with 0.1 M $KHCO_3$–0.1 M K_2CO_3 (80:3; pH 9; 1 × 1/3 vol) and the aq. phase acidified again to pH 2.5 and repartitioned with Et_2O. The Et_2O extract was dried (dry Na_2SO_4) and evaporated to a gum (3.4 g), 1.7 g of which were purified on a column of DEAE-Sephadex A-25 (2 × 50 cm). The elution was performed with a discontinuous gradient of HOAc in 80% MeOH according to ref. [7]. The diol was eluted with 0.25 M HOAc (ABA-containing fractions). TLC of this fraction (0.3 mm Si gel GF_{254}: C_6H_6–Me_2CO–EtOAc–HOAc, 40:10:5; 1) gave ABA (R_f 0.52) and the diol (R_f 0.21, eluted with EtOAc–MeOH, 1:1) which was then methylated with ethereal CH_2N_2 and purified by TLC (0.3 mm Si gel CF_{254}: $CHCl_3$–EtOAc, 1:1, R_f 0.3).

Preparation of 1',4' - *cis* - *and* 1',4'; - trans - *diol of ABA.* (+) - ABA - Me prepared from (+)-ABA (ethereal CH_2N_2 followed by TLC in the system (R_f 0.76) used to purify the Me ester of the diol), isolated from immature *V. faba* seeds during these experiments was reduced in 5 ml MeOH–H_2O (2:1) containing some crystals of $NaBH_4$ for 2 hr at room temp. according to ref. [8]. The MeOH was evaporated and the aq. remainder partitioned at pH 7.0 with Et_2O. The Et_2O extract was separated on TLC (Si gel GF_{254}; $CHCl_3$–MeOH, 1:1) to give the 1',4'-*cis*-diol of (+)-ABA-Me (R_f 0.33) and *trans*-diol (R_f 0.61). 1',4' - *Cis* - diol of ABA-Me MS (15 eV) *m/z* (rel. int.): 280 $(M)^+$ (27), 262 (42), 244 (23), 248 (20), 230 (28), 224 (39), 206 (65), 192 (44), 174 (84), 146 (98), 125 (100), 111 (84). 1',4' - *Trans* - diol of ABA-Me. MS (15 eV) *m/z* (rel. int.): 280 $[M]^+$ (8), 262 (42), 244 (38), 248 (10), 230 (33), 224 (16), 206 (48), 192 (31), 174 (65), 146 (80), 125 (100), 111 (75).

Bioassay. Wheat seedling bioassay was performed as described previously [9].

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8β-HYDROXY DEHYDROZALUZANIN C FROM *ANDRYALA PINNATIFIDA**

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Key Word Index—*Andryala pinnatifida*; Compositae; sesquiterpene lactone; guaianolide.

Abstract—The roots of *Andryala pinnatifida* afforded 8β-hydroxy dehydrozaluzanin C.

From the genus *Andryala* (tribe Lactuceae), so far only the isolation of taraxasterol from *A. pinnatifida* Ait (= *A. canariensis*) has been reported [1]. A re-investigation of the roots of this species afforded, in addition to taraxasteryl acetate and cinnamic acid, small amounts of a sesquiterpene lactone, molecular formula $C_{15}H_{16}O_4$. The ^1H NMR spectrum (Table 1) indicated the presence of a methylene lactone with two further exomethylene groups. As the signals for one of these groups were downfield shifted doublets as in dehydrozaluzanin C [2], a guaianolide with a 3-keto group was indicated. The presence of an additional hydroxyl group followed from the IR spectrum and a broad signal at δ 4.46, which was coupled

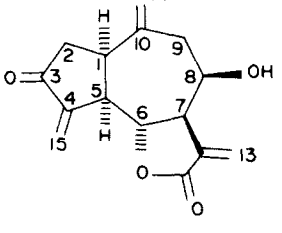
*Part 419 in the series "Naturally Occurring Terpene Derivatives". For Part 418, see Bohlmann, F., Adler, A., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 1169.

