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CARYOPHYLLENE DERIVATIVES AND A HELIANGOLIDE FROM *LYCHNOPHORA* SPECIES*

FERDINAND BOHLMANN,† CHRISTA ZDERO,† HAROLD ROBINSON‡ and ROBERT M. KING‡

†Institute for Organic Chemistry, Technical University Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12, W. Germany; ‡Smithsonian Institution, Washington, DC 20560, U.S.A.

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Key Word Index—*Lychnophora salicifolia*; *L. hakeaefolia*; *L. phylicaefolia*; Compositae; new caryophyllenic acids; new heliangolide.

Abstract—The investigation of three *Lychnophora* species afforded three new caryophyllenic acids and a new heliangolide closely related to 15-desoxygoyazensiolide. All three species contain lupeol, lupeyl acetate and eremanthine. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

The genus *Lychnophora* seems to be restricted to Brazil and is placed in the tribe Vernonieae [1]. So far little is known about the chemistry of this genus. Recently, however, the isolation of lychnophorolic acid, a caryophyllene derivative, has been reported [2]. From two further species the presence of flavone glycosides is reported [3]. The investigation of all three further species afforded in all cases lupeol, its acetate and eremanthine. One species contains three further caryophyllene derivatives, while *L. hakeaefolia* yielded a new heliangolide, closely related to 15-desoxygoyazensolide.

RESULTS AND DISCUSSION

The aerial parts of *Lychnophora salicifolia* Mart. contained the pentaynene (**1**), the enetetraynene (**2**), caryophyllene (**3**), lupeyl acetate, costunolide (**4**) [4], eremanthine (**5**) [5], and several sesquiterpene acids. The main constituent was a crystalline acetate, molecular formula $C_{17}H_{24}O_2$, which afforded on reaction with diazomethane a methyl ester and a pyrazoline, formed by addition of diazomethane to a conjugated double bond, its presence already being indicated by the corresponding IR band and by a low field double doublet in the ^{1}H NMR spectrum (Table 1). The ^{1}H NMR spectrum of the pyrazoline was interpreted by extensive double resonance experiments (Table 1). Irradiation of the broadened threefold doublet at δ 2.55 collapsed the signals at 2.00, 1.62 and 1.75 to doublets and sharpened the signals of two methylene protons at 5.04 and 4.93, indicating that these signals may be assigned to 1-H, 9-H, 10-H and 12-H of a caryophyllene derivative. Irradiation of the 9-H signal collapsed the signal at 5.37 to a doublet indicating an 8α-position of the *O*-acetate function. Further decoupling experiments led to the assignments of all other signals (Table 1). However, the ^{1}H NMR spectra of the free acid and its methyl ester were more complex. Most signals were accompanied by smaller signals, which must be due to a second conformer. In C_6D_6 at 75° all these additional signals disappeared, but now most signals were heavily broadened, indicating a rapid equilibrium of different conformers (Table 1). However, all data were in good agreement with structures **8c** and **8d**, respectively. Compound **8c** is the acetate of lychnophorolic acid (**8a**) isolated before from *Lychnophora affinis* [2]. Compound **8a** was present also in the more polar fractions and was transformed to the methyl ester **8b** and, by heating with acetic anhydride, to a lactone, again establishing the configuration at C-8. The ^{1}H NMR spectral data (Table 1) indicated that the additional ring changed the conformation of the eleven-membered ring of **8a** as seen from the altered coupling constants. Inspection of models showed good agreement with the observed couplings. The angles between 9-H and 8-H, as well as between 8-H and 7β-H, are nearly 90°. The signals of the methylene protons (12-H) were collapsed to a singlet. Addition of Eu(fod)$_3$, however, led to a clear separation. The induced shifts again established the assignments of all signals (Table 1).

The less polar fraction contained two further acids with molecular formulae only differing by two hydrogens. The ^{1}H NMR spectra of the corresponding methyl esters showed that we were dealing with the esters **6b** and **7b**. The spectrum of **6b**, however, could only be interpreted in C_6D_6 at 77°, while at room temperature most signals were broad multiplets. Again double resonance experiments established the assignments though some signals were still overlapped. The second acid could be purified only as its methyl ester (**7b**). The ^{1}H NMR spectrum of this ester surprisingly was much more distinct than that of **6b** indicating a stable conformation (Table 1). Eu(fod)$_3$-induced shifts allowed further assignments of those signals which were overlapped in the original spectrum. The configuration at C-5 cannot be given with certainty. However, inspection of models indicated a β-position of the carboxyl group at C-6. Also the ^{13}C NMR spectral data of **3**, **7b** and **9** (Table 2) were in agreement with this

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*Part 283 in the series "Naturally Occurring Terpene Derivatives". For Part 282 see Bohlmann, F. and Fritz, U. (1980) *Phytochemistry* **19**, 2471.

