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# EUDESMANOLIDES AND KAURENE DERIVATIVES FROM *WEDELIA HOOKERIANA**

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**Key Word Index**—*Wedelia hookeriana*; Compositae; sesquiterpene lactones; eudesmanolides; diterpenes; ent-kaurene derivatives.

**Abstract**—From the aerial parts of *Wedelia hookeriana* eight new eudesmanolides, all derivatives of ivangustin, and a new ent-kaurenic acid derivative together with its methyl ester have been isolated. The structures were elucidated by high field $^1$H NMR spectroscopy. The chemotaxonomic situation is discussed briefly.

## INTRODUCTION

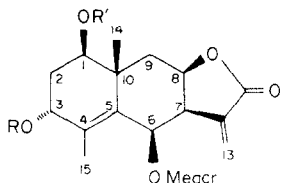
From the large genus *Wedelia* (Compositae, tribe Heliantheae, subtribe Ecliptinae) some species have already been investigated chemically. In addition to thiophene acetylenes [1] ent-kaurene derivatives [2–4] are widespread in this genus. From one species a pseudoguaianolide [5] and from two others eudesmanolides [6, 7] were reported. We now have studied the constituents of *Wedelia hookeriana* and the results are discussed in this paper.

## RESULTS AND DISCUSSION

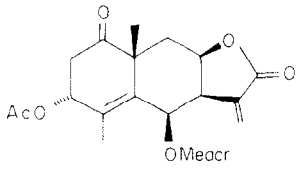
The roots of *Wedelia hookeriana* Gardn. afforded the thiophene acetylene **23** [1] as well as the corresponding dithio derivative **24** [1], caryophyllene, germacrene D, bicyclogermacrene, sabinene, isocomene (**25**), 7$\alpha$H-silphiperfol-5-ene (**26**) [8] and the ent-kaurene derivatives **10**, **13**, **14**, **16** [1], **17** [10] and **19**. The aerial parts gave germacrene D, bicyclogermacrene, sabinene, ent-kaurene derivatives **10–17**, **19**, **20** and two further ones, the acetate **18a** as well as its methyl ester **18b**. Furthermore the ent-beyerene derivatives **21** and **22** and a complex mixture of minute amounts of sesquiterpene lactones were present. Repeated separations finally gave the eudesmanolides **1–8**.

The structure of **18a** and **18b** could be easily deduced from the $^1$H NMR spectra, which were similar to those of other 15$\alpha$-acyloxy derivatives with a 9$\beta$-hydroxy group, which caused a typical downfield shift of the H-15 signal (see Experimental). Esterification of **18a** afforded **18b**. The separation of the sesquiterpene-containing fractions by TLC only led to the isolation of **1** and **2**. The remaining lactones could be partly separated by HPLC (reversed phase), which gave **3**, **5** and **8**, while the mixture of the lactones **4**, **6** and **7**, also containing **5**, could not be separated. The structure of **1** was deduced from the $^1$H NMR (Table 1) and the mass spectrum, which only showed a $[M-HOAc]^+$ peak. As, however, the $^1$H NMR spectrum clearly showed the presence of an acetate group, the molecular formula could be calculated as $C_{21}H_{26}O_7$, indicating the presence of two ester groups and a hydroxy group. Accordingly the IR spectrum showed bands at 3620 (OH), 1775 (lactone), 1735, 1240 (OAc) and 1720 cm$^{-1}$ (unsaturated ester). The nature of the latter followed from the typical $^1$H NMR signals of a methacrylate residue (6.14 *br s*, 5.67 *dq* and 1.98 *br s*). Spin decoupling in a mixture of deuteriochloroform and benzene allowed the assignment of all signals. The presence of an eudesmanolide with a 4,5-double bond followed from the signals of H-6–H-9, which were similar to those of 6$\beta$-tigloyloxyivangustin [11] isolated from a *Steiractinia* species, which also is placed in the subtribe Ecliptinae. The couplings observed required an $\alpha$-orientation of the protons at C-6–C-8. The signals of H-1–H-3 showed that the remaining oxygen functions were at C-1 and C-3, the hydroxy group at C-1 and the acetoxy group at C-3. This decision followed from the chemical shifts of H-1 and H-3 and that of H-14, which would have been more downfield if an acetate group was at C-1 [11]. The couplings observed indicated the given stereochemistry, which was further supported by the downfield shift of H-1 when compared with the shift of the corresponding 3-desacyloxy derivative [11]. Obviously H-1$\alpha$ was deshielded by the $\alpha$-acetoxy group. The observed Eu(fod)$_3$-induced shifts, however, did not clearly support this assignment (Table 1), as both, the acetoxy and the hydroxy group seemed to be complexed to the same extent as followed from the shifts of H-1 and H-3. We therefore have transformed **1** to the corresponding ketone **9** by oxidation with pyridinium chlorochromate. The $^1$H NMR spectrum of **9** showed that the keto group was at C-1, as could be deduced from the downfield shift