Table 1. ^{1}H NMR spectral data of compound **1** (400 MHz, $CDCl_3$, TMS as int. standard)

H-1	3.10*ddd*	H-9α	2.58*dd*
H-2α	2.69*dd*	H-9β	2.52*dd*
H-2β	2.58*dd*	H-13	6.47*d*
H-5	3.26*dddd*	H-13'	5.69*d*
H-6	4.54*dd*	H-14	5.02*s*
H-7	3.17*dddd*	H-14'	4.77*s*
H-8	4.46(*br*)	H-15	6.28*d*(*br*)
		H-15'	5.92*d*(*br*)

J (Hz): 1, 2α = 8.5; 1, 2β = 2.5; 1, 5 = 9; 2α, 2β = 18.5; 5, 6 = 6, 7 = 9.5; 5, 15 = 3; 7, 8 ~ 2; 7, 13 = 3.5; 7, 13' = 3; 8, 9α = 2.5; 8, 9β = 5; 9α, 9β = 13.5.

with two geminal coupling double doublets at δ 2.58 and 2.52 and a four-fold doublet at δ 3.17. As the latter was further coupled with the doublets at δ 6.47 and 5.69 (H-13) as well as with the double doublet at δ 4.54, the signals of H-6 to H-9 could be assigned. Irradiation at δ 4.54 collapsed a four-fold doublet at δ 3.26 to an unresolved broad doublet, while the latter was further coupled with the exomethylene signals at δ 6.28 and 5.92 as well as with a three-fold doublet at δ 3.10. The latter was coupled further with two double doublets at δ 2.69 and 2.58, obviously the signals of H-2. Consequently, the structure of the lactone was **1**. The observed couplings $J_{8,9}$ were small, as required for the given stereochemistry at C-7 and C-8. Inspection of a model showed that the β-orientation of the 8-hydroxy group led to a near 90° angle between H-7 and H-8α and that because the signals of H-14 were singlets with nearly no allylic couplings H-1 and H-9 were more or less in plane with the β-orientated exomethylene group at C-10. In this conformation, the angles between H-8α and H-9 agreed with the couplings observed (J = 5 and 2.5 Hz), while in the other possible conformation $J_{8\alpha,9\beta}$ should be large. All data, therefore, were in agreement with the presence of 8β-hydroxy dehydrozaluzanin C, the 8-epimer of a lactone already isolated from *Vernonia* species [3]. ^{1}H NMR spectral data of the 8-epimer differed in the expected manner from those of **1**. Thus the chemical shift of H-13' was as usual much more downfield in



1

the 8α-hydroxy epimer, while in the 8β-epimer the H-6 signal was shifted downfield due to the deshielding effect of the 8β-hydroxy group (Δ 0.62 ppm). The corresponding 4β,15-dihydro compound of **1** has been isolated from *Crepis virens* [4]. Its ^{1}H NMR spectral data are in part similar to those of **1**.

As so far from the tribe Lactuceae mainly guaianolides related to lactucin have been isolated [5, 6], the presence of **1** in an *Andryala* species may be of importance for the placement of this genus, which has been transferred recently from the subtribe Crepidinae [7] to the *Tolpis* group and placed in the same subgroup as *Tolpis* and *Hieracium* [8]. From these genera so far no lactones have been reported. Clearly much more work has to be done on the Lactuceae.

EXPERIMENTAL

The air-dried plant material, collected in September 1980 on Tenerife (voucher Ten 5/80, deposited in the Herbarium of the Inst. for Org. Chem., Technical University of Berlin), 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 ^{1}H NMR spectra with those of authentic material. The roots (20 g) afforded 50 mg taraxasteryl acetate, 20 mg cinnamic acid and 2 mg **1** (Et_2O–petrol, 3:1), colourless gum, which could not be induced to crystallize, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.): 260.105 $[M]^+$ (2) ($C_{15}H_{16}O_4$), 242 $[M-H_2O]^+$ (2), 166 $[M-C_6H_6O]^+$ (28), 57 (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+10 \quad +12 \quad +18 \quad +24} \quad (CHCl_3;\ c\ 0.1).$$

The aerial parts (150 g) gave 500 mg taraxasteryl acetate and 200 mg of a 1:1 mixture of stigmasterol and sitosterol.

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