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EUDESMANOLIDES AND OTHER CONSTITUENTS FROM *CRATYSTYLIS CONOCEPHALA*

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Key Word Index—*Cratystylis conocephala*; Compositae; sesquiterpenes; eudesmanolides; costic acid derivatives; 2α-acetoxygermacra-1(10)*E*,4*E*,11(13)-trien-12-oic acid; thiophene acetylenes.

Abstract—A representative of the small Australian genus *Cratystylis* afforded in addition to widespread compounds six previously unreported eudesmanolides, four derivatives of costic acid, a new germacratriene acid and three thiophene acetylenes. The structures were elucidated by high field ^{1}H NMR spectroscopy. The chemotaxonomy is discussed briefly.

INTRODUCTION

The small Australian genus *Cratystylis* (Compositae, tribe Inuleae, subtribe Inulinae) belongs to the more deviating genera whose stigmatic rows fuse near the base and cover nearly the entire surface [1]. It looks extremely isolated and its relationship still is not settled. Nothing is known on the chemistry of this genus. We therefore have investigated *Cratystylis conocephala* (F. Muell) S. Moore. The results are discussed in this paper.

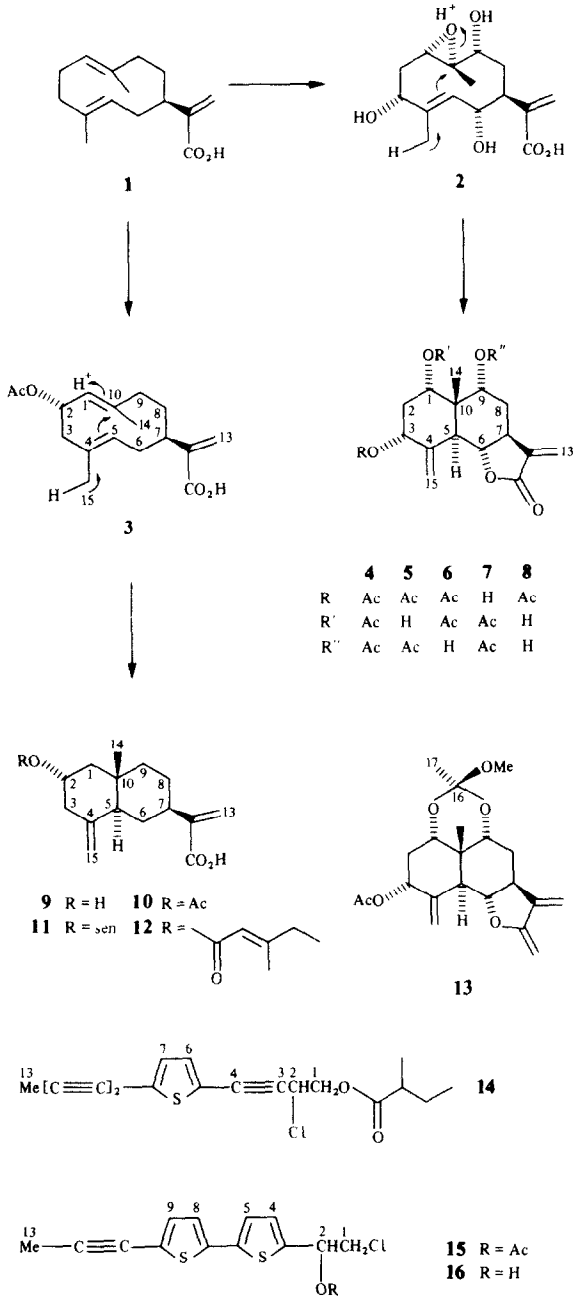
RESULTS AND DISCUSSION

The extract of the aerial parts of the plant gave in addition to widespread compounds (see Experimental) two main compounds in high concentration, 2α-hydroxycostic acid (**9**) and the eudesmanolide **4** which we have named cratystyolide triacetate. Furthermore the related lactones **5**–**8** and **13** as well as the costic acid derivatives **10**–**12** were present. The roots gave thymohydroquinone dimethyl ether, tridecapentaynene, the monothiophene derivative **14** as well as the dithiophenes **15** and **16**. The latter has been isolated previously from an *Epaltes* species [2], and accordingly, the ^{1}H NMR spectrum of **15** was very similar (see Experimental to that reported). Due to the exchange of an acetoxy for a hydroxy group the H-2 signal was shifted downfield. The ^{1}H NMR spectrum of **14** (Experimental) was close to that of the corresponding isovalerate which was isolated from a *Pluchea* species [3]. Evidence for the presence of a 2-methylbutyrate was provided by the typical ^{1}H NMR signals.