Table 1. ^{1}H NMR spectral data of compounds **6a**, **6b**, **7b**, **8b**, **8c**, **8d**, **9** and **10** (270 MHz, TMS as internal standard)

	6a ($CDCl_3$)	**6b** (C_6D_6)	**7b** (C_6D_6)*	+ Eu(fod)$_3$	**8b** ($CDCl_3$)	**8c***	**8d** ($CDCl_3$)*	C_6D_6*	C_6D_6 75°	**9**	Δ†	**10**
1-H	2.65 *m*	2.67 *m*	2.35 *ddd*	2.58 *m*	2.48 *ddd* (*br*)	2.68 *ddd* (*br*)	2.63 *ddd* (*br*)	2.67 *ddd* (*br*)	2.63 *m*	2.56 *ddd* (*br*)	0.17	2.55 *ddd*(*br*)
3α-H	2.33 *m*	2.24 *m* 2.09 *m* 2.31 *m*				2.15–2.6 *m*	2.15–2.6 *m*	1.9–2.4 *m*	2.1 *m*	2.48 *ddd*	0.11	2.39 *m*
3β-H										1.99 *ddd*	0.11	1.90 *m*
4α-H	2.25 *m*									2.22 *dddd*	0.47	1.39 *dddd*
4β-H										2.36 *dddd*	0.13	1.75 *m*
5-H	6.22 *m*	5.88 *dd*	2.07 *dddd* 2.35 *m*	3.03 *m* 2.58 *m*	6.22 *dd*	6.34 (6.22) *dd*	6.21 (6.07) *dd*	5.87 (5.55) *dd*	5.95 *m*	6.19 *ddd*	0.15	2.34 *dddd*
6-H		—		3.56 *m*		—	—	—	—			
7α-H	2.25 *m*	2.31 *m*		2.80 *m*	2.1 *m*	2.10 *dd*	2.10 *dd*	2.05 *dd*	2.1 *m*	3.17 *dddd*	0.15	2.81 *d* (*br*)
7β-H		2.24 *m*		2.58 *m*	2.95 *dd*	3.13 (2.96) *dd*	3.07 (2.93) *dd*	3.36 (3.09) *dd*	3.32 *m*	2.78 *m*	0.22	3.36 *dd*
8α-H	1.45 *m*	1.59 *n*		1.83	—	—	—	—	—	—	—	—
8β-H		1.37 *m*		1.57 *m*	4.06 *m*	5.17 (5.00) *ddd*	5.15 (4.97) *ddd*	5.47 (5.10) *ddd*	5.40 *m*	4.40 *d* (*br*)	0.15	5.37 *dd*(*br*)
9-H		1.95 *m*	1.91 *ddd*	2.20 *m*	1.93 *dd*	1.83 (1.78) *ddd*	1.82 *dd*	1.84 *dd*	1.88 *m*	2.35 *d*	0.22	2.00 *dd*
10α-H	1.65 *m*	1.70 *dd*	1.66 *dd*	1.83 *m*	1.48 *dd*	1.53 *dd*	1.51 *dd*	1.51 *dd*	1.56 *dd*	1.43 *dd*	0.08	1.62 *dd*
10β-H		1.75 *dd*	1.76 *dd*		1.58 *dd*	1.64 *dd*	1.62 *dd*	1.60 *dd*	1.66 *m*	1.86 *dd*	−0.03	1.75 *dd*
12-H	5.03 *d*	5.06 *d*	4.97 (5.04) *s* (*br*)	5.01 *s* (*br*)	4.97 *s* (*br*)	5.01 (5.11) *s*(*br*)	4.94 (5.03) *s* (*br*)	4.98 (5.08) *s* (*br*)	5.02 *s* (*br*)	5.16 *s*	0.12	5.04 *s* (*br*)
12′-H	4.88 *d*	4.85 *d*	4.88 (4.81) *s* (*br*)	4.93 *s* (*br*)	4.82 *s* (*br*)	4.89 (4.97) *s* (*br*)	4.79 (4.88) *s* (*br*)	4.76 (4.87) *s* (*br*)	4.82 *s* (*br*)		0.16	4.93 *s* (*br*)
13-H	1.02 *s*	1.04 *s*	0.94 (1.01) *s*	0.98 *s*	1.22 *s*	1.13 (1.14) *s*	1.13 (1.14) *s*	1.17 (1.19) *s*	1.17 *s*	1.14 *s*	0.14	1.07 *s*
14-H	1.00 *s*	0.98 *s*	0.90 (0.97) *s*		1.14 *s*	1.05 (1.00) *s*	1.04 (1.01) *s*	1.04 (1.06) *s*	1.05 *s*	1.09 *s*	0.17	0.99 *s*
OMe	—	3.49 *s*	3.44 *s*	4.54 *s*	3.70 *s*	—	3.71 (3.70) *s*	3.46 (3.40) *s*	3.47 *s*	—	—	3.67 *s*
OAc	—	—	—	—		2.05 (2.06) *s*	2.05 (2.06) *s*	1.74 (1.73) *s*	1.77 *s*	—	—	1.88 *s*
16-H	—	—	—	—	—	—	—		—	—		4.94 *dd*
16′-H	—	—	—	—	—	—	—	—	—			3.97 *dd*

