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EIGHT ALIPHATIC ALDEHYDES FROM *CIRSIUM DIPSACOLEPIS* AND THEIR STEREOSELECTIVE SYNTHESIS

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Key Word Index—*Cirsium dipsacolepis*; Compositae; roots; unsaturated aliphatic aldehydes; aplotaxene; cyperene; synthesis.

Abstract—Two new and six known aliphatic aldehydes have been isolated from the roots of *Cirsium dipsacolepis*, *viz*. 7-octenal, (2*E*)-2,8-nonadienal, (2*E*)-2,9-decadienal, (2*E*)-2,10-undecadienal, (2*E*,4*E*)-2,4,10-undecatrienal, (2*E*,4*E*)-2,4,11-dodecatrienal, (2*Z*,4*Z*)-2,4,11-dodecatrienal and (2*E*,4*Z*)-2,4,11-dodecatrienal. The aldehydes were identified and synthesized stereoselectively from alkane-α,ω-diynes.

INTRODUCTION

Cirsium dipsacolepis is a perennial herb that grows on dry plains. The roots have been used for foods such as pickles in Japan. There are a few reports on its constituents and only the presence of aplotaxene and a few triterpenes has been reported [1]. Now we wish to report the isolation and identification of hydrocarbons and eight aliphatic aldehydes, 7-octenal, (2*E*)-2,8-nonadienal, (2*E*)-2,9-decadienal, (2*E*)-2,10-undecadienal, (2*E*,4*E*)-2,4,10-undecatrienal, and (2*E*,4*E*)-, (2*Z*,4*Z*)- and (2*E*,4*Z*)-2,4,11-dodecatrienal, from the root of *C. dipsacolepis*. This paper also deals with the stereoselective syntheses of the aldehydes.

RESULTS AND DISCUSSION

Hydrocarbons

A main component (*ca* 82%) of the volatile oil of *C. dipsacolepis* is aplotaxene (**1**), and dihydro- (**2**), tetrahydro- (**3**) and hexahydroaplotaxene (1-heptadecene) also occur as minor components. These compounds were identified by spectral and GC comparison with authentic samples synthesized from the corresponding C_{18} acids by decarboxylation [2,3]. However, the same compounds have already been found as constituents of *C. japonicum* [4]. Other minor components shown in Table 1 were also identified by GC-MS analysis. It is noteworthy that many aliphatic hydrocarbons with a vinyl group are present in the roots of *C. dipsacolepis*.


1


2


3

PHOTO 26/2-H

Table 1. Hydrocarbons of *Cirsium dipsacolepis*

n-Dodecane
2-Methyldodecane
n-Tridecane
3-Methyltridecane
n-Tetradecane
2-Methyltetradecane
n-Pentadecane
3-Methylpentadecane
n-Hexadecane
2-Methylhexadecane
n-Heptadecane
n-Octadecane
n-Nonadecane
n-Eicosane

1-Dodecene
1-Tetradecene
1-Pentadecene
1-Hexadecene
1-Heptadecene
1-Octadecene
Aplotaxene
Dihydroaplotaxene
Tetrahydroaplotaxene
Cyperene

7-Octenal and aliphatic dienals

It was easily deduced from spectral data that aldehyde **4** was 7-octenal. Moreover, **4** was hydrogenated with Pd-C as catalyst in *n*-hexane at room temperature overnight to afford 1-octanal. Further confirmation was made by comparing various spectral data of **4** with those of 7-octenal synthesized from 1,8-nonadiene by ozonolysis.

IR absorption bands at 1687, 990 and 910 cm^{-1} suggested that aldehyde **5** had a conjugated carbonyl group and a vinyl group. Catalytic hydrogenation of **5** under the same conditions as described above afforded 1-nonanal. Moreover, in the ^1H NMR spectrum of **5**, an olefinic proton at 6.11 ppm (*dd*, J = 15.5, 7.8 Hz) couples with an aldehyde proton at 9.49 ppm (*d*, J = 7.8 Hz) and with an olefinic proton at 6.83 ppm (*dt*, J = 15.5, 6.9 Hz). The coupling constants of the above two olefinic protons (15.5 Hz) clearly indicate a *trans*-relationship. Based on these results, the structure of aldehyde **5** is established to be (2*E*)-2,8-nonadienal.