The main constituent **4** gave no molecular ion in its mass spectrum. However, the ^{1}H NMR spectrum (Table 1) clearly indicated the presence of a triacetate and the highest mass ion (*m/z* 346; $C_{19}H_{22}O_6$) in the mass spectrum was obviously the result of acetic elimination. After addition of C_6D_6 all signals in the ^{1}H NMR spectrum of **4** could be assigned by spin decoupling. The low field signal at δ5.29 showed a small coupling with the exomethylene signals (H-15) and with a pair of doublet triplets at δ1.82 and 1.70 which also were coupled with a proton which gave rise to a triplet at δ4.74. Hence, the locations of acetoxy groups at C-1 and C-3 were established. Diagnostic for the stereochemistry were the magnitude of the coupling constants of H-1 and H-3. Irradiation at the frequency of H-7 (δ2.84) changed the signals of H-6 (δ3.61, *t*), H-8α (1.82, *m*), H-8β (1.54, *br t*), H-13 (5.95, *d*) and H-13′ (5.16, *d*). As irradiation at δ1.54 collapsed the triplet at δ4.86 to a doublet a third acetoxy group was located at C-9. Again the coupling constants required an α-orientated oxygen function. Finally the large couplings of H-6 indicated the presence of a derivative of β-cyclocostunolide.

The ^{1}H NMR spectrum of the inseparable mixture of **5** and **6** (Table 1) showed that we were dealing with two isomeric desacetyl derivatives of compound **4**. All signals could be assigned due to small differences in concentration and by spin decoupling. The resulting sequences required the presence of a 1- and 9-desacetyl derivative of **4**. Furthermore the 9α-acetoxy group in **5** caused a clear shielding effect on H-7. Reaction of the mixture in methanol with *p*-toluenesulphonic acid at room temperature gave the *ortho* ester **13** which also was isolated from the extract. The structure again could be deduced from its ^{1}H NMR spectrum (Table 1) which differed from that of **4** mainly by the upfield shift of the H-1 and H-9 signals and by the additional methyl singlets at δ3.28 and 1.51. The chemical shift of the latter signal indicated that the corresponding methyl must be placed at a carbon with oxygen functions which was in agreement with the mass spectral data. Therefore an *ortho* ester structure was very likely. This was confirmed by the ^{13}C NMR spectrum (Experimental) and by NOE difference spectroscopy which also clarified the configuration at C-16. NOEs were observed between methoxy and H-1 (3%), between H-14, H-1 (6%), H-9 (6%), H-6 (8%), H-2β (5%) and H-8β (4%) while H-17 only gave a NOE with the methoxy methyl (8%) and not with H-1, H-9 and H-14. Small differences in the coupling constants indicated small changes in conformations. Most likely in compounds **4**–**8** the accumulation of 1,3-diaxial substituents led to small deviation of a chair conformation.

The ^{1}H NMR spectra of **7** and **8** (Table 1) again indicated that desacetyl derivatives of **4** were present. The



3a and **9a**–**12a** are the corresponding methyl esters

positions of the free hydroxy groups followed from the chemical shift differences and by spin decoupling. Thus in the spectrum of **7** the H-3 signal was shifted upfield while in that of **8** two signals (H-1 and H-9) were shifted upfield. In agreement with the remaining data therefore **7** was a 1-*O*-9-*O*-diacetate and **8** a 3-*O*-monoacetate.

The ^{1}H NMR spectra of **9** and **9a** (Table 2) were in part very close to those of costic acid and its methyl ester. Spin decoupling indicated that an α-hydroxy group was at C-2. Compound **9** has been isolated from a *Sphaeranthus* species [4].