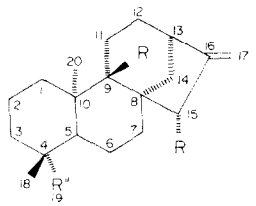
*Part 447 in the series "Naturally Occurring Terpene Derivatives". For Part 446 see Bohlmann, F. and Rotard, W. (1982) *Justus Liebigs Ann. Chem.* (in press).



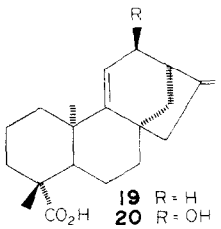

| | 1 | 2 | 3 | 4 | 5 | 6 | 6a | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| R | Ac | COEt | *i*Bu | MeBu | *i*Val | Tigl | Tigl | Sen | Ac |
| R' | H | H | H | H | H | H | Ac | H | Tigl |



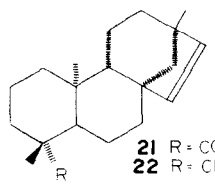

**9**



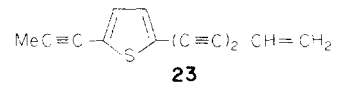
| | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18a | 18b |
|---|---|---|---|---|---|---|---|---|---|---|
| R | H | H | OAc | OAng | OSen | OTigl | OAng | OSen | OAc | OAc |
| R' | H | H | H | H | H | H | OH | OH | OH | OH |
| R'' | $CO_2H$ | $CH_2OH$ | $CO_2H$ | $CO_2H$ | $CO_2H$ | $CO_2H$ | $CO_2H$ | $CO_2H$ | $CO_2H$ | $CO_2Me$ |



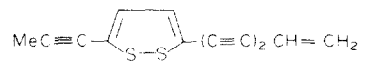

**19** R = H
**20** R = OH




**21** R = $CO_2H$
**22** R = $CH_2OH$




**23**

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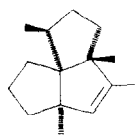

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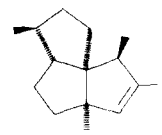

**26**

of H-14 and H-9. The couplings $J_{2,3}$ showed that the introduction of a third $sp^2$-carbon led to a conformation with a quasi equatorial 3-acetoxy group. Inspection of a model showed that the observed differences in the spectra of **1** and **9** could be deduced from the most stable conformations. The structure of **1** being settled, those of **2–8** could then be deduced from their $^1H$ NMR spectral data (Table 1). Obviously all lactones were methacrylates with a free 1$\beta$-hydroxy group except **8** and they differed only in the nature of the ester group at C-3. Though this assumption was not rigorously established, the fact that the chemical shift of H-6 was not altered in the spectra of the different diesters, strongly supported this assignment, as the chemical shift of a proton under a saturated and an unsaturated ester group always differs typically. Accordingly the chemical shifts of H-3 differed in **2–5** and **6** and **7**, respectively. The last lactone was the tiglate **8**. The relative position of the acetate group followed from the chemical shift of H-1, which differed from that of **6a** obtained by acetylation of the mixture of **4–7** after separation by HPLC. As in the lactone from *Steiractinia* [11], in addition to the downfield shift of the H-1 signal also those of H-6, H-9 and H-14 were altered.