The similarity of the ^1H NMR and IR spectra of aldehydes **6** and **7** to those of aldehyde **5** suggests that both are homologues of **5**. Furthermore, catalytic hydrogenation of **6** and **7** gave 1-decanal and 1-undecanal, respectively. These results indicate that the structures of **6** and **7** are established to be (2*E*)-2,9-decadienal and (2*E*)-2,10-undecadienal, respectively.

Aliphatic trienals

IR absorption bands at 1675, 990 and 910 cm^{-1} suggest that aldehyde **9** has a conjugated carbonyl group and a vinyl group. Its UV spectrum showed an absorption maximum at 273 nm, which indicated the presence of a conjugated dienal group. Moreover, catalytic hydrogenation of **9** under the same conditions as those described above afforded 1-dodecanal. These results indicated that **9** was 2,4,11-dodecatrienal. Furthermore, the ^1H NMR signals of the conjugated dienal group of **9** coincided in chemical shifts and coupling pattern with those of authentic (2*E*,4*E*)-decadienal. Based on these results, the structure of aldehyde **9** is established to be (2*E*,4*E*)-2,4,11-dodecatrienal, which is reported for the first time as a natural product.

IR and UV spectra of aldehyde **11** were similar to those of **9**. Catalytic hydrogenation of **11** also gave 1-dodecanal, which showed that **11** was the stereoisomer of **9**. Since the coupling constants of H_2–H_3 and H_4–H_5 are 15.0 and 10.8 Hz respectively, **11** is established to be (2*E*,4*Z*)-2,4,11-dodecatrienal, which has been reported in *Silphium* species [5].

Aldehyde **10** was rather unstable and a trace component, which was obtained as a mixture containing **9** (11%), **11** (21%) and **10** (68%). However, catalytic hydrogenation of this mixture afforded only 1-dodecanal, and **10** gradually changed to **9** and **11**. Based on these results and the coupling constants of H_2–H_3 and H_4–H_5 (each 11.4 Hz), the new aldehyde **10** most likely was (2*Z*,4*Z*)-2,4,11-dodecatrienal.

Aldehyde **8** was deduced to be a homologue of **9**, since the ^1H NMR and IR spectra of **8** were similar to those of **9**. Furthermore, catalytic hydrogenation of **8** gave 1-undecanal. These results indicate that **8** is probably (2*E*,4*E*)-2,4,10-undecatrienal.

Synthesis

Dienals, **5**, **6** and **7**, and the four stereoisomers of 2,4,11-dodecatrienal and (2*E*,4*E*)-2,4,10-undecatrienal were synthesized in order to confirm their structures unambiguously (Figs. 1 and 2). Diyne **12** was hydrogenated with a Lindlar catalyst in the presence of quinoline in ethanol at room temperature until one mole equivalent of hydrogen was absorbed. Diene-acetal **15** was synthesized from enyne **13** via enyne-acetal **14** by the method described by Bohlmann *et al.* [6]. Treatment of **15** in 4% sulphuric acid–acetone (1:5) afforded the dienals, **5**–**7**, which were purified by vacuum distillation (yields 16–17% from diyne **12**).

(2*Z*)-2,9-Decadienal (**17**) was obtained by treatment of (2*Z*)-2,9-decadienal diethylacetal (**16**) with a catalytic amount of *p*-toluenesulphonic acid [7] (Fig. 2). After treatment of the vinylphosphonium salt (**20**) [8, 9] with lithium ethoxide in THF at room temperature, **17** or **18** dissolved in THF was added dropwise and the reaction was continued for 12 hr at room temperature. The reaction was worked up [10, 11], and fractionation of this crude oil by HPLC on LiChrosorb Si-60 afforded pure acetal **22** or **21** in 50–82% yields from **17** or **18**.

