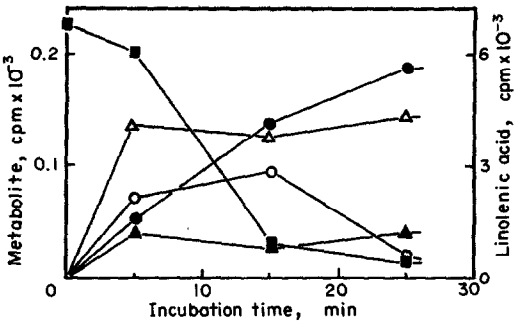
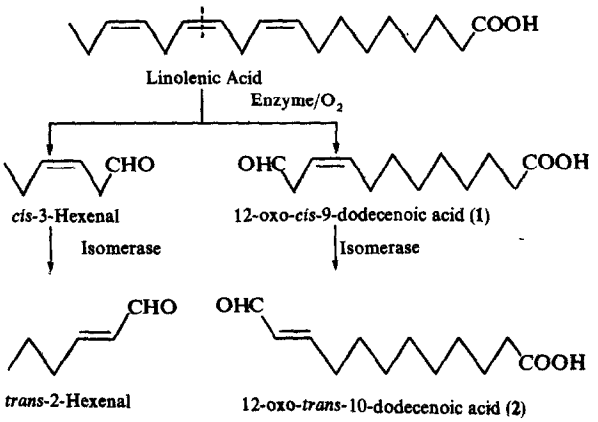


Fig. 2. Time course of C_{12}-oxo-acid formation from linolenic acid-[1-^{14}C]. Reaction mixture with linolenic acid-[1-^{14}C] was incubated at 20° for an initial 5 min and then at 40°. —■— Linolenic acid; —○—12-oxo-*cis*-9-dodecenoic acid; —●— 12-oxo-*trans*-10-dodecenoic acid; —▲— 9-oxo-nonanoic acid; —△— unknown.



Scheme 1. Biosynthetic pathway of leaf aldehyde.

Based on these findings and the results previously reported [3], the biosynthetic pathway of leaf aldehyde, *trans*-2-hexenal, and 12-oxo-*trans*-dodecenoic acid from linolenic acid was demonstrated to be as shown in Scheme 1.

EXPERIMENTAL

Material. Chloroplasts were prepared from leaves of *Thea sinensis* var. *Yabukita* harvested on the 18th August 1976 according to the method of ref. [4]. Authentic samples of 12-oxo-*cis*-9-dodecenoic acid (**1**) and 12-oxo-*trans*-10-dodecenoic acid (**2**) were synthesized by an unequivocal route [5].

Radio gas chromatography (GC–RC). A GC–RC equipped with an FID and gas phase radio detector was used. Column: 1 m × 3 mm stainless steel packed with 60–80 mesh, Chromosorb W coated with 10% Silicone GE SE-30. Column temp. 100–200° at 3°/min. Carrier gas flow rate: 60 ml N_2/min. The radio detector was 1 kcpm. One nCi of toluene-[1-^{14}C] was determined as 52 counts under these conditions.

Incorporation of linolenic acid-[1-^{14}C] *into* C_{12}*-oxo-acids.* A mixture of linolenic acid-[1-^{14}C] (5 μCi, sp. act. 50 mCi/mmol, Radiochemical Centre, Amersham), linolenic acid (9.5 mg) and chloroplasts (300 mg) in 10 ml of 4-diluted McIlvaine's buffer, pH 6.3. containing 0.4 M sucrose, was vigorously shaken for 5 min at 20°. After 10 min incubation at 40°, the reaction mixture was extracted with Et_2O (10 ml × 3). The combined Et_2O extract was washed with H_2O, dried and concd. Products were methylated with CH_2N_2 at −20° and unlabelled methyl-12-oxo-*cis*-9-dodecenoate, methyl-12-oxo-*trans*-10-dodecenoate and methyl-9-oxo-nonanoate added to the conc extracts as marker compounds. After the soln was made up to 1.0 ml, 50 μl of the radioactive extract was analyzed by GC–RC.

REFERENCES

1. Brady, A. V. and Zimmerman, D. C. (1976) *Plant Physiol.* **57**, 780.
2. Tressl, R. and Drawert, F. (1973) *J. Agr. Food Chem.* **21**, 560.
3. Hatanaka, A., Kajiwara, T. and Sekiya, J. (1976) *Phytochemistry* **15**, 1125.
4. Sekiya, J., Numa, S., Kajiwara, T and Hatanaka, A. (1976) *Agric. Biol. Chem.* **40**, 185.
5. Kajiwara, T., Sekiya, J., Kido, Y. and Hatanaka, A. (1977) *Agric. Biol. Chem.* **41**, 8.

Phytochemistry, 1977, Vol. 16, pp. 1829–1831. Pergamon Press. Printed in England.