The spectrum of **10a** (Table 2) differed from that of **9a** mainly by the downfield shift of the threefold doublet (H-2) and the presence of an acetoxy singlet. Thus **10a** was the acetate of **9a**. Accordingly, acetylation of **9a** afforded an acetate which was identical with **10a**.

The ^{1}H NMR spectrum of **11a** (Table 2) clearly showed that the corresponding senecioate was present while that of **12a** (Table 2) showed the typical signals of a 4-methylsenecioate. The configuration of the ester double bond followed from the chemical shift of the olefinic methyl (δ2.16, *d*).

Most of the compounds of this species are closely related. The common precursor for the sesquiterpenes is the hitherto unknown, germacrane derivative **1** which by allylic oxidation can be transformed to the desacetyl derivative of compound **3**. Proton attack then would lead to compound **9**. Similar allylic oxidation and epoxidation of **1** would lead to **2**, which by proton attack would give the desacetyl derivative of **4** (cratystyolide). The high concentration of **9** may be an indication that the turnover of germacratriene acids is very fast. This may be the reason that such acids are extremely rare. So far only 8β-acyloxy derivatives were reported from a *Pegolettia* species [5] which is placed in the same subtribe. The absence of eudesmanolides derived from **9** in the *Cratystylis* species is remarkable.

The overall picture of the chemistry of this genus indicated relationships to *Sphaeranthus* by the cooccurrence of thiophene acetylenes [6] and 2α-hydroxycostic acid. However, similar thiophenes and eudesmane derivatives are also common in *Pluchea* [3] and *Epaltes* species [2] which are less closely related to *Cratystylis*. The main genera of the subtribe like *Inula*, however, show a different chemistry. Clearly further related genera have to be investigated to obtain more information on the chemotaxonomy of this difficult subtribe.

EXPERIMENTAL

The air-dried plant material (voucher RMK 9621, collected in east Australia, voucher deposited in the U.S. National Herbarium) was extracted with MeOH–Et_2O–petrol (1:1:1). The extract of the aerial parts (from 900 g) gave by standing in Et_2O 1.4 g crystals of **4**. The remaining mixture was first separated by CC (silica gel) into four fractions; 1: petrol and petrol–Et_2O (9:1); Fr. 2: petrol–Et_2O 3:1, 1:1 and 1:3); Fr. 3: Et_2O and Fr. 4: Et_2O–MeOH (9:1). TLC of Fr. 1 (Et_2O–petrol, 1:9) gave 20 mg thymohydroquinone dimethyl ether, 10 mg lupeyl acetate and 10 mg taraxasteryl acetate. Fraction 2 was a mixture of acids which were separated as methyl esters by TLC (Et_2O–petrol, 1:3) affording each 20 mg sitosterol and stigmasterol and two mixtures (Fr. 2/1 and Fr. 2/2). HPLC of Fr. 2/1 (MeOH–H_2O, 17:3, always RP 8, *ca* 100 bar) gave 150 mg **11a** (R_t 7.7 min) and 50 mg **12a** (R_t 10.0 min). HPLC of Fr. 2/2 (same conditions) afforded 1.8 mg **3a** (R_t 3.4 min) and 15 mg **10a** (R_t 3.8 min). From CC fraction 3 by crystallization 1.2 g **9** were obtained. TLC of CC fraction 4 (Et_2O–petrol–MeOH, 15:4:1) gave 2 mg **13** R_f 0.7), 80 mg **4** (R_f 0.45), 20 mg **5** and **6** (ratio *ca* 9:10), inseparable by TLC or HPLC (MeOH–H_2O, 11:9, R_t 3.8 min), and a mixture which gave by HPLC (MeOH–H_2O, 11:9) 4 mg **7** (R_t 2.5 min) and 8 mg **8** (R_t 4.0 min). The extract of 200 g roots gave by CC three fractions; Fr. 1:petrol; Fr. 2: Et_2O–petrol (1:9) and Fr. 3:Et_2O–petrol (1:1). TLC of fraction 1 gave 1 mg tridecapentayne and fraction 2 afforded 50 mg thymohydroquinone dimethyl ether. TLC of fraction 3 (Et_2O–petrol, 1:3) gave 1 mg **14** (R_f 0.5), 5 mg **15** (R_f 0.43) and 3 mg **16** (R_f 0.22). Known compounds were

