of glutamic acid of 0.38, and was present to the extent of 20 mg per g of dried leaves (as compared with e.g. 0.2 mg of aspartic acid, 0.6 mg of glutamic acid, and 0.5 mg of leucine).

Isolation of alliin. An extract, produced by disintegrating dried leaves of *A. alliaceum* (50 g) in three 500-ml portions of boiling 70% MeOH, was filtered and concd to near dryness *in vacuo*. The residue was dissolved in H_2O (30 ml), and the solution was extracted with 3 × 40 ml of $CHCl_3$. The aq. phase was transferred to an Amberlite IR 120 (H^+, 2.5 × 40 cm) column and the total amino acid fraction was further divided into a major fraction, containing the neutral and acidic amino acids (3.3 g), and another, comprising the basic amino acids and amines (1.2 g), by methods previously described [5, 6]. Further separation of the acidic (0.2 g) from the neutral amino acids (2.8 g) was likewise conducted as described [6]. Recrystallization of the latter fraction from H_2O gave a semicrystalline residue (655 mg) which was further purified by prep. HVE at pH 1.9, followed by prep. PC (PhOH–H_2O–12 M NH_3, 120:30:1, w/v/v) and chromatography on Dowex 50 W (× 8, 200–400 mesh, H^+, 0.7 × 10 cm). Washing with water (35 ml) and elution of the column with 1 M Py (25 ml) resulted in the isolation of a virtually homogeneous material, indistinguishable from authentic alliin on PC, HVE, and amino acid analysis. The ^1H NMR spectrum, in D_2O (pH 6), exhibited signals at 3.2 (2H, *m*), 3.7 (2H, *m*), 4.1 (1H, *dd*), and 4.5–6.0 ppm (3H, *m*); the same solution was characterized by a ^{13}C NMR spectrum with signals (cf. formula **4**), at 51.6 (C-5, *t*), 52.6 (C-3, *t*), 57.1 (C-2, *d*), 126.4 (C-6, *d*), 127.5 (C-7, *t*), and 173.2 ppm (C-1, *s*). The circular dichroism curve (in H_2O) displayed a negative extremum at 218 nm in accordance with the published data for alliin (**4**) [7].

Acknowledgements—The authors are grateful to Prof. R. Gmelin for authentic amino acid specimens, to Mr. O. Malver for experimental assistance, and to Dr. G. Borch for performing the CD-measurements.

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Phytochemistry, Vol. 20, No. 4, pp. 823–824, 1981.
Printed in Great Britain.

0031-9422/81/040823-02 $02.00/0
Pergamon Press Ltd.

A CARLINA OXIDE DERIVATIVE FROM *CARLINA DIAE**

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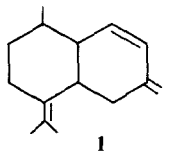
(*Received* 28 *April* 1980)

Key Word Index—*Carlina diae*; Compositae; new carlina oxide derivative; new phenyl heptene diyne.

From the genus *Carlina*, tribe Cynareae, subtribe Carlineae, several acetylenic compounds have been isolated [1], which clearly showed a difference from the other subtribes. We now have investigated *C. diae* (Rech. f.) Meusel et Kästner, a species which was transferred from *Lyrolepsis* to *Carlina* [2], to see whether the chemistry supports this classification or not. The roots afforded in addition to β-sesquiphellandrene (**1**) and the acetylenes **2**–**8** [1] only two, **5b** and 13-methoxy carlina oxide (**8**), the structures clearly follow from the spectra data. While most of the ^1H NMR-data of **8** are very similar to those of **7**, the presence of a 13-methoxy group can be deduced from the aromatic proton signals, which all showed vicinal couplings indicating an *ortho*-disubstituted phenyl group (see Experimental). **8** is an unusual compound as the oxygen function is not in the *meta*-position. Only a few compounds of this type are known [3]. Most probably **8** is formed via the unknown carboxylic acid **14** by oxidation and methylation. This would indicate that carlina oxide (**7**) and **8** may be formed in the same way as shown for phenyl heptatriyne by intramolecular aldol condensation [1],

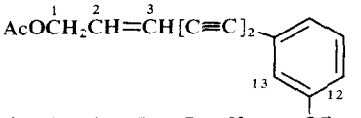
* Part 259 in the series "Polyacetylenic Compounds". For Part 258 see Bohlmann, F., Jakupovic, J., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19**, 2760.