The chemistry of *W. hookeriana* agrees with that of *W. trilobata* [7] and partly with that of the other species so far investigated. Perhaps eudesmanolides may have been overlooked in some of these species as the concentrations seem to be very low. Further

Table 1. $^1$H NMR spectral data of compounds **1–9** (400 MHz, $CDCl_3$, TMS as int. standard)

| | **1** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $CDCl_3$ | Δ | $CDCl_3$–$C_6D_6$ | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** |
| H-1 | 4.06 *dd* | 0.31 | 3.87 *br d* | 4.06 *dd* | 4.06 *dd* | | 4.06 *dd* | | 4.06 *dd* | 5.23 *dd* | — |
| H-2 | 1.99 *m* | 0.17 | 1.76 *ddd* | 2.01 *m* | 2.05 *m* | | 2.04 *m* | | 2.04 *m* | 2.0 *m* | 2.88 *dd* |
| H-2′ | 1.83 *m* | 0.23 | 1.61 *ddd* | 1.82 *m* | 1.79 *ddd* | | 1.8 *m* | | 1.8 *m* | | 2.42 *dd* |
| H-3 | 5.24 *br d* | 0.31 | 5.14 *br d* | 5.28 *br d* | 5.26 *br d* | | 5.28 *br d* | | 5.32 *br d* | 5.27 *br d* | 5.77 *dd* |
| H-6 | 5.88 *d* | 0.08 | 5.46 *d* | 5.88 *d* | 5.88 *d* | | 5.87 *d* | | 5.88 *d* | 5.95 *d* | 5.90 *d* |
| H-7 | 3.50 *dddd* | 0.06 | 3.06 *dddd* | 3.51 *dddd* | 3.52 *dddd* | | 3.52 *dddd* | | 3.52 *dddd* | 3.47 *br d* | 3.47 *dddd* |
| H-8 | 4.86 *ddd* | 0.06 | 4.37 *ddd* | 4.87 *ddd* | 4.87 *ddd* | | 4.86 *ddd* | | 4.86 *ddd* | 4.83 *ddd* | 4.78 *ddd* |
| H-9 | 2.64 *dd* | 0.15 | 2.90 *dd* | 2.66 *dd* | 2.69 *dd* | | 2.66 *dd* | | 2.66 *dd* | 2.0 *m* | 3.20 *dd* |
| H-9′ | 1.91 *dd* | 0.12 | 1.62 *dd* | 1.91 *dd* | 1.90 *dd* | | 1.92 *dd* | | 1.92 *dd* | | 2.03 *dd* |
| H-13 | 6.37 *d* | 0.09 | 6.14 *d* | 6.37 *d* | 6.37 *d* | | 6.37 *d* | | 6.36 *d* | 6.38 *d* | 6.39 *d* |
| H-13′ | 5.87 *d* | 0.06 | 5.72 *d* | 5.87 *d* | 5.87 *d* | | 5.87 *d* | | 5.86 *d* | 5.86 *d* | 5.84 *d* |
| H-14 | 1.09 *s* | 0.09 | 0.94 *s* | 1.10 *s* | 1.10 *s* | | 1.12 *s* | | 1.12 *s* | 1.26 *s* | 1.21 *s* |
| H-15 | 1.68 *s* | 0.11 | 1.57 *s* | 1.68 *s* | 1.68 *s* | | 1.68 *s* | | 1.69 *s* | 1.73 *s* | 1.81 *s* |
| OMeacr | 6.14 *br s* | 0.03 | 6.02 *dq* | 6.15 *br s* | 6.15 *br s* | | 6.14 *br s* | | 6.14 *br s* | 6.13 *br s* | 6.13 *br s* |
| | 5.67 *dq* | 0.02 | 5.39 *dq* | 5.64 *dq* | 5.67 *dq* | | 5.67 *br s* | | 5.67 *br s* | 5.65 *dq* | 5.68 *dq* |
| | 1.98 *br s* | 0.05 | 1.83 *dd* | 1.99 *br s* | 1.99 *dd* | | 1.98 *br s* | | 1.98 *br s* | 1.98 *br s* | 1.98 *br s* |
| OCOR | 2.04 *s* | 0.18 | 1.90 *s* | 2.33 *q* | 2.55 *qq* | 2.55 *dq* | 2.19 *d* | 6.88 *qq* | 5.67 *br s* | 6.86 *qs* | 2.10 *s* |
| | | | | 1.12 *t* | 1.14 *d* | 0.89 *t* | 2.04 *m* | 1.81 *br d* | 2.15 *d* | 1.80 *dq* | — |
| | | | | | | 1.11 *d* | 0.95 *d* | 1.80 *br s* | 1.89 *d* | 1.84 *dq* | — |
| OAc | — | — | — | — | — | — | — | — | — | 2.09 *s* | — |

