(Si gel, $CHCl_3$). The fraction eluted with petrol–C_6H_6 (9:1) gave lupeol (720 mg), mp 215°. The next fractions eluted with the same eluent gave stigmasterol (330 mg), mp 168°. Elution with petrol–C_6H_6 (3:1) gave 11,13-dihydrodeoxyelephantopin (**1**). This was purified by prep. TLC (Si gel, $CHCl_3$) and on crystallization from $CHCl_3$–petrol (1:1) gave white needles (12 mg), mp 234°. MS *m/z* (rel. int.): 346 (1.62), 290 (1.15), 277 (0.84), 260 (22.15), 232 (8.94), 214 (24.62), 203 (11.86), 188 (9.71), 175 (11.62), 147 (9.96), 121 (14.40), 91 (20.13), 83 (49.48), 69 (100), 55 (40), 41 (100). Accurate mass of peak *m/z* 260 ($C_{15}H_{16}O_4$): 260.1037 $C_{15}H_{16}O_4$ requires 260.1047. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3020, 1765, 1740, 1700, 1630, 1260. UV λ_{max}^{MeOH} 217 nm (ϵ = 15,500). ^1H NMR (90 MHz, $CDCl_3$): δ 1.24 (3H, *d*, *J* = 8 Hz, H-13), 1.85 (3H, *d*, *J* = 1 Hz, H-15), 1.96 (3H, *d*, *J* = 1 Hz, H-18), 2.5–3.2 (6H, *m*, H-3, H-7, H-9), 4.52 (1H, *m*, H-8), 4.9 (1H, *d*, *J* = 12 Hz, H-15), 5.4–5.5 (2H, *m*, H-2, H-6), 5.68 (1H, *d*, *J* = 1 Hz, H-19), 6.16 (1H, *d*, *J* = 1 Hz, H-19), 6.84 (1H, *s*, H-1).

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ENT-BEYER-15-ENE DERIVATIVES FROM *NIDORELLA ANOMALA**

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Key Word Index—*Nidorella anomala*; Compositae; Astereae; diterpenes; *ent*-beyerene derivatives.

Abstract—*Nidorella anomala* afforded in addition to known beyerene derivatives three new ones.

Six species from the South African genus *Nidorella* (Compositae, tribe Astereae) have been investigated chemically. These species all contain dehydrofalcarinone or its derivatives[1, 2], while only three species afforded diterpenes, most of them being *ent*-clerodanes[1, 2]. Two species contained *seco*-clerodane or *seco*-labdane derivatives[1, 2]; two sesquilimonene derivatives[1, 2] and coumarins such as obliquin were isolated from two species[1, 2]. We have now investigated *Nidorella anomala* Steetz, which differs from all the other species by its 3–4-lobed, non-radiate outer flowers, with sparse pappus shorter than the tube[3]. The roots afforded the dehydrofalcarinone derivative **10**[1], while the aerial parts gave coumarin, obliquin (**11**)[4] and the *ent*-beyer-15-ene derivatives **1**[5], **3**[6] and **4**[7] as well as three further ones, the hydroxy acid **5**, the malonate **7** and the diester **9**. The structure of **5**, which was transferred to its methyl ester, followed from the ^1H NMR spectrum (Table 1). Most signals were close to those of **2**, only the additional downfield signals at δ 3.07 and 3.32 indicated the presence of a hydroxyl group. The former signal was a three-fold doublet and coupled with the broadened doublet at δ 3.32. The couplings observed showed that an equatorial hydroxyl group was present, which obviously was hydrogen bonded with the carbomethoxy group as followed from the IR spectrum, the large coupling observed in the ^1H NMR spectrum and the downfield shift signal of H-18 if compared with the chemical shift of this signal in the spectrum of **2**. The second diterpene was transformed to the methyl ester **8**. The structure followed from the mass spectrum and the ^1H NMR spectral data (Table 1). In addition to the molecular formula ($C_{24}H_{36}O_4$), the elimination of $O{=}C{=}CHCO_2Me$, HO_2CCH_2Me and $CH_2OCOCH_2CO_2Me$ supported the presence of the malonate residue. The ^1H NMR spectrum showed the typical doublets of H-19 and a two-proton singlet at δ 3.38, typical of a malonate, while the chemical

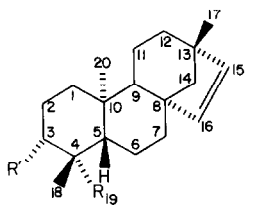
*Part 410 in the series "Naturally Occurring Terpene Derivatives". For Part 409 see Bohlmann, F., Zdero, C., Robinson, H. and King, R. M. (1982) *Phytochemistry* **21** (in press).

