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UNUSUAL DITERPENES AND SESQUITERPENE XYLOSIDES FROM *NIDORELLA HOTTENTOTICA**

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Key Word Index—*Nidorella hottentotica*; Compositae; Astereae; diterpenes; *seco*-labdane derivatives; sesquiterpenes; sesquiterpene xylosides; unusual carbon skeleton.

Abstract—The investigation of the South African species *Nidorella hottentotica* afforded in addition to known compounds several diterpene lactones, most of them being *seco*-labdanes with a ten-membered ring. Furthermore five unusual xylosides were isolated in which one or two derivatives of sesquilimonene were linked with the sugar. The structures were elucidated by spectroscopic methods and some chemical transformations. The chemotaxonomy of the genus is discussed briefly.

The genus *Nidorella* (Compositae) with *ca* 20 species belongs to the tribe Astereae. So far four species have been investigated chemically. All contain dehydrofalcarinone derivatives [1] and diterpenes, while from one species sesquilimonene derivatives were isolated [1]. We have now investigated a further species from Transvaal, *N. hottentotica*. The roots afforded the acetylenic compounds **1-3** also found in the other species [2]. The aerial parts contained **3** as well as phytol, phytol linolenoate, squalene, germacrene D, α-humulene, coumarin, obliquine (**4**) [3], prenyletin (**5**) [4], the flavonol **6** [5] and a complex mixture of diterpene lactones and sesquiterpene glycosides whose separation was extremely difficult. The main constituent was the xyloside **18**, but the epimer **17**, the ketone **15**, the desoxy compound **14** and **25** were also present. As the oxidation of **17** and **18** afforded the same ketone, which was identical with the natural compound **15**, an oxygen function was at the same location in each compound. Acetylation of **17** and **18** afforded the triacetates **19** and **20**, while reduction of **18** gave the sesquiterpene diol **23**, which on acetylation afforded the diacetate **24**. Upon reduction of **18** the xyloside **25** was also obtained, which was identical with the natural compound. Its acetylation afforded the triacetate **26**. As the ^{1}H NMR spectral data of **18** (Table 1) clearly indicated the presence of an unsaturated ester, the diol **23** obviously was formed by reduction of the ester group. The corresponding acid **21** was also isolated from the mixture of the natural products. Esterification gave the methyl ester **22** and its ^{1}H NMR spectral data (Table 2) fully corresponded to those of a part of **18**. The structure of **22** and the ester moiety of **18** clearly followed from the ^{1}H NMR spectrum, which was close to that of methyl nidorellaurinoate [1]. However, the additional hydroxyl group and the position of the double bonds caused some changes. Spin decoupling showed that the allylic hydroxyl was at C-6 and that H-5 had three large couplings, indicating the equatorial position of the hydroxyl and the *iso*-propenyl group. Consequently the ^{1}H NMR spectral data were in part close to those of carveol, while those of **15** were in part close to the spectral data of carvone. The stereochemistry at C-6 was supported by the fact that carvone on reduction with sodium borohydride only gave the equatorial alcohol for which the ^{1}H NMR data were nearly identical with the relevant signals in the spectrum of **18**. The nature of the sugar moiety of **18** followed from the couplings observed in the spectrum of the triacetates **20** (Table 1) and **26** (Table 2), as all signals could be assigned by spin decoupling. The position of the ester group was deduced from the ^{1}H NMR spectrum of **18**, as the H-4′ signal was shifted downfield, while the position of the second sesquiterpene part followed from the nearly unchanged chemical shifts of H-1′ in the spectra of **18** and **20** as well as from that of **25** and **26** (Table 1). The structures of the second sesquiterpene moiety were also deduced from the spectral data of **25** and **26**. While several signals were nearly identical with those of limonene, the additional side chain followed from the ^{1}H NMR signals of the $CH(Me)CH_2OR$ part, though the signals of H-7″, H-11″, H-12″ and H-13″ were overlapping multiplets. The signals of H-14″ were double doublets, which were coupled with a multiplet at δ 1.72. However, the latter was also coupled with the methyl group (H-15″). The corresponding signals in the spectrum of **18** were identical with those of **25**. The mass spectrum of **18** only gave a $[M-H_2O]^+$ peak, but chemical ionization showed the expected $[M+1]^+$ peak at *m/z* 587, but here also *m/z* 569 was much more pronounced. Elimination of the sesquiterpene part led to the base

*Part 401 in the series "Naturally Occurring Terpene Derivatives". For Part 400 see Bohlmann, F. and Fritz G. (1981) *Tetrahedron Letters* 4803.