*J*(Hz): 1, 2 = 12; 1, 2′ = 4; 2, 2′ = 14; 2, 3 = 5; 2′, 3 = 1.3; 6, 7 = 7, 13 = 2; 7, 8 = 7.5; 8, 9 = 4; 8, 9′ = 3; 9, 9′ = 15.5; OMeacr: 3′, 4′ ~ 1; OProp: 2′, 3′ = 7; O*i*Bu: 2′, 3′ = 2′, 4′ = 7; OMeBu: 2′, 3′ = 2′, 5′ = 3′, 4′ = 7; O*i*Val: 2′, 3′ = 3′, 4′ = 3′, 5′ = 7; OTigl: 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.3; OSen: 2′, 4′ = 2′, 5′ = 1.

genera placed in the same subtribe which contain eudesmanolides are *Baltimora* [12], *Dimerostemma* [13–15], *Encelia* [16–19], *Podanthus* [20], *Zexmenia* [21], *Steiractinia* [11] and *Zinnia* [22]. Ent-kaurene derivatives have been isolated from the following genera of the subtribe Ecliptinae: *Aspilia* [23], *Oyedaea* [24], *Perymenium* [25], *Steiractinia* [11], *Verbesinia* [26] and *Zexmenia* [21]. Though these diterpenes are widespread in the Compositae the co-occurrence with eudesmanolides may be important. Further investigations are necessary to see whether these compounds are really useful chemotaxonimic markers. It should be mentioned that there are several genera placed in the subtribe Ecliptinae where these compounds so far have not been isolated. Here the co-occurrence of thiophene acetylenes like **23** may be of interest.

## EXPERIMENTAL

The air-dried plant material, collected in the province Bahia, Brazil (vouchers RMK 8680 and 8781, deposited in the U.S. National Herbarium, Washington) was extracted with $Et_2O$–petrol (1:2) and the resulting extracts were separated first by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the $^1H$ NMR spectra with those of authentic material. The roots (20 g) afforded 6 mg germacrene D, 5 mg bicyclogermacrene, 4 mg caryophyllene, 15 mg sabinene, 5 mg **25**, 5 mg **26** (hydrocarbons separated by $AgNO_3$–Si gel), 100 mg **10**, 20 mg **13**, 10 mg **14**, 5 mg **16**, 2 mg **17**, 50 mg **19**, 3 mg **23** and 1 mg **24**, while the aerial parts (590 g) gave 50 mg germacrene D, 30 mg bicyclogermacrene, 10 mg spathulenol, 5 mg stigmasterol, 3 g **10**, 5 mg **11**, 10 mg **12**, 10 mg **13**, 5 mg **14**, 5 mg **15**, 15 mg **16**, 3 mg **17**, 30 mg **18a** ($Et_2O$–petrol, 1:1), 6 mg **18b** ($Et_2O$–petrol, 1:3), 2 g **19**, 10 mg **20**, 50 mg **21**, 10 mg **22** and a mixture of **1–8**. TLC ($Et_2O$–petrol, 3:1, then $Et_2O$–$C_6H_6$–$CHCl_3$, 1:1:1) afforded 10 mg **1**, 4 mg **2**, and a mixture of **3–8**. HPLC (reversed phase, MeOH–$H_2O$, 7:3) of this mixture gave 3 mg **3**, 4 mg **4–7** (*ca* equal amounts), 2 mg **7** and 1 mg **8**.

