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STUDIES ON TERPENOIDS AND STEROIDS - 18[1]

BALAENONOL, BALAENOL AND ISOBALAENDIOL: THREE NEW 14(15)-ENE-QUINONE-METHIDE TRITERPENOIDS FROM CASSINE BALAE[2,†]

H. CHANDRASIRI FERNANDO, A.A. LESLIE GUNATILAKA*
Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka
AND
YASUHIRO TEZUKA, TOHRU KIKUCHI*
Research Institute for Wakan-Yaku, Toyama Medical and Pharmaceutical University, Sugitani, Toyama 930 01, Japan

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Abstract - The three new 14(15)-ene-quinone-methide triterpenoids, balaenonol, balaenol and isobalaendiol, isolated from *Cassine balae* have been shown to be 3,21β-dihydroxy-2,22-dioxo-3,5,7,10(1),14(15)-pentaen-(14→15)-D:A-*friedo*-24,29-dinoroleanane (**1**), 3,21β-dihydroxy-2-oxo-3,5,7,10(1),14(15)-pentaen-(14→15)-D:A-*friedo*-24,29-dinoroleanane (**2**) and 3,21β,22β-trihydroxy-2-oxo-3,5,7,10(1),14(15)-pentaen-(14→15)-D:A-*friedo*-24,30-dinoroleanane (**3**), respectively, on the basis of spectroscopic evidence. The possible biosynthetic origin of these 14(15)-ene-quinone-methides from pristimerin is discussed.

INTRODUCTION

Ene-quinone-methide triterpenoids are a small group of natural products peculiar to plants of the closely related families, Celastraceae and Hippocrateaceae and represented by netzahualcoyone (**5**),[3] netzahualcoyonol (**6**),[4] netzahualcoyondiol (**7**),[4] netzahualcoyene (**8**),[4] netzahualcoyol (**9**),[4] pristimerinene (**11**),[5] hydroxypristimerinene (**12**)[5] and Salacia quinone-methide (**13**).[6] In our continuing search for anti-tumour agents in Sri Lankan plants we have investigated the quinone-methide triterpenes in the endemic Celastraceae species, *Cassine balae* Kosterm. (= *Elaeodendron balae* Kosterm.) and in this paper we report the isolation and structure elucidation of three new 14(15)-ene-quinone-methides, balaenonol (**1**), balaenol (**2**) and isobalaendiol (**3**) in addition to pristimerin (**14**), tingenone (**15**), 22β-hydroxytingenone (**16**) and 20-hydroxytingenone (**17**). A minor impurity present in certain samples of balaenol was identified to be isobalaenol (**4**). The structure (**10**) earlier proposed[7] for an ene-quinone-methide identical with balaenonol has been revised as (**1**). Previous investigation of *C. balae* has led to the isolation of (**14**), (**15**), (**17**), olean-12-en-3β,11α-diol, 3β,29-dihydroxy-D:B-*friedo*-olean-5-ene and an ene-quinone-methide whose structure was erroneously postulated as (**10**).[7]

†Dedicated with great admiration and affection to Professor Sir Derek Barton on the occasion of his seventieth birthday and in appreciation to his contributions in the fields of terpenoids and steroids.

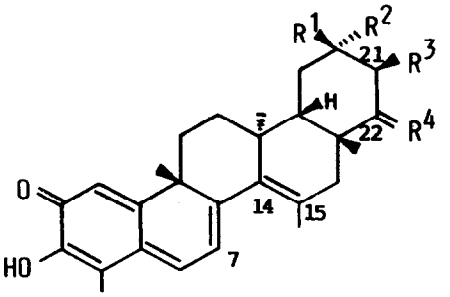
RESULTS AND DISCUSSION

The hot hexane extract of the outer root bark of *C. balae* on fractionation by medium-pressure liquid chromatography (MPLC) over Si gel afforded pristimerin (**14**), tingenone (**15**), 22β-hydroxytingenone (**16**), 20-hydroxytingenone (**17**) and three new ene-quinone-methides, named as balaenonol, balaenol and isobalaendiol. Structures of these ene-quinone-methides were elucidated with the help of spectroscopic methods as described below.

The UV spectrum (λ_{max} ,446 nm) of balaenonol, $C_{28}H_{34}O_4$, m.p.205-208°,$[\alpha]_D$ +110°, suggested that it had a chromophore with a greater conjugation than in pristimerin (UV λ_{max}, 423 nm)[6]; but identical with those reported for netzahualcoyone (**5**),[3] pristimerinene (**11**)[5] and Salacia quinone-methide (**13**).[6] The IR spectrum showed the presence of hydroxy (3450-3200 cm^{-1}), six-membered ring carbonyl (1705 cm^{-1}) and conjugated carbonyl (1602 cm^{-1}) functions. The ^1H NMR spectrum in the olefinic region was comparable with that of pristimerin. However, differences were observed in the chemical shifts of the singlets due to some methyl groups (see Table 1); two methyl groups attached to unsaturated centres were present, one corresponding to C4-methyl of pristimerin. This together with the above UV λ_{max} suggested balaenonol to be a 9(11)- or 14(15)-ene-quinone-methide with a methyl group at the terminus of the conjugated system. The 14(15)-ene-quinone-methide structure (**1**) was favoured based on the following evidence.

