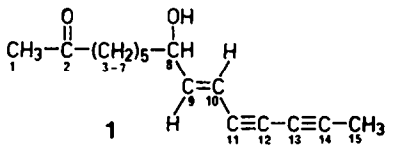

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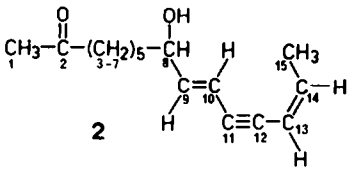

2

spectrum of **1** showed the presence of a C≡C group (2200 cm^{-1}), a C=O group (1700 cm^{-1}) and an OH group (3390 cm^{-1}). The UV spectrum indicated the presence of a diyn-ene chromophore [7, 8]. Similar data were reported by Schulte *et al.* [7] for a compound of undetermined structure from *E. angustifolia*.

Compound **1** exhibited a molecular ion peak at *m/z* 232, which was compatible with the molecular formula $C_{15}H_{20}O_2$. The ^1H NMR spectrum showed two deshielded methyl groups at 1.98 and 2.13 ppm, which suggested methyl groups adjacent to a carbonyl group and an unsaturated system. A signal at 4.17 ppm was attributable to the proton of a C<u>H</u>–OH group, while the chemical shift and couplings of the methylene group at 2.42 ppm were characteristic of a methylene group next to a carbonyl group. Signals at 6.25 and 5.72 ppm indicated the presence of a *trans* double bond ($J_{9,10}$ = 15.9). These assignments were confirmed by the ^{13}C NMR spectrum which also showed four high field quaternary carbons characteristic of internal acetylenic carbons.

Cross peaks from the 2D ^1H COSY spectrum of the mixture of **1** and **2** allowed the unambiguous identification of the fragment CH_2-3 to H-10 of both compounds and indicated a long range coupling between H-10 and CH_3-15 in **1**. These data, together with those above indicate **1** is 8-hydroxypentadeca-9*E*-ene-11,13-diyn-2-one.

Compound **2** could only be obtained by HPLC as a 1:1 mixture with **1**. Its structure was determined by comparing the data of **1** with the mixture. The IR spectra showed the same structural elements. In the mass spectrum of the mixture a second molecular ion peak at *m/z* 234 was compatible with the molecular formula $C_{15}H_{22}O_2$. The ^1H COSY spectrum clearly showed the common and different structural elements of **1** and **2**. The high field protons were identical in both molecules and indicated that both had identical structural elements C-1 to C-10. The position of the *cis* double bond in **2** was immediately evident from the COSY spectrum and indicated **2** was a reduced form of **1**. Thus compound **2** is 8-hydroxypentadeca-9*E*,13*Z*-diene-11-yn-2-one. Both compouds **1** and **2** are new.

Since **1** and **2** could not be found in fresh roots of *Echinacea pallida* but in root powder which had been stored for several days, **1** and **2** have to be regarded as artifacts arising during storage. In contrast to a preliminary communication [9], compounds **1** and **2** cannot be confirmed as constituents of *E. angustifolia* due to the fact that commercial roots of *E. angustifolia* are mixed with *E. pallida*. In addition, up to now we could not observe the formation of **1** and **2** in authentic *E. angustifolia* roots. So there is now some evidence that these two plants are chemically different.

EXPERIMENTAL

Authentic roots from flowering plants of *Echinacea pallida* were obtained from the Botanical Garden of Munich and identified by Dr. G. Heubl (voucher specimen deposited in the Herbarium of the Institute of Pharmaceutical Biology, Munich). Dried and ground roots (1 kg) of *E. angustifolia* (purchased from GALKE, Gittelde/Harz, F.R.G.; batch no. 460/4, 07.10.85 (USA), voucher specimen deposited) were extracted in a Soxhlet with $CHCl_3$, yielding 22 g of resinous material. 9 g of the $CHCl_3$ extract were fractionated by CC on silica gel, eluting with toluene–ethyl acetate (93:7). The crude fraction of **1** and **2** (120 mg) was first purified by preparative TLC (silica; toluene–ethyl acetate 19:4) and then by preparative HPLC (LiChrosorb RP 18, 7 μ) using 40% acetonitrile as mobile phase, yielding a mixture of **1** and **2** (30 mg). **1** crystallized from $CHCl_3$ (14 mg). Analytical HPLC was performed with a gradient system (acetonitrile–water, 40% to 80% in 30 min), using a LiChrospher 100-CH18, 5 μ, Hibar 125-4 column (Merck) as stationary phase. The first major peak was observed at 5.8 min, **1** at 7.2 min and **2** at 7.7 min (210 nm).

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded at ambient temperature on a Bruker VM-400 NMR spectrometer locked to the deuterium resonance of the solvent, $CDCl_3$. A 2D ^1H COSY spectrum of a mixture of the two compounds (*ca* 1:1) was recorded with a 90°-t_1-FID (t_2) pulse sequence. All 1D and 2D spectra were recorded using the standard Bruker software package. EI mass spectra were taken on AEI 902S and Kratos MS 80 RFA mass spectrometers.

