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LABDANE DERIVATIVES FROM *HEMIZONIA* SPECIES*

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Key Word Index—*Hemizonia fitchii*; *H. lutescens*; *H. congesta*; Compositae; diterpenes; labdanes; sesquiterpene; cubebol derivative; chromene derivatives.

Abstract—The investigation of three *Hemizonia* species afforded in addition to known compounds seven new labdane derivatives, all derived from labd-13-en-15-ol. The absolute configuration of these diterpenes was determined by degradation of the triol by periodate cleavage, which afforded a known norditerpene ketone. From *H. fitchii* two new chromene esters and the *cis*-isomer of a known coumarate were isolated. *H. congesta* afforded in addition to labdane derivatives a hydroxycubebol.

INTRODUCTION

The genus *Hemizonia* (Compositae, tribe Heliantheae) is placed in the subtribe Madiinae [1]. So far little is known on the chemistry of this Californian genus. The presence of an acetylenic thiophene has been reported in the roots of two species [2]. To obtain a better understanding of the chemistry of this genus we have now investigated the aerial parts of three species in detail. Two species afforded mainly labdane derivatives, several of them isolated for the first time, while one species only gave chromenes and *p*-coumarates. From *H. congesta* a hydroxycubebol was isolated.

RESULTS AND DISCUSSION

The aerial parts of *Hemizonia fitchii* A. Gray afforded squalene, the chromenes **15**–**17** [3–5] together with a mixture of two esters of **17**, the isovalerate **18** and the methyl butyrate **19**. The structures were deduced from the ^{1}H NMR data of the mixture (Table 1). In addition to the coumarate **14** [6] the corresponding *cis*-isomer **13** was present. Its structure followed from the ^{1}H NMR spectral data (Table 1), which were characteristically different from those of **14**.

The aerial parts of *H. lutescens* (Greene) Keck. afforded *n*-hexadecanol 2-methylbutyrate, the geraniol esters **10**–**12** and a complex mixture of diterpenes. Finally, in addition to the known labdane **1** [7] seven other labdanes were isolated. Inspection of the ^{1}H NMR spectral data (Table 2) led to structures **2**–**8**. The ^{1}H NMR spectral data of **2** were similar to those of **1**; but the signals for the side-chain protons were different. The signal of the olefinic methyl protons was replaced by a doublet, while multiplets at δ 3.66 and 3.46 clearly showed the presence of hydroxy groups at C-14 and C-15, as followed from spin decouplings, especially with C_6D_6 as the solvent. The molecular formula of **3** indicated that this diterpene had an additional hydroxy group. As the signal of H-16 was a singlet, this group had to be placed at C-13. Consequently, periodate splitting led to the known ketone **9** [8, 9]. The ^{1}H NMR spectral data of **4**–**6** (Table 1) clearly showed that these diterpenes were monoacetates of **2** and **3**, respectively. Since H-14 and H-15 gave first-order signals the relative position of the acetoxy groups could be deduced easily from the chemical shifts. The ^{1}H NMR spectral data of **8**, molecular formula $C_{20}H_{34}O_2$, showed that the epoxide of **1** was present. Consequently, the signal of H-14 was a double doublet at δ 2.97, while the H-15

Table 1. ^{1}H NMR spectral data of compounds **12**, **13**, **17** and **18** ($CDCl_3$, 400 MHz, TMS as internal standard)

	17	**18**		**12**	**13**
H-3	5.45 *d*		H-2,6	7.69 *d*	7.46 *d*
H-4	6.26 *d*		H-3,5	6.88 *d*	6.90 *d*
H-5	6.95 *s*		H-7	6.84 *d*	7.64 *d*
H-8	6.32 *s*		H-8	5.82 *d*	6.29 *d*
H-9	6.14 *q*		OMe	3.73 *s*	3.79 *s*
H-10	1.45 *d*	1.44 *d*	H-1′	4.53 *br d*	4.53 *br d*
H-11	1.42 *s*		H-2′	5.48 *qqt*	5.48 *qqt*
H-12	1.41 *s*		H-4′	1.80 *br s*	1.80 *br s*
OMe	3.78 *s*		H-5′	1.74 *br s*	1.74 *br s*
OCOR	2.20 *d*	2.55 *tq*			
	2.11 *tq*	1.68 *ddq*			
	0.95 *d*	1.45 *m*			
	0.94 *d*	0.86 *t*			
		1.14 *d*			