The MS had significant peaks at m/z 294, 279 and 253 arising due to a *retro*-Diels-Alder cleavage of ring D giving (**22**) followed by the loss of CH_3 or C_3H_5 groups resulting in (**23**) and (**24**), respectively (Scheme 1). These fragments were also observed for balaenol and isobalaendiol (see Experimental Section). It is noteworthy that the presence of a peak at m/z 279 has also been observed for pristimerinene (**11**),[5] hydroxypristimerinene (**12**)[5] and netzahualcoyone (**5**).[3] An NOE enhancement of 10% of the doublet due to 7-H at δ 6.21 on irradiation at δ 1.77 (signal due to methyl group at C-15) further supported the 14(15)-ene-quinone-methide structure (**1**) for balaenonol and not the previously assigned 9(11)-ene-quinone-methide structure (**10**).[7] Recently, it has been pointed out that the ^1H NMR spectrum of pristimerinene (**11**) is superimposable upon that of netzahualcoyene (**8**).[4] Furthermore, there is no special reason as to why the 9(11)-ene-quinone-methides such as pristimerinene (**11**) and Salacia quinone-methide (**13**) should exist in quinone-methide form and not in their more stable aromatic forms (**18**) and (**19**), respectively.

Having established the presence of 14(15)-ene-quinone-methide system in balaenonol it remained to determine the nature and location of the remaining two oxygen functions. The IR band at 1705 cm^{-1} and the presence of a D_2O exchangeable signal at δ 3.67 (br d, J= 1.5 Hz) in the ^1H NMR spectrum suggested, respectively, the presence of a six-membered ring carbonyl and chelated hydroxy functions probably on adjacent carbon atoms. This is possible only at C-21 and C-22 of the ring E and was confirmed by comparison of the ^1H NMR signal due to C*H*OH of balaenonol (δ 4.64, dd, J= 6 and 1.5 Hz) with that of 22β-hydroxytingenone (δ 3.67, s),[9] which further suggested that the OH group is at C-21 and the carbonyl at C-22. On addition of D_2O, the double doublet due to 21-C*H*OH collapsed to a doublet (J= 6 Hz). The stereochemical dispositions of the C-20-Me and C-21-OH groups in ring E were determined with the aid of ^1H NMR coupling constant data and NOE studies (see Fig. 1).



(1) R^1 =Me; R^2 =H; R^3 =OH; R^4 =O

(2) R^1 =Me; R^2 =H; R^3 =OH; R^4 =H_2

(3) R^1 =H; R^2 =Me; R^3 =OH; R^4 =β-OH,α-H

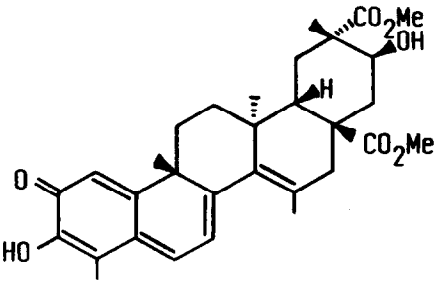
(4) R^1 =H; R^2 =Me; R^3 =OH; R^4 =H_2

(5) R^1 =Me; R^2 =CO_2Me; R^3 =OH; R^4 =O

(6) R^1 =Me; R^2 =CO_2Me; R^3 =OH; R^4 =H_2

(7) R^1 =Me; R^2 =CO_2Me; R^3 =OH; R^4 =β-OH,α-H

(8) R^1 =Me; R^2 =CO_2Me; R^3 =H; R^4 =H_2



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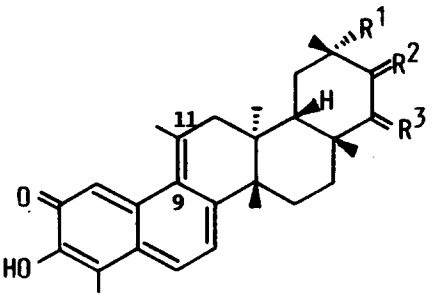
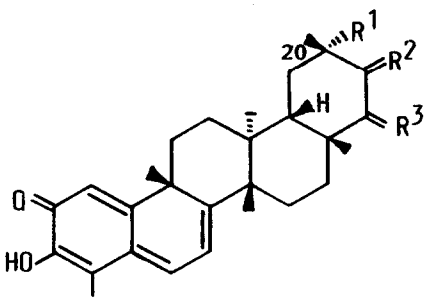


