N-*Isobutyl*-2(E), 4(E)-*decadienamide* (**2a**). The ester, **5** (2.6 g, 0.015 mol) was refluxed with 8% ethanolic KOH (*ca* 50 ml) for 4 hr. The EtOH was removed under red. pres. H_2O (*ca* 40 ml) was added, the soln was neutralized with aq. HCl (1:1) and thereafter extracted with Et_2O. The organic layer was washed with H_2O, dried and concd.

The crude acid was treated with excess oxalyl chloride (2.5 ml, 0.03 mol) in dry C_6H_6 (*ca* 30 ml) at room temp. for 30 min and then refluxed for another 30 min. Removal of the solvent and excess of the reagent furnished the acid chloride as an oily residue. This was taken up in dry Et_2O (20 ml) to which was added, with stirring, isobutylamine (4 ml, 0.04 mol) in dry Et_2O (*ca* 10 ml). After 1 hr the mixture was poured into H_2O (*ca* 50 ml) and extracted with Et_2O. The extract was washed successively with 1 N H_2SO_4, aq. $NaHCO_3$ soln and H_2O, concd and then chromatographed. The product, a colourless solid, mp 72°, was obtained in the C_6H_6 eluates (yield 900 mg, 30% from the ester). ^{1}H NMR; ($CDCl_3$) δ: 0.92 [*d*, J = 6.5 Hz, H-3′, H-4′ (merged with H-10)], 1.05–1.50 (*m*, H-6–H-9), 6.05 (*m*, H-4, H-5), *ca* 7.10 (*m*, H-3), 5.72 (*d*, J = 14.9 Hz, H-2), 5.55 (*br s*, –NH–), 3.13 (*t*, J = 7.1 Hz, H-1′), *ca* 1.65 (*m*, H-2′).

N-*Isobutyl*-4, 5-*epoxy*-2(E)-*decadienamide* (**3**), *m*-Chloroperbenzoic acid (400 mg, 2.3 mmol) in dry CH_2Cl_2 (10 ml) was added to a soln of **2a** (500 mg, 2.3 mmol) in dry CH_2Cl_2 (25 ml) with stirring. After 16 hr the ppted *m*-chlorobenzoic acid was filtered off. Et_2O (*ca* 50 ml) was added and the mixture was washed with 3% NaOH and then H_2O. The organic layer was dried and concd. The product was finally crystallized from petrol as shining crystals (350 mg, 65%), mp 152–153°. IR ν_{max}^{KBr} cm^{-1}: 3300 (*br*), N–H; 1642, C=C; 1603, C=O; 1248, epoxide; 985, *trans* double bond. ^{1}H NMR ($CDCl_3$) δ: 0.91 [*d*, J = 6.1 Hz (merged with H-10), H-3′, H-4′], 1.05–1.65 (*m*, H-6–H-9), 2.83 (*d* of *t*, J = 5.0, 2.1 Hz, H-5), *ca* 3.15 (*m*, H-4), 6.60 (*dd*, J = 16, 6 Hz, H-3), 6.06, (*d*, J = 16 Hz, H-2), 5.95 (*br s*, –NH–), 3.12 (*t*, J = 6.4 Hz; H-1′), *ca* 1.70 (*m*, H-2′).

(±)*Erythro*-N-*isobutyl*-4, 5-*dihydroxy*-2(E)-*decenamide* (**1**). Compound **3** (300 mg, 1.25 mmol) in THF (*ca* 48 ml) was cooled to 10°. *Ca* 3 ml 30% $HClO_4$ soln was added and the mixture kept at 15° for 15 hr. The solvent was removed, H_2O (*ca* 50 ml) added and the mixture extracted with Et_2O. The Et_2O extract was washed with $NaHCO_3$ soln and then H_2O and dried. Upon concn the extract gave the product (160 mg, 50%) as a crystalline solid (Me_2CO–petrol), mp 122°. IR ν_{max}^{KBr} cm^{-1}: 3300 (*br*), N–H and O–H; 1670, C=C; 1630, C=O; 1082 and 1041, C–O; 981, *trans* double bond. ^{1}H NMR, (d_6-Me_2CO) δ: 0.83 [*d*, J = 6.6 Hz (merged with H-10), H-3′, H-4′], 1.00–1.50 (*m*, H-6–H-9), *ca* 3.52 (*m*, H-5 and OH-5), 4.02 (H-4 and OH-4), 6.76 (*dd*, J = 15.4, 5.2 Hz, H-3), 6.06 (*d*, J = 15.4 Hz, H-2), 7.14 (*br s*, NH), 2.99 (*t*, J = 6.4 Hz; H-1′) *ca* 1.60 (*m*, H-2′). ^{13}C NMR (d_6-DMSO) δ: 13.96 (13.97), C-10; 22.17 (22.17), C-9; 31.51 (31.50), C-8; 24.96 (24.96), C-7; 32.66 (32.65), C-6; 73.48 (73.48), C-5; 73.79 (73.81), C-4; 143.29 (143.29), C-3; 123.81 (123.82), C-2; 165.03 (165.06), C-1; 46.13 (46.14), C-1′; 28.15 (28.14), C-2′; 20.18 (20.18), C-3′, C-4′. Values given in parentheses are those for the corresponding carbons of the natural sample recorded at the same concn and with the same machine.

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ONTOGENETIC VARIATIONS IN C_{17} HYDROCARBON COMPOSITION IN ROOT OIL OF *CIRSIUM JAPONICUM*

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Key Word Index—*Cirsium japonicum*; Compositae; root oil; *n*-C_{17}-hydrocarbons.

Abstract—Large decreases occur in the amounts of four unsaturated hydrocarbons present in the root oil of *Cirsium japonicum* during the months of February and March. These decreases are correlated with the onset of flowering.

Dihydroaplotaxene **2**, tetrahydroaplotaxene **3** and *cis*-8,9-epoxyheptadeca-1-en-11,13-diyn-10-ol from *Cirsium japonicum* have been the subject of previous studies [1, 2]. The *n*-C_{17}-hydrocarbons, aplotaxene **1**, **2**, **3** and hexahydroaplotaxene **4**, are the main components of the root oil. In order to study the changes in hydrocarbon composition during growth, root oils were prepared monthly and the contents of **1**–**4** determined by GC.

$$Me\text{–}CH_2\text{–}CH{=}CH\text{–}CH_2\text{–}CH{=}CH\text{–}CH_2\text{–}CH{=}CH\text{–}(CH_2)_5\text{–}CH{=}CