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GUAIANOLIDES RELATED TO ARBORESCIN FROM *ARTEMISIA ADAMSII*

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Key Word Index—*Artemisia adamsii*, Compositae, sesquiterpene lactones, guaianolides

Abstract—The aerial parts of *Artemisia adamsii* afforded, among several known compounds, arborescin as the main constituent Furthermore, 11 new guaianolides, all related to arborescin, were present in minute quantities The structures were elucidated by spectroscopic methods and the biogenetic relationships are discussed briefly

INTRODUCTION

More than 100 species have been studied chemically from the large genus *Artemisia* (tribe Anthemideae) Although many different types of sesquiterpene lactones have been reported, eudesmanolides and guaianolides are the most common [1] We have now studied a Mongolian species, *Artemisia adamsii* Bess, which so far has only given phenolic compounds [2]

RESULTS AND DISCUSSION

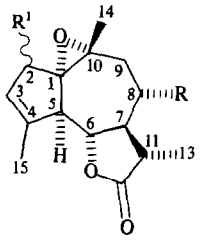
The aerial parts of *A adamsii* afforded camphor, bisabolol, 4β,10α-dihydroxyaromadendran [3], the coumarins scopoletin, *O*-methylscopoletin, di-*O*-methylfraxetin, 11β,13-dihydrohanphyllin [4], desacetoxymatricarin [5], 11β,13-dihydrokaunolide [6], arborescin **1** [7] and 11 further guaianolides which are all related to **1** Careful ^{1}H NMR investigations led to the structures **2**–**13** From comparison of the ^{1}H NMR spectrum of **2** (Table 1) with that of **1**, the presence of 8α-hydroxyarborescin could be deduced The additional low-field signal at δ3 85, which was coupled with H-7, showed two larger couplings indicating that the corresponding hydrogen was β-orientated As expected, the hydroxyl group caused small downfield shifts of the neighbouring protons

The lactone **5** obviously was a hydroperoxide, as could be deduced from the low-field signal at δ8 07 Accordingly, triphenylphosphine reduction afforded **5a** As followed from the ^{1}H NMR spectrum of **5a** (Table 1), the Δ^3-double bond of **1** was replaced by a Δ^2-double bond (δ5 63 *d* and 6 26 *d*, J = 6 Hz), and instead of an olefinic methyl signal, a singlet at δ1 55 was present In agreement with the molecular formula therefore an additional hydroxyl group, most likely at C-4, had to be assumed All other signals were close to those of **1**, which could all be clearly assigned by spin decoupling The only remaining question therefore was the configuration at C-4 This was established by NOE difference spectroscopy Clear effects were visible between H-15 and H-3 and H-6, between H-2 and H-14, between H-6 and H-11, and between OH and H-5 These results further allowed the assignment of the signals of the isolated double-bond protons (H-2 and H-3) and confirmed the configuration of the epoxide The ^{1}H NMR data of **6a** and **6b** (Table 1) were very close to those of **5a**, but the molecular formula was different Although no molecular ion was detectable, *m/z* 267 obviously was formed by loss of methyl As only the signals of H-2, H-3, H-5 and H-15 showed shift differences, most likely these lactones differed only in the stereochemistry at C-1 As in the ^{1}H NMR spectrum of **6a** the H-5 signal was at lower field compared with the shift in the spectrum of **6b**, the 1-hydroxyl group most likely was α-orientated in **6a** Therefore, both compounds were artefacts formed by hydrolysis of the epoxides during the lengthy separation

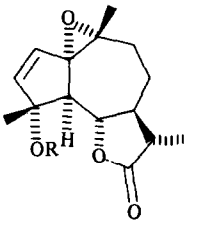
The ^{1}H NMR spectrum of **7** (Table 2) again indicated the presence of a hydroperoxide Triphenylphosphine reduction afforded a diol (**7a**), the ^{1}H NMR spectrum of which showed that the signals of H-5 and H-6 were shifted as in the case of **5** and **5a** Accordingly, the hydroperoxide was at C-4 and not at C-1, where the second hydroxyl group should be placed The presence of an *exo*-methylene group at C-10 could be deduced from the corresponding signals (δ4 97 and 4 77 *br s*) Spin decoupling allowed the assignment of all signals, thus leading to the proposed structure of **7** A clear NOE between H-15 and H-6 and H-3 indicated the presence of a 4β-methyl group

