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TRANSFORMATION PRODUCTS OF FUROEREMOPHILANES AND OTHER CONSTITUENTS FROM *EURYOPS ARABICUS*

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Key Word Index—*Euryops arabicus*; Compositae; sesquiterpenes; furoeremophilanes; eremophilanolides; seco-furoeremophilanes; rearranged sesquiterpenes; quercetin glycosides; glucopyranoside derivatives.

Abstract—The aerial parts of *Euryops arabicus* afforded in addition to several known furoeremophilanes four new ones as well as four eremophilanolides, two seco derivatives and a rearranged spiro lactone. Furthermore two quercetin derivatives and an unusual diester of glucose were present. The structures were elucidated by high field NMR techniques and the biosynthesis of the unusual compounds is discussed.

INTRODUCTION

The genus *Euryops* with nearly 100 species with the majority in southern Africa is placed in the tribe Senecioneae, subtribe Othonninae [1]. One-third of the species have been studied chemically [2]. Most common are furoeremophilanes which are characteristic for large parts of the whole tribe [3]. The only species known outside Africa is *E. arabicus* Steud. We therefore have studied this species to see whether the chemistry differs from that of the South African species. The results are discussed in this paper.

RESULTS AND DISCUSSION

The aerial parts of *E. arabicus* afforded in addition to known compounds (see Experimental) the furoeremophilanes **5** and **8**–**11**, the seco derivatives **12** and **14** as well as the eremophilanolides **17**–**20**, the rearranged spiro lactone **21**, the quercetin derivatives **22** and **23** as well as a derivative of glucose (**24**). The structure of **5** directly followed from the ^{1}H NMR spectrum (Table 1) which is very close to that of **1**–**4**.

The ^{1}H NMR spectra of **8** and **9** (Table 1) clearly indicated that isomeric methoxy derivatives of 9-desoxycacalol were present. Accordingly, the data were in part close to those of **7** [4]. However, due to the replacement of the keto by a methoxy group several signals were shifted upfield. The configuration at C-1 was determined by NOE difference spectroscopy. Small couplings of H-1 in the case of **8** required an axial orientation of the methoxy group. Accordingly, a NOE between H-15 and the axial H-2 required a 1α-methoxy group. The ^{13}C NMR data (Table 2) also agreed with the proposed structure.

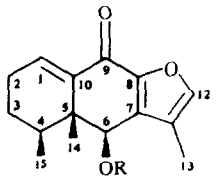
Similarly the coupling of H-1 in the ether **9** and **10** indicated an equatorial ether group. Thus compound **9** is the epimer of **8**. The ^{1}H NMR data of **11** (Table 1) showed that the corresponding Δ^1 derivative of desoxycacalol was present. Accordingly, spin decoupling clearly indicated the sequence of H-1 (H-9) through H-4 (H-15).

The ^{1}H NMR spectrum of **12** (Table 1) differed more pronouncedly from those of **8**–**11**. The presence of a benzofuran followed from the typical signals while the relative position and the nature of the side chain could be deduced by spin decoupling. Thus a small allylic coupling of H-9 with H-1 was visible while no meta-coupling of H-9 could be detected which excluded a 6-methyl derivative. Most likely **12** is formed by fragmentation of a derivative of a 6-acyloxyfuroeremophilane with additional oxygen functions at C-1 and C-9. The carbinol **12** we have named seco-eurabicol.

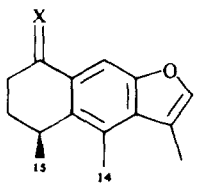
The ^{1}H NMR spectrum of **14** (Table 1) indicated again the presence of a benzofuran. A low field triplet at δ9.69 required a saturated aldehyde in the side chain. Spin decoupling established the whole sequence of the side chain. The chemical shift of the proton at the methyl-bearing carbon further showed that it was benzylic. Similarly the ^{1}H NMR spectrum of the acetal **14a** (Table 1), which was obtained during the separation, led to the structure of the corresponding side chain. The relative position of the latter followed from a NOE of H-6 with H-13 and H-14. The ^{13}C NMR data (Table 2) also supported the proposed structure. Most likely **14** was biogenetically formed by fragmentation of **13** followed by rearrangement of the intermediate **13a** induced by loss of the C-6 acyloxy group. The aldehyde **14** we have named seco-eurabicanal.