J(Hz): compounds **12** and **13**: 2,3 = 8.5; 1′,2′ = 6.5; 7,8 = 12.5 (compound **13**: 7,8 = 16); compounds **17** and **18**: 3,4 = 10; 9,10 = 6.5; OiVal: 2′,3′ = 3′,4′ = 3′,5′ = 7; OMeBu: 2′,3′ = 2′,5′ = 3′,4′ = 7; $3'_1$, $3'_2$ = 14.

*Part 369 in the series "Naturally Occurring Terpene Derivatives". For Part 368 see Bohlmann, F., Jakupovic, J., Zdero, C., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20** (in press).

Table 2. ^{1}H NMR spectral data of compounds **2**–**8** ($CDCl_3$, 400 MHz, TMS as int. standard)

	2 ($CDCl_3$)	**2** (C_6D_6)	**3**	**4**	**5**	**6**	**7***	**8**
H-5	1.08 *dd*	1.04 *dd*	1.07 *dd*	1.08 *dd*	1.08 *dd*	1.08 *dd*	1.13 *dd*	1.07 *dd*
H-6α		1.69 *br d*						
H-6β		1.34 *dddd*						
H-7α	1.96 *ddd*	2.02 *ddd*	1.96 *ddd*	1.96 *ddd*	1.96 *ddd*	1.96 *ddd*	1.82 *br d*	1.95 *ddd*
H-7β	2.37 *ddd*	2.45 *ddd*	2.38 *ddd*	2.37 *ddd*	2.37 *ddd*	2.38 *ddd*	2.49 *ddd*	2.38 *ddd*
H-9		1.73 *m*			1.77 *m*			
H-13		1.58 *m*	—		—			
H-14	3.66 *m*	3.49 *m*	3.75 *m*	3.63 *ddd*	3.68 *brd*	4.74 *ddd*	5.13 *dd*	2.97 *dd*
H-15	3.46 *m*	3.34 *m*		4.19 *dd*	4.27 *dd*	3.74 *dd*	4.53 *dd*	3.80 *dd*
H-15′				4.00 *dd*	4.02 *dd*	3.67 *dd*	4.15 *dd*	3.60 *dd*
H-16	0.89 *d*	0.88 *d*	1.17 *s*	0.94 *d*	1.16 *s*	0.93 *d*	1.29 *s*	1.30 *s*
H-17	4.80 *br s*	5.03 *br s*	4.82 *br s*	4.81 *br s*	4.81 *br s*	4.80 *br s*	4.80 *br s*	4.83 *br s*
H-17′	4.49 *br s*	4.76 *br s*	4.53 *br s*	4.49 *br s*	4.51 *br s*	4.50 *br s*	4.48 *br s*	4.50 *br s*
H-18	0.86 *s*	0.92 *s*	0.86 *s*	0.86 *s*	0.86 *s*	0.86 *s*	0.92 *s*	0.86 *s*
H-19	0.79 *s*	0.87 *s*	0.79 *s*	0.79 *s*	0.79 *s*	0.79 *s*	0.85 *s*	0.79 *s*
H-20	0.66 *s*	0.81 *s*	0.68 *s*	0.66 *s*	0.68 *s*	0.66 *s*	0.74 *s*	0.67 *s*
OAc	—	—	—	2.10 *s*	2.10 *s*	2.10 *s*	2.18 *s*	—

J (Hz): 5,6α = 2.5; 5,6β = 12.5; 6α,6β = 13; 6α,7α = 2.5; 6α,7β = 12.5; 6β,7α = 12.5; 6β,7β = 4.5; 7α,7β = 12.5; 13,14 = 6.5; 13,16 = 6.5; 14,15 = 2.7; 14,15′ = 8; 15,15′ = 11 (compound **8**: 14,15 = 4; 14,15′ = 6.8; 15,15′ = 12).