Table 1. ^{1}H NMR spectral data of compounds **4–8** and **13** ($CDCl_3$, 400 MHz, δ values)

H	**4** $CDCl_3$–C_6D_6 (2:1)	**5**	C_6D_6	**6**	C_6D_6	**7**	**8**	**13***
1	4.74 *t*	3.79 *dt*	3.57 *dt*	4.91 *t*	4.73 *t*	5.04 *t*	3.94 *br t*	3.89 *dd*
2α	1.82 *m*	2.10 *m*	1.77 *dt*	2.28 *dt*	2.20 *dt*	2.06 *m*	2.19 *dt*	2.13 *br d*
2β	1.70 *dt*	2.10 *m*	1.58 *dt*	2.10 *m*	1.52 *dt*		2.03 *dt*	1.95 *dt*
3	5.29 *dd*	5.52 *dd*	5.46 *dd*	5.42 *m*	5.38 *dd*	4.30 *br t*	5.60 *br t*	5.27 *dd*
5	3.39 *dt*	3.51 *br d*	3.43 *m*	3.43 *br d*	3.43 *m*	3.59 *dt*	3.38 *dt*	3.65 *dt*
6	3.61 *t*	4.09 *t*		4.08 *t*		4.09 *t*	4.08 *t*	4.08 *t*
7	2.84 *ddddd*	3.15 *ddddd*	2.78 *ddddd*	3.45 *ddddd*	3.19 *ddddd*	3.10 *ddddd*	3.45 *ddddd*	3.24 *ddddd*
8α	1.82 *m*	2.04 *m*	1.58 *ddd*	2.03 *m*	1.70 *ddd*	2.15 *ddd*	2.12 *ddd*	2.13 *br* d
8β	1.54 *br t*	1.90 *m*	1.27 *ddd*	2.15 *m*	1.20 *br t*	1.98 *ddd*	1.87 *ddd*	1.89 *ddd*
9	4.86 *t*	5.21 *t*	5.06 *t*	3.99 *br t*	3.50 *br t*	5.05 *t*	4.03 *t*	4.07 *t*
13	5.95 *d*	6.10 *d*	5.97 *d*	6.14 *d*	5.99 *d*	6.13 *d*	6.09 *d*	6.10 *d*
13′	5.16 *d*	5.41 *d*	4.76 *d*	5.42 *d*	4.84 *d*	5.40 *d*	5.41 *d*	5.39 *d*
14	0.51 *s*	0.86 *s*	0.16 *s*	0.89 *s*	0.19 *s*	0.95 *s*	0.80 *s*	0.83 *s*
15	5.28 *br s*	5.41 *br s*	5.27 *br s*	5.41 *br s*	5.27 *br s*	5.32 *d*	5.43 *d*	5.33 *d*
15′	5.05 *d*	5.31 *br s*	5.19 *br s*	5.31 *br s*	5.19 *br s*	5.23 *d*	5.32 *d*	5.16 *d*
OAc	1.86 *s*	2.11 *s*	1.85 *s*	2.14 *s*	1.66 *s*	2.12 *s*	2.11 *s*	2.03 *s*
	1.86 *s*	2.08 *s*	1.61 *s*	2.03 *s*	1.58 *s*	2.06 *s*	—	—
	1.79 *s*							
OH	—	2.95 *d*	2.82 *d*	3.70 *br s*	3.36 *br* s	2.06 *m*	3.68 *br* s	

*H-17 1.51 s, OMe 3.28 s.

J [Hz]: 1,2α = 1,2β = 8α,9 = 8β,9 ~ 2.5; 2α,2β = 16; 2α,3 = 2; 2β,3 = 4; 5,6 = 6,7 = 11; 5,15 = 5,15′ ~ 1.5; 7,8α = 3; 7,8β = 8α,8β = 13; 7,13 = 3 (compound **5**: 1,OH = 6.5; compound **7**: 2α,3 = 2β,3 = 3; compound **8**: 2α,3 = 2.5; 2β,3 = 3.5; compound **13**: 1,2α = 2.5; 1,2β = 4).