*In parentheses are signals of the second conformer.

†Δ-Values after addition of Eu(fod)$_3$.

J(Hz): **6a**/**b**: 1, 9 = 10.5; 1, 10α = 10; 1, 10β = 10; 3α, 4α = 4; 4α, 5 = 11; 4β, 5 = 6; 4α, 4β = 12; 7α, 8β = 10; 7β, 8β = 6; 7α, 7β = 12; 8β, 9 = 10; 10α, 10β = 10.5; **7b**: 5, 6 = 6, 7β = 7; 6, 7α = 2.5; 5, 5′ = 14; 4, 5 – 7; **9**: 1, 10β = 8; 3α, 3β = 13; 3α, 4α = 4; 3α, 4β = 12; 3β, 4β = 4; 4β, 7α ~ 1.5; 5, 7α = 1.5; 7α, 7β = 12.5; 7α, 8 = 6.5; **10**: 1, 10α = 8.5; 5, 16 = 8; 5, 16′ = 11; 16, 16′ = 16.5

Table 2. ^{13}C NMR spectral signals of compounds **3**, **7b** and **9** (CDCl$_3$)

	3*	**7b**	**9**
C-1	48.2 *d*	43.7 *d*	44.2 *d*
C-2	154.3 *s*	152.9 *s*	150.7 *s*
C-3	40.4 *t*	37.8 *t*	38.9 *t*†
C-4	29.4 *t*	27.3 *t*	38.0 *t*†
C-5	124.5 *d*	31.0 *t*	143.3 *d*
C-6	135.0 *s*	45.6 *d*	129.2 *s*
C-7	34.8 *t*	34.9 *t*	41.3 *t*
C-8	28.4 *t*	28.3 *t*	75.7 *d*
C-9	53.6 *d*	54.9 *d*	59.2 *d*
C-10	30.1 *t*	29.4 *t*	31.0 *t*
C-11	40.0 *s*	33.5 *s*	34.0 *s*
C-12	111.8 *t*	110.1 *t*	116.2 *t*
C-13	30.1 *q*	29.9 *q*	30.0 *q*
C-14	22.6 *q*	22.0 *q*	21.7 *q*
C-15	16.3 *q*	176.9 *s*	170.6 *s*
OMe	—	51.3 *q*	—

*Assignments supported by measuring the corresponding epoxide and by addition of Yb(fod)$_3$.

†May be interchangeable.

assumption. The chemical shift of C-1 in the spectra of **7b** and **9** was at higher field as in the spectrum of caryophyllene (**3**), indicating a shielding effect of the C-6 carbonyl group.

The roots of *L. phylicaefolia* DC only contained **1**, polyisoprene, eremanthine (**5**), lupeol and lupeyl acetate, while the aerial parts afforded **3**, **5**, lupeol, lupeyl acetate and an isomer of lupeol (**11**). Furthermore, sakuranetin (**13**) [6] and persicogenin (**14**) [7] were present.