On treatment of acetal **21** with a small amount of 0.1 N sulphuric acid in acetone, the new (2*Z*,4*E*)-2,4,11-dodecatrienal **23** was obtained, whereas treatment of acetal **21** in 4% sulphuric acid–acetone (1:5) afforded (2*E*,4*E*)-2,4,11-dodecatrienal **9**. The former treatment of acetal **22** gave the new (2*Z*,4*Z*)-2,4,11-dodecatrienal **10**. Prolonged treatment of **22** for three days afforded a mixture of trienal **11** and **10** (9:1). Purification of these trienals by HPLC gave pure trienals, **9**, **23**, **10** and **11** (yields 18–50% from **17** or **18**). The new (2*E*,4*E*)-2,4,10-undecatrienal **8** was synthesized from (2*E*)-2,8-nonadienal by the method described under the synthesis of **9**. The synthetic aldehydes were shown to be identical with natural aldehydes **5**–**11** by spectral and GC chromatographic comparison. Interestingly, the four isomers of 2,4,11-dodecatrienal and (2*E*,4*E*)-2,4,10-undecatrienal have odours different from one another.

EXPERIMENTAL

Extraction and isolation. Plant material was collected in Nagano Prefecture in October 1980. Roots of *C. dipsacolepis* (Maxim.) Matsum. were extd with acetone and then with *n*-hexane. Both filtrates were concd, satd with NaCl and extd with Et_2O to give oily materials. Volatile oil was obtained by steam distillation of these oily materials under red. press. (45–50 mmHg) in 0.038% yield from the root. The neutral fraction of the volatile oil was sepd into 4 fractions using CC on silica gel. The first fraction (*n*-pentane) contained hydrocarbons such as aplotaxene. These hydrocarbons were sepd into 6 fractions using CC on $AgNO_3$–silica gel (13:87) with *n*-pentane–Et_2O as eluents. Cyperene, tetrahydro- and dihydro-aplotaxene and aplotaxene were isolated. The second fraction (*n*-pentane–Et_2O (9:1)) contained esters and aldehydes. Eight aldehydes were isolated from this fraction by repeated HPLC on LiChrosorb Si-60 followed by prep. GC (5% Thermon 3000 on Chromosorb W).

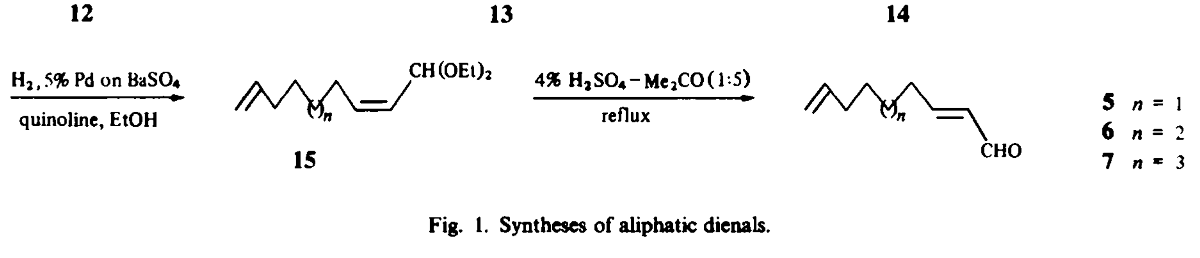

Fig. 1. Syntheses of aliphatic dienals.