Table 1. ^{1}H NMR spectral data of compounds **14–16**, **18** and **20** (400 MHz, $CDCl_3$, TMS as int. standard)

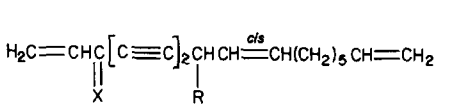
	14	**15**	**16**	**18**†	**20***
H-2	5.44 *br s*	6.76 *br s*	6.75 *br s*	5.53 *br s*	5.64 *br d*
H-5		2.57 *ddd* 2.35 *dd*			1.47 *dddd*
H-6		–	–	4.23 *br dd*	5.49 *br dd*
H-9	4.70 *br s*	4.80 *br s* 4.74 *br s*	4.82 *br s* 4.77 *br s*	4.72 *br s*	4.74 *br s* 4.91 *br s*
H-10	1.74 *br s*	1.75 *br s*	1.76 *br s*	1.74 *br s*	1.73 *br s*
H-12	6.79 *br t*	6.76 *br t*	6.74 *br t*	6.82 *br t*	6.72 *br t*
H-15	1.85 *br s*	1.81 *br s*	1.79 *br s*	1.85 *br s*	1.79 *br s*
H-1′	4.49 *d*	4.48 *d*	4.48 *d*	4.47 *d*	4.47 *d*
H-2′	3.57 *br dd*	3.56 *br dd*	4.96 *dd*	3.56 *br dd*	4.94 *dd*
H-3′	3.82 *br dd*	3.80 *br dd*	5.22 *dd*	3.80 *br dd*	5.22 *dd*
H-4′	4.89 *ddd*	4.87 *ddd*	4.96 *m*	4.87 *ddd*	4.94 *ddd*
H-5′$_1$	4.14 *dd*	4.13 *dd*	4.18 *dd*	4.12 *dd*	4.17 *dd*
H-5′$_2$	3.48 *dd*	3.45 *dd*	3.38 *dd*	3.46 *dd*	3.37 *dd*
H-2″	5.40 *br s*	5.40 *br s*	5.40 *br s*	5.40 *br s*	5.39 *br s*
H-9″	4.70 *br s*	4.70 *br s*	4.71 *br s*	4.69 *br s*	4.70 *br s*
H-10″	1.74 *br s*	1.73 *br s*	1.74 *br s*	1.73 *br s*	1.71 *br s*
H-13″					1.72 *m*
H-14$_1$″	3.63 *dd*	3.62 *dd*	3.63 *dd*	3.62 *dd*	3.62 *dd*
H-14″$_2$	3.37 *dd*	3.36 *dd*	3.30 *dd*	3.36 *dd*	3.29 *dd*
H-15	0.93 *d*	0.93 *d*	0.93 *d*	0.92 *d*	0.87 *d*
OAc	—	—	2.03 *s*	—	2.01 *s*
			2.06 *s*	—	2.05 *s*
					2.08 *s*

*H-3 2.15–1.95 *m*, H-4 2.28 *br dd*, H-11 2.2 *m*.

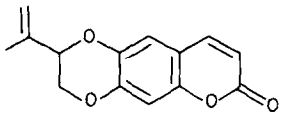
†**17**: H-2 5.73 *br s*, H-6 4.14 *dd* (J = 6.5, 6.5 Hz), **19**: H-2 5.71 *br s* H-6 5.21 *dd* (J = 6.5, 6.5 Hz), H-12 6.66 *br t*.