A low-field broad singlet at δ7 63, which disappeared on addition of triphenylphosphine, in the spectrum of **8** (Table 1) again indicated the presence of a hydroperoxide Irradiation of the broadened triplet at δ5 06 sharpened the H-6 doublet Accordingly, homoallylic coupling was present and the oxygen function was at C-3 However, the stereochemistry at this carbon could not be established as no clear NOEs were obtained and the couplings of H-3 did not allow a definite decision The ^{1}H NMR spectrum of **9** was identical with that of the product obtained by reduction of **8** All signals in the spectra of **8** and **9** could be assigned by spin decoupling. The couplings observed clearly indicated that the stereochemistries at C-6, C-7 and C-11 were the same as those in arborescin, which surely was the precursor of **8**

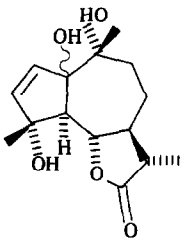
The spectrum of **10** (Table 1) showed that a keto group



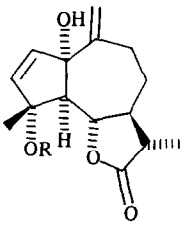
	1	2	3	4
R	H	OH	H	H
R^1	H	H	αOH	βOH



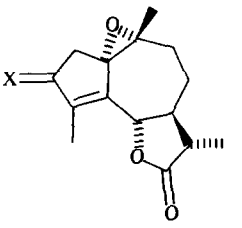
5 R=OH
5a R=H



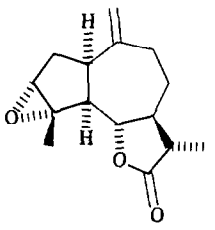
6a 1α OH
6b 1β OH



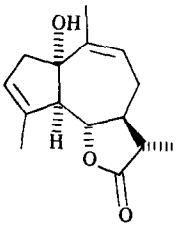
7 R=OH
7a R=H



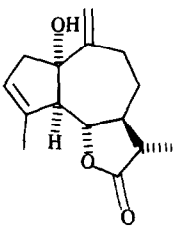
8 X=OOH,H
9 X=OH,H
10 X=O



11



12



13

was at C-3 Accordingly, now the H-2 signals were downfield-shifted doublets (δ2 48 and 2 57) All the other signals were close to those of **9** Therefore the configurations at C-6, C-7 and C-11 were obviously the same

The ^{1}H NMR spectra of **3** and **4** (Table 1) were similar but differed characteristically in a few signals Spin decoupling allowed the location of the functional groups and the presence of a hydrogen bond in **3** followed from the clear coupling $J_{2,OH}$ and from the IR spectrum Accordingly, **3** was the 2α-hydroxy derivative of **1** and **4** was the 2β-isomer

The ^{1}H NMR spectral data of **11** (Table 2) was very similar to that of estafiatin [8] However, the signals of the methylene protons were replaced by a methyl doublet Accordingly, most likely 11β,13-dihydroestafiatin was present The stereochemistry was established by NOE difference spectroscopy, which showed clear effects between H-15 and H-6 and between H-1 and H-9α

The ^{1}H NMR spectrum of **12** and **13** (Table 2) showed that these lactones differed only in the position of one of the double bonds While **13** obviously had a 10,14-double bond, spin decoupling showed that in the spectrum of **12** the broadened double-doublet at δ5 42 was due to H-9 and the methyl signal at δ1 90 was that of H-14 The sequences obtained by the decoupling experiments led to the proposed structures

The chemistry of this *Artemisia* species is characterized by the presence of 11β,13-dihydroguaianolides all closely related to dihydrokaunolide [6], the precursor of desacetoxymatricarin, and arborescin, the precursor of **2–10** The coumarins isolated have been reported in many *Artemisia* species The co-occurrence of coumarins and arborescin-derived lactones may be of chemotaxonomic importance, since this is observed only in a group of *Artemisia* species

Table 1 ^{1}H NMR spectral data of **1**–**6** and **8**–**10** (400 MHz, $CDCl_3$, TMS as internal standard)

	1	**2**	**3**	**4**	**5**	**5a**	**6a**	**6b**	**8**	**9**	**10**
H-2α	2 76 *br d*	2 76 *br d*	—	4 28 *br s*	5 71 *d*	5 63 *d*	5 87 *d*	5 77 *d*	2 26 *dd*	2 37 *dd*	2 57 *d*
H-2β	2 14 *br d*	2 13 *br d*	4 66 *br d*						2 01 *dd*	2 23 *dd*	2 48 *d*
H-3	5 55 *br s*	5 55 *br s*	5 69 *br s*	5 79 *br s*	6 36 *d*	6 26 *d*	6 08 *d*	6 03 *d*	5 06 *br t*	4 81 *br t*	—
H-5	2 82 *br d*	2 87 *br d*	2 67 *br d*	3 12 *br d*	2 89 *d*	2 52 *d*	2 61 *d*	2 37 *d*	—	—	—
H-6	4 00 *dd*	4 05 *dd*	3 72 *dd*	3 94 *dd*	4 04 *dd*	4 09 *dd*	4 63 *dd*	4 70 *dd*	4 99 *br d*	4 99 *br d*	5 27 *d*
H-7	1 32 *dddd*	1 63 *dddd*	1 72 *m*	1 36 *m*	1 46 *m*	1 43 *m*	2 13 *m*	2 11 *m*	1 75 *m*	1 66 *m*	1 77 *m*
H-8α	1 62 *dddd*	—	1 96 *m*	2 00 *m*	1 64 *dddd*	1 67 *dddd*	1 83 *m*	1 84 *m*	1 83 *m*	1 71 *m*	1 86 *m*
H-8β	1 45 *dddd*	3 85 *br dd*	1 38 *m*	1 48 *m*	1 43 *m*	1 43 *m*	1 66 *m*	1 60 *m*	1 40 *m*	1 40 *m*	1 42 *m*
H-9α	2 14 *ddd*	2 20 *dd*	2 35 *m*	2 30 *m*	2 18 *m*	2 19 *m*	2 36 *m*	2 31 *m*	1 85 *m*	1 83 *m*	2 15 *m*
H-9β	1 93 *ddd*	2 31 *dd*	1 50 *m*	1 63 *m*	2 00 *m*	1 98 *m*	1 55 *m*		1 65 *m*	1 58 *m*	1 48 *m*
H-11	2 20 *dq*	2 54 *dq*	2 23 *dq*	2 20 *dq*	2 21 *dq*	2 25 *dq*	2 22 *dq*	2 28 *dq*	2 29 *dq*	2 28 *dq*	2 39 *dq*
H-13	1 18 *d*	1 40 *d*	1 22 *d*	1 13 *d*	1 13 *d*	1 21 *d*	1 23 *d*	1 19 *d*	1 21 *d*	1 21 *d*	1 26 *d*
H-14	1 33 *s*	1 35 *s*	1 46 *s*	1 50 *s*	1 41 *s*	1 41 *s*	1 35 *s*	1 32 *s*	1 28 *s*	1 25 *s*	1 28 *s*
H-15	1 93 *tq*	1 94 *tq*	1 96 *br s*	2 02 *br s*	1 50 *s*	1 55 *s*	1 42 *s*	1 46 *s*	1 91 *br s*	1 89 *br s*	1 87 *br s*
OH(OOH)	—	1 55 *br s*	2 30 *d*	—	8 07 *s*	—	—	—	7 63 *br s*	—	—

J (Hz) 5, 6 = 11, 6, 7 = 10; 7, 8α = 2 5, 7, 8β = 12, 7, 11 = 12, 8α, 8β = 13, 8α, 9α = 8α, 9β = 3, 8β, 9α = 12, 8β, 9β = 2 5, 9α, 9β = 15, 11, 13 = 7, compounds **1** and **2** 2α, 2β = 18, 2α, 3 = 2β, 3 = 2α, 15 = 2β, 15 = 3, 15 ~ 1 5, compound **2**, 7, 8β = 8β, 9α = 10; 8β, 9β = 4, 9α, 9β = 14 5, compound **3** 2, OH = 8 5, compounds **5**, **5a**, **6a** and **6b** 2, 3 = 6, compounds **8** and **9** 2, 2′ = 18 5, 2, 3 = 6 5, compound **10** 2, 2′ = 18 5

Table 2 ^{1}H NMR spectral data of 7, 7a and 11–13 (400 MHz, $CDCl_3$, TMS as internal standard)

