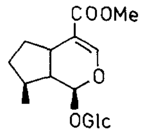

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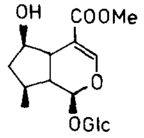

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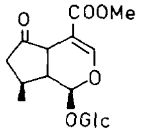

3

The results presented in Table 1 show that the incorporation of **1** into **2** and **3** in *V. offinalis* was extremely efficient in young shoots. During the flowering period, however, the incorporation decreased significantly. Previously, we had shown [3] that the incorporation of **1** into **3** in *V. officinalis* plants, past the flowering stage, was too small to be measured by ^{2}H NMR ($< 0.5\%$).

These results suggest that immature plants should be used in biosynthetic experiments with advanced precursors, unless other information is at hand.

EXPERIMENTAL

The experimental techniques, as well as the synthesis and physical properties of the precursor, have been described previously [1].

Acknowledgements—We wish to thank The Danish Natural Science Research Council for financial support and for access to NMR facilities. Access to MS facilities from The Danish Council for Scientific and Industrial Research is acknowledged.

REFERENCES

1. Damtoft, S., Jars, M. U., Kirk, O., Jensen, S. R. and Nielsen, B. J., (1983) *Phytochemistry* **22**, 695.
2. Horodysky, A. G., Waller, G. R. and Eisenbraun, E. J. (1969) *J. Biol. Chem.* **244**, 3110.
3. Damtoft, S. (1980) Thesis, The Technical University of Denmark, Lyngby.

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GUAIANOLIDES FROM *CENTAUREA KOTSCHYI*

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Key Word Index—*Centaurea kotschyi*; Compositae; sesquiterpene lactones; guaianolides.

Abstract—The aerial parts of *Centaurea kotschyi* (var. *kotschyi*) afforded, besides three known sesquiterpene lactones, a new derivative of linichlorin B. The structure was determined by spectral analysis.

INTRODUCTION

In continuation of our phytochemical investigation of the genus *Centaurea* [1], we report here the isolation and structure elucidation of a new guaianolide.

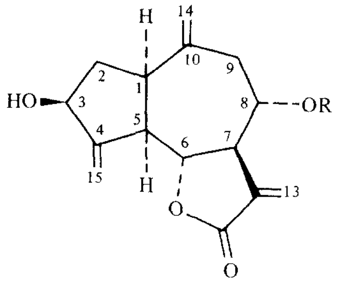
Centaurea kotschyi Boiss., endemic to Turkey, had not been investigated chemically. The aerial parts of the plant gave, in addition to the three known guaianolides desacylcynaropicrin (**1**) [2], cynaropicrin (**2**) [3] and linichlorin B (**3**) [4], a new lactone (**4**) which is closely related to linichlorin B.

RESULTS AND DISCUSSION

Compound **4**, $C_{19}H_{24}O_7$, $[M]^+$ 364, exhibited the typical IR absorption bands of an α,β-unsaturated-γ-lactone group ($1750\,cm^{-1}$), hydroxyl group(s) ($3400\,cm^{-1}$) and an acyl group (1730 and $1270\,cm^{-1}$). The ^{1}H NMR spectrum (Table 1) showed that compound **4** was very similar to linichlorin B, and that they both had the same ring structure, therefore the only difference was in the side chain. A pair of doublets at δ 3.87 and 3.64 ($J = 11$ Hz) indicated the presence of a $-CH_2-O-$ group [5, 6] and a methyl singlet δ 1.40, in addition to the signals that were assigned for the ring protons, suggested that the acyl group was an α,β-dihydroxyisobutyryl moiety. In the mass spectrum peaks at m/z 244 $[M - C_4H_8O_4]^+$ and 119 corroborated the presence of this group.

EXPERIMENTAL

Extraction and isolation. The dried, aerial parts of *C. kotschyi* (var. *kotschyi*) (1.5 kg), collected near Ankara in July 1980 (voucher No. 45503 deposited at the herbarium of the Faculty of



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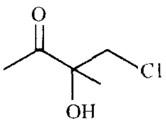
3 R =



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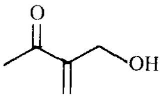

4 R =

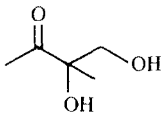

Table 1. ^{1}H NMR spectral data of **4** (400 MHz, CHCl$_3$, TMS as internal standard)

H	δ
1α	2.99 *ddd*
2α	1.71 *ddd*
2β	2.21 *ddd*
3α	4.57 *t*(*br*)
5α	2.81 *t*(*br*)
6β	4.28 *dd* (10.5; 9)*
7α	3.18 *dddd*
8β	5.15 *ddd* (5.5; 4; 9.5)
9α	2.68 *dd* (5.5; 14.5)
9β	2.47 *dd* (3.5; 15)
13	6.24 *d* (3.4)
13′	5.60 *d* (3)
14	5.16 *s* (*br*)
14′	5.09 *s*(*br*)
15	5.50 *s*(*br*)
15′	5.37 *s*(*br*)
-CCH$_2$-OH	3.87 *d* (11) 3.64 *d* (11)
-C(OH)CH$_3$	1.40 *s*

**J* (Hz).

Pharmacy, Istanbul), were extracted with EtOH, evapd to small vol. *in vacuo*, and worked up in the usual manner by using an aq. soln of 4% lead acetate [1]. The residue (13.6 g) was chromatographed on a silica gel column and eluted with CHCl$_3$ containing increasing amounts of MeOH. The fractions yielded **1**, **2**, **3** and **4** (90, 25, 50 and 17 mg), respectively.

Compound **4**. This product was purified by prep. TLC; IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1750 (γ-lactone), 1730 and 1270 (CO$_2$R), 1635 (double bond); UV λ_{max}^{MeOH} nm: 215; MS *m/z* (rel. int.): $C_{19}H_{24}O_7$, 364 $[M]^+$ (7.0), 261 $[M-C_4H_7O_3]^+$ (11.4), 244 $[M-C_4H_8O_4]^+$ (36.9), 119 (35), 91 (74.8) 75 (100).

REFERENCES

1. Oksuz, S., Ulubelen, A., Aynechi, Y. and Wagner, H. (1982) *Phytochemistry* **21**, 2747.
2. Gonzales, A. G., Bermejo, J., Massanet, G. M. and Perez, J. (1973) *An. Quim.* **69**, 1333.
3. Rustaiyan, A., Niknejad, A., Zdero, C. and Bohlmann, F. (1981) *Phytochemistry* **20**, 2427.
4. Gonzales, A. G., Bermejo, J., Amaro, J. M., Massanet, G. M., Galindo, A. and Cabrera, I. (1978) *Can. J. Chem.* **56**, 491.
5. Gonzales, A. G., Bermejo, J., Breton, L., Massanet, G. M. and Triana, J. (1974) *Phytochemistry* **13**, 1193.
6. Suchy, M., Samek, Z., Herout, V. and Sorm, F. (1968) *Collect. Czech. Chem. Commun.* **33**, 2238.