J(Hz): 11, 12 = 13″, 15″ = 7; 13″, 14″$_1$ = 6.5; 13″, 14″ = 6; 14″$_1$, 14″$_2$ = 9.5; 1′, 2′ = 6.5; 2′, 3′ = 8.5; 3′, 4′ = 8.5; 4′, 5′$_1$ = 5; 4′, 5′$_2$ = 8.5; 5′$_1$, 5′$_2$ = 12; compound **15**: 3α, 5α = 1.5; 4, 5α = 3.5; 4, 5β = 12.5; 5α, 5β = 16; compounds **18** and **20**: 3, 4 = 4, 5β ~ 12; 5α, 6 ~ 7; 5β, 6 ~ 10.

peak m/z 347 $[M+1-C_{15}H_{26}O]^+$ in the CI spectrum, while in the EI spectrum m/z 214 ($C_{15}H_{18}O$) was one of the stronger fragments, obviously formed from the ester part by elimination of two molecules of water leading to the corresponding ketene. The changed nature of the ester part was deduced from the ^{1}H NMR spectrum of **14** (Table 1). Several signals were similar to those in the spectrum of limonene. The structure was further supported by the mass spectrum. Again only chemical ionization gave a clear $[M+1]^+$ ion and m/z 349 $[M+1-C_{15}H_{26}O]^+$ was also present. We propose the name nidohottin for compound **14**. The sesquiterpene moiety **21** (without any oxygen functions) we now name sesquilimonene in place of the old name cycloisopropenmyrcene, which was proposed for a hydrocarbon obtained from myrcene and isoprene [6]. The carbon skeleton has only been observed previously in a benzofuran derivative [7]. Compound **21** therefore is 6-hydroxysesquilimonen-14-oic acid. The diterpene lactones present in the mixture of the polar compounds could only be partially separated. The main constituent was the angelate **9**, which was separated from a mixture of **10–12**, which obviously differed from **9** only by the nature of the ester groups. The angelate residue was replaced by *iso*-butyrate, methylbutyrate and *iso*-valerate. Furthermore a diterpene was present in which the ester group was replaced by a free hydroxyl (**8**). ^{1}H NMR investigations of **9** (Table 3) allowed the assignment of the sequences **A** and **B** by spin decoupling as the chemical shift of H-12 (sequence **A**) required an acyloxy residue at this carbon. Furthermore two methyl singlets were visible. The molecular formula, $C_{25}H_{32}O_7$, followed from the mass spectrum of **9**, though electron impact conditions showed no molecular ion. Chemical ionization gave a clear $[M+1]^+$ peak (m/z 445) followed by elimination of angelic acid. Sodium borohydride reduction afforded an alcohol, as shown by the ^{1}H NMR spectral data (Table 3) and the CI mass spectrum, which in addition to the changed $[M+1]^+$ peak (m/z 447) showed elimination of water (m/z 429). The ^{1}H NMR spectrum of the alcohol showed that the keto group had to be placed α to the ester group, as a vicinal coupling between the corresponding protons could be shown by decoupling. Consequently sequence **A** must be completed by an additional keto group. The presence of a lactone was evident from the IR spectrum. However, the observed frequency at 1780 cm^{-1}, was unexpected for a δ-lactone, which followed from sequence **A**.



	1	2	3
X	O	H,OH	H,OH
R	H	H	OAc



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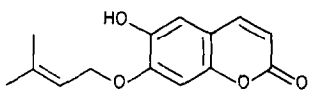

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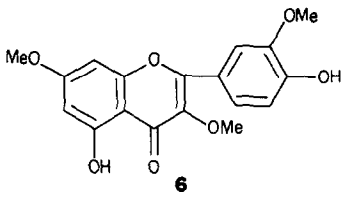

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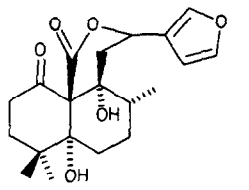