Table 1. ^{1}H NMR spectral data of compounds **6**, **8** and **9** (400 MHz, $CDCl_3$, TMS as int. standard) and ^{13}C NMR spectrum of compound **9**

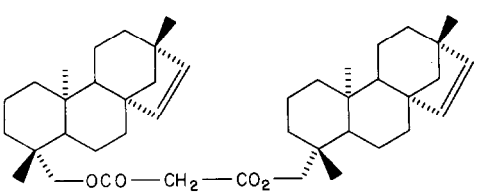
	^{1}H NMR						
	6	**8**	**9**	^{13}C NMR	($CDCl_3$) of **9**		
H-3	3.07 *ddd*	—	—	C-1	39.0	C-11	20.2
H-15	5.69 *d*	5.65 *d*	5.64 *d*	C-2	18.2	C-12	33.2
H-16	5.47 *d*	5.46 *d*	5.46 *d*	C-3	36.2	C-13	43.6
H-17	1.00 *s*	1.00 *s*	1.00 *s*	C-4	39.0	C-14	61.1
H-18	1.40 *s*	0.95 *s*	1.95 *s*	C-5	56.8	C-15	134.9
H-19	—	4.35 *d*	4.34 *d*	C-6	20.2	C-16	136.0
H-19′	—	3.95 *dd*	3.93 *dd*	C-7	37.1	C-17	24.9
H-20	0.57 *s*	0.74 *s*	0.74 *s*	C-8	49.0	C-18	27.4
OCOR	—	3.38 *s*	3.36 *s*	C-9	52.9	C-19	68.3
OMe	3.67 *s*	3.75 *s*	—	C-10	37.3	C-20	15.7
OH	3.32 *d*	—	—	CO_2R	166.8	—	—
				CH_2	41.8	—	—

J (Hz): 15,16 = 5.5; compound **6**: 2α,3β = 3β, OH = 11.5; 2β,3β = 4; compound **8**: 5,19′ = 1; 19,19′ = 11.

shifts of H-19 agreed with the proposed stereochemistry at C-4. All other signals were similar to those in the spectrum of **3**. The structure elucidation of **9** caused some difficulties, as the mass spectrum gave a clear peak at *m/z* 330 ($C_{22}H_{34}O_2$) followed by elimination of ketene, although no acetate groups were present. The polarity ruled out an additional oxygen function. Accordingly, no reaction with diazomethane or acetic anhydride occurred. As the ^{1}H NMR spectrum (Table 1) was almost identical with that of **8** except for the methoxy signal, a very similar structure was assumed. The ^{13}C NMR spectrum also gave no indication of further functions. All signals agreed well with those of **3**. However, the one-proton singlet in the ^{1}H NMR spectrum at δ 3.36 led to the assumption that a diester of malonic acid may be present. This was confirmed by the CI mass spectrum, which gave a clear $[M+1]^+$ peak. A fragment at *m/z* 330 was formed by a McLafferty fragmentation. The structure was further supported by acid-catalysed methanolysis, which led to **3** and **8**. Compound **7** seemed to be the first compound, where two units of a diterpene were esterified with a dicarboxylic acid. We have given the name nidoanomalin to compound



	1	2	3	4	5	6	7	8
R	CO_2H	CO_2Me	CH_2OH	CH_2OH	CO_2H	CO_2Me	$CH_2OCOCH_2CO_2H$	$CH_2OCOCH_2CO_2Me$
R′	H	H	H	OH	OH	OH	H	H



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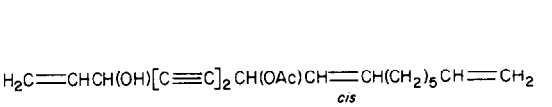

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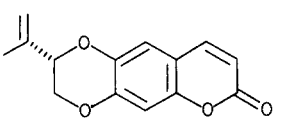

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7. These diterpenes probably belong to the *ent*-beyerene series, as the optical rotations of **2–4** were the same as those of the known compounds and those of **6**, **8** and **9** had the same signs.