The aerial parts of *L. hakeaefolia* Mart. also contained lupeyl acetate and lupeol. The polar fractions, however, afforded a sesquiterpene lactone with the molecular formula C$_{20}$H$_{22}$O$_6$. ^{1}H NMR investigations led to structure **12**, closely related to 15-desoxygoyazensolide, isolated from a *Vanillosmopsis* species [8]. The presence of an angelate followed from the characteristic ^{1}H NMR spectral signals (6.09 *qq*, $J = 7$, 1.5 Hz; 1.90 *dq*, $J = 7$, 1.5 Hz and 1.80 *dq*, $J = 1.5$, 1.5 Hz), while the sequence 5-H through 9-H was established by double resonance studies. The 7-H was located by irradiation of the fourfold doublet at 3.72, as the 13-H-doublets at 6.23 and 5.44 collapsed to singlets. Furthermore, the signals at 5.30 and 4.54 were simplified to a doublet quartet and to a double doublet, respectively. These two signals therefore must be assigned to 6- and 8-H. Irradiation at 4.54 further collapsed the double doublets at 2.49 and 2.32 (9α- and 9β-H) to doublets, which apparently were adjacent to a quaternary carbon. The olefinic methyl (2.09 *dd*) was coupled to 5-H (6.02 *dq*) and 6-H (5.30 *ddq*). The presence of a furanone moiety was indicated by the typical low field singlet at 5.72 and IR bands at 1700 and 1590 cm^{-1}, while the stereochemistry at C-10 followed from the downfield shifts of the signals of 7-H and 9α-H. The stereochemistry at C-6 through C-8 finally was established by the coupling constants $J_{5,6}$, $J_{6,7}$ and $J_{6,8}$ (Table 3). Inspection of models indicated that the corresponding angles were in good agreement with the observed coupling constants, though they were slightly different from those reported for 15-desoxygoyazensolide [8]. In particular $J_{7,8}$ is reported to have the value 2.5 Hz. The similarity of all other signals excluded a *cis*-annelated lactone ring, especially as the CD curve was similar to the ORD maxima of 15-desoxygoyazensolide. The presence of an 8,12-lactone clearly followed from the chemical shift of 8-H, which would not be in agreement with a 6,12-lactone, where the coupling constants $J_{7,13}$ are typically smaller [9]. We have named the new lactone lychnopholide. The roots afforded **1**, polyisoprene, lupeol and its acetate and again eremanthine (**5**).

Table 3. ^{1}H NMR spectral data of compound **12** (270 MHz, CDCl$_3$)

2-H	5.72 *s*	13-H	6.23 *d*
5-H	6.02 *dq*	13-H	5.44 *d*
6-H	5.30 *ddq*	14-H	1.54 *s*
7-H	3.72 *dddd*	15-H	2.09 *dd*
8-H	4.54 *ddd*	3′-H	6.09 *qq*
9α-H	2.49 *dd*	4′-H	1.90 *dq*
9β-H	2.32 *dd*	5′-H	1.80 *dq*

J(Hz): 5,6 = 3; 5,15 = 1.7; 6,7 = 5; 6,15 = 2.7; 7,8 = 2.5; 7,13 = 3.2; 7,13 = 2.8; 8,9α = 12; 8,9β = 2; 9α,9β = 14; 3′,4′ = 7; 3′,5′ = 4′,5′ = 1.5.

The compounds isolated from *Lychnophora* species indicate a close relationship to other genera of the tribe Vernonieae. In particular, the occurrence of eremanthine (**5**) and the new lactone **12** shows that *Lychnophora* may be closely related to *Eremanthus* [10], *Centratherum* [11], and *Vanillosmopsis* [8], where similar heliangolides are present. However, more species have to be investigated and the importance of the caryophyllene derivatives has to be clarified. Triterpenes of the lupane type and eremanthine, are also present in *Vernonia* species [12], a genus which is not very homogenous.

EXPERIMENTAL

^{1}H NMR: 270 MHz, TMS as internal standard; MS: 70 eV, direct inlet; optical rotation: CHCl$_3$. The air-dried plant material, collected in north-eastern Brazil, was chopped and extracted with Et$_2$O–petrol (1:2). The resulting extracts were separated first by CC (Si gel, grade II) and then by TLC (Si gel GF 254). Known compounds were identified by comparison of the IR and NMR spectra with those of authentic material.