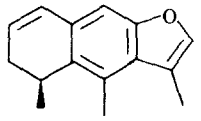
The ^{1}H NMR spectra of **17** and **18** (Table 3) were close to that of **16** [5]. The nature of the altered substituents at C-6 followed from the typical signals of a methacryloyloxy and ethoxy residue respectively. In the spectrum of **19** (Table 1) the H-6 signal was shifted downfield if compared with the shift in the spectrum of **17**. NOE difference spectroscopy established the configurations at C-6. Thus a clear effect of H-6 with H-14 and H-15 was obtained in the case of **18** while H-6 in **19** gave NOE with H-4.

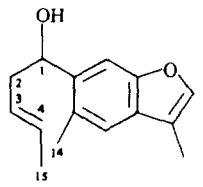
The molecular formula of **21** ($C_{15}H_{18}O_2$) indicated that an isomer of **15** was present. However, the ^{1}H NMR spectrum of **21** (Table 3) was very different. The signal at δ6.38 only could be that of H-6 as a small coupling with



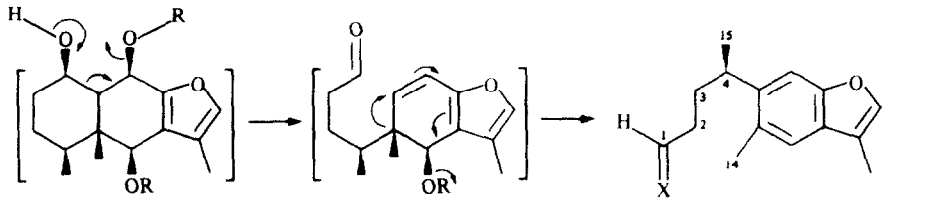
1 R = Meacr **2** R = Ang **3** R = *i*Bu **4** R = Sen **5** R = Epmeacr
6 R = Epang **1a/2a** 1,10αH; **1b/2b** 4αOH,1,10αH; **1c–3c** 1β,10β-epoxide



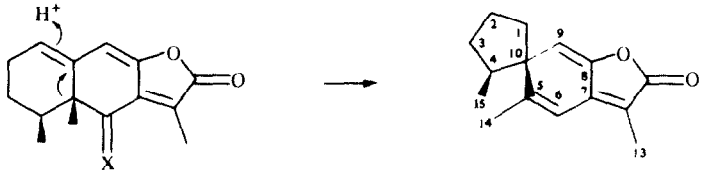




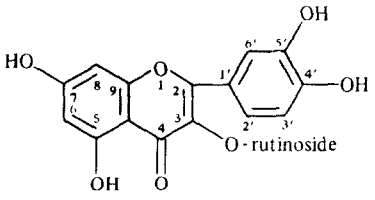
7 X = O **8** X = αOMe,H **11** **12**
9 X = βOMe,H **10** X = βOEt,H

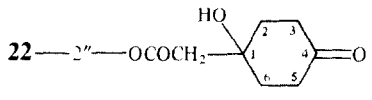


13 **13a** **14** X = O **14a** X = $(OMe)_2$



15 X = H_2 **16** X = αOH,H **17** X = αOMeacr,H **21**
18 X = αOEt,H **19** X = βOMeacr,H **20** X = βOAng,H





22 **23**

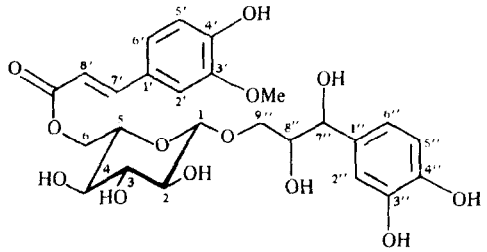


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Table 1. ^{1}H NMR spectral data of **5**, **8–12**, **14** and **14a** ($CDCl_3$, 400 MHz, δ-values)