	7	7a	11	12	13
H-1	—	—	2 90 *br dd*	—	—
H-2	5 73 *d*	5 60 *d*	2 11 *m*	2 62 *br d*	2 95 *br d*
H-2′			1 79 *ddd*	2 53 *br d*	2 41 *br d*
H-3	6 05 *d*	5 92 *d*	3 37 *br s*	5 57 *br s*	5 52 *br s*
H-5	2 65 *d*	2 39 *d*	2 29 *dd*	2 58 *br d*	2 66 *br d*
H-6	4 05 *dd*	4 11 *dd*	3 97 *dd*	3 90 *dd*	3 81 *dd*
H-7	2 35 *dddd*	2 33 *dddd*	1 91 *dddd*	2 11 *dddd*	2 03 *dddd*
H-8α	2 17 *m*	2 25 *m*	2 11 *m*	2 01 *m*	2 16 *m*
H-8β	1 31 *m*	1 30 *m*	1 34 *dddd*	2 16 *m*	1 29 *dddd*
H-9α	2 82 *ddd*	2 82 *ddd*	2 29 *m*	5 47 *br d*	2 48 *ddd*
H-9β	2 29 *br d*	2 25 *m*	2 11 *m*		2 35 *m*
H-11	2 23 *dq*	2 24 *dq*	2 22 *dq*	2 22 *dq*	2 16 *dq*
H-13	1 26 *d*	1 25 *d*	1 21 *d*	1 24 *d*	1 22 *d*
H-14	4 97 *br s*	4 95 *br s*	4 90 *br s*	1 90 *br s*	5 12 *br s*
H-14′	4 77 *d*	4 74 *d*	4 83 *br s*		5 03 *br s*
H-15	1 30 *s*	1 32 *s*	1 58 *s*	1 95 *br s*	1 89 *br s*

J (Hz) Compounds 7 and **7a** 2, 3 = 6, 5, 6 = 11, 6, 7 = 10, 7, 8α = 2 5, 7, 8β = 10, 7, 11 = 12, 8α, 9α = 4, 8β, 9α = 9α, 9β = 13, 9β, 14′ = 1, 11, 13 = 7, compound **11** 1, 2 = 9, 1, 2′ = 10, 1, 5 = 8, 2, 2′ = 14, 2, 3 = 1, 5, 6 = 6, 7 = 10 5, 7, 8α = 5, 7, 8β = 12, 7, 11 = 12, 8α, 8β = 15, 8β, 9β = 5, 8β, 9α ~ 10, 11, 13 = 7, compound **13** 2, 2′ = 17, 5, 6 = 6, 7 = 10, 7, 8α = 4, 7, 8β = 11, 7, 11 = 12, 8α, 8β = 13, 8β, 9α = 12, 8β, 9β = 4, 11, 13 = 7, compound **12** 2, 2′ = 16, 5, 6 = 11, 6, 7 = 10, 7, 8α = 4, 7, 8β = 10, 7, 11 = 12, 8α, 9 = 2, 8β, 9 = 4, 11, 13 = 7

