMR spectrum (Table 2) allows to fix the chain as 1-methylpropyl and to assign structure **3** to nemorosonol B. Nemorosonol B is the first modified alkyl-aryl ketone found in nature.

### REFERENCES

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