8-Hydroxypentadeca-9E-ene-11,13-diyn-2-one (**1**). UV λ_{max} (nm): 281, 263, 250, 236. IR ν_{max}, film, cm^{-1}: 3390, 1700, 2200. MS *m/z* (rel. int.) 232 $[M]^+$ (30), 189 $[M-CH_3CO]^+$ (12), 174 [189 − Me]$^+$ (38), 161 (8), 147 (77), 133 (100), 119 (40), 95 (50), 43 (18); ^1H NMR (400 MHz, $CDCl_3$, TMS int. std.) δ: 1.3–1.5 (4H, *m*, $H_{5,6}$) 1.5–1.6 (4H, *m*, $H_{4,7}$), 1.98 (3H, *d*, $J_{15,10}$ = 0.9, H_{15}), 2.13

Table 1. ^{13}C NMR data for **1** and **2** (100 MHz, $CDCl_3$, TMS int. std)*

Carbon	1	2
1	29.87 (*q*)	29.68 (*q*)
2	208.94 (*s*)	‡
3	43.61 (*t*)	43.57 (*t*)
4	23.69 (*t*)	23.64 (*t*)
5	29.02 (*t*)	28.96 (*t*)
6	24.99 (*t*)	24.95 (*t*)
7	36.73 (*t*)	36.78 (*t*)
8	72.08 (*d*)	72.25 (*d*)
9	148.53 (*d*)	144.86 (*d*)
10	108.94 (*d*)	110.24 (*d*)†
11	80.12 (*s*)†	‡
12	75.17 (*s*)†	‡
13	72.44 (*s*)†	110.04 (*d*)†
14	64.38 (*s*)†	138.49 (*d*)
15	4.58 (*q*)	15.96 (*q*)

*Multiplicities were obtained from ^{13}C DEPT spectra.

†Signal assignments are interchangeable in vertical column.

‡Signal not observed.

(3H, *s*, H_1), 2.42 (2H, *t*, $J_{3,4}$ = 7.3, H_3), 4.17 (1H, *m*, $J_{8,7}$ = 5.9, H_8), 5.72 (1H, *ddd*, $J_{10,9}$ = 15.9, $J_{10,8}$ = 1.2, H_{10}), 6.25 (1H, *dd*, H_9); ^{13}C NMR: Table 1.

8-Hydroxypentadeca-9E,13Z-diene-11-yn-2-one (2). MS *m/z* (rel. int.): 234 $[M]^+$ (70), 219 $[M-Me]^+$ (45), 193 (35), 176 (32), 159 (40), 149 (45) 135 (60), 121 (72), 95 (73), 83 (100), 71 (75), 55 (98); ^{1}H NMR (400 MHz, $CDCl_3$, TMS int. std.) δ: the signals for protons H_{1-8} were the same as for **1**, 1.89 (3H, *d*, $J_{15,14}$ = 6.8, H_{15}), 5.59 (1H, *ddd*, $J_{10,9}$ = 15.9, $J_{10,8}$ = 1.6, H_{10}), 5.99 (1H, *dq*, H_{14}), 6.12 (1H, *dd*, H_9); ^{13}C NMR: Table 1.

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(7*R*)-*TRANS,TRANS*-NEPETALACTONE FROM *NEPETA ELLIPTICA*

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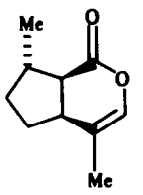
Key Word Index—*Nepeta elliptica*; Labiatae; nepetalactone; cyclopentanoid monoterpene; ^{13}C NMR spectra.

Abstract—The major component of the essential oil from the aerial parts of *Nepeta elliptica*, gathered in the Kumaun Region of India, has been identified as (7*R*)-*trans,trans*-nepetalactone primarily by comparison of its IR spectrum with those of its four (7*S*)-stereoisomers and its mass spectrum and ^{1}H and ^{13}C NMR spectra with those of its three diastereomers.

INTRODUCTION

Several members of the genus *Nepeta* produce one or more diastereomers of (7*S*)-nepetalactone [1–4]. *Nepeta cataria* [1–3] and *N. mussini* [3], the two most thoroughly studied species, give essential oils that contain, respectively, (7*S*)-*cis,trans*- and (7*S*)-*cis,cis*-nepetalactone **1a** and **1b** as the major components and (7*S*)-*trans,cis*-nepetalactone **1c** and **1a** as minor components. significantly, the ^{1}H and ^{13}C NMR spectra of **1a–c** have been described [3], and all four (7*S*)-nepetalactones **1a–d** have been synthesized [5].

We describe here the isolation and characterization of the fourth naturally occurring diastereomer of nepetalactone and the first with the (*R*)-configuration at C_7. (7*R*)-*trans,trans*-Nepetalactone **1d'** was obtained as the major component (80%) of the essential oil from the aerial parts of *Nepeta elliptica* Royle ex Benth., which grows at altitudes of 1500–3000 m in the Kumaun region of India [6].



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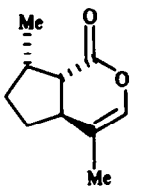

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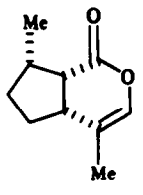

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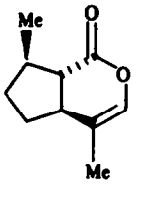

1d'