(10) R^1 =H; R^2 =β-OH,α-H; R^3 =O

(11) R^1 =CO_2Me; R^2 =R^3 =H_2

(12) R^1 =CO_2Me; R^2 =H, OH; R^3 =H_2

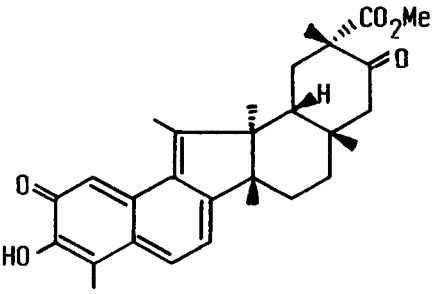


(14) R^1 =CO_2Me; R^2 =R^3 =H_2

(15) R^1 =H; R^2 =O; R^3 =H_2

(16) R^1 =H; R^2 =O; R^3 =β-OH,α-H

(17) R^1 =OH; R^2 =O; R^3 =H_2



(13)

Table 1. ^{1}H NMR data (δ/ppm; 397.78 MHz) of balaenonol (1), balaenol (2), isobalaendiol (3), isobalaenol (4), netzahualcoyone (5), pristimerinene (11) and pristimerin (14)

Proton	(1)	(2)	(3)	(4)	(5)[a]	(11)[b]	(14)[c]
1-H	6.57 d (J= 1)	6.57 d (J= 1)	6.56 d (J= 1.5)	6.57 d (J= 1)	6.55 brs	6.48 d (J= 1)	6.53 d (J= 1.3)
6-H	7.18 dd (J= 7,1)	7.18 dd (J= 7,1)	7.19 dd (J= 7,1.5)	7.18 dd (J= 7,1)	7.15 brd (J= 7)	7.10 dd (J= 7,1)	7.02 dd (J= 7,1.3)
7-H	6.21 d (J= 7)	6.17 d (J= 7)	6.18 d (J= 7)	6.17 d (J= 7)	6.18 d (J= 7)	6.10 d (J= 7)	6.35 d (J= 7)
4-CH_3	2.27 s	2.26 s	2.26 s	2.26 s	2.24 s	2.23 s	2.21 s
9-CH_3	1.29 s	1.27 s	1.28 s	1.27 s			1.45 s
13-CH_3	0.94 s	0.84 s	0.84 s	0.84 s			0.53 s
14-CH_3	-	-	-	-			1.26 s
15-CH_3	1.77 s	1.73 s	1.73 s	1.73 s	1.77 s	1.70 s	-
17-CH_3	1.41 s	1.20 s	1.36 s	1.20 s			1.10 s
20-H	2.59 m	2.15 m	1.77 m	2.15 m			-
20β-CH_3	0.78 d (J= 7)	0.95 d (J= 7)	-	-			1.18 s
20α-CH_3	-	-	1.03 d (J= 6.5)	1.04 d (J= 6.5)			-
21α-H	3.67 d (J= 1.5)	3.98 d (J= 5)	3.46 dd (J= 11,3)		3.65 brs		-
22α-H	-	1.59 t (J= 12)	3.40 d (J= 3)				

[a,b,c]Data from references 3,5 and 10, respectively.

Table 2. ^{13}C NMR data (δ/ppm; 100 MHz, $CDCl_3$) of balaenonol (1), balaenol (2), isobalaendiol (3), and pristimerin (14)

Carbon	(1)	(2)	(3)	(14)	Carbon	(1)	(2)	(3)	(14)
1	120.2 d	120.0 d	120.0 d	119.6 d	15	126.5 s	127.7 s	128.8 s	28.7 t
2	178.2 s	178.1 s	178.1 s	178.4 s	16	38.4 t	39.4 t	37.7 t	36.4 t
3	146.4 s	146.3 s	146.3 s	146.1 s	17	49.4 s	31.6 s	40.0 s	30.6 s
4	116.7 s	116.8 s	116.9 s	117.0 s	18	46.1 d	42.3 d	43.1 d	44.4 d
5	128.2 s	128.2 s	127.8 s	127.5 s	19	30.6 t	32.2 t	34.3 t	30.9 t
6	134.1 d	134.7 d	134.5 d	133.9 d	20	35.9 d	34.5 d	33.0 d	40.4 s
7	122.2 d	121.8 d	121.5 d	118.1 d	21	73.99 d	68.3 d	74.2 d	29.9 t
8	159.6 s*	160.1 s*	160.1 s*	169.9 s	22	215.3 s	43.4 t	80.0 d	34.8 t
9	44.2 s	44.5 s	44.6 s	42.9 s	23	10.4 q	10.4 q	10.4 q	10.2 q
10	157.6 s*	159.6 s*	159.4 s*	164.7 s	25	28.97 q	29.3 q	29.4 q	38.3 q
11	37.3 t	37.5 t	37.5 t	33.6 t	26	22.0 q	22.0 q	21.9 q	21.6 q
12	36.1 t	36.0 t	35.15 t	35.15 t	27	24.3 q	24.3 q	24.4 q	18.3 q
13	42.1 s	42.7 s	42.5 s	39.4 s	28	22.3 q	31.6 q	27.4 q	31.6 q
14	136.4 s	135.8 s	136.4 s	45.0 s	30	11.5 q	10.6 q	18.6 q	32.7 q

*Assignments may be exchanged.