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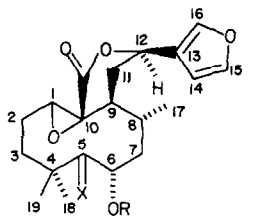
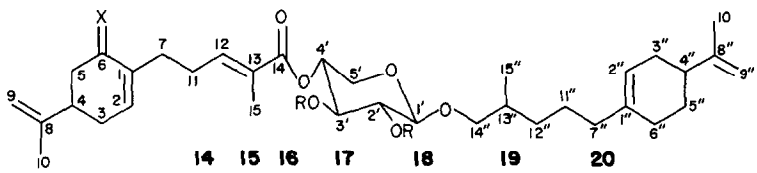
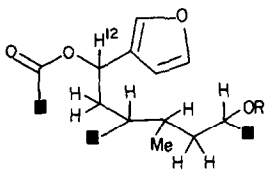


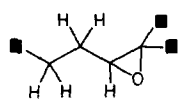
	8	9	10	11	12	13
R	H	Ang	iBu	Mebu	iVal	Ang
X	O	O	O	O	O	H,OH



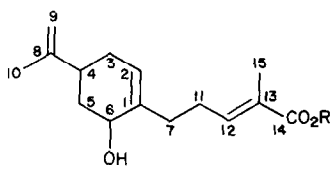
	14	15	16	17	18	19	20
X	H_2	O	O	H,αOH	H,βOH	H,αOAc	H,βOAc
R	H	H	Ac	H	H	Ac	Ac



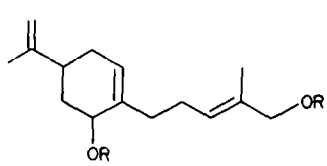
A



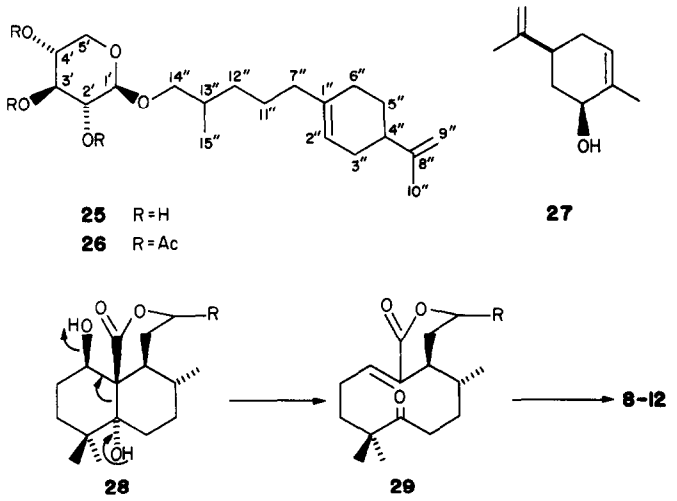
B



21 R = H
22 R = Me



23 R = H
24 R = Ac



25 R=H
26 R=Ac

27

28 **29**

Obviously the IR band was influenced by the α-epoxide grouping. This effect was also observed in γ-lactones, where the lactone band was shifted to 1800 cm^{-1} [8]. Combination of the sequences now led to structure **9** as the only logical structure. The large couplings $J_{6,7}$ and $J_{7,8}$ required equatorial orientations of the ester group at C-6 and the methyl group at C-8, which was supported by the downfield shift of H-8 in the spectrum of **8**. The stereochemistry at C-1 and C-10 could not be assigned with certainty. The ^{13}C NMR spectrum further supported the structure of **9**. The absolute configuration could not be determined. The structures of **8** and **10–12** were also established, as the ^1H NMR spectra clearly showed identical stereochemistry in all cases. We have given the name *seco*-nidorella lactone to compound **8**. In addition to

Table 2. ^1H NMR spectral data of compounds **22** and **24–27** (400 MHz, $CDCl_3$, TMS as int. standard)