*OCOEt 2.37 *q*, 1.18 *t* (*J* = 7.5).

protons showed double doublets at 3.80 and 3.60. Obviously all diterpenes were closely related, **1** being the precursor, which can be transformed to the epoxide **8**. Hydrolysis then would give **3**, while reduction produces **2**. As the optical rotation of the degradation product of **3** had the same sign as other simple labdanes, most probably all diterpenes belong to this series and, therefore, so also do the diterpenes from *Morithamnus* [8]. However, the stereochemistry at C-13 and C-14 was not determined.

The aerial parts of *H. congesta* DC. afforded farnesol, phytol, **2**, **3**, **14**, **15**, **16**, **20** and the diol **23**, whose structure could be deduced from the ^{1}H NMR and ^{13}C NMR spectral data (Table 3).

Compound **23** was transformed by traces of acid to the diene **24**, by protonation of the 4-hydroxy group followed by opening of the cyclopropane ring (see Scheme 1). The ^{13}C NMR spectral data of **23** showed the presence of a tricyclic system with two tertiary hydroxyls (80.2 *s* and 73.9 *s*). The high-field doublet at 20.2 probably was that of a cyclopropane carbon. The C-5 signal was deshielded by the neighbouring hydroxyl (30.7 *d*). Though the assignment of the other signals caused no problems, some signals may be interchangeable. The ^{1}H NMR spectral data of **23** also showed the presence of a cyclopropane derivative. Spin decoupling in different solvents allowed the assignment of all signals, though some were overlapping multiplets. Starting with the signal of H-5, which probably was that of a cyclopropane led to the sequence H-5–H-10. The couplings observed allowed the assignment of the stereochemistry at C-5, C-6, C-7 and C-10. Obviously the six-membered ring was in a chair conformation, since in a boat form $J_{6,7}$ should be larger. However, this excluded a 10β-methyl, as $J_{9\alpha,10}$ was 13 Hz. The stereochemistry at C-4 could not be assigned with certainty but as the $Eu(fod)_3$-induced shifts indicated that the hydrogens at C-5 and C-6 both were near the hydroxyl groups, the proposed configuration at C-4 was very likely. This was further supported by the shift of H-14. The ^{1}H NMR spectral data of **24** were also assigned by spin decoupling, though again several signals were overlapping multiplets. Compound **23** is a derivative of the rare cubebol, where the stereochemistry at C-4 is known [10]. The absolute configuration was not determined but the proposed structure is very likely, as most sesquiterpenes from the Compositae have a 7β-isopropyl group.

The compounds isolated from the *Hemizonia* species may be of chemotaxonomic interest. So far little is known about the constituents of the aerial parts of representatives of the subtribe Madiinae. Only the acetylenic compounds from the roots show relationships to the genera *Achyrachaena*, *Calycadenia*, *Layia* and *Madia* [2], which are all placed in this subtribe.

EXPERIMENTAL

The air-dried plant material, collected in California, summer 1980, was extrd with Et_2O–petrol (1:2) and the resulting extracts were sepd by CC on Si gel and further by repeated TLC on Si gel. Known compounds were identified by comparing their ^{1}H NMR spectra with those of authentic compounds.

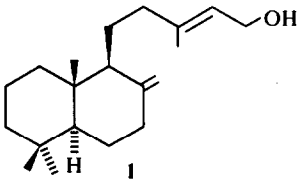
Hemizonia fitchii (*voucher RMK* 8426). The aerial parts (250 g) afforded 5 mg squalene, 10 mg **13** (Et_2O–petrol, 1:3), 10 mg **14**, 50 mg **15**, 100 mg **16**, 50 mg **17** as well as 8 mg **18** and **19** (*ca* 1:1) (Et_2O–petrol, 1:4).

Hemizonia lutescens (*voucher RMK* 8404). The aerial parts (170 g) afforded 7 mg *n*-hexadecanol-2-methylbutyrate, 5 mg **1**,

Table 3. ^{1}H NMR spectral data of compounds **23** and **24** (400 MHz, TMS as int. standard).