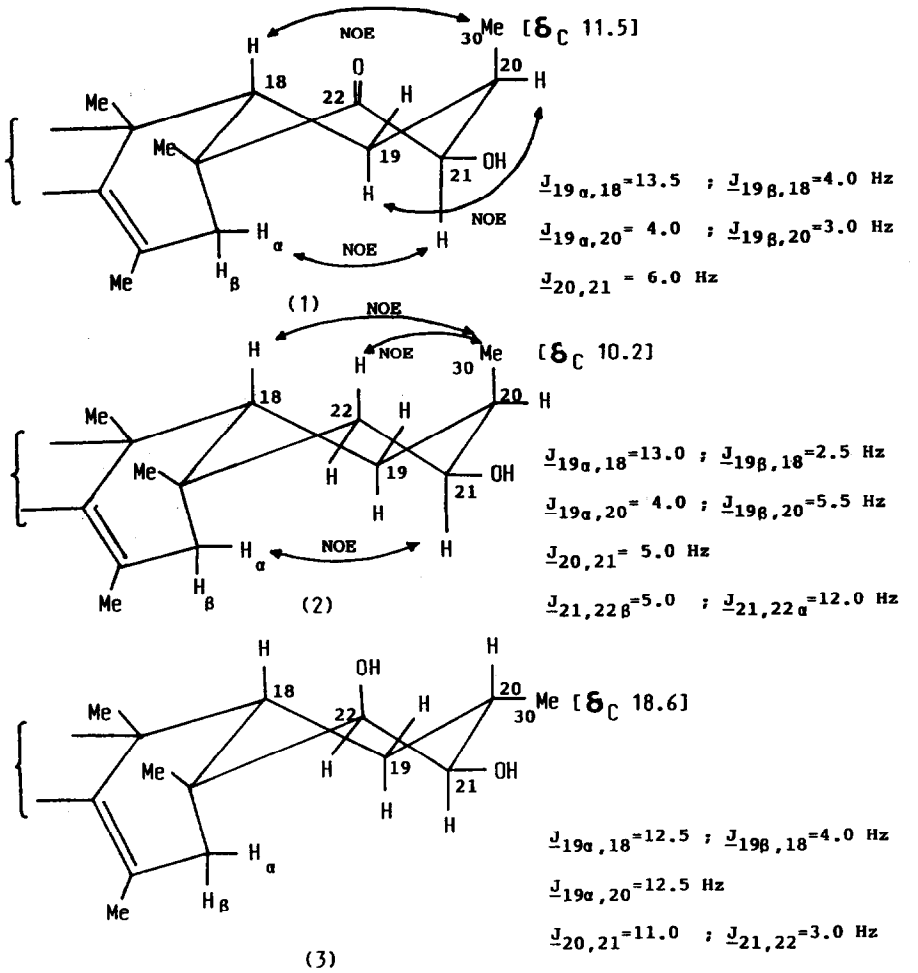


Fig.1

Further evidence for the proposed structure of balaenonol (1) came from its ^{13}C NMR spectral data, assignments of which were made by comparison with our data for pristimerin (14) (Table 2) obtained by application of 2D ^{1}H-^{1}H and ^{1}H-^{13}C shift correlation techniques, extensive decoupling and NOE studies.[10] As expected, significant differences in chemical shifts were observed for C-8, C-14, C-15, C-21, C-22 and C-27. The shielding experienced by C-28 of (1) compared to (14) and (2) may be explained as due to the paramagnetic effect of the C-22 carbonyl function. Detailed analysis of ^{13}C NMR spectra of 14(15)-ene-quinone-methides will be published elsewhere. The CD curves of pristimerin and balaenonol are presented in Fig. 2.

Balaenol, $C_{28}H_{34}O_3$, m.p. 139-140°, $[\alpha]_D$ +152°, had a UV spectrum similar to that of (1) (see Experimental). Its IR spectrum indicated the presence of hydroxy (3500-3200 cm^{-1}) and conjugated carbonyl (1596 cm^{-1}) functions. The ^1H NMR spectrum in the low field region was almost superimposable with that of balaenonol (1) and the singlets due to two methyl groups attached to unsaturated centres appeared at δ 2.26 and 1.73 (Table 1). These observations along with the UV λ_{max} suggested the ene-quinone-methide structure for balaenol. The presence of a secondary OH at C-21 was apparent from its ^1H NMR spectrum in which the C*H*OH appeared as a dt (*J*= 12 and 5 Hz) at δ 3.98. The coupling constants observed for the signals due to ring E protons along with NOE data (Fig. 1) confirmed that both C-20-Me and C-21-OH are of β-orientation. The ^{13}C NMR data also supported the structure (2) proposed for balaenol. The assignments were made by comparison with the data for pristimerin (14) and balaenonol (1) (Table 2).