H	5	8	9	10	11	12	14	14a
1	7.00 *t*	4.28 *dd*	4.50 *dd*	4.56 *br dd*	6.49 *dd*	5.00 *ddd*	9.69 *t*	4.33 *t*
2	2.25 *m*	2.07 *dddd* 2.01 *dddd*	2.08 *m** 1.93 *m**	2.09 *m** 1.94 *m**	5.89 *ddd*	2.48 *ddd* 2.35 *ddd*	2.36 *dt*	1.80–1.50 *m*
3	1.65–1.45 *m*	2.25 *dddd* 1.62 *dddd*	1.98 *m** 1.84 *m**	2.00 *m** 1.84 *m**	2.58 *dddd* 2.25 *ddd*	5.59 *br dt*	1.97 *dt*	
4	2.02 *m*	3.28 *ddq*	3.23 *m*	3.23 *m*	3.29 *br dq*	5.63 *br dq*	3.12 *tq*	3.05 *tq*
6	6.49 *s*	—	—	—	—	7.27 *br s*	7.29 *br s*	7.27 *br s*
9	—	7.22 *br s*	7.45 *br s*	7.47 *br s*	6.99 *br s*	7.60 *br s*	7.27 *br s*	7.28 *br s*
12	7.40 *br s*	7.29 *q*	7.28 *q*	7.28 *q*	7.28 *q*	7.36 *q*	7.32 *q*	7.31 *q*
13	1.93 *br s*	2.39 *d*	2.39 *d*	2.39 *d*	2.39 *d*	2.22 *d*	2.21 *d*	2.20 *d*
14	1.01 *d*	2.60 *br s*	2.59 *br s*	2.59 *br s*	2.58 *br s*	2.43 *br s*	2.40 *br s*	2.42 *br s*
15	1.17 *s*	1.16 *s*	1.24 *d*	1.23 *d*	1.10 *d*	1.72 *br d*	1.27 *d*	1.26 *d*
OR	1.65 *s*	3.42 *s*	3.46 *s*	3.74 *dq*	—	2.02 *d*	—	3.28 *s*
	3.24 *d*			3.58 *dq*				3.26 *s*
	2.89 *d*			1.30 *t*				

*Not first order.

J[Hz]: 12,13 = 1.5; 4,15 = 7; compound **5**: 1,2 = 4; compound **8**: 1,2 = 1,2′ = 2,3′ = 2′,3′ = 3; 2,2′ = 2′,3 = 13; 2,3 = 3,4 = 5; 3′,4 = 2; compounds **9** and **10**: 1,2 = 7; 1,2′ = 9; compound **11**: 1,2 = 9.5; 1,3 = 2,3 = 3; 2,3′ = 6; 3,3′ = 17; 3,4 = 7; 3′,4 = 1.5; compound **12**: 1,2 = 1, OH = 3; 1,2′ = 2,3 = 2′,3 = 4, 15 = 6.5; 2,2′ = 13.5; 3,4 = 15.5; compound **14**: 1,2 = 12,13 = 1.5; 2,3 = 3,4 = 7; compound **14a**: 1,2 = 5.5; 3,4 = 7; 12,13 = 1.5; OEpmeacr: 3,3′ = 5.5; OEt: 1,1 = 9; 1,2 = 7.

Table 2. ^{13}C NMR spectral data of **8**, **14** and **21** ($CDCl_3$, δ-values)

C	8	14	21
1	77.6 *d*	202.4 *d*	34.4 *t*
2	25.4 *t*	42.1 *t*	24.5 *t*
3	22.2 *t*	29.9 *t*	37.7 *t*
4	28.7 *d*	34.1 *d*	47.9 *d*
5	132.1 *s*	129.7 *s*	142.8 *s*
6	129.4 *s*	120.4 *s*	117.1 *d*
7	127.0 *s*	126.9 *s*	146.5 *s*
8	153.8 *s*	154.7 *s*	153.8 *s*
9	110.8 *d*	107.7 *d*	116.4 *d*
10	134.6 *s*	141.1 *s*	56.0 *s*
11	116.2 *s*	115.2 *s*	112.2 *s*
12	141.9 *d*	141.1 *d*	172.8 *s*
13	11.4 *q*	7.9 *q*	8.1 *q*
14	14.6 *q*	20.0 *q*	13.7 *q*
15	21.1 *q*	22.2 *q*	23.2 *q*
OMe	56.3 *q*	—	—

Table 3. ^{1}H NMR spectral data of **17–21** ($CDCl_3$, 400 MHz, δ-values)