Lychnophora salicifolia (*voucher RMK* 8148). The roots (100 g) afforded 0.5 mg **1**, 0.1 mg **2**, 20 mg lupeyl acetate and 5 mg **5**. The aerial parts (1 kg) gave 0.1 mg **1**, 0.2 mg **2**, 15 mg **3**, 5 mg **4**, 20 mg **5**, 100 mg **6a** (Et$_2$O–petrol, 1:3), 120 mg **7a** (Et$_2$O–petrol, 1:3), 30 mg lupeol, 200 mg **8c** (Et$_2$O–petrol, 1:1) and 50 mg **8a** [2].

L. hakeaefolia (*voucher RMK* 8135). The roots (200 g) afforded 0.1 mg **1**, 20 mg polyisoprene, 40 mg lupeyl acetate, 20 mg lupeol, 5 mg **4** and 20 mg **5**. The aerial parts (330 g) gave 20 mg lupeyl acetate, 120 mg lupeol and 15 mg **12** (Et$_2$O–petrol, 1:1).

L. phylicaefolia (*voucher RMK* 8054). The roots (200 g) afforded 0.2 mg **1**, 10 mg **5**, 50 mg lupeol, 100 mg lupeyl acetate and 200 mg polyisoprene. The aerial parts (1.2 kg) gave 5 mg **3**, 20 mg **5**, 500 mg lupeol, 200 mg lupeyl acetate, 100 mg **11**, 5 mg **13** and 5 mg **14**.

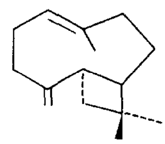
Caryophyllen-15-oic acid (**6a**). Colourless gum IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400, 2500, 1690 (C=CCO$_2$H); C=CH$_2$ 1640, 900; MS *m/e* (rel.

$Me[C\equiv C]_5CH=CH_2$

1

$MeCH=CH[C\equiv C]_4CH=CH_2$

2



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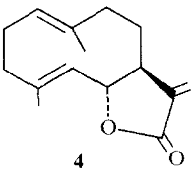

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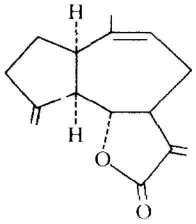

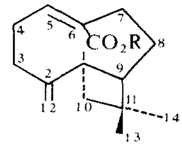

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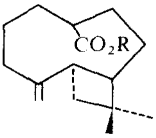
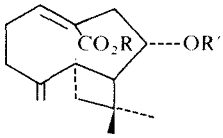
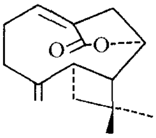
6b R = Me



7a R = H
7b R = Me



8a R = R′ = H
8b R = Me, R′ = H
8c R = H, R′ = Ac
8d R = Me, R′ = Ac



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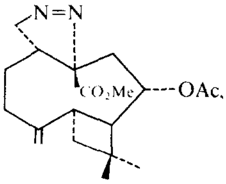

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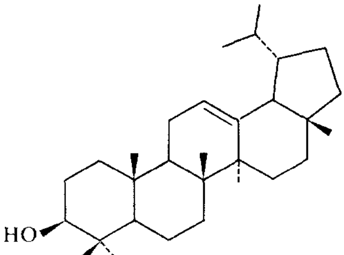

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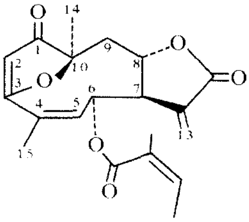

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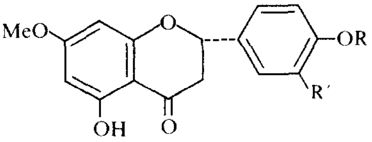

13 R = R′ = H
14 R = Me, R′ = OH

int.): 234.162 (M^+, 3) ($C_{15}H_{22}O_2$), 219 (M − Me, 8); 69 ($C_5H_9^+$, 100). To 35 mg **6b** in 3 ml Et_2O excess CH_2N_2 in Et_2O was added. After 3 min the soln was evapd and the residue was purified by TLC (Et_2O–petrol, 1:10), yielding 35 mg **6b**, colourless oil; IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 1717, 1620 (C=CCO$_2$R); 3080, 1640, 895 (C=CH$_2$); MS *m/e* (rel. int.): 248.197 (M^+, 3) ($C_{16}H_{24}O_2$); 233 (M − Me, 7), 216 (M − MeOH, 4), 201 (216 − Me, 5), 179 (233 − $C_4H_6CH_2$, 33), 147 (179 − MeOH, 57), 69 ($C_5H_9^+$, 100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546\,\text{nm}}{+2.75 \quad +2.8 \quad +2.9}\,(c = 3.2).$$