During our ^1H NMR studies we found that certain samples of balaenol was contaminated upto *ca.* 30% with its isomer, isobalaenol (4). Attempted separation of the two isomers by HPLC under varying conditions was unsuccessful and resulted in decomposition. The differences in the ^1H NMR were observed for the signals due to 30-H (20β-Me and 20α-Me, see Table 1). The major difference in the ^{13}C NMR was also observed for the C-30; in balaenol it appeared at δ 10.6 whereas in isobalaenol it was found at δ 18.5 identical with the position of the C-30 signal of isobalaendiol (3) (see Fig. 1 and below). The CD curve of balaenol was found to be superimposable with that of balaenonol (Fig. 2).

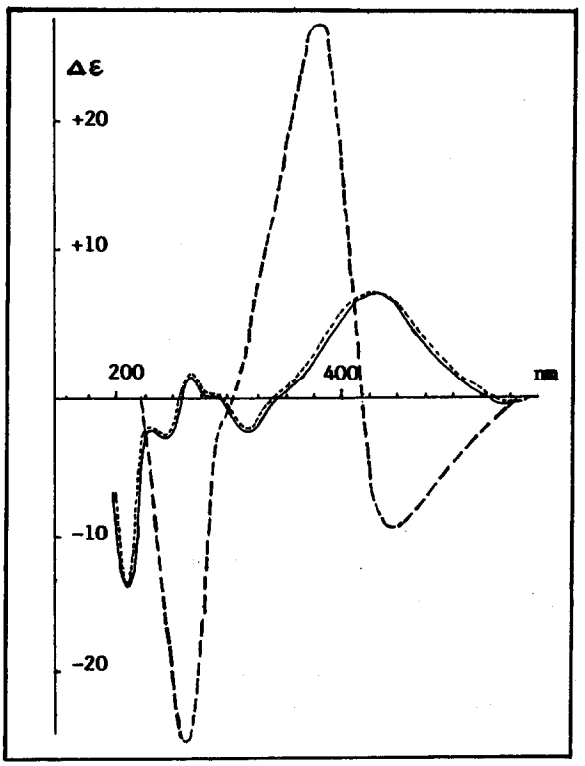
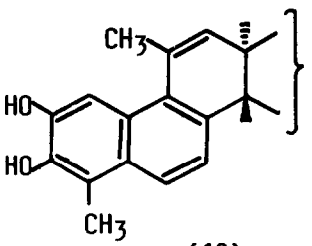
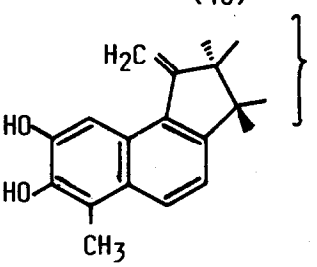


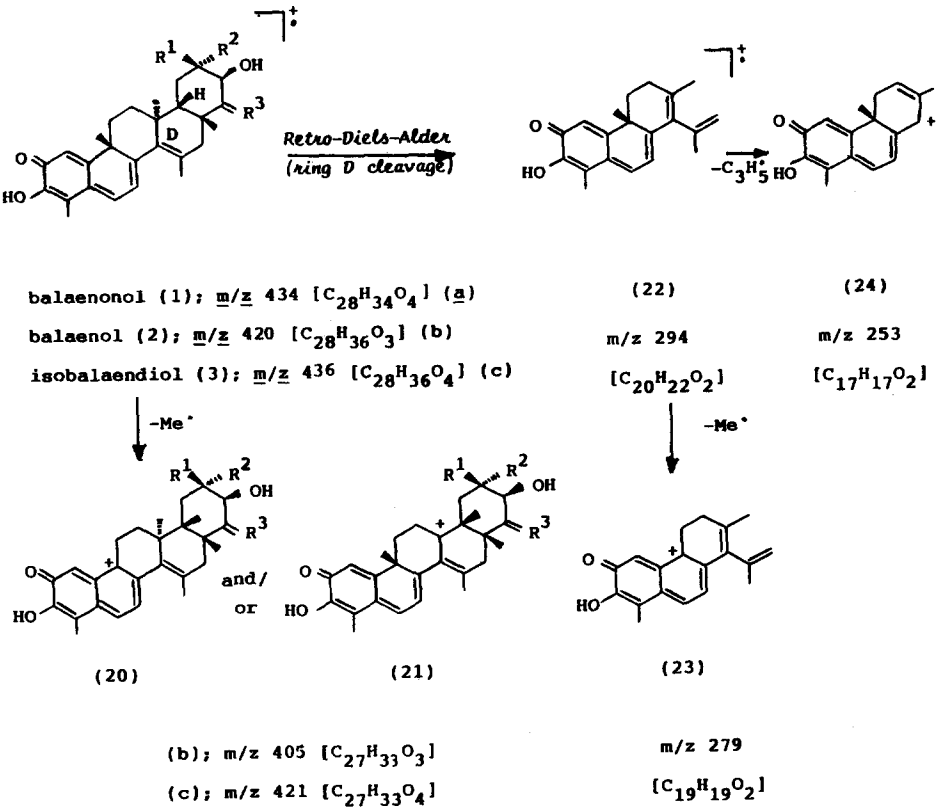
Fig. 2. CD Curves (in CH_3CN) of — balaenonol (1), ----- balaenol (2), and - - - pristimerin (14)