The isolation of the *ent*-beyerene derivatives showed that *N. anomala* may be somewhat isolated in the genus, while the presence of **10** indicated the relationship to the other species. However, compounds like **10** have also been isolated from a few other genera of the tribe. An *ent*-beyerene derivative has been reported previously in the tribe only from a *Baccharis* species [8].

EXPERIMENTAL

The air-dried plant material collected in Transvaal (voucher 81/280, deposited in the Herbarium of the Botanic Research Institute, Pretoria), was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by CC (Si gel) and repeated TLC (Si gel). Compounds were identified by comparing the ^1H NMR spectra with those of authentic material. The roots (5 g) afforded 2 mg **10**, while the aerial parts (30 g) gave 4 mg coumarin, 20 mg **1**, 10 mg **3**, 6 mg **4**, 3 mg **5** (Et_2O–petrol, 3:1), 11.5 mg **7** (Et_2O–petrol, 3:1), 15 mg **9** (Et_2O–petrol, 1:10) and 1 mg **11**.

3α-Hydroxystachen-19-oic acid (**5**). Colourless gum, purified as its methyl ester **6** (CH_2N_2 in Et_2O), colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3550 (OH, hydrogen bonded), 1710 (CO_2R); MS *m/z* (rel. int.): 332.235 $[M]^+$ (62) ($C_{21}H_{32}O_3$), 314 $[M-H_2O]^+$ (47), 300 $[M-MeOH]^+$ (42), 282 $[300-H_2O]^+$ (44), 275 (64), 135 (82), 119 (80), 105 (97), 93 (100). $[\alpha]_D$ positive.

Erythoxylol A-malonate (**7**). Colourless gum, purified as its methyl ester **8** (CH_2N_2 in Et_2O), colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1760, 1740 ($OCOCH_2CO_2R$); MS *m/z* (rel. int.): 388.261 $[M]^+$ (44) ($C_{24}H_{36}O_4$), 373 $[M-Me]^+$ (2), 288 $[M-O{=}C{=}CHCO_2Me]^+$ (8), 270 $[M-HO_2CCH_2CO_2Me]^+$ (12), 257 $[M-CH_2OCOCH_2CO_2Me]^+$ (19), 148 (48), 135 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+17 \quad +17.5 \quad +20 \quad +35} \quad (CHCl_3;\ c\ 1.15).$$

Nidoanomalin (**9**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1750, 1735 (CO_2R), 3040, 1645 (C=C); MS *m/z* (rel. int.): 330.256 (24) ($C_{22}H_{34}O_2$, McLafferty), 288 [330–ketone]$^+$ (11), 135 (100); CIMS (*iso*-butane) *m/z* (rel. int.): 645 $[M+1]^+$ (5), 272 $[C_{20}H_{32}]^+$ (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+19.7 \quad +19.7 \quad +22.1 \quad +37.6} \quad (CHCl_3;\ c\ 0.29).$$

To 5 mg **9** in 1 ml MeOH 10 mg *p*-toluene sulfonic acid was added. After 14 hr standing at room temp. TLC (Et_2O–petrol, 1:10) afforded 2 mg **3** (identical with the natural compound), 3 mg **8** (identical with the methyl ester of **7**) and 3 mg unchanged **9**.

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TWO CHROMONE GLYCOSIDES FROM *CASSIA MULTIJUGA*

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Key Word Index—*Cassia multijuga*; Leguminosae; leaves; chromone glycosides.

Abstract—Two new 2-methylchromone glycosides have been identified in the leaves of *Cassia multijuga*.

INTRODUCTION

Species of *Cassia* are rich sources of flavonoids [1, 2], anthraquinones [3, 4] and polysaccharides [5] and the plants possess important medicinal properties. All these compounds showed considerable antibiotic activity against Gram-positive organisms.

From the leaves of *Cassia multijuga*, 5 - acetonyl - 7 - hydroxy - 2 - methylchromone, 5 - acetonyl - 2 - methylchromone - 7 - *O* - β - D - glucopyranoside and