5,6-*Dihydrocaryophyllen*-15-*oic acid* (**7a**). Purified as its methyl ester **7b**, colourless oil; IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 1735 (CO$_2$R); 3080, 1640, 895 (C=CH$_2$); MS: *m/e* (rel. int.): 250.193 (M^+, 15) ($C_{16}H_{26}O_2$), 235 (M − Me, 20), 218 (M − MeOH, 10), 191 (M − CO_2Me, 29), 190 (M − HCO_2Me, 21), 175 (190 − Me, 17), 147 (191 − C_4H_6, 39), 69 ($C_5H_9^+$, 100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-4.4 \quad -4.6 \quad -5.0 \quad -6.9}\,(c = 10.4).$$

8*β*-*Acetoxy-caryophyllen*-15-*oic acid* (**8c**). Colourless crystals, mp 170° (Et_2O); IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 3300–2600, 1690 (CO$_2$H); 1640, 905 (C=CH$_2$); MS *m/e* (rel. int.): 292.167 (M^+, 0.2) ($C_{17}H_{24}O_4$), 250 (M − ketene, 3), 232 (M − HOAc, 12), 217 (232 − Me, 6), 43 ($MeCO^+$, 100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+40.5 \quad +42.0 \quad +48.0 \quad +84.6}\,(c = 3.2).$$

To 50 mg **8c** in 3 ml Et_2O excess CH_2N_2 was added. After 10 min the soln was evapd. The residue afforded 20 mg **8d**, colourless gum; MS *m/e* (rel. int.): 306.183 (M^+, 7) ($C_{18}H_{26}O_4$), 275 (M − OMe, 5), 246 (M − HOAc, 23), 85 ($C_4H_5O_2$, 100). The more polar fraction afforded 30 mg **10**, colourless crystals, mp 86° (Et_2O–petrol); IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 1740, 1240 (OAc), 1715 (CO$_2$R), 2080, 1640, 900 (C=CH$_2$); MS *m/e* (rel. int.): 320.199 (M − N_2, 1), ($C_{19}H_{28}O_4$), 289 (320 − OMe, 2), 260 (320 − HOAc, 10), 43 ($MeCO^+$, 100).

Lychnophorolic acid methyl ester (**8b**). Obtained after esterification of **8a** with CH_2N_2, colourless oil; ^{1}H NMR spectrum, see Table 1. 30 mg **8a** were heated with 2 ml Ac_2O at 70°. TLC afforded 25 mg **9**, colourless crystals, mp 126° (Et_2O), IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 1770 (*γ*-lactone), 3075, 1640, 905 (C=CH$_2$); MS *m/e* (rel. int.): 232.146 (M^+, 12) ($C_{15}H_{20}O_2$), 217 (M − Me, 3), 199 (217 − H_2O, 3), 131 ($C_{10}H_{11}^+$, 100), 117 ($C_9H_9^+$, 33), 91 ($C_7H_7^+$, 45).

Lychnopholide (**12**). Colourless crystals from Et_2O–petrol, mp 128°, IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 1765 (lactone), 1710, 1655 (C=CCO$_2$R); 1700, 1590 (furanone); MS *m/e* (rel. int.): 358.142 (M^+, 55) ($C_{20}H_{22}O_6$), 275 (M − COC_4H_7, 22), 258 (M − $C_4H_7CO_2H$, 3), 83 ($C_4H_7CO^+$, 100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,\text{nm}}{-56.9 \quad -57.3 \quad -56.5 \quad +32.7 \quad +970.4}\,(c = 0.26).$$

CD (MeCN): $\Delta\varepsilon_{313}$ + 4.64, $\Delta\varepsilon_{304}$ + 4.32, $\Delta\varepsilon_{257}$ − 1.31, $\Delta\varepsilon_{235}$ + 0.41, $\Delta\varepsilon_{226}$ − 3.15.

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