

## TWO NEW QUINONE-METHIDES FROM CASSINE BALAE: REVISED STRUCTURE OF BALAENONOL<sup>1</sup>

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**Abstract:** The structure of balaenol, a new quinone-methide triterpene isolated from *Cassine balae* has been deduced as 1 and the structure of the previously isolated balaenonol has been revised as 2 from their spectral data including 2-D heteronuclear <sup>1</sup>H-<sup>13</sup>C shift correlated NMR spectra and n.o.e studies.

In our continuing interest on quinone-methide and phenolic triterpenoids of Celastraceae, we have investigated the triterpenoid pigments of the root outer bark of *Cassine balae* [= *Elaeodendron balae*] and in this paper we report the structure of two 14(15)-ene-quinone-methides, balaenol (1) and balaenonol (2). The structure (4) previously proposed<sup>2</sup> for balaenonol has been revised as (2). The structure of the only one related ene-quinone-methide known in nature thus far, netzahualcoyone(3) has recently been determined by X-ray analysis.<sup>3</sup> Previous investigations of *C. balae* have led to the isolation of pristimerin, tingenone, 20-hydroxytingenone, olean-12-en-3 $\beta$ ,11 $\alpha$ -diol, 3 $\beta$ ,29-dihydroxy-D:B-friedo-olean-5-ene and an ene-quinone-methide whose structure was erroneously postulated as (4).<sup>2</sup>

The phenolic fraction of the hot light petroleum extract of the outer root bark of *C. balae* on chromatography afforded, in addition to several other pigments, two reddish brown quinone-methides, balaenonol and balaenol. Balaenonol, C<sub>28</sub>H<sub>34</sub>O<sub>4</sub>,<sup>4</sup> m.p. 205-208°C, had a UV spectrum [  $\lambda_{\max}$  (EtOH, log  $\epsilon$ ) 256(4.00) and 446(4.02)] suggesting that it had a chromophore with a greater conjugation than in pristimerin (UV 423 nm);<sup>5</sup> but identical with those reported for pristimerinene (5)<sup>6,7</sup>, hydroxy-pristimerinene (6)<sup>6,7</sup> and netzahualcoyone (3).<sup>3</sup> The IR spectrum showed the presence of hydroxy (3450-3200 cm<sup>-1</sup>), six-ring carbonyl (1705 cm<sup>-1</sup>) and conjugated carbonyl (1602 cm<sup>-1</sup>) functions. Its <sup>1</sup>H NMR spectrum at low field is very similar to those of (3), (5) and (6). Analysis of <sup>1</sup>H NMR, <sup>1</sup>H-<sup>1</sup>H COSY NMR, <sup>13</sup>C NMR (off-resonance and broad-band decoupled) and <sup>1</sup>H-<sup>13</sup>C shift correlated NMR spectra (Fig. 1) allowed assignment of all the <sup>1</sup>H and <sup>13</sup>C signals (Fig.3). An n.o.e. enhancement of 10% of the doublet due to 7-H at  $\delta$  6.21 on irradiation at  $\delta$  1.77 (signal due to methyl group at C-15) further suggested the structure of balaenonol as (2) and not the previously assigned structure (4). The stereochemistry at C-20 and C-21 was tentatively assigned as  $\beta$  on the basis of coupling constants and the n.o.e. data (see Fig. 4).