(18)



(19)



balaenonol (1); m/z 434 [$C_{28}H_{34}O_4$] (a)
balaenol (2); m/z 420 [$C_{28}H_{36}O_3$] (b)
isobalaendiol (3); m/z 436 [$C_{28}H_{36}O_4$] (c)

(20) (21) (22) (23) (24)

(22) m/z 294 [$C_{20}H_{22}O_2$]

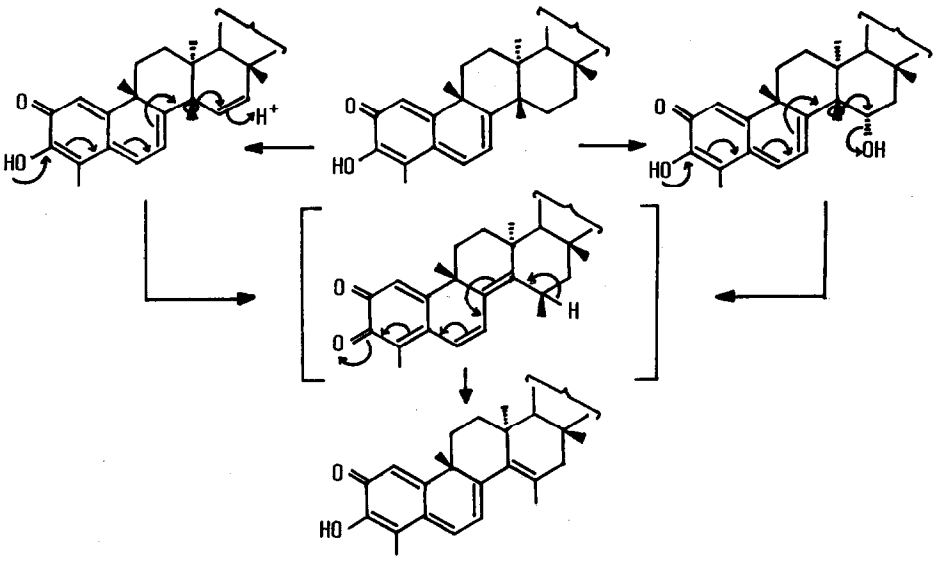
(24) m/z 253 [$C_{17}H_{17}O_2$]

(b); m/z 405 [$C_{27}H_{33}O_3$]
(c); m/z 421 [$C_{27}H_{33}O_4$]

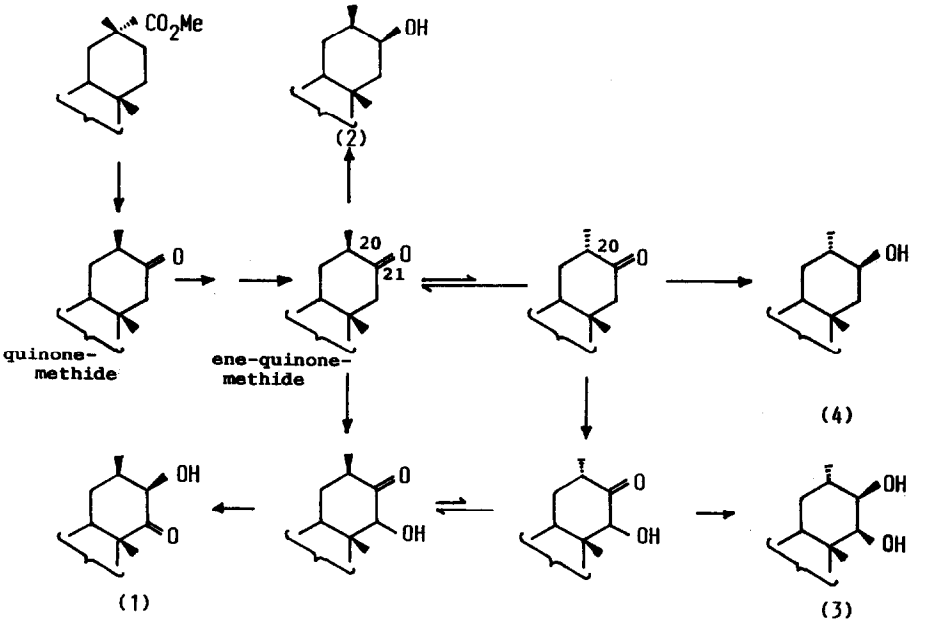
(23) m/z 279 [$C_{19}H_{19}O_2$]