H	17	18	19	20	21
1	5.98 *dd*	5.94 *dd*	5.96 *dd*	5.97 *dd*	2.0 *m*
4	2.38 *m*	2.39 *m*	1.90 *m*	1.92 *m*	2.16 *ddq*
6	5.84 *s*	4.17 *s*	6.13 *q*	6.18 *q*	6.38 *br s*
9	6.04 *br s*	5.98 *br s*	5.99 *br s*	6.01 *br s*	5.55 *br s*
13	2.11 *br s*	2.06 *br s*	1.81 *d*	1.81 *d*	1.92 *br s*
14	0.98 *s*	0.85 *s*	1.15 *s*	1.15 *s*	2.02 *br s*
15	0.93 *d*	0.95 *d*	0.96 *d*	0.96 *d*	0.76 *d*
OR	6.04 *br s*	3.50 *dq*	6.27 *br s*	6.33 *qq*	—
	5.57 *dq*	3.33 *dq*	5.75 *dq*	2.11 *dq*	
	1.89 *dd*	1.17 *t*	2.04 *dd*	2.00 *dq*	

J[Hz]: Compounds **17–20**: 1,2 = 1,2′ = 4; 4,15 = 7 (compounds **19** and **20**: 6,13 = 2); compounds **21**: 3,4 = 6.5; 3′,4 = 12; 4,15 = 7; OMeacr: 3,3′ = 3,4 = 3′,4 = 1.5; OAng: 3,4 = 7; 3,5 = 4,5 = 1.5; OEt: 1,1′ = 9; 1,2 = 7.

H-13 and H-14 could be detected. Furthermore the chemical shift of the second olefinic proton (δ5.55) required an enol ester function. Thus the proposed assignment was very likely and further supported by the ^{13}C NMR spectrum (Table 2). The remaining ^{1}H NMR signals required the presence of a spiro compound. This and the stereochemistry was determined from the NOE's. Clear effects were obtained between H-6, H-14 and H-13, between H-4 and H-9 as well as between H-14 and H-15. The spiro compound **21** surely is formed biogenetically by a rearrangement induced by protonation at C-1 (Scheme). Lactone **21** we have named spiroeuryolide. In addition to the furoeremophilanes and related compounds isointermedeol [6] was isolated. It is identical with a carbinol which has been proposed to be the corresponding eremophilane [7]. Therefore the proposed compound does not exist (compound **12a** in lit. [7]). The stereochemistry was established by NOE difference spectroscopy.

The ^{13}C NMR spectrum of **22** nicely agreed with that of quercetin-3-*O*-rutinoside [8] and that of **23** was very similar (Table 4). However, additional signals indicated that the sugar moiety was different. The ^{1}H NMR spectrum (Experimental) clearly indicated that the glucopyranoside moiety was esterified at C-2″ if the data were compared with those of **22**. The additional signals were nearly identical with those of methyl-[1-hydroxy-4-oxocyclohexyl]-acetate [9]. The tetradehydro derivative is

Table 4. ^{13}C NMR spectral data of **22** and **23** (δ-values)

C	22*	23†	C	22	23
2	156.4	159.3	1″	101.5	102.3
3	133.6	134.5	2″	74.2	75.6
4	177.4	178.8	3″	76.8	76.9
5	161.2	162.8	4″	70.8	72.2
6	98.8	99.8	5″	76.1	75.8
7	163.9	165.8	6″	67.1	68.4
8	93.6	94.8	1‴	100.7	100.7
9	156.9	158.3	2‴	70.4	72.0
10	104.2	105.7	3‴	70.4	71.6
1′	121.6	123.2	4‴	72.2	72.8
2′	115.3	116.1	5‴	68.2	69.6
3′	144.6	145.7	6‴	17.5	17.8
4′	148.3	149.6			
5′	116.5	117.5			
6′	121.6	123.5			

*In DMSO-d_6.

†In deuterio methanol, signals of the ester residue: δ37.2 *t* (2×), 37.5 *t* (2×), 47.8 *t*, 70.1 *s*, 171.9 *s*, 214.4 *s*.

present in several *Senecio* species [3]. As expected compound **23** gave no molecular ion, but FAB-MS data showed the calculated mass for $C_{35}H_{40}O_{19}$.

From the ^1H NMR spectrum of **24** the presence of a ferulate residue and a substituted phenylpropane moiety could be deduced. Further signals indicated that these groups were linked with glucose. Acetylation afforded a heptaacetate. Its ^1H NMR signals (Experimental) could be fully assigned by spin decoupling. The relative positions of the ferulate and the phenylpropane residue followed from the chemical shifts.