POLYUNSATURATED COMPOUNDS OF *CENTAUREA SCABIOSA*

ANNIE B. ANDERSEN, JØRGEN LAM and PER WRANG
Department of Organic Chemistry, Chemical Institute, University of Aarhus, 8000 Aarhus C, Denmark

(*Received* 11 *February* 1977)

Key Word Index—*Centaurea scabiosa*; Cynareae; Compositae; polyacetylenes; polyenes.

Abstract—Roots, green parts, and flower heads of *Centaurea scabiosa* were examined separately. Twenty-five polyacetylenes, 4 polyenic aldehydes, 1,8,11,14-heptadecatetraene, and the flavone apigenin were isolated and characterized. Three C_{17} hydrocarbons with from one to three isolated double bonds and a series of minor compounds were also isolated.

INTRODUCTION

Previous investigations of green parts and roots of *Centaurea scabiosa* have shown the presence of compound **2** [1, 2]. Furthermore, polyunsaturated aldehydes and compounds **2** and **8** have been detected in *C. scabiosa* subsp. *scabiosa* [3]. As no data on the flower heads of *C. scabiosa* have been published, and as UV spectra of extracts of wild flowering plants showed the presence of considerable amounts of polyunsaturated compounds, a new investigation was carried out at this laboratory.

RESULTS AND DISCUSSION

The investigation revealed a large number of polyacetylenes, some of which are characteristic of the tribe Cynareae and others which are widely distributed in the Compositae. Among the more characteristic ones are the chlorohydrins in the flower heads, the long chain aldehydes with non-conjugated aldehyde groups present in the leaves, and the epoxides occurring in flower heads and roots. The compounds **2–7**, **9–10**, **26–27**, and **33–34** are commonly found in the Compositae, especially in the tribes Heliantheae and Cynareae. Compound **1** has previously been reported [4, 5]. Apigenin (**36**) is a flavone common in the family Compositae [6, 7]. The polyacetylenes and the tetraenic aldehydes reported here have earlier been isolated from various plants [3].

The investigation was carried out on 3 separate parts, roots, leaves and stems, and flower heads. The petrol and ether extracts from these parts were subjected to column and repeated preparative-TLC.

Roots

The following compounds were identified:

1 $MeCH_2(CH{=}^{c}CHCH_2)_3(CH_2)_4CH{=}CH_2$,

2 $MeCH{=}CH(C{\equiv}C)_4CH{=}CH_2$,

3 $Me(C{\equiv}C)_5CH{=}CH_2$,

4 $MeCH{=}CH(C{\equiv}C)_3(CH{=}CH_2H$,

5 $Me(C{\equiv}C)_4(CH{=}CH)_2H$,

6 $MeCH{=}CH(C{\equiv}C)_2(CH{=}CH)_2(CH_2)_4CH{=}CH_2$,

7 $Me(C{\equiv}C)_3(CH{=}CH)_2(CH_2)_4CH{=}CH_2$,

8 $MeCH{=}CH(C{\equiv}C)_4CH{-}CH_2$ (O)

9 $MeCH{=}CH(C{\equiv}C)_2(CH{=}CH)_2CHCH_2CH_2$ (OAc, OAc)

10 $Me(C{\equiv}C)_3(CH{=}CH)_2CHCH_2CH_2$ (OAc, OAc).

From the fraction containing **1** 3 other hydrocarbons (**11–13**) were isolated. These compounds were not fully characterized although their MS data exhibiting M^+ (*m/e*): 238 for **11**, 236 for **12**, and 234 for **13**, suggested the presence of C_{17} hydrocarbons with 1, 2, and 3 double bonds, respectively. Their IR spectra exhibit vinylic double bonds (1630, 990, 910 cm^{-1}). The PMR data (100 MHz) clearly show the similarities between the compounds **1** and **11–13**. They all have methylene groups next to double bonds and to saturated (methylene) groups (2 δ, *m*). **1** and **13** show a methylene group between two double bonds (2.8 δ, *m*). **1**, **12** and **13** exhibit double bond protons between methylene groups (5.4 δ, *m*). They all show vinyl protons (**1**: 4.88 δ, *dm*, J = 9.8 Hz; 4.92 δ, *dm*, J = 17.1 Hz, and 5.75 δ, *ddt*, J = 6.8 + 9.8 + 17.1 Hz. **11**: 4.9 δ, *dm*, J = 9.5 Hz; 4.94 δ, *dm*, J = 17 Hz, and 5.77 δ, *ddt*, J = 6.5 + 9.5 + 17 Hz. **12** and **13**: 4.97 δ, *dm*, J = 10 Hz, 5.02 δ, *dm*, J = 17 Hz, and 5.86 δ, *ddt*, J = 6.5 + 10 + 17 Hz), and methyl protons (**1**: 0.97 δ, *t*, J = 7.5 Hz. **11–13**: 0.91 δ, *m*) corresponding to the terminal groups of these compounds.

1 and **11–13** are all C_{17}-hydrocarbons and they may be related to linolenic, stearic, oleic, and linoleic acids, respectively, and may thus have been formed from these acids by β-oxidation. The proposed structures of **11–13** are then:

11 $Me(CH_2)_{14}CH{=}CH_2$,

12 $Me(CH_2)_7CH{=}^{c}CH(CH_2)_5CH{=}CH_2$,

13 $Me(CH_2)_4(CH{=}^{c}CHCH_2)_2(CH_2)_4CH{=}CH_2$.