	22	**24**	**25**	**26**	**27**
H-1′	—	—	4.37 *d*	4.46 *d*	—
H-2	5.52 *br s*	5.63 *br s*	5.41 *br s*	5.39 *br s*	5.50 *br s*
H-2′	—	—	3.47 *dd*	4.91 *d*	—
H-3	2.07 *br d* 1.95 *br dd*	—	—	—	2.07 *dddq* 1.96 *dddq*
H-3′	—	—	3.61 *dd*	5.15 *dd*	—
H-4	2.29 *br dd*	—	—	—	2.27 *ddddd*
H-4′	—	—	3.36 *dd*	3.36 *dd*	—
H-5	2.17 *m* 1.50 *m*	—	—	—	2.16 *dddd* 1.50 *ddd*
H-5′$_1$	—	—	4.04 *dd*	4.11 *dd*	—
H-5′$_2$	—	—	3.38 *dd*	3.36 *dd*	—
H-6	4.26 *br dd*	5.50 *br dd*	—	—	4.19 *br dd*
H-7	2.17 *m*	4.72, 4.70 *br s*	—	—	1.76 *dddd*
H-9	4.74 *br s*	—	4.71 *br s*	4.69 *br s*	4.73 *br s*
H-10	1.74 *br s*	1.72 *br s*	1.74 *br s*	1.73 *br s*	1.74 *dd*
H-11	2.38 *m*	—	—	—	—
H-12	6.78 *br t*	5.43 *br t*	—	—	—
H-13	—	—	1.7 *m*	1.7 *m*	—
H-14	—	4.43 *br s*	3.64 *dd*	3.61 *dd*	—
H-14′	—		3.38 *dd*	3.28 *dd*	—
H-15	1.85 *br s*	1.64 *br s*	0.94 *d*	0.87 *d*	—
OMe	3.73 *s*	—	—	—	—
OAc	—	2.08 *s*	—	2.04 *s* (6H)	—
		2.07 *s*	—	2.03 *s*	—

J (Hz): see Table 1; compound **27**: 2,3α ~ 3; 2,3β = 2, 6 = 2, 7 ~ 1; 3α,3β = 17; 3α,5α = 1.5; 3α,7 ~ 1; 3β,7 ~ 1; 3α,4α = 5; 3β,4α = 10; 4α,5α = 5; 4α,5β = 12.5; 4α,9 ~ 1; 5α,5β = 12.5; 5α,6 ~ 5; 5β,6 = 9.5; 6,7 ~ 1.

Table 3. ^{1}H NMR spectral data of compounds **7–9** and **13** (400 MHz, $CDCl_3$ TMS as int. standard)

	7	8	9*	13†
H-1	—	3.10 *br d*	3.07 *br d*	2.98 *br d*
H-2	2.10 *ddd*	2.30 *m*	2.36 *m*	
H-2′	1.92 *ddd*	2.20 *m*	2.14 *m*	
H-3	1.69 *ddd*		2.23 *m*	not detected
		2.33 *m*		
H-3′	1.80 *ddd*		2.45 *m*	
H-6	1.79 *m*			
		3.75 *ddd*	5.64 *dd*	5.51 *dd*
H-6′	1.60 *m*			
H-7	1.53 *m*	1.81 *ddd*	1.75 *ddd*	1.65 *m*
H-7′	1.20 *m*	1.49 *ddd*	1.58 *ddd*	
H-8	1.97 *m*	2.41 *m*	1.91 *m*	1.9 *m*
H-9	—	2.75 *ddd*	2.67 *ddd*	2.76 *ddd*
H-11	2.78 *dd*	2.55 *ddd*	2.54 *ddd*	2.57 *ddd*
H-11′	2.24 *dd*	2.04 *ddd*	1.91 *ddd*	1.9 *m*
H-12	5.45 *d*	5.27 *dd*	5.26 *dd*	5.29 *dd*
H-14	6.36 *dd*	6.43 *dd*	6.40 *dd*	6.41 *dd*
H-15	7.45 *dd*	7.42 *dd*	7.42 *dd*	7.43 *dd*
H-16	7.43 *dd*	7.49 *dd*	7.47 *dd*	7.48 *dd*
H-17	1.24 *d*	1.12 *d*	1.14 *d*	1.22 *d*
H-18	1.09 *s*	1.38 *s*	1.41 *s*	1.30 *s*
H-19	0.99 *s*	1.31 *s*	1.18 *s*	1.04 *s*
OR	—	3.58 *d*	6.14 *qq*	6.14 *qq*
			2.05 *dq*	2.05 *dq*
			1.96 *dq*	1.98 *dq*

*Data of compounds **10–12** nearly identical with those of **9** except ester signals *i*Bu: 2.30 *qq*, 1.18 *d*; MeBu: 1.11 *d*, 0.93 *t*; *i*Val: 0.97 *d* and H-6 5.54 *dd*.

