32 $Me(C{\equiv}C)_4CH{=}CHCH{-}CH_2$ (Cl, OH)

33 $MeCH{=}CH(C{\equiv}C)_2(CH{=}CH)_2(CH_2)_3OH$,

34 $Me(C{\equiv}C)_3(CH{=}CH)_2(CH_2)_3OH$,

35 $MeCH{=}CH(C{\equiv}C)_3CH{=}CHCH{-}CH_2$ (OH, OH)

36 Apigenin (flavone).

Two compounds exhibiting TLC behaviour identical with those of **14** and **15**, respectively, could also be detected in the flower heads; they were, however, present in amounts insufficient for complete characterization (less than 20 μg).

It should be noted that the flower heads contain a large number of compounds with relatively large amounts of Cl-containing substances. With regard to *Centaurea* species, these substances have only been reported, up till now, from the section Centaurium Cass. [3, 10]. It is now clear that *C. scabiosa* belonging to the section Acrocentron Cass. [10] also contains chlorohydrins.

EXPERIMENTAL

Roots (1.2 kg) (washed and air-dried); 600 g of leaves and stems, and 1.5 kg of flower heads from *Centaurea scabiosa* L. were collected in Kasted, close to the city of Aarhus. Each portion was ground and extracted, first with petrol and then with Et_2O. The extracts were subjected to column chromatography (Si gel) using petrol and petrol containing increasing proportions of Et_2O as eluants. For further separation repeated TLC (Si gel and Si gel containing 5% caffeine) was used.

Compounds isolated from roots. 150 mg of **1**, 9 mg of **2**, 0.4 mg of **3**, 0.2 mg of **4**, 0.1 mg of **5**, 1 mg of **6**, 0.3 mg of **7**, less than 0.1 mg of **8**, 0.8 mg of **9**, 0.3 mg of **10**, 10 mg of **11**, 6 mg of **12**, 5 mg of **13**, less than 0.05 mg of **14** and less than 0.05 mg of **15**.

Compounds isolated from leaves and stems. 10 mg of **16–19** (non-separable), 1.2 mg of **20**, 1.2 mg of **21**, 0.1 mg of **22**, and 0.1 mg of **23–25** (non-separable).

Compounds isolated from flower heads. Less than 0.1 mg of **2**, 0.5 mg of **3**, 0.1 mg of **4**, 2 mg of **5**, 0.4 mg of **6**, 0.8 mg of **7**, 0.6 mg of **8**, 0.4 mg of **26**, 0.1 mg of **27**, less than 0.1 mg of **28**, less than 0.1 mg of **29**, 4 mg of **30**, 65 mg of **31**, 18 mg of **32**, 0.1 mg of **33**, 0.4 mg of **34**, 50 mg of **35**, and 1.2 g of **36**.

Hydrolysis of **14** *and* **15**. Half the total amounts of **14** and **15**, respectively, were dissolved in 3 ml MeOH. 100 mg of KOH were added, and the solns heated to 50° for 15 min. After acidification of the soln with 4N H_2SO_4 and extractions with Et_2O the extracts were dried. The products obtained exhibited TLC data identical with those of **33** and **34**.

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A C_{15} ALDEHYDE FROM *CUCUMIS SATIVUS*

THOMAS R. KEMP

Department of Horticulture, University of Kentucky, Lexington, KY 40506, U.S.A.

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Key Word Index—*Cucumis sativus*; Cucurbitaceae; cucumber; *cis*-8-pentadecenal; MS; IR.

Abstract—*cis*-8-Pentadecenal was isolated from a concentrate of cucumber volatiles and characterized by spectral analyses and ozonolysis. The biochemical origin of this compound and other long chain aldehydes isolated from cucumber is discussed.

INTRODUCTION

Previous analyses of volatile flavor concentrates of the Cucurbits, especially cucumber have resulted in the characterization of several unusual compounds, principally aldehydes [1–4]. We have now isolated and characterized an additional aldehyde constituent, *cis*-8-pentadecenal, of cucumber volatile concentrate. To our knowledge this compound has not been previously reported in the literature.