Table 2. ^{1}H NMR spectral data of compounds **9a–12a** ($CDCl_3$, 400 MHz, δ-values)

H	**9a**	**10a**	**11a**	**12a**
1α	1.23 *br t*	1.33 *t*	1.33 *t*	1.35 *t*
1β	1.82 *ddd*	1.82 *ddd*	1.84 *ddd*	1.86 *ddd*
2	3.87 *tt*	4.96 *tt*	4.99 *tt*	5.00 *tt*
3α	1.98 *br t*	2.05 *br t*	2.08 *br t*	2.07 *br t*
3β	2.65 *ddd*	2.69 *ddd*	2.71 *ddd*	2.72 *ddd*
5	1.87 *br d*	1.89 *br d*	1.91 *br d*	1.92 *br d*
6α	1.67 *br d*	1.68 *br d*	1.69 *br d*	1.69 *br d*
6β	1.25 *ddd*	1.26 *dd*	1.26 *ddd*	1.29 *ddd*
7	2.54 *br tt*	2.55 *br tt*	2.55 *br tt*	2.55 *br tt*
8α	1.62 *m*	1.60 *m*	1.68 *m*	1.65 *m*
8β	1.45 *dddd*	1.45 *dddd*	1.44 *dddd*	1.46 *dddd*
9α	1.35 *ddd*	1.38 *ddd*	1.41 *ddd*	1.50 *m*
9β	1.57 *m*	1.57 *m*	1.57 *m*	1.57 *m*
13	6.15 *br s*	6.16 *d*	6.16 *br s*	6.17 *d*
13′	5.56 *t*	5.57 *t*	5.57 *t*	5.57 *t*
14	0.74 *s*	0.79 *s*	0.81 *s*	0.81 *s*
15	4.81 *q*	4.85 *q*	4.85 *q*	4.86 *q*
15′	4.50 *q*	4.55 *q*	4.55 *q*	4.55 *q*
OCOR	—	2.02 *s*	5.64 *qq*	5.63 *tq*
			2.16 *d*	2.16 *dq*
			1.89 *d*	1.07 *t*
				2.15 *d*
OMe	3.75 *s*	3.76 *s*	3.76 *s*	3.76 *s*

J [Hz]: 1α,1β = 1α,2 = 2,3α = 3α,3β ~ 12; 1β,2 = 2,3β = 4.5; 3α,15 = 3β,15 = 5,15 ~ 1.5; 5,6β = 6β,7 = 7,8β = 12; 5,6α = 6α,7 ~ 2.5; 7,8α = 3; 7,13′ = 13,13′ = 0.7; 8α,8β = 8β,9α = 9α,9β = 13; 8α,9β = 3; OSen: 2,4 = 2,5 = 1; OMeSen: 2,4 = 2,6 = 1; 4,5 = 7.

identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.

*Methyl-2α-acetoxy-germacra-*1(10)E,4E,11(13)*-trien-*12*-oate* (**3a**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1250 OAc), 1725 (C=CCO_2R); MS *m/z* (rel. int.): 306.183 $[M]^+$ (0.2) (calc. for $C_{18}H_{26}O_4$: 306.183), 264 $[M-ketene]^+$ (2), 246 $[M-HOAc]^+$ (14), 214 $[246-MeOH]^+$ (6), 199 $[214-Me]^+$ (10), 171 $[199-CO]^+$ (12), 97 $[C_6H_9O]^+$ (100); ^{1}H NMR ($CDCl_3$): δ 4.42 (*br d*, H-1), 5.61 (*ddd*, H-2), 4.30 (*br d*, H-5), 6.12 and 5.53 (*br s*, H-13), 1.57 (*br s*, H-14), 1.60 (*br s*, H-15), 2.07 (*s*, OAc), 3.76 (*s*, OMe) (*J* [Hz]: 1,2 = 2,3 = 5,6 = 10; 1,2′ = 5); $[\alpha]_D^{24°}$ + 82° ($CHCl_3$; *c* 0.17).