SCHEME 1

Isobalaendiol, $C_{28}H_{36}O_4$, m.p. 210-213°, $[\alpha]_D$ +65°, had UV and IR spectra similar to those of balaenol. The MS exhibited significant fragments at m/z 421, 294, 279 and 253 and these can be interpreted as due to the fragments shown in Scheme 1. The additional oxygen was suspected to be present as an OH and this was confirmed by the ^{1}H NMR spectrum which had two C*H*OH signals at δ 3.40 (d, *J*= 2 Hz) and 3.46 (dd, *J*= 11 and 2 Hz) instead of one C*H*OH signal at δ 3.98 (dt, *J*= 12 and 5 Hz) in balaenol (2). The other significant differences were observed for the signals due to 20-H and 20-Me (see Table 1). The stereochemical disposition of 20-Me, 21-OH and 22-OH were determined with the help of proton coupling constants and NOE studies (Fig. 1). The ^{13}C NMR spectral assignments are given in Table 2. The chemical shift (δ 18.6) of C-30 in isobalaendiol compared with those of balaenonol (δ 11.5) and balaenol (δ 10.6) further confirmed that the C-20-methyl group of isobalaendiol has α-orientation as opposed to balaenonol and balaenol where it has β-orientation. Thus, isobalaendiol should have the structure (3).



SCHEME 2



SCHEME 3

Biosynthetic aspects

It is possible that 14(15)-ene-quinone-methides are biosynthesised from the corresponding quinone-methides *via* a dehydrogenation and rearrangement or hydroxylation followed by concommitant dehydration and rearrangement mechanisms as depicted in Scheme 2.

The 14(15)-ene-quinone-methides encountered in *Cassine balae* differ only in ring E. Their biosynthetic origin can be explained by a series of transformations given in Scheme 3, which is analogous to that proposed previously.[5] The isomerisation of 20β-methyl to 20α-methyl could occur in the 21-keto intermediate. However, it is surprising that isotingenone (structure identical with **15** except for the α-orientation of C-20-Me group) has thus far not being encountered in nature.

EXPERIMENTAL

General methods. The general experimental details were the same as those described previously[11] except the following. IR spectra were recorded for KBr discs with Shimadzu IR 408 spectrometer and UV spectra were recorded in ethanol on a Shimadzu UV 160 spectrometer. ^{1}H NMR spectra were in $CDCl_3$ at 397.78 MHz with TMS as internal reference on a JEOL GX-400 spectrometer. The ^{13}C NMR spectra were recorded on the same spectrometer operating at 100.57 MHz. Mass spectra were obtained using JEOL D-300 mass spectrometer (ionization voltage, 70 eV; accelerating voltage 3 kV) using a direct inlet system. MPLC were carried out using Si gel (230-400 mesh); a pressure pump was employed to apply pressure.

Extraction of C. balae root outer bark and fractionation of the hexane extract. The dried and powdered root outer bark (1.0 kg) of *C. balae* collected in Monaragala district, Sri Lanka, was exhaustively extracted with hot hexane. Evaporation afforded hexane extract (160.5 g; 16%). A portion (49 g) of this was subjected to MPLC with solvent gradients ranging from hexane-EtOAc to EtOAc to 1% MeOH in EtOAc. A total of 78 fractions of 50 ml were collected. Similar eluates (by TLC) were combined and subjected to further purification by flash chromatography and PLC to obtain six triterpenoid pigments.

Isolation of pristimerin (**14**), tingenone (**15**) and 22β-hydroxytingenone (**16**). Combined column fractions 4-10 (8.31 g) was further separated by flash chromatography over a Si gel column made up in hexane and increasing the polarity gradiently upto hexane-EtOAc (9:1) to give crude pristimerin, tingenone and 22β-hydroxytingenone. These were separately purified by PLC. Pristimerin (**14**) obtained as orange yellow crystals (32 mg, 0.0032%), m.p. 215-217°, $[\alpha]_D$ -168°, was identical (mixed m.p., co-IR, ^{1}H NMR) with an authentic sample.[11] Tingenone (**15**) was obtained as an orange red crystalline solid (50 mg, 0.005%), m.p.187-190° (lit.[12] m.p. 189-192°; lit.[9] m.p. 203-204°), $[\alpha]_D$ -197° (c, 1.00 in $CHCl_3$). Spectral properties (UV, IR, ^{1}H NMR) were identical with those reported for tingenone.[9] Detailed analysis of ^{1}H and ^{13}C NMR spectra of pristimerin and tigenone will be presented elsewhere.[10]

The column fraction which yielded pristimerin and tingenone were subjected to PLC [Si gel GF_{254}; eluant: hexane-EtOAc (8.5:1.5), multiple elution] to obtain 22β-hydroxytingenone as an orange red crystalline solid (38 mg, 0.0038%), m.p. 210-212° (lit.[9] m.p. 210-211°), $[\alpha]_D$ -179° (c, 2.5 in $CHCl_3$). Spectral properties (UV, IR, ^{1}H NMR) were identical with those reported for 22β-hydroxytingenone.[9]