*3α-Acetoxy-6β-methacryloyloxyivangustin* (**1**). Colourless crystals ($Et_2O$–petrol), mp 190°, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3620 (OH), 1775 (γ-lactone), 1735, 1240 (OAc), 1720 (C=CCO$_2$R); MS *m/z* (rel. int.): 330.147 [M − HOAc]$^+$ (2) ($C_{19}H_{22}O_5$), 304 [M − $C_3H_5CO_2H$]$^+$ (3), 262 [304 − ketene]$^+$ (90), 244 [304 − HOAc]$^+$ (42), 229 [244 − Me]$^+$ (9), 216 [244 − CO]$^+$ (44), 69 [$C_3H_5CO$]$^+$ (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589\ \ 578\ \ 546\ \ 436\ \text{nm}}{+38\ \ +43\ \ +48\ \ +75}\ (CHCl_3;\ c0.04).$$

5 mg **1** in 1 ml $CHCl_3$ was stirred for 2 hr with 50 mg pyridinium chlorochromate. TLC ($Et_2O$) afforded 1.5 mg **9**, colourless gum, $^1H$ NMR spectrum see Table 1; MS *m/z* (rel. int.): 328.131 [M − HOAc]$^+$ (4) ($C_{19}H_{20}O_5$), 302 [M − $C_3H_5CO_2H$]$^+$ (4), 260 [302 − ketene]$^+$ (17), 242 [302 − HOAc]$^+$ (9), 69 [$H_3H_5CO$]$^+$ (100).

*3α-Propioyloxy-6β-methacryloyloxyivangustin* (**2**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3600 (OH), 1780 (γ-lactone), 1725 (CO$_2$R, C=CCO$_2$R); MS *m/z* (rel. int.): 386 [M − $H_2O$]$^+$ (0.2), 348 [M − O=C=CHMe]$^+$ (2), 330.147 [M − $HO_2CEt$]$^+$ (3) ($C_{19}H_{22}O_5$), 318 [M − $C_3H_5CO_2H$]$^+$ (8), 262 [318 − O=C=CHMe]$^+$ (83), 244 [318 − $HO_2CEt$]$^+$ (20), 229 [244 − Me]$^+$ (6), 216 [244 − CO]$^+$ (19), 201 [216 − Me]$^+$ (9), 69 [$C_3H_5CO$]$^+$ (100), 57 [EtCO]$^+$ (78).

*3α-Isobutyryloxy-6β-methacryloyloxyivangustin* (**3**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3610 (OH), 1780 (γ-lactone), 1725 (CO$_2$R, C=CCOR); MS *m/z* (rel. int.): 332.162 [M − $C_3H_5CO_2H$]$^+$ (6) ($C_{19}H_{24}O_5$), 330 [M − $C_3H_7CO_2H$]$^+$ (3), 262 [332 − $Me_2C$=C=O]$^+$ (75), 244 [332 − $Me_2CHCO_2H$]$^+$ (22), 216 [244 − CO]$^+$ (17), 201 [216 − Me]$^+$ (7), 71 [$C_3H_7CO$]$^+$ (81), 69 [$C_3H_5CO$]$^+$ (100).

*3α-(2-Methylbutyryloxy)-, tigloyloxy- and senecioyloxy-6β-methacryloyloxyivangustin* (**4**, **6** and **7**). Colourless gum, not free from **5**, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3600 (OH), 1775 (γ-lactone), 1725 (CO$_2$R, C=CCO$_2$R); MS *m/z* (rel. int.): 346.178 [M − $C_3H_5CO_2H$]$^+$ (1) ($C_{20}H_{26}O_5$), 344 [M − $C_3H_5CO_2H$]$^+$ (2) ($C_{20}H_{24}O_5$), 330 [M − $C_4H_7CO_2H$ and $C_4H_9CO_2H$]$^+$ (0.7), 262 [346 − $C_5H_8O$ and 344 − $C_5H_6O$]$^+$ (18), 244 [344 and 346 − $RCO_2H$]$^+$ (5), 85 [$C_4H_9CO$]$^+$ (10), 83 [$C_4H_7CO$]$^+$ (100), 69 [$C_3H_5CO$]$^+$ (25), 57 [85 − CO]$^+$ (17), 55 [83 − CO]$^+$ (18).