Cratystyolide triacetate (**4**). Colourless crystals; mp 196–98°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1775 (γ-lactone), 1740, 1265 (OAc); MS *m/z* (rel. int.): 346.142 $[M-HOAc]^+$ (2.5) (calc. for $C_{19}H_{22}O_6$: 346.142), 304 $[346-ketene]^+$ (5.5), 287 $(346-OAc]^+$ (3), 286 $[346-HOAc]^+$ (3.3), 244 $[304-HOAc]^+$ (42), 226 $[286-HOAc]^+$ (100), 211 $[226-Me]^+$ (24); $[\alpha]_D^{24°}$ + 112° ($CHCl_3$; *c* 0.73).

*Cratystyolide-l-*O*,3-*O*-diacetate and* 3-O,9-O*-diacetate* (**5** and **6**). Colourless crystals; mp 172–174°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1745, 1255 (OAc); MS *m/z* (rel. int.): 304.131 $[M-HOAc]^+$ (12) (calc. for $C_{17}H_{20}O_5$: 304.131), 244 $[304-HOAc]^+$ (64), 226 $[244-H_2O]^+$ (76), 211 $[226-Me]^+$ (32), 105 (100). To 5 mg **5** and **6** in 1 ml MeOH 5 mg *p*-Ts were added. After 20 min at room temp. usual work-up and TLC gave 4 mg **13**, identical with the isolated material.

*Cratystyolide-*1-O,9-O*-diacetate* (**7**). Colourless crystals, mp 236°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610 (OH), 1770 (γ-lactone), 1740, 1260 (OAc); MS *m/z* (rel. int.): 304.131 $[M-HOAc]^+$ (11) (calc. for $C_{17}H_{20}O_5$: 304.131), 262 $[304-ketene]^+$ (26), 244 $[304-HOAc]^+$ (56), 229 $[244-Me]^+$ (54), 226 $[244-H_2O]^+$ (28), 53 (100).

*Cratystyolide-*3-O*-acetate* (**8**). Colourless crystals, mp 222–223°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540, 3400 (OH), 1770 (γ-lactone), 1740, 1240 (OAc); MS *m/z* (rel. int.): 304.131 $[M-H_2O]^+$ (2.5)

(calc. for $C_{17}H_{20}O_5$: 304.131), 280 [M − ketene]$^+$ (6), 262 [M − HOAc]$^+$ (36), 244 [304 − HOAc]$^+$ (38), 226 [244 − H_2O]$^+$ (68), 106 (100); $[\alpha]_D^{24°}$ + 133° ($CHCl_3$ *c*0.25).

2α-Hydroxycostic acid (**9**). Colourless crystals, mp 182°; addition of CH_2N_2 afforded the methyl ester **9a** (TLC: Et_2O–petrol, 1:1, R_f 0.35); MS *m/z* (rel. int.): 264.173 [M]$^+$ (11) (calc. for $C_{16}H_{24}O_3$: 264.173), 246 [M − H_2O]$^+$ (51), 231 [246 − Me]$^+$ (28), 214 (246 − MeOH]$^+$ (27), 199 (214 − Me]$^+$ (47), 171 [199 − CO]$^+$ (51), 119 (100). Acetylation of **9a** (Ac_2O, 1 hr, 70°) gave **10a**, identical with the natural product.

Methyl 2α-acetoxycostoate (**10a**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735 (OAc, CO_2R), 1650, 1630 (C=C); MS *m/z* (rel. int.): 306.183 [M]$^+$ (0.1) (calc. for $C_{18}H_{26}O_4$: 306.183), 275 [M − OMe]$^+$ (5.4), 246 [M − HOAc]$^+$ (100), 214 [246 − MeOH]$^+$ (10), 199 [214 − Me]$^+$ (31), 171 [199 − CO]$^+$ (30); $[\alpha]_D^{24°}$ + 16° ($CHCl_3$; *c* 1.11).