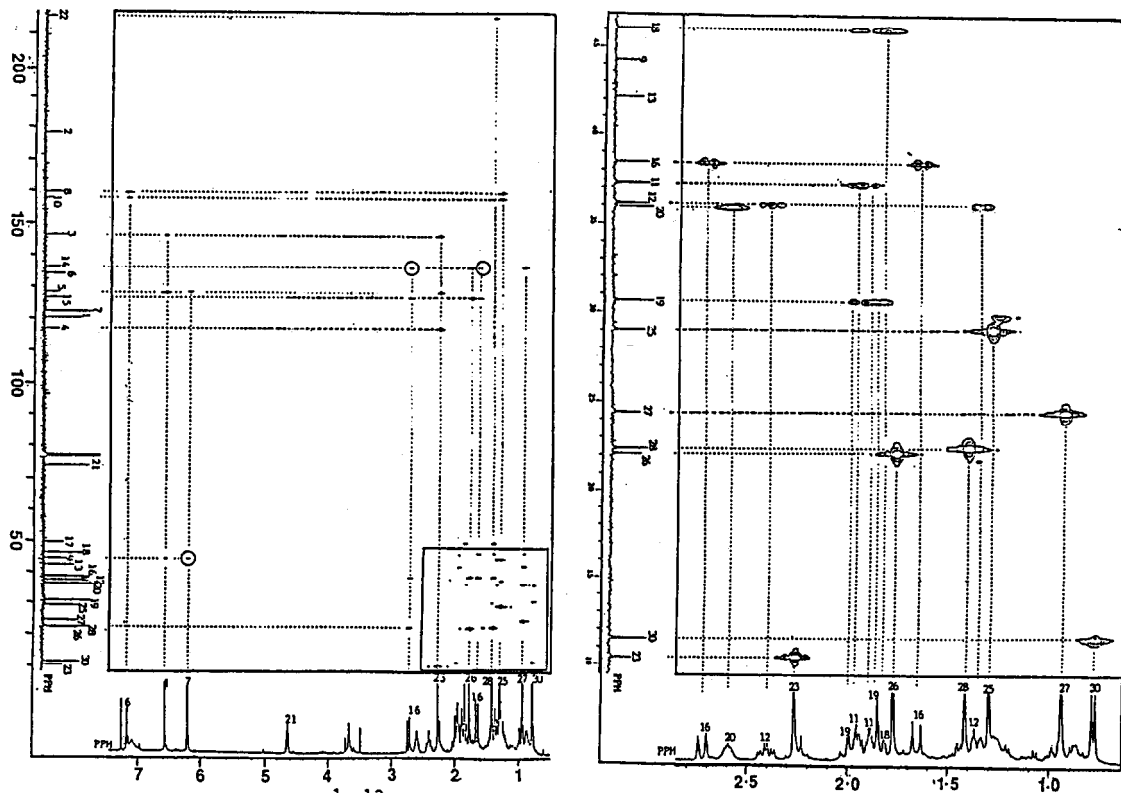
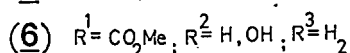
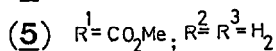
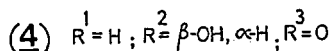
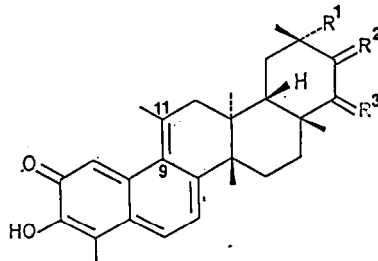
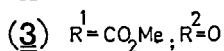
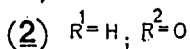
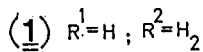
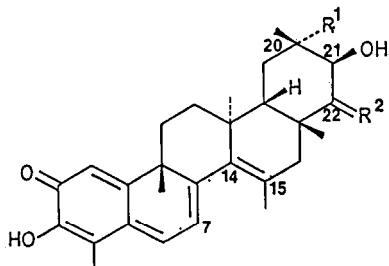


Fig. 1. Contour plot of the  $^1H$ - $^{13}C$  shift-correlated NMR spectrum of Balaenol (2).

The  $^1H$  shifts are shown on the abscissa and the  $^{13}C$  shifts on the ordinate. The multiplicities of the carbon signals were determined by means of off-resonance, and are indicated as s, d, t, and q: spectrum obtained with the usual pulse sequence and data processing was performed with the standard JEOL software. The spectral widths were 1700 Hz in  $f_1$  and 6000 Hz in  $f_2$ , giving digital resolutions of 6.6 and 5.8 Hz with a 512 x 2048 data point matrix.