	23 $CDCl_3$	**23** C_6D_6	Δ*	**24** C_6D_6	**23** ^{13}C NMR ($CDCl_3$)	
H-2	2.45 *m*			2.0 *m*	C-1	33.4 *s*
H-3α	1.84 *ddd*			2.72 *m*‡	C-2	29.7 *t*
H-3β	2.45 *m*			2.08 *m*	C-3	35.7 *t*
H-5α	0.82 *d*	1.02 *d*	~1.9	6.06 *br s*	C-4	80.2 *s*
H-6β	1.07 *dd*	1.38 *dd*	2.02	2.93 *m*	C-5	30.7 *d*
H-7α	1.24 *m*†	1.42 *m*	2.99	1.46 *ddd*	C-6	20.2 *d*
H-8α	2.45 *m*			1.3 *m*	C-7	50.2 *d*
H-8β	0.79 *br ddd*	0.74 *br ddd*	1.50	1.62 *m*	C-8	26.2 *t*
H-9α	0.53 *br ddd*	0.51 *br ddd*	0.93	1.35 *m*	C-9	31.9 *t*
H-9β	1.61 *m*			2.0 *m*	C-10	39.5 *d*
H-10β	1.64 *m*			—	C-11	73.9 *s*
H-12	1.26 *s*	1.45 *s*	0.74	1.14 *s*	C-12	29.3 *q*
H-13	1.22 *s*	1.33 *s*	1.21	1.10 *s*	C-13	28.3 *q*
H-15	1.17 *s*	1.30 *s*	0.94	1.71 *br s*	C-14	18.8 *q*
H-14	0.92 *d*	0.95 *d*	0.64	1.69 *br s*	C-15	23.6 *q*

* Δ values after addition of $Eu(fod)_3$ at 57°.
† In MeOD 1.29 *ddd*.
‡ In $CDCl_3$ 2.69 *ddd*.
J (Hz): compound **23**: 2α,3α = 2β,3α = 9; 3α,3β = 7α,8β = 8α,8β = 8β,9α = 9α,10β = 13; 5,6 = 6,7 = 3; 10,14 = 6; compound **24**: 6β,7α = 8; 7α,8α = 3.3; 7α,8β = 11.



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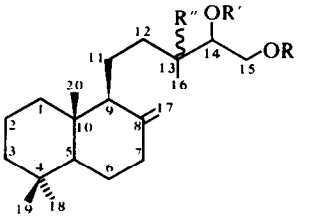
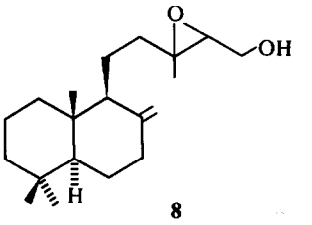


	2	**3**	**4**	**5**	**6**	**7**
R	H	H	Ac	Ac	H	Ac
R′	H	H	H	H	Ac	Prop
R″	H	OH	H	OH	H	OH



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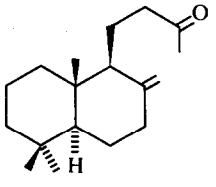

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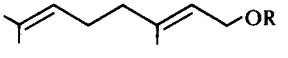
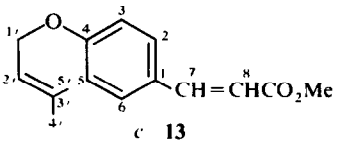
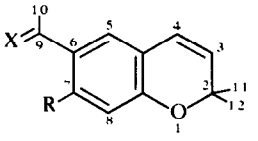


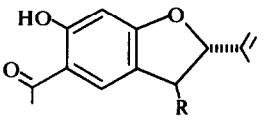
10 R = iBu
11 R = iVal
12 R = Mebu



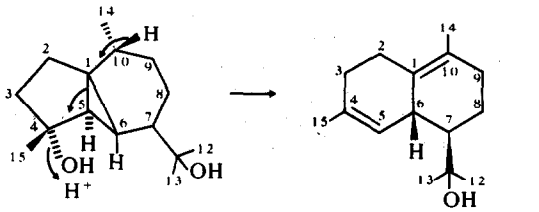
c **13**
t **14**



	15	**16**	**17**	**18**	**19**	**20**
R	OH	OMe	OMe	OMe	OMe	H
X	=O	=O	H,OH	H,OiVal	H,OMeBu	=O



21 R = H
22 R = OH



23 24*

Scheme 1.

* Same numbering as in **23**.