EXPERIMENTAL

The air-dried aerial parts (600 g, collected in the Mongolian Peoples Republic near Bulgam, July 1983, voucher 28, deposited at the Academy of Science, Institute of Biochemistry at Halle, G D R) was extracted with MeOH–Et_2O–petrol (1 1 1) The extract obtained was stored in Et_2O for several days at −25°, affording 500 mg crystalline arborescin **1**, mp 144° (lit [7] 145°) The remaining extract was worked up in the usual way [9] Fractions obtained by CC (SiO_2) were as follows 1 (petrol and Et_2O–petrol, 1 9), 2 (Et_2O–petrol, 1 3 and Et_2O–petrol, 1 1), 3 (Et_2O) and 4 (Et_2O–MeOH, 9 1) TLC (SiO_2) of fraction 1 (Et_2O–petrol, 1 9) afforded 110 mg camphor and 7 mg bisabolol Fraction 2 gave, on TLC (Et_2O–petrol, 1 3), 15 mg scopoletin, 7 mg *O*-methylscopoletin and 20 mg di-*O*-methyl fraxetin, while TLC of fraction 3 (Et_2O–petrol, 3 1) afforded 43 mg desacetoxymatricarin, 100 mg 11β,13-dihydrohanphyllin, 10 mg 11β,13-dihydrokauniolide, 150 mg **1**, 1 mg 4β,10α-dihydroxyaromadendrane Fraction 4 was separated again by CC into two fractions (4/1 and 4/2) TLC (C_6H_6–CH_2Cl_2–Et_2O, 1 1 1) of 4/1 gave four bands (4/1/1–4/1/4) HPLC (RP 8, MeOH–H_2O, 1 1, always *ca* 100 bar, flow rate 3 ml/min) of 4/1/1 gave 4 mg **8** (R_t 4 5 min) and 7 mg **5** (R_t 6 5 min) TLC of 4/1/2 (C_6H_6–CH_2Cl_2–Et_2O, 1 1 1) gave three bands (4/1/2/1–3) HPLC (RP 8, MeOH–H_2O, 3 2) of 4/1/2/1 gave 3 mg **11** (R_t 9 5 min), HPLC of 4/1/2/2 (MeOH–H_2O, 1 1) gave 1 mg **13** (R_t 12 8 min) and 2 mg **12** (R_t 14 3 min) and that of 4/1/2/3 gave 4 mg **7** (R_t 7 5 min) HPLC of 4/1/3 (MeOH–H_2O, 1 1) gave 7 mg **7** (R_t 7 5 min) and HPLC of 4/1/4 (MeOH–H_2O, 11 9) 1 mg **3** (R_t 10 4 min) TLC of 4/2 (C_6H_6–CH_2Cl_2–Et_2O, 1 1 1) gave two bands (4/2/1 and 2) HPLC of 4/2/1 (MeOH–H_2O, 11 9) afforded 2 mg **4** (R_t 9 7 min) and 1 mg **3** (R_t 10 4 min) HPLC of 4/2/2 (MeOH–H_2O, 11 9) gave a fraction, which after the addition of triphenylphosphine and TLC (C_6H_6–CH_2Cl_2–Et_2O, 1 1 1) and HPLC (see above) gave 6 mg **6a** (R_t 3 1 min), 9 mg **10** (R_t 6 5 min) and a mixture which after the addition of triphenylphosphine on repeated HPLC (MeOH–H_2O, 13 7) afforded 1 mg **6b** (R_t 3 4 min) and 1 mg **9** (R_t 3 7 min) Due to the minute amounts obtained, the lactones **2–13** could not be induced to crystallize They were homogeneous by TLC and HPLC in different solvent systems and showed no impurities in the 400 MHz ^{1}H NMR spectra

8α-Hydroxyarborescin (**2**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1780 (γ-lactone), MS *m/z* (rel int) 264 136 $[M]^+$ (16) (calc for $C_{15}H_{20}O_4$ 264 136), 231 $[M-H_2O-Me]^+$ (24), 203 $[231-CO]^+$ (32), 107 (86), 96 (100)

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+58 \quad +60 \quad +66 \quad +197} \text{ (CHCl}_3\text{, } c \text{ 0 2)}$$

2α-Hydroxyarborescin (**3**) Colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3500 (OH), 1770 (γ-lactone), MS *m/z* (rel int) 264 136 $[M]^+$ (2 5) (calc for $C_{15}H_{20}O_4$ 264 136), 246 $[M-H_2O]^+$ (3), 218 $[246-CO]^+$ (5), 203 $[218-Me]^+$ (3 5), 55 (100)

2β-Hydroxyarborescin (**4**) Colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3600 (OH), 1770 (γ-lactone), MS *m/z* (rel int) 264 136 $[M]^+$ (3) (calc for $C_{15}H_{20}O_4$ 264 136), 249 $[M-Me]^+$ (6), 246 $[M-H_2O]^+$ (10), 231 $[246-Me]^+$ (9), 55 (100)

4α-Hydroperoxy-2,3-dehydro-3,4-dihydroarborescin (**5**) Colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3520 (OH), 1770 (γ-lactone), MS (CI, isobutane) 281 $[M+1]^+$ (39), 263 $[281-H_2O]^+$ (83), 247 $[281-H_2O_2]^+$ (100),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-105 \quad -110 \quad -126 \quad -200} \text{ (CHCl}_3\text{, } c \text{ 0 5)}$$

To 5 mg **5** in 0 5 ml $CDCl_3$, 10 mg triphenylphosphine was added After 5 min the ^{1}H NMR spectrum had completely changed to that of **5a** (Table 1)

Products of hydrolysis of **5a** **6a** Colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3600 (OH), 1770 (γ-lactone), MS *m/z* (rel int)