Methyl 2α-senecioyloxycostoate (**11a**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730, 1650, 1630 (C=CCO$_2$R); MS *m/z* (rel. int.): 346.214 [M]$^+$ (0.1) (calc. for $C_{21}H_{30}O_4$: 346.214), 315 [M − OMe]$^+$ (1.5), 246 [M − RCO$_2$H]$^+$ (68), 214 [246 − MeOH]$^+$ (6), 83 [RCO]$^+$ (100); $[\alpha]_D^{24°}$ − 5° ($CHCl_3$; *c* 1.11).

Methyl 2α-[3-ethyl-but-2Z-enoyloxy]-costoate (**12a**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730, 1655, 1630 (C=CCO$_2$R); MS *m/z* (rel. int.): 360.230 [M]$^+$ (0.1) (calc. for $C_{22}H_{32}O_4$: 360.230), 329 [M − OMe]$^+$ (1.3), 246 [M − RCO$_2$H]$^+$ (44), 214 [246 − MeOH]$^+$ (3), 97 [RCO]$^+$ (100); $[\alpha]_D^{24°}$ − 6.5° ($CHCl_3$; *c*0.64).

Cyclocratystyloide (**13**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1765 (γ-lactone), 1730, 1230 (OAc); MS *m/z* (rel. int.) 378.168 [M]$^+$ (0.4) (calc. for $C_{20}H_{26}O_7$: 378.168), 347 [M − OMe]$^+$ (32), 346 [M − MeOH]$^+$ (41), 286 [346 − HOAc]$^+$ (24), 244 [286 − C_2H_2O]$^+$ (82), 227 [286 − $C_2H_3O_2$]$^+$ (100); ^{13}C NMR ($CDCl_3$, C-1–C-17): 71.0*, 31.2, 70.6*, 140.7, 39.5, 73.2*, 43.4, 27.0, 78.9*, 39.1, 139.1, 170.4, 116.9, 15.8, 115.4, 112.3, 22.5, (*may be interchangeable).

2-[Penta-1,3-diyn-1-yl]-5-[4-(2-methylbutyryloxy)-3-chloro-but-1-yn-1-yl]-thiophene (**14**). Yellow coloured oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2200 (C≡C), 1740 (CO$_2$R); UV $\lambda_{max}^{Et_2O}$ nm: 340, 318; MS *m/z* (rel. int.): 332.065 [M]$^+$ (4.5) (calc. for $C_{18}H_{17}O_2$ SCl: 332.065), 230 [M − RCO$_2$H]$^+$ (84), 195 [230 − Cl]$^+$ (26], 85 [RCO]$^+$ (28), 57 [85 − CO]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ4.43 and 4.40 (*dd*, H-1), 4.96 (*dd*, H-2), 7.11 (*d*, H-6), 7.07 (*d*, H-7), 2.05 (*s*, H-13), OCOR: 2.45 (*m*, H-2), 1.74 and 1.51 (*m*, H-3), 0.93 (*t*, H-4), 1.18 (*d*, H-5) *J* [Hz]: 1,1 = 7; 1,2 = 3; 6,7 = 4; OCOR: 2,5 = 3,4 = 7).

2-Prop-1-ynyl-5-[1-acetoxy-2-chloroethyl]-dithiophene (**15**). Yellow coloured oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2220 (C≡C), 1750, 1235 (OAc); UV $\lambda_{max}^{Et_2O}$ nm: 340, 328; MS *m/z* (rel. int.): 324.005 [M]$^+$ (45) (calc. for $C_{15}H_{13}O_2S_2Cl$: 324.005), 288 [M − HCl]$^+$ (27), 275 [M − CH_2Cl]$^+$ (1.5), 265 [M − OAc]$^+$ (21), 246 [288 − ketene]$^+$ (32), 233 [275 − ketene]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ3.86 and 3.80 (*dd*, H-1), 6.17 (*dd*, H-2), 7.01 (*d*, H-4), 6.99 (*d*, H-5, H-8), 6.97 (*d*, H-9), 2.09 (*s*, H-13), 2.14 (*s*, OAc) (*J*[Hz]: 1,1 = 11.5; 1,2 = 7.5; 1,2′ = 5; 4,5 = 8,9 = 3.5).

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