†H-5 3.70 *br d*, OH 3.43.

J (Hz): 14,15 = 2; 14,16 = 15, 16 ~ 5; compound **7**: 2,2′ = 13; 2,3 = 4; 2,3′ = 10.5; 2′,3 = 9; 2′,3′ = 4.5; 3′,3′ = 13; 8,17 = 7; 11,11′ = 13; 11,12 = 9; 11′,12 = 4.5; compounds **8–13**: 1,2 = 3; 6,7 = 2; 6,7′ = 12; 7,7′ = 14; 7,8 = 11; 7′,8 = 4; 8,9 = 5; 8,17 = 7; 9,11 = 8.5; 9,11′ = 12.5; 11,11′ = 12.5; 11,12 = 6; 11′,12 = 11 (compound **8**: 6, OH = 12; compound **13**: 5,6 = 4; 5, OH = 11).

compounds **8–12** a further diterpene lactone was isolated which most probably has structure **7**. The ^{1}H NMR spectral data (Table 3) differed from those of **8–12** in the splitting and chemical shifts of H-11, since one vicinal coupling was missing and both signals were shifted downfield. Furthermore the epoxide and the ester groups were missing. Spin decoupling allowed the assignment of the signals of H-11 through H-15 and H-6 through H-8. As the presence of a ■–CH_2CH_2–■ sequence was shown, which must be linked with a keto group since the signals were at lower fields, the combination of the sequences led to structure **7**, if the missing neighbours of H-6 and H-8 were tertiary alcohol groups. This, however, only followed indirectly from the mass spectrum, because even by chemical ionization only a $[M - H_2O]^+$ fragment was visible. However, as the number of the protons which could be recognized in the ^{1}H NMR spectrum did not agree with a molecular formula $C_{20}H_{24}O_5$, a second hydroxyl had to be assumed, which can only be placed at C-5. Therefore structure **7** was most likely but it could not be established with certainty. The stereochemistry at C-5 and the absolute configuration could not be determined. We have named compound **7** nidorella lactone. Probably compounds **8–12** were formed via **28** by fragmentation leading to **29**, which by further oxidation would lead to **8–12**, while by further oxidation **28** could also be transformed to compound **7**.

The chemistry of *N. hottentotica* again shows that in addition to dehydrofalcarinone-like compounds such as **1–3**, sesquilimonene derivatives may also be useful markers for this genus, while the nature of the diterpenes differs in the species, which have been investigated so far. However, the fact that they are always highly oxygenated may be characteristic.

EXPERIMENTAL

The air-dried plant material, collected in Transvaal, voucher 81/2 (deposited in the Botanical Research Institute, Pretoria) was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated 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 (30 g) gave 3 mg **1**, 8 mg **2** and 5 mg **3**, while the aerial parts (180 g) afforded 16 mg germacrene D, 8 mg α-humulene, 30 mg squalene, 6 mg phytol, 8 mg of its linolenoate, 6 mg coumarin, 30 mg **3**, 12 mg **4**, 15 mg **5**, 2 mg **6**, 5 mg **7** (CH_2Cl_2–Et_2O, 3:1), 50 mg **8** (CH_2Cl_2–Et_2O, 3:1 and twice with C_6H_6–Et_2O, 17:3), 30 mg **10–12** (same solvents, not separated, proportions *ca* 2:1:2), 5 mg **13** (CH_2Cl_2–Et_2O, 3:1), 25 mg **14** (Et_2O–petrol, 3:1), 4 mg **15** (Et_2O–petrol, 3:1), 10 mg **17** (Et_2O, twice), 180 mg **18** (CH_2Cl–Et_2O, 3:1 and Et_2O), 5 mg **21** (same solvents) and 19 mg **25** (CH_2Cl_2–Et_2O, 3:1).