The isolation of the seco derivatives **12** and **14** as well as the rearranged spiro compound **21** may be of chemotaxonomic relevance as similar compounds have not been isolated from other *Euryops* species. Also the desoxycacalols **7–11** are unusual, as so far the ketone **7** has only been isolated from a *Senecio* species [4]. However, all other furoeremophilanes are typical *Euryops* constituents. Seco-furoeremophilanes are also present in *E. tenuissimus* [3] which is related morphologically to *E. arabicus* [1].

EXPERIMENTAL

The air-dried aerial parts (1 kg, collected in Abha province Saudi Arabia, voucher no. 55 deposited in the Faculty of Agriculture, King Saud University, Saudi Arabia) were extracted with MeOH–Et_2O–petrol (1:1:1), and worked-up as reported previously [10]. CC (silica gel) gave six fractions (1: petrol; 2: Et_2O–petrol, 1:9; 3: Et_2O–petrol, 1:3; 4: Et_2O–petrol, 1:1; 5: Et_2O–MeOH, 9:1 and 6: MeOH). Fraction 1 contained 200 mg caryophyllene and 300 mg δ-cadinene. Fraction 2 gave 100 mg angelic acid and 150 mg methacrylic acid. Fraction 3 was separated by flash chromatography affording six fractions (3/1–3/6, petrol with raising amounts of Et_2O). HPLC (MeOH–H_2O, 4:1, always RP 8, *ca* 100 bar) of fraction 3/1 gave 4 mg **8** (R_t 10.5 min), 5 mg **9** (R_t 11.3 min) and 20 mg **11** (R_t 14.5 min). HPLC of fraction 3/2 (MeOH–H_2O, 4:1) afforded 5 mg **12** (R_t 7.0 min), 7 mg **10** (R_t 14.0 min), 3 mg **8** and 6 mg **9**. TLC of fraction 3/3 (Et_2O–petrol, 3:7) gave 50 mg **12** (R_f 0.41), 25 mg **15** (R_f 0.5) and a mixture which gave by HPLC (MeOH–H_2O, 4:1) a mixture which gave by TLC (Et_2O–petrol, 1:3) 40 mg **8** (R_f 0.83) and 10 mg **17** (R_f 0.66), 40 mg **14a** (R_t 12.7 min) and 7.5 mg **20**. Fraction 3/4 afforded by HPLC (MeOH–H_2O, 3:1) a mixture, which gave by TLC (Et_2O–petrol, 1:3) 15 mg isointermedeol [6], 15 mg **12** (R_t 8.7 min), a mixture, which afforded by TLC (Et_2O–petrol, 1:3) 15 mg **18** (R_f 0.75) and 50 mg **21** (R_f 0.65), a further mixture, which was separated by TLC (Et_2O–petrol, 1:3) to give 10 mg **15** [11], 40 mg **21** and 20 mg **7** (R_f 0.8) [7], 100 mg isointermedeol (R_t 15.0 min) and a mixture, which gave by TLC (Et_2O–petrol, 1:3) 40 mg **14a** and 15 mg **19** (R_f 0.62). TLC of fraction 3/5 (Et_2O–petrol, 3:7) gave 100 mg isointermedeol and TLC of fraction 3/6 (Et_2O–petrol, 3:7) afforded 12 mg **1b** [3], 18 mg **1a** [3] and 13 mg **2** [12]. Repeated CC and TLC of CC fraction 4 afforded 2 g **3** [13], 1.8 g **1** [3], 2 g **4** [14] and 3 g **2**. HPLC of CC fraction 5 (MeOH–H_2O, 13:7) gave 20 mg vanillin, 4 mg **3** [13], 5 mg **16** [5], 2 mg **1b** [16], 10 mg **5**, 20 mg **6** [13], 4 mg **2c** [15], 5 mg **1c** [16], 2 mg **3c** [15] and 3 mg **2b** [16]. CC fraction 6 gave by HPLC (MeOH–H_2O, 1:1) 100 mg **22**, 50 mg **23** and 20 mg **24**. IR and mass spectral data (Table 5). Known compounds were identified by comparing the 400 MHz ^1H NMR spectra with those of authentic material.