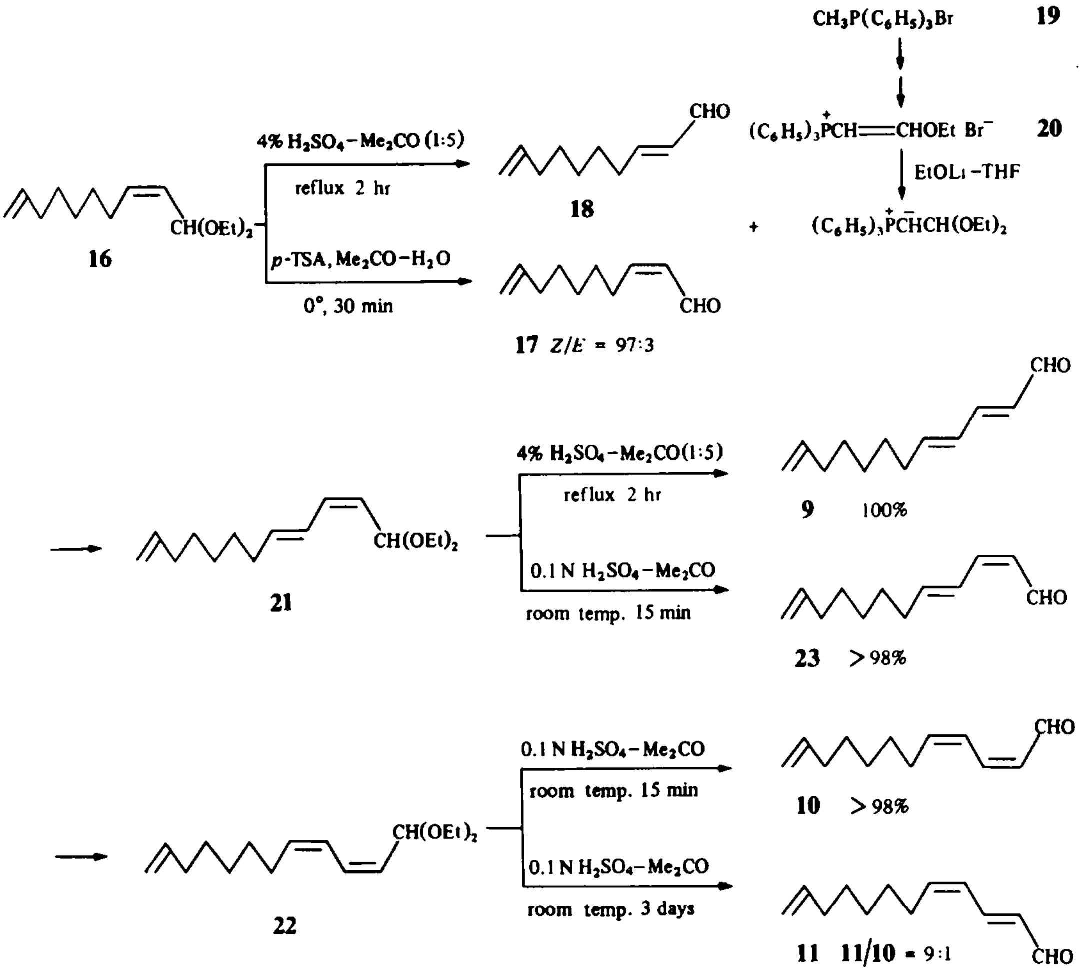

Fig. 2. Syntheses of aliphatic trienals.

(2E)-2,8-*Nonadienal* (**5**). Oil; ^{1}H NMR (270 MHz, CDCl$_3$) δ1.3–1.6 (2H, *m*, H-5,6), 2.07 (2H, *dt*, J = 6.9, 6.7 Hz, H-7), 2.33 (2H, *dt*, J = 6.9, 6.8 Hz, H-4), 4.95 (1H, *m*, H-9c), 5.00 (1H, *ddt*, J = 16.9, 1.8, 1.5 Hz, H-9t), 5.78 (1H, *ddt*, J = 16.9, 10.3, 6.7 Hz, H-8), 6.11 (1H, *dd*, J = 15.5, 7.8 Hz, H-2), 6.83 (1H, *dt*, J = 15.5, 6.8 Hz, H-3), 9.49 (1H, *d*, J = 7.8 Hz, H-1); IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1687, 1630, 990 and 910; EIMS *m/z* 138 ([M]$^+$, $C_9H_{14}O$).

(2E)-2,9-*Decadienal* (**6**). Oil; EIMS *m/z* 152 ([M]$^+$, $C_{10}H_{16}O$).

(2E)-2,10-*Undecadienal* (**7**). Oil; EIMS *m/z* 166 ([M]$^+$, $C_{11}H_{18}O$).