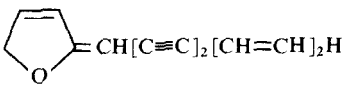
1

$ROCH_2CH{=}CH[C{\equiv}C]_3[CH{=}CH]_2H$

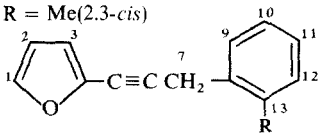
2; R = Ac **3**: R = H



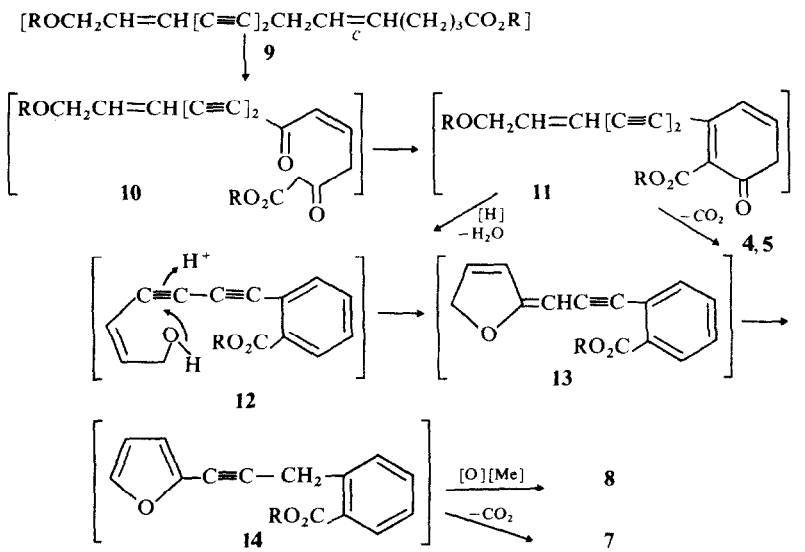
4: R = Ac **5a**: R = H **5b**: R = Me(2.3-*cis*)



6



7: R = H **8**: R = OMe



which could explain the formation of **4**, **7** and **8**. Several of the steps involved are established in the biogenesis of similar compounds [1]. The compounds isolated clearly indicate that this species belongs to *Carlina*.

EXPERIMENTAL

Air dried roots (57 g) were extracted with Et_2O–petrol (1:2). The resulting extract was first separated by column chromatography (Si gel, act. grade II) and further by TLC (Si gel, GF 254). 16 mg **1**, 2 mg **2**, 1 mg **3**, 1 mg **4**, 1 mg **5a**, 1 mg **5b**, 1 mg **6**, 45 mg **7** and 8 mg **8** (Et_2O–petrol: 1:10) were obtained.

13-*Methoxy carlina oxide* (**8**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1607, 1593, 1490, 1470, 1445, 1250, 1120, 1045; UV (λ_{max}, Et_2O): 250 nm; MS: M^+ *m/e* (rel. int. %) 212.084 (32) ($C_{14}H_{12}O_2$); 197 (100) (M^+ − Me); 181 (13) (M^+ − OMe); 169 (22) (197 −CO); 152 (20) (197 −CHO); 141 (32) (169 −CO). ^1H NMR (270 MHz, $CDCl_3$, TMS int. standard): 7.36 *dd* (1-H), 6.37 *dd* (2-H), 6.52 *d(br)* (3-H), 3.82 *s(br)* (7-H), 7.53 *d(br)* (9-H), 6.97 *dd(br)* (10-H), 7.21 *ddd* (11-H), 6.87 *d(br)* (12-H), 3.96 *s* (OMe) (*J*/Hz): 1,2 = 1.5; 1,3 = 0.5; 2,3 = 3.5; 9,10 = 7.5; 9,11 = 1.5; 10,11 = 8.

1,12-*Diacetoxy-7-phenylhept-2c-ene-4,6-diyne* (**5b**). Yellow oil, MS: *m/e* (rel. int.) 254,094 (M^+, 100) ($C_{16}H_{14}O_3$), 239 (M − Me, 11), 211 (239–CO, 88); ^1H NMR ($CDCl_3$): 4.88 (*dd*, H-1, *J* = 7, 1.5), 6.19 (*dt*, H-2, *J* = 10, 7), 5.79 (*dt*, H-3, *J* = 10, 1.5), 7.10 (*dbr*, H-9, *J* = 8), 7.23 (*dd*, H-10, *J* = 8, 8), 6.93 (*dd*, H-11, *J* = 8, 2), 7.03 (*sbr*, H-13), 2.10 (*s*, OAc), 3.80 (*s*, OMe).

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