*3α-Isovaleryloxy-6β-methacryloyloxyivangustin* (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3610 (OH), 1780 (γ-lactone), 1730 (CO$_2$R, C=CCO$_2$R); MS *m/z* (rel. int.): 346.178 [M − $C_3H_5CO_2H$]$^+$ (6) ($C_{20}H_{26}O_5$), 330 [M − $C_4H_9CO_2H$]$^+$ (4), 262 [346 − $Me_2CHCH$=C=O]$^+$ (100), 244 [346 − $C_4H_9CO_2H$]$^+$ (23), 216 [244 − CO]$^+$ (20), 85 [$C_4H_9CO$]$^+$ (61), 69 [$C_3H_5CO$]$^+$ (76), 57 [85 − CO]$^+$ (70).

*3α-Tigloyloxy-6β-methacryloyloxyivangustin acetate* (**8**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1780 (γ-lactone), 1735 (OAc), 1720 (C=CCO$_2$R); MS *m/z* (rel. int.): 412 [M − HOAc]$^+$ (0.3), 386 [M − $C_3H_5CO_2H$]$^+$ (0.3), 372 [M − $C_4H_7CO_2H$]$^+$ (1), 330.147 [372 − ketene]$^+$ (22) ($C_{19}H_{22}O_5$), 286 [386 − $C_4H_7CO_2H$]$^+$ (11), 262 [344 − $C_3H_5CO$]$^+$ (50), 55 [83 − CO]$^+$ (58).

Acetylation of the mixture of **5–7** afforded the acetates ($Ac_2O$, 4-pyrrolidinopyridine [27], $CHCl_3$, 24 hr), one of them, the tiglate **6a** could be obtained pure by HPLC (MeOH–$H_2O$, 7:3); $^1H$ NMR ($CDCl_3$, 400 MHz): 5.18 (*dd*, H-1), 1.99 (*m*, H-2), 3.35 (*br d*, H-3), 5.93 (*d*, H-6), 3.49 (*dddd*, H-7), 4.82 (*ddd*, H-8), 2.27 (*dd*, H-9), 1.93 (*dd*, H-9'), 6.38 (*d*, H-13), 5.87 (*d*, H-13'), 1.21 (*s*, H-14), 1.72 (*s*, H-15); OMeacr: 6.14 *br s*, 5.67 *dq*, 1.99 *br s*; OTigl: 6.93 *br q*, 1.81 *br d*, 1.82 *br s*; OAc: 2.07 *s* [*J*(Hz): see Table 1].

*9β-Hydroxy-15α-acetoxy-ent-kaurenic acid* (**18a**). Colourless gum, which was transformed to the methyl ester by addition of $CH_2N_2$ affording **18b** identical with the natural ester, colourless crystals, mp 162° (petrol), IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3620 (OH), 1730, 1245 (OAc, CO$_2$Me); MS *m/z* (rel. int.): 390.241 [M]$^+$ (0.5) ($C_{23}H_{34}O_5$), 372 [M − $H_2O$]$^+$ (0.3), 330 [M − HOAc]$^+$ (28), 312 [330 − $H_2O$]$^+$ (10), 298 [330 − MeOH]$^+$ (4), 270 [298 − CO]$^+$ (11), 161 [$C_{12}H_{17}$]$^+$ (51), 138 [$C_{10}H_{18}$]$^+$ (100); $^1H$ NMR ($CDCl_3$, 400 MHz, TMS int. standard): 2.78 *br s* (H-13), 5.94 *br s* (H-15), 5.13 *br s* (H-17), 5.10 *br s* (H-17'), 1.17 *s* (H-18), 0.96 *s* (H-20), 2.07 *s* (OAc), 3.65 *s*(OMe).

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