50 mg **2** (Et_2O), 20 mg **3** (Et_2O–MeOH, 20:1), 8 mg **4** (Et_2O–petrol, 3:1), 30 mg **5** (Et_2O), 5 mg **6** (Et_2O), 6 mg **7** (Et_2O–petrol, 3:1), 6 mg **8** (Et_2O–petrol, 3:1) and 10 mg **10**–**12** (not sepd, *ca* 1:1:1).

Hemizonia congesta (*voucher RMK* 8425). The aerial parts (120 g) afforded 8 mg farnesol, 30 mg phytol, 520 mg **2**, 280 mg **3**, 12 mg **14**, 12 mg **15**, 50 mg **16**, 15 mg **20** and 500 mg **23** (Et_2O), while the roots (40 g) gave traces of tridecapentaynene, 4 mg **2**, 5 mg **3**, 6 mg **10**, 3 mg **20**, 3 mg **21** and 4 mg **22**.

14,15-*Dihydroxy-labd*-8(17)-*ene* (**2**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3360 (OH), 3070, 1640, 895 (C=CH_2); MS *m/z* (rel. int.): 308.272 $[M]^+$ (9) ($C_{20}H_{36}O_2$), 293 $[M - Me]^+$ (10), 275 $[293 - H_2O]^+$ (7), 257 $[275 - H_2O]^+$ (6), 191 $[M - {}^{\cdot}CH_2CH_2CH(Me)CH(OH)CH_2OH]^+$ (27), 137 $[C_{10}H_{17}]$ (100), 95 $[C_7H_{11}]^+$ (87), 81 $[C_6H_9]^+$ (95).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+82 \quad +86 \quad +96 \quad +150} \quad (c = 0.71,\ CHCl_3).$$

13,14,15-*Trihydroxy-labd*-8(17)-*ene* (**3**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3420 (OH), 3090, 1650, 900 (C=CH_2); MS *m/z* (rel. int.): 324.266 $[M]^+$ (4) ($C_{20}H_{36}O_3$), 306 $[M - H_2O]^+$ (8), 291 $[306 - Me]^+$ (5), 288 $[306 - H_2O]^+$ (3), 273 $[291 - H_2O]^+$ (6), 263 $[M - {}^{\cdot}CH(OH)CH_2OH]^+$ (6), 245 $[263 - H_2O]^+$ (78), 137 (100), 95 (81), 81 (83).

Compound **3** (20 mg) in 2 ml MeOH was stirred with 50 mg H_5IO_6 for 1 hr. The reaction products were sepd by TLC (Et_2O–petrol, 1:10). The ketone **9** (14 mg) obtained was identical with that isolated from a *Morithamnus* species (IR and ^1H NMR spectrum).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+20.5 \quad +21.0 \quad +23.9 \quad +35.1} \quad (c = 0.56,\ CHCl_3).$$

15-Acetoxy-14-hydroxy-labd-8(17)-ene (**4**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740, 1235 (OAc), 3080, 1650, 900 (C=CH_2); MS *m/z* (rel. int.): 350.282 $[M]^+$ (14) ($C_{22}H_{38}O_3$), 335 $[M - Me]^+$ (14), 290 $[M - AcOH]^+$ (6), 277 $[M - CH_2OAc]^+$ (12), 191 $[C_{14}H_{23}]^+$ (17), 137 (100), 95 (71), 81 (79). $[\alpha]_D = +3$ ($c = 0.6$, $CHCl_3$).

15-*Acetoxy*-13,14-*dihydroxy-labd*-8-(17)-*ene* (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600, 3460 (OH), 1740, 1240 (OAc), 2080, 1640, 890 (C=CH_2); MS *m/z* (rel. int.): 366.277 $[M]^+$ (1) ($C_{22}H_{38}O_4$), 348 $[M - H_2O]^+$ (2), 333 $[348 - Me]^+$ (2), 315 $[333 - H_2O]$ (2), 306 $[M - AcOH]^+$ (1), 288 $[306 - H_2O]^+$ (3), 263 $[M - CH(OAc)CH_2OH]^+$ (5), 245 $[263 - H_2O]^+$ (52), 137 (100), 95 (61), 81 (68).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+10 \quad +11 \quad +11 \quad +17} \quad (c = 0.8,\ CHCl_3).$$

14-*Acetoxy*-15-*hydroxy-labd*-8(17)-*ene* (**6**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740, 1240 (OAc), 3080, 1640, 900 (C=CH_2); MS *m/z* (rel. int.): 350.282 $[M]^+$ (4) ($C_{22}H_{38}O_3$), 335 $[M - {}^{\cdot}Me]^+$ (3), 319 $[M - CH_2OH]^+$ (1), 307 $[335 - CO]$ (1), 290 $[M - AcOH]^+$ (7), 275 $[335 - AcOH]^+$ (6), 137 (100), 95 (70), 81 (67).