RESULTS AND DISCUSSION

The compound was obtained by reduced pressure steam distillation–extraction of the fruit and purified by GLC using an SE-30 and a DEGS column. MS yielded a low intensity molecular ion (M^+) peak at *m/e* 224 and diagnostic peaks at *m/e* 206 (M^+-H_2O) and *m/e* 180 (M^+-CH_2CHOH). The overall fragmentation pattern was similar to those of C_{16} and C_{17} monounsaturated aldehydes [3]. An IR spectrum revealed bands at 2700

(—CHO), 1730 (C=O) and 720 cm^{-1} (—CH=CH—, *cis*) but no band in the 960–970 cm^{-1} region (—CH=CH—, *trans*) indicating an aliphatic aldehyde with *cis* unsaturation. The MS and IR spectra were consistent with a C_{15} aldehyde containing one double bond. Ozonolysis of the compound yielded heptanal, as shown by GLC retention data, which established the position of the double bond at C-8. Collectively, the spectral and ozonolysis data led to the conclusion that the compound is *cis*-8-pentadecenal.

cis-8-Pentadecenal bears the same structural relationship to the naturally occurring fatty acid, palmitoleic acid (*cis*-8-hexadecenoic acid) as the other long chain (C_{17}–C_{10}) aldehydes isolated from cucumber [3] bear to the common fatty acids palmitic, oleic, linoleic and linolenic acids. That is, this series of aldehydes would result from the sequential removal of carbon from the carboxyl end of the fatty acid) Recently, Galliard and Matthew [5] partially purified and studied an enzyme system from cucumber which catalyzes the removal of carbon atoms from the carboxyl end of fatty acids to form aldehydes (α-oxidation). Using palmitic acid as a substrate they found that a homologous series of *n*-alkanals starting with pentadecanal was formed. In light of their research and structural considerations, it seems probable that this enzyme system gives rise to *cis*-8-pentadecenal and other long chain (C_{17}–C_{10}) aldehydes which we have isolated from volatile concentrates of cucumber fruit. *cis*-8-Pentadecenal has a weak odour which apparently does not contribute significantly to the flavour of the fruit.

EXPERIMENTAL

The concentrate of volatile compounds was prepared by red. press. steam distillation–extraction of macerated cucumber fruit (*Cucumis sativus* L.) in a H_2O recycling apparatus according to the procedure described previously [3]. *cis*-8-Pentadecenal was separated from the volatile concentrate by GLC using a 1.8 m × 6 mm O.D. stainless steel column packed with 20% SE-30 coated on 60–80 mesh, acid washed, silanized Chromosorb W. The column temp. was programmed from 100° to 180° at 1°/min. The peak which eluted from SE-30 immediately before pentadecanal was collected and rechromatographed on a 1.8 m × 6 mm O.D. stainless steel column packed with 10% diethylene glycol succinate (DEGS) coated on 60–80 mesh, acid washed, silanized Chromosorb W. A MS of the purified compound was recorded with an ionizing energy of 70 eV, *m/e* (rel. int.): 41 (100), 55 (98), 43 (63), 69 (57), 67 (47), 57 (42), 56 (37), 81 (35), 54 (33), 82 (32), 83 (32), 70 (31), 95 (21), 96 (20) and 84 (19). An IR spectrum was obtained with the aid of a NaCl microcell and a mirror beam condenser; spectral grade CS_2 was used as the solvent. Ozonolysis was carried out using a micro-ozonizer according to the procedure of Beroza and Bierl [6].

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NEUE GERMACROLIDE AUS *PLATYCARPHA GLOMERATA**

FERDINAND BOHLMANN und CHRISTA ZDERO

Institut für Organische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-1000 Berlin 12, Deutschland

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Key Word Index—*Platycarpha glomerata*; Compositae; new germacrolides; thiophenacetylenes.

Abstract—The roots of *Platycaroha glomerata* contain five thiophenes which have been isolated before only from *Berkheya* species. A new diol is also present. The aerial parts contain two new germacrolides, their structures being elucidated by spectroscopic methods. On the basis of the identification of these root constituents, this plant appears to be closely related to other genera in the tribe Arctotideae.

Die botanische Stellung der südafrikanischen Gattung *Platycarpha* ist teilweise unstritten. Wir haben daher *P. glomerata* näher untersucht. Die Wurzeln enthalten die bereits bekannten Thiophenacetylenverbindugen **1**–**5** [1], Isohumulen (**8**| [2] sowie eine weitere Thiophenverbindung, die bisher noch nicht isoliert wurde. Die Konstitution **6** folgt aus den spektroskopischen Daten und dem Ergebnis der Mangandioxid-Oxydation zum Keton **7**:

Die oberirdischen Teile liefern zwei schwer trennbare Lactone, ein Methylenlacton und offenbar die entsprechende Dihydroverbindung. Das ^{1}H-NMR-Spektrum des Methylenlactons in Deuteriobenzol ist weitgehend 1. Ordnung. interpretierbar. Systematische Entkopplungen fürhen zur Konstitution **9**, obwohl einige Signale

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