267 $[M-Me]^+$ (6), 264 136 $[M-H_2O]^+$ (6) (calc for $C_{15}H_{20}O_4$ 264 136), 246 $[264-H_2O]^+$ (8), 231 $[246-Me]^+$ (8), 111 (71), 95 (100) **6b** Colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3600 (OH), 1770 (γ-lactone), MS *m/z* (rel int) 267 $[M-Me]^+$ (15), 264 136 $[M-H_2O]^+$ (10) (calc for $C_{15}H_{20}O_4$ 264 136), 246 $[264-H_2O]^+$ (12), 188 (68), 55 (100)

1α-*Hydroxy*-4α-*hydroperoxy*-11β*H*-*guaia*-2,10(14)-*dien*-6α,12-*olide* (**7**) Colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3500 (OH), 1770 (γ-lactone), MS *m/z* (rel int) 262 120 $[M-H_2O]^+$ (1 5) (calc for $C_{15}H_{18}O_4$ 262 129), 247 $[M-OOH]^+$ (4), 219 $[262-OOH]^+$ (3), 55 (100) Addition of triphenylphosphine gave **7a**, colourless oil, ^1H NMR see Table 1

3-*Hydroperoxy*-4,5-*dehydro*-3,4-*dihydroarborescin* (**8**) Colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3580 (OH), 1770 (γ-lactone), MS *m/z* (rel int) 262 120 $[M-H_2O]^+$ (2) (calc for $C_{15}H_{18}O_4$ 262 120), 246 $[M-H_2O_2]^+$ (3), 188 (8), 73 (100), MS (CI, isobutane) 281 $[M+1]^+$ (44), 263 $[281-H_2O]^+$ (100), 247 $[281-H_2O_2]^+$ (88)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-8 \quad -9 \quad -10 \quad -15} (CHCl_3,\ c\ 0\,3)$$

Addition of triphenylphosphine afforded an alcohol, identical to **9** (^1H NMR)

3-*Hydroxy*-4,5-*dehydro*-3,4-*dihydroarborescin* (**9**) Colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3600 (OH), 1770 (γ-lactone), MS *m/z* (rel int) 264 136 $[M]^+$ (4) (calc for $C_{15}H_{20}O_4$ 264 136), 246 $[M-H_2O]^+$ (8), 231 $[246-Me]^+$ (4), 218 $[246-CO]^+$ (9), 203 $[218-Me]^+$ (21), 188 (24), 55 (100)

3-*Oxo*-4,5-*dehydro*-3,4-*dihydroarborescin* (**10**) Colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1780 (γ-lactone), 1720 (C=O), MS *m/z* (rel int) 262 120 $[M]^+$ (1) (calc for $C_{15}H_{18}O_4$ 262 120), 234 $[M-CO]^+$ (10), 219 $[234-Me]^+$ (2), 165 (24), 55 (100)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-25 \quad -26 \quad -30 \quad -67} (CHCl_3,\ c\ 0\,6)$$

3α,4α-*Epoxy*-11β*H*-*guaia*-10(14)-*en*-6α,12-*olide* (**11**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1780 (γ-lactone), MS *m/z* (rel int) 248 141 $[M]^+$ (6) (calc for $C_{15}H_{20}O_3$ 248 141), 233 $[M-Me]^+$ (36), 97 (79), 55 (100)

1α-*Hydroxy*-11β,13-*dihydrokaumolide* (**12**) Colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3600 (OH), 1770 (γ-lactone), MS *m/z* (rel int) 248 141 $[M]^+$ (56) (calc for $C_{15}H_{20}O_3$ 248 141), 233 $[M-Me]^+$ (30), 230 $[M-H_2O]^+$ (22), 220 $[M-CO]^+$ (22), 215 $[230-Me]^+$ (18), 205 $[220-Me]^+$ (18), 150 (82), 55 (100)

1α-*Hydroxy*-5α,11β*H*-*guaia*-3,10(14)-*dien*-6α,12-*olide* (**13**) Colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3600 (OH), 1765 (γ-lactone), MS *m/z* (rel int) 248 141 $[M]^+$ (37) (calc for $C_{15}H_{20}O_3$ 248 141), 233 $[M-Me]^+$ (9), 230 $[248-H_2O]^+$ (8), 205 $[233-CO]^+$ (32), 175 (87), 55 (100)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+18 \quad +21 \quad +23 \quad +43} (CHCl_3,\ c\ 0\,1)$$

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