The following fractions representing slightly increasing polarity yielded the compounds **2–10**. From the region containing **6** and **7** an acetylene with an ene-diyne chromophore was isolated (λ_{max}: 240, 253, 268, and 283 nm). It has a MW of 226 (MS) indicating the presence of a C_{17}-hydrocarbon ($C_{17}H_{22}$) and in addition two isolated double bonds in the structure. Biosynthetically it might be related to **1** and **11–13**, and a possible structure might be

$$MeCH{=}CH(C{\equiv}C)_2CH_2CH{=}CH(CH_2)_5CH{=}CH_2$$

which is a compound reported earlier [8, 9].

Another two compounds **14** and **15** containing an ene-diyne-diene and a triyne-diene chromophore, respectively, were isolated from the roots. On TLC examination they showed R_f values identical with those exhibited by $MeCH{=}CH(C{\equiv}C)_2(CH{=}CH)_2(CH_2)_3OAc$ and $Me(C{\equiv}C)_3(CH{=}CH)_2(CH_2)_3OAc$, and their hydrolytic products gave the same TLC data as the corresponding alcohols **33** and **34** present in the flower heads. According to these data we suggest the structures of **14** and **15**: $MeCH{=}CH(C{\equiv}C)_2(CH{=}CH)_2(CH_2)_3OAc$ and $Me(C{\equiv}C)_3(CH{=}CH)_2(CH_2)_3OAc$ respectively. This assumption is supported by the finding of two compounds in the roots showing an ene-diyne-diene and a triyne-diene chromophore, respectively. These compounds exhibited the same TLC data as the alcohols **33** and **34**. Hence they are believed to be identical with these alcohols.

Leaves and stems

From these parts of the plant compounds **16–25** were characterized, the different chain lengths being determined by MS;

16–19 $MeCH_2(CH{=}CH)_4(CH_2)_nCHO$, n = 4–7,

20–21 $MeCH{=}CH(C{\equiv}C)_2(CH{=}CH)_2(CH_2)_nCHO$, n = 4–5,

22 $Me(C{\equiv}C)_3(CH{=}CH)_2(CH_2)_5CHO$,

23–25 $MeCH{=}CH(C{\equiv}C)_2(CH{=}CH)_2(CH_2)_nCH_2OH$, n = 2–4.

From the fraction containing **23–25** traces (less than 50 μg) of compounds with tetraene and triyne-diene chromophores were isolated; these compounds are probably alcohols.

Flower heads

Compounds **2–8** and the following compounds were isolated from the flower heads:

26 $Me(C{\equiv}C)_3(CH{=}CH)_3H$,

27 $MeCH{=}CH(C{\equiv}C)_2(CH{=}CH)_3H$,

28 $MeCH{=}CH(C{\equiv}C)_3CH{=}CHCH{-}CH_2$ (O)

29 $Me(C{\equiv}C)_5CH{-}CH_2$ (O)

30 $MeCH{=}CH(C{\equiv}C)_3CH{=}CHCH{-}CH_2$ (OH, Cl)

31 $MeCH{=}CH(C{\equiv}C)_3CH{=}CHCH{-}CH_2$ (Cl, OH)

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**.

REFERENCES

1. Löfgren, N. (1949) *Acta Chem. Scand.* **3**, 82.
2. Bohlmann, F., Postulka, S. and Ruhnke, J. (1958) *Chem. Ber.* **91**, 1642.
3. Bohlmann, F., Burkhardt, T. and Zdero, C. (1973) *Naturally Occurring Acetylenes*. Academic Press, London.
4. Romanuk, M., Herout, V. and Sorm, F. (1959) *Collection Czech. Chem. Commun.* **24**, 2018.
5. Binder, R. G., Haddon, W. F., Lundin, R. E. and Waiss, A. C. (1975) *Phytochemistry* **14**, 2085.
6. Hegnauer, R. (1964) in *Chemotaxonomie der Pflanzen*, Bd. III. Birkhauser Verlag, Basel.
7. Harborne, J. B. (1973) in *Phytochemistry*, Vol. II (Miller, L. P. ed.). Van Nostrand, New York.
8. Bohlmann, F., Mönch, H. and Niedballa, U. (1966) *Chem. Ber.* **99**, 586.
9. Bohlmann, F. and Zdero, C. (1969) *Chem. Ber.* **102**, 1691.
10. Hoffmann, O. (1889–94) in *Die naturlichen Pflanzenfamilien* Engler Prantl ed.) Vol. IV/5 p. 87–387. Engelmann, Leipzig.

Phytochemistry, 1977, Vol. 16, pp. 1831–1832. Pergamon Press. Printed in England.

A C_{15} ALDEHYDE FROM *CUCUMIS SATIVUS*

THOMAS R. KEMP

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

(*Received* 10 *March* 1977)

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