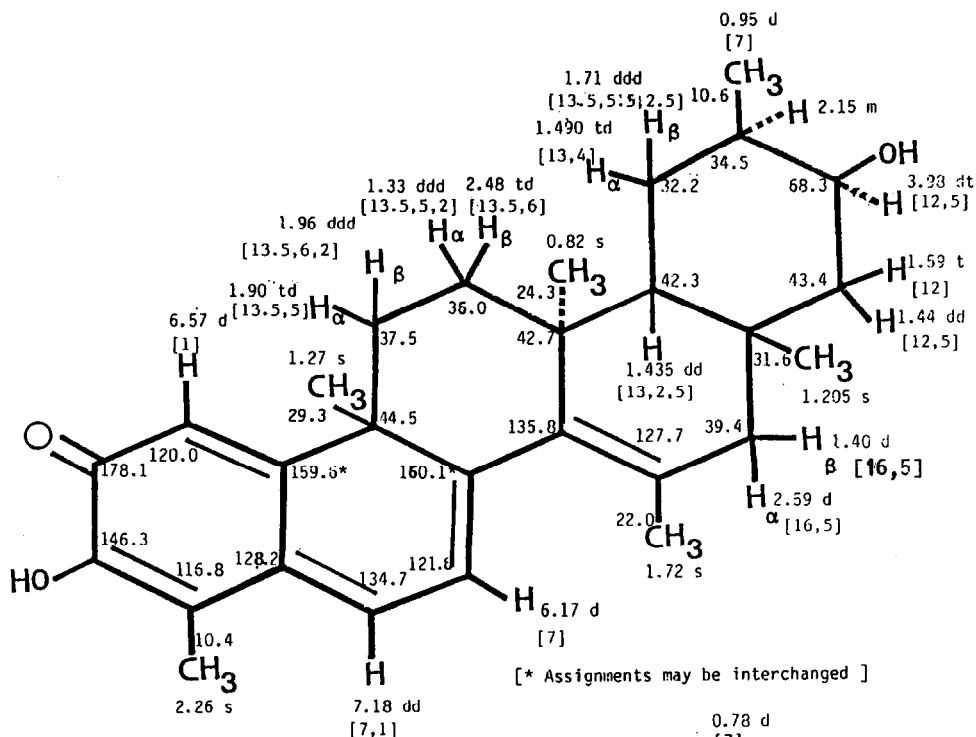


Fig. 2

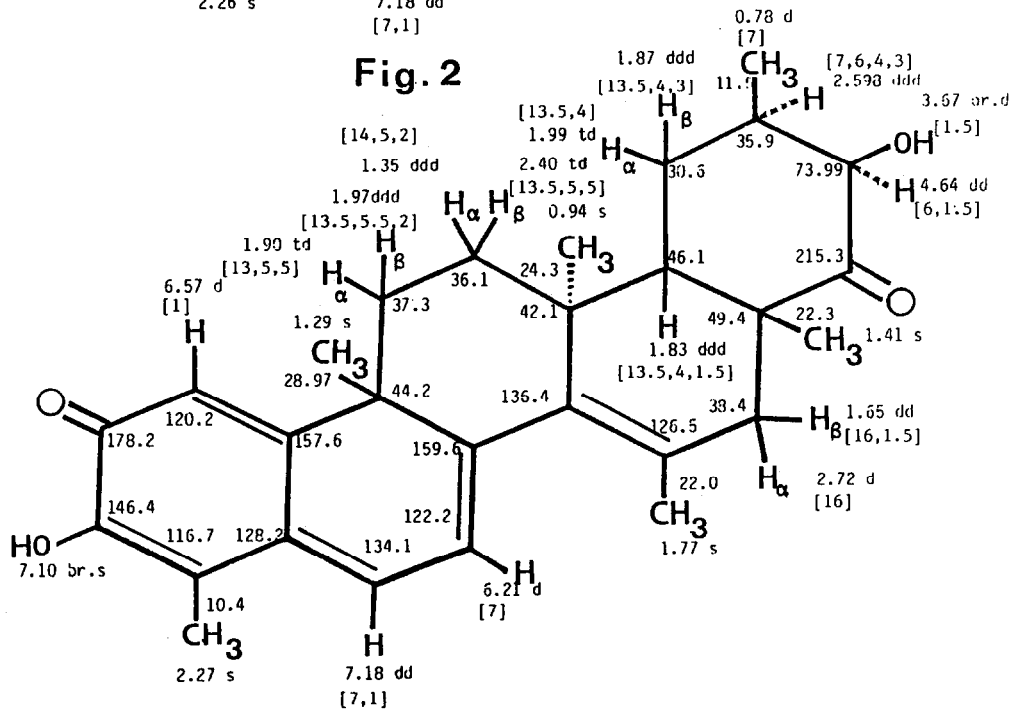


Fig. 3

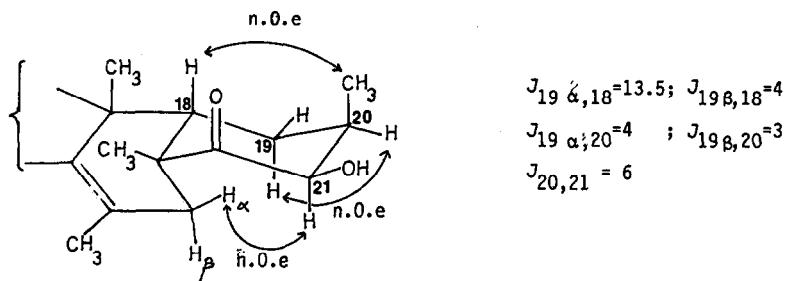
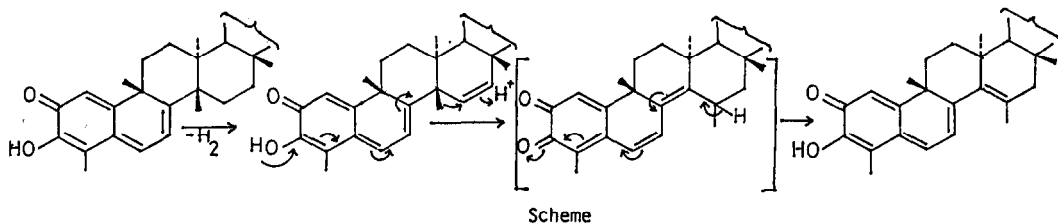


Fig. 4



Balaenol,  $C_{28}H_{36}O_3$ ,<sup>4</sup> m.p. 139-140°C, had a UV spectrum similar to that of balaenonol. Its IR spectrum indicated the presence of hydroxy ( $3500-3200\text{ cm}^{-1}$ ) and conjugated carbonyl ( $1596\text{ cm}^{-1}$ ) functions.  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals were assigned as for balaenonol (2) and by comparison with those for pristimerin. These assignments are shown in Fig. 2. These spectral data suggested structure (1) for balaenol.

Biosynthetically, 14(15)-ene-quinone-methides could arise from the corresponding quinone-methides by a dehydrogenation followed by a series of rearrangements (Scheme).

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