Isolation of balaenonol (**1**). Combined column fraction 19-21 on standing precipitated an orange crystalline solid (0.7 g) which was further purified by flash chromatography over Si gel. Elution with 5% EtOAc in hexane followed by PLC [Si gel; 0.5 mm;eluant: hexane-EtOAc (6:4)] afforded balaenonol (**1**) (28 mg, 0.0028%) as orange brown plates; m.p. 205-208° (from acetone), $[\alpha]_D$ +109° (c, 1.05 in $CHCl_3$) (lit.[7] m.p. 204-205°, $[\alpha]_D$ +105°); UV (EtOH) 256 (log ε 3.94), 444 (4.02) nm; IR (KBr) 3450-3200, 1705, 1602, 1555, 1435, 1205 and 1115 cm^{-1}; for ^{1}H and ^{13}C NMR data, see Tables 1 and 2, respectively; MS, m/z 434 ($\underline{M}^+$, 100%) $C_{28}H_{34}O_2$, 331 (18) $C_{23}H_{23}O_2$, 294 (8) $C_{20}H_{22}O_2$, 279 (16) $C_{19}H_{19}O_2$, 265 (11) $C_{18}H_{17}O_2$, 253 (17) $C_{17}H_{17}O_2$, 241 (28) $C_{16}H_{17}O_2$, 227 (30) $C_{15}H_{15}O_2$, 201 (45) $C_{13}H_{13}O_2$; $\underline{M}^+$ 434.2488. Calc. for $C_{28}H_{34}O_4$, $\underline{M}$ 434.2458.

Isolation of balaenol (2). Further elution of the above column from which balaenonol was obtained gave crude balaenol which on purification by PLC [Si gel; eluant: hexane-EtOAc (6:4)] afforded pure balaenol (2) (26 mg, 0.0026%) as a crystalline solid, m.p. 139-142°; $[\alpha]_D$ +152° (c, 2.40 in $CHCl_3$); UV (EtOH) 252 (log ε 3.09), 446 (4.14) nm; IR (KBr) 3500-3200, 1596, 1500, 1446, 1382, 1292, 1211, 1071, 1021 cm^{-1}; for ^1H and ^{13}C NMR data, see Tables 1 and 2, respectively; MS, m/z 420 (M$^+$, 100%) $C_{28}H_{36}O_3$, 405 (24) $C_{27}H_{33}O_3$, 294 (14) $C_{20}H_{22}O_2$, 279 (18) $C_{19}H_{19}O_2$, 265 (13) $C_{18}H_{17}O_2$, 254 (13) $C_{17}H_{18}O_2$, 227 (28) $C_{15}H_{15}O_2$, 202 (42) $C_{13}H_{12}O_2$; M$^+$ 420.2691. Calc. for $C_{28}H_{36}O_3$, M 420.2664.

Isolation of 20-hydroxytingenone (17). Combined column fractions 30-35 (231 mg) was further separated by repeated PLC [Si gel; 0.5 mm; eluant-dichloromethane:MeOH (97:3), R_F 0.4 and then with hexane:EtOAc (4:6), R_F 0.5] afforded 20-hydroxytingenone (17) as an orange red crystalline solid (26 mg, 0.0026%), m.p. 208-210° (from acetone) (lit.[5] m.p. 207-208°); $[\alpha]_D$ +122° (c, 2.10 in $CHCl_3$); UV (EtOH) 253 (log ε 3.51), 420 (4.09) nm; IR (KBr) 3300-3400, 1717, 1597, 1547, 1512, 1442, 1352, and 1122 cm^{-1}; detailed analysis of ^1H and ^{13}C NMR spectra will be presented elsewhere.[10]

Isolation of isobalaendiol (3). This was isolated from the same combined column fractions from which 20-hydroxytingenone was isolated (see above). PLC separation [Si gel; 0.5 mm; eluant- dichloromethane:MeOH (97:3), R_F 0.35 and then with hexane:EtOAc (4:6), R_F 0.4] afforded isobalaendiol (3) as an orange red crystalline solid (23 mg, 0.0023%), m.p. 210-212° (from dichloromethane-ether); $[\alpha]_D$ +65° (c, 4.5 in $CHCl_3$); UV (EtOH) 256 (log ε 3.02), 441 (4.01) nm ; IR (KBr) 3500-3200, 1584, 1526, 1442, 1379, and 1204 cm^{-1}; for ^1H and ^{13}C NMR data, see Tables 1 and 2, respectively; MS, m/z 436 (M$^+$, 100%) $C_{28}H_{36}O_4$, 294 (6) $C_{20}H_{22}O_2$, 281 (19) $C_{19}H_{21}O_2$, 279 (11) $C_{19}H_{19}O_2$, 265 (7) $C_{18}H_{17}O_2$, 253 (8) $C_{17}H_{17}O_2$, 241 (8) $C_{16}H_{17}O_2$, 227 (14) $C_{15}H_{15}O_2$, 201 (15) $C_{13}H_{13}O_2$; M$^+$ 436.2595. Calc. for $C_{28}H_{36}O_4$, M, 436.2613.

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