Nidorella lactone (**7**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550 (OH), 1780 (lactone), 1735 (C=O), 880 (furan); MS *m/z* (rel. int.): 344 $[M-H_2O]^+$ (12) ($C_{20}H_{24}O_5$), 326 $[344-H_2O]^+$ (3), 316 $[344-CO]^+$ (2), 298 $[316-H_2O]^+$ (4), 95$[C_5H_3O_2]^+$ (47), 57 (100), CIMS-(*iso*-butane): 345 $[M+1-H_2O]^+$ (100).

Seco-nidorella lactone (**8**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550 (OH), 1770 (lactone), 1690 (C=O, hydrogen bonded), 880 (furane); CIMS (*iso*-butane) *m/z* (rel. int.): 363 $[M+1]^+$ (10), 345 $[363-H_2O]^+$ (82), 141 (100).

Seco-nodorella lactone-6-O-*angelate* (**9**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (lactone), 1720, 1710 (C=O, C=CCO_2R), 880 (furane); CIMS (*iso*-butane) *m/z* (rel. int.): 445 $[M+1]^+$ (22), 345 $(445-HOAng]^+$ (100), 101 $[AngOH+1]^+$ (35), 83 $[101-H_2O]^+$ (34). ^{13}C NMR ($CDCl_3$, 67.5 MHz, C-1 through C-20): 59.0, 19.7, 34.6, 46.9, not detected, 71.4, 32.8, 34.0, 54.2, 61.6, 29.4, 72.3, 124.1, 108.4, 139.0, 143.9, 22.3, 18.2, 16.8, not detected (OAng 127.7, 139.9, 15.9, 20.7) (a few signals may be interchangeable).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-7.7 \quad -8.3 \quad -10.2 \quad -25.9} \ (CHCl_3;\ c\ 0.64).$$

To 10 mg **9** in 1 ml *iso*-propanol 10 mg $NaBH_4$ was added. After 10 min dil. H_2SO_4 was added. TLC (Et_2O–petrol, CH_2Cl_2–Et_2O, 3:1) afforded 8 mg **13**, colourless gum, CIMS (*iso*-butane) *m/z* (rel. int.): 447 $[M+1]^+$ (100), 429 $[447-H_2O]^+$ (63), 347 $[447-HOAng]^+$ (62), 329 $[347-H_2O]^+$ (67).

Seco-nidorella lactone-6-O-iso-*butyrate, 2-methylbutyrate and isovalerate* (**10–12**). Unseparated colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (lactone), 1730 (CO_2R), 1710 (C=O), 880 (furane); CIMS (*iso*-butane) *m/z* (rel. int.): 447, 443 $[M+1]^+$ (10 and 8), 345 $[M+1-HO_2CR]^+$ (100).

Nidohottin (**14**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1725 (C=CCO_2R); CIMS (*iso*-butane) *m/z* (rel. int.): 571 $[M+1]^+$ (16), 553 $[571-H_2O]^+$ (3), 349 $[571-C_{15}H_{26}O]^+$ (20), 235 $[RCO_2H+1]^+$ (30).

Nidohottin-6-*one* (**15**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3530 (OH), 1720, 1650 (C=CCO_2R), 1680 (C=CC=O), 900 (C=CH_2); Acetylation (Ac_2O, 70°) afforded **16**, colourless gum; CIMS (*iso*-butane) *m/z* (rel. int.): 464 $[M+1-C_{15}H_{24}]^+$ (6), 447 $[M+1-C_{15}H_{25}OH]^+$ (90), 231 $[RCO]^+$ (100).

Nidohottin-6α-*ol* (**17**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 568 $[M-H_2O]^+$ (0.5), 364 $[M-C_{15}H_{25}OH]^+$ (7), 214 $[A]^+$ (52), 55 (100). Acetylation (Ac_2O, CH_2Cl_2, 4-dimethylaminopyridine DMAP) afforded **19**, colourless gum, ^1H NMR see Table 1.