Quercetin-3-O-[*rutinoside*-2″-O-[1-*hydroxy*-4-*oxo*-*cyclohexyl*]-*acetate*] (**23**). Yellow gum; ^1H NMR (MeOD): δ6.18 (*d*, H-6, J = 2 Hz), 6.36 (*d*, H-8, J = 2), 7.57 (*d*, H-2′, J = 1.5), 6.86 (*d*, H-5′, J = 8), 7.56 (*dd*, H-6′, J = 8, 1.5), 5.42 (*d*, H-1″, J = 7.5), 5.00 (*dd*, H-2″, J = 7.5, 9.5), 3.59 (*t*, H-3″, J = 9.5), 3.31 (*m*, H-4″), 3.37 (*m*, H-5″), 3.81 and 3.37 (*m*, H-6″); rhamnoside: 4.49 (*d*, H-1, J = 1.5), 3.62 (*dd*, H-2, J = 3, 1.5), 3.51 (*dd*, H-3, J = 3, 9), 3.26 (*t*, H-4, J = 9), 3.42 (*dd*, H-5, J = 7, 9), 1.09 (*d*, H-6, J = 7); ester group: 2.78 and 2.67 (*d*, H-7, J = 13.5), 2.67, 2.15, 2.10, 1.99 (*m*, H-2, 3, 5, 6).

1-O-[6,7-*Dihydroxydihydroconiferyl*]-β-D-*glucopyranoside*-6-O-*ferulate* (**24**). Colourless gum; ^1H NMR ($CDCl_3$): ferulate: δ7.18 (*d*, H-2, J = 2), 6.81 (*d*, H-5, J = 8), 7.05 (*dd*, H-6, J = 8, 2), 7.58 (*d*, H-7, J = 16), 6.36 (*d*, H-8, J = 16), 3.89 (*s*, OMe); phenyl propane moiety: δ6.97 (*d*, H-2, J = 2), 6.71 (*d*, H-5, J = 8), 6.82 (*dd*, H-6, J = 8, 2), 3.68 and 3.57 (*dd*, H-9, J = 10, 5), 3.81 (*s*, OMe); glucose part: 4.62 (*d*, H-1), 4.48 (*dd*, H-6, J = 12, 2), 4.27 (*dd*, H-6′, J = 12, 5). Acetylation afforded **24**Ac; colourless gum; ^1H NMR ($CDCl_3$): ferulate: δ7.14 (*d*, H-2), 7.05 (*d*, H-5), 7.13 (*dd*, H-6), 7.64 (*d*, H-7), 6.39 (*d*, H-8), 3.88 (*s*, OMe); phenylpropane moiety: 6.96 (*d*, H-2), 6.99 (*d*, H-5), 6.95 (*dd*, H-6), 5.95 (*d*, H-7, J = 7), 5.26 (*ddd*, H-8, J = 4, 4, 7), 3.69 and 3.63 (*dd*, H-9, J = 12, 4); glucose part:

Table 5. Infrared and mass spectral data of compounds **5**, **8–12**, **14** and **17–21**

	IR (ν_{max} cm^{-1})	MS*
5	1735	330.147 (0.6), 228 (100), 213 (64)
8	1620, 1580	244.146 (52), 213 (77), 212 (91), 197 (100)
9	1620, 1570	244.146 (61), 213 (100), 212 (16), 197 (64)
10	1630, 1550	258.162 (42), 213 (100), 212 (44), 197 (82)
11	1565, 860	212.120 (81), 197 (100), 182 (52)
12	3600	230.131 (6), 175 (100) [M − C_4H_7]
14	2750, 1740	230.131 (32), 173 (100) [M − CH_2CH_2CHO]
17	1800, 1720	314.152 (22), 228 (32), 213 (52), 69 (100)
18	1780	274.157 (92), 228 (46), 213 (100), 185 (62)
19	1790, 1730	314.152 (22), 228 (18), 213 (32), 69 (100)
20	1800, 1730	328.167 (6), 228 (8), 213 (23), 133 (100), 83 (72)
21	1760	230.131 (26), 215 (6), 174 (100) [M − C_4H_8]

*First value [M]$^+$ determined by high resolution corresponding to the calculated ones.

δ4.54 (*d*, H-1), 5.02 (*dd*, H-2, $J = 9.5, 7.5$), 5.24 (*t*, H-3, $J = 9$), 5.12 (*t*, H-4, $J = 9$), 3.73 (*ddd*, H-5), 4.31 (*dd*, H-6, $J = 12.5, 4.5$), 4.27 (*dd*, H-6′, $J = 12.5, 3$) (remaining couplings as in **24**).

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