(2E,4E)-2,4,11-*Dodecatrienal* (**9**). Oil; ^{1}H NMR (CDCl$_3$) δ1.2–1.5 (6H, *m*, H-7,8,9), 2.05 (2H, *dt*, J = 6.0, 7.0 Hz, H-10), 2.22 (2H, *dt*, J = 6.0, 7.0 Hz, H-6), 4.95 (1H, *m*, H-12c), 5.00 (1H, *ddt*, J = 17.0, 1.8, 1.5 Hz, H-12t), 5.80 (1H, *ddt*, J = 17.0, 10.0, 6.6 Hz, H-11), 6.07 (1H, *dd*, J = 15.1, 8.0 Hz, H-2), 6.2–6.4 (2H, *m*, H-4,5), 7.08 (1H, *dd*, J = 15.1, 9.7 Hz, H-3), 9.54 (1H, *d*, J = 8.0 Hz, H-1); IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1675, 1635, 990 and 910; UV $\lambda_{\max}^{\text{EtOH}}$ nm: 273; EIMS *m/z* 178 ([M]$^+$ $C_{12}H_{18}O$).

(2E,4E)-2,4,10-*Undecatrienal* (**8**). Oil; EIMS *m/z* 164 ([M]$^+$ $C_{11}H_{16}O$).

(2Z,4Z)-2,4,11-*Dodecatrienal* (**10**). Oil; ^{1}H NMR (CDCl$_3$) δ1.3–1.5 (6H, *m*, H-7,8,9), 2.06 (2H, *dt*, J = 6.5, 6.4 Hz, H-10), 2.30 (2H, *dt*, J = 7.3, 7.2 Hz, H-6), 4.95 (1H, *m*, H-12c), 5.00 (1H, *ddt*, J = 17.2, 1.8, 1.5 Hz, H-12t), 5.80 (1H, *ddt*, J = 17.2, 10.3, 6.5 Hz, H-11), 5.86 (1H, *dd*, J = 11.4, 8.0 Hz, H-2), 6.02 (1H, *dt*, J = 11.4, 7.3 Hz, H-5), 6.99 (1H, *dd*, J = 11.9, 11.4 Hz, H-4), 7.30 (1H, *dd*, J = 11.9, 11.4 Hz, H-3), 10.23 (1H, *d*, J = 8.0 Hz, H-1).

(2E,4Z)-2,4,11-*Dodecatrienal* (**11**). Oil; ^{1}H NMR (CDCl$_3$) δ1.2–1.5 (6H, *m*, H-7,8,9), 2.06 (2H, *q*, J = 6.8 Hz, H-10), 2.34 (2H, *dt*, J = 7.7, 7.0 Hz, H-6), 4.95 (1H, *m*, H-12c), 5.00 (1H, *ddt*, J = 17.0, 1.8, 1.5 Hz, H-12t), 5.80 (1H, *ddt*, J = 17.0, 10.3, 6.8 Hz, H-11), 6.00 (1H, *dt*, J = 10.8, 7.7 Hz, H-5), 6.14 (1H, *dd*, J = 15.0, 7.9 Hz, H-2), 6.27 (1H, *dd*, J = 11.3, 10.8 Hz, H-4), 7.44 (1H, *dd*, J = 15.0, 11.3 Hz, H-3), 9.61 (1H, *d*, J = 7.9 Hz, H-1).

(2Z,4E)-2,4,11-*Dodecatrienal* (**23**). Oil; ^{1}H NMR (CDCl$_3$) δ1.2–1.5 (6H, *m*, H-7,8,9), 2.06 (2H, *dt*, J = 7.3, 6.6 Hz, H-10), 2.24 (2H, *dt*, J = 7.3, 6.8 Hz, H-6), 4.95 (1H, *m*, H-12c), 5.00 (1H, *ddt*, J = 17.0, 1.8, 1.5 Hz, H-12t), 5.79 (1H, *dd*, J = 7.7, 10.8 Hz, H-2), 5.81 (1H, *ddt*, J = 17.0, 10.0, 6.6 Hz, H-11), 6.17 (1H, *dt*, J = 14.3, 7.1 Hz, H-5), 6.91 (1H, *dd*, J = 10.8, 11.2 Hz, H-3), 7.04 (1H, *dd*, J = 14.3, 11.2 Hz, H-4), 10.17 (1H, *d*, J = 7.7 Hz, H-1).

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