Nidohottin-6β-*ol* (**18**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3530 (OH), 1725 (C=CCO_2R); MS *m/z* (rel. int.): 568 $[M-H_2O]^+$ (0.5), 364 $[M-C_{15}H_{25}OH]^+$ (8), 346 $[364-H_2O]^+$ (12), 214 $[A]^+$ (50), 55 (100); CIMS (*iso*-butane) 487 $[M+1]^+$ (6), 569 $[587-H_2O]^+$ (57), 551 $[569-H_2O]^+$ (12), 347 $[569-C_{15}H_{25}OH]^+$ (100). Compound **18** (20 mg) was acetylated as above (Ac_2O–DMAP) affording 18 mg **20**, colourless gum, ^1H NMR see Table 1. Compound **18** (10 mg) in 2 ml Et_2O was reduced with 20 mg $LiAlH_4$ (30 min room temp.). TLC (Et_2O) afforded 1 mg **25**, identical with the natural compound, and 2 mg **23**, colourless gum, MS *m/z* (rel. int.): 218 $[M-H_2O]^+$ (6), 203 $[218-Me]^+$ (17), 175 $[203-CO]^+$ (71), 69 $[C_5H_9]^+$ (81), 55 $[C_4H_7]^+$ (100); CIMS (*iso*-butane): 237 $[M+1]^+$ (1), 219 $[237-H_2O]^+$ (100), 201 $[219-H_2O]^+$ (31). Acetylation (Ac_2O, 70°) afforded **24**, colourless gum CIMS (*iso*-butane) *m/z* (rel. int.): 321 $[M+1]^+$ (1), 261 $[321-HOAc]^+$ (100), 201 $[261-HOAc]^+$ (31). Compounds **17** (5 mg) and **18** (5 mg) respectively were stirred for 2 hr in Et_2O with 50 mg MnO_2. TLC afforded **15** identical with the natural ketone.

6β-*Hydroxysesquilimonen*-14-*oic acid* (**21**). Colourless gum, which was purified as its methyl ester **22** (TLC: Et_2O–petrol, 1:1); colourless gum, MS *m/z* (rel. int.): 264 $[M]^+$ (5), 249.150 $[M-Me]^+$ (19) ($C_{15}H_{21}O_3$), 232 $[M-MeOH]^+$ (9), 217 $[232-Me]^+$ (12), 205 $[M-CO_2Me]^+$ (8), 204 $[232-CO]^+$ (7), 151 $[C_{10}H_{15}O]^+$ (17), 133 $[151-H_2O]^+$ (33), 55 (100).

14-*Hydroxy*-12,13-*dihydrosesquilimonene*-14-O-(1)-*xyloide* (**25**). Colourless gum; CIMS (*iso*-butane) *m/z* (rel. int.): 355 $[M+1]^+$ (11), 337 $[355-H_2O]^+$ (14), 223 $[C_{15}H_{26}O+1]^+$ (100), purified as its triacetate **26**, colourless gum; MS *m/z* (rel. int.): 481 $[M+1]^+$ (1), 421 $[481-HOAc]^+$ (1), 361 $[421-HOAc]^+$ (1), 319 $[361-ketene]^+$ (15), 259 $[M-C_{15}H_{26}O]^+$ (100), 199 $[259-HOAc]^+$ (38), 169 $[199-CH_2O]^+$ (78), 139 $[199-HOAc]^+$ (9).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-5.6 \quad -5.8 \quad -6.7 \quad -10.5} \ (CHCl_3;\ c\ 1.1).$$

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REFERENCES

1. Bohlmann, F. and Fritz, U. (1978) *Phytochemistry* **17**, 1769.
2. Bohlmann, F., Burkhardt, T. and Zdero, C. (1973) *Naturally Occurring Acetylenes*. Academic Press, London.
3. Dean, F. M. and Parton, B. (1969) *J. Chem. Soc.* 526.
4. Schwenker, G., Kloss, P. and Engels, W. (1967) *Pharmazie* **22**, 724.
5. Frazer, A. W. and Lewis, J. K. (1973) *Phytochemistry* **12**, 1787.
6. Ruzicka, C. and Boch, W. (1931) *Helv. Chim. Acta* **14**, 1336.
7. Winheimer. A. J. and Washecheck. I. H. (1969) *Tetrahedron Letters*, 3315.
8. Bohlmann, F., Fritz, U., King, R. M. and Robinson, H. (1980) *Phytochemistry* **20**, 743.