15-*Acetoxy*-13-*hydroxy*-14-*propionyloxy-labd*-8(17)-*ene* (**7**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1750 (CO_2R); MS *m/z* (rel. int.): 422.303 $[M]^+$ (2) ($C_{25}H_{42}O_5$), 404 $[M - H_2O]^+$ (7), 362 $[M - AcOH]^+$ (1), 344 $[404 - AcOH]^+$ (7), 270 $[344 - EtCO_2H]^+$ (21), 263 $[M - CH(O\,Prop)CH_2OAc]^+$ (6), 245 $[263 - H_2O]^+$ (21), 137 (100), 95 (57), 81 (71).

15-*Hydroxy*-14,15-*epoxylabd*-8(17)-*ene* (**8**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 3080, 1640, 890 (C=CH_2); MS *m/z* (rel. int.): 306.256 $[M]^+$ (2) ($C_{20}H_{34}O_2$), 291 $[M - Me]^+$ (2), 273 $[291 - H_2O]^+$ (2), 245 $[273 - CO]^+$ (27), 137 (100), 95 (67), 81 (80).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+7 \quad +8 \quad +9 \quad +17} \quad (c = 0.4,\ CHCl_3).$$

Methyl-cis-*coumarate* [*dimethyl allyl ether*] (**13**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (CO_2R), 1610 (C=C); MS *m/z* (rel. int.): 246.126 $[M]^+$ (5) ($C_{15}H_{18}O_3$), 178 $[M - isoprene]^+$ (100), 147 $[178 - OMe]^+$ (63), 119 [147–CO] (8), 69 $[Me_2C{=}CHCH_2]^+$ (49).

2,2-*Dimethyl*-7-*methoxy*-6-[1-*hydroxyethyl*]-*chromene isovalerate and* [2-*methyl butyrate*] (**18** and **19**). Colourless gum, which could not be sepd even by HPLC, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R), 1615 (C=C); MS *m/z* (rel. int.): 318.183 $[M]^+$ (1) ($C_{19}H_{26}O_4$), 233 $[M - RCO]^+$ (100), 201 $[233 - MeOH]^+$ (23).

11-*Hydroxy cubebol* (**23**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3340 (OH), 1465, 1450, 1400, 1383, 1372, 1315, 1300, 1230, 1202, 1173, 1140, 1100, 1085, 1055, 1040, 970, 950, 935, 920, 860; MS *m/z* (rel. int.): 238.193 $[M]^+$ (1) ($C_{15}H_{26}O_2$), 220 $[M - H_2O]^+$ (8), 205 $[220 - Me]^+$ (12), 187 $[205 - H_2O]^+$ (5), 162 $[220 - Me_2CO]^+$ (72), 147 $[162 - Me]^+$ (38), 59 $[MeC{=}O^+H]$ (100).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,nm}{-33.7 \quad -34.3 \quad -39.4 \quad -69.1 \quad -108.6} \quad (c = 0.35,\ CHCl_3).$$

Compound **2** (20 mg) in 1 ml $CHCl_3$ containing a trace of HCl on standing at room temp for 12 hr afforded 12 mg **24**, colourless oil, MS *m/z* (rel. int.): 202.172 $[M - H_2O]^+$ (29) ($C_{15}H_{22}$), 187 $[202 - Me]^+$ (43), 174 $[202 - C_2H_4]^+$ (22), 162 $[M - Me_2CO]^+$ (51), 159 $[174 - Me]^+$ (57), 134 $[M - CH_2{=}CHC(OH)Me_2$, RDA$]^+$ (30), 119 $[134 - Me]^+$ (40), 59 $[Me_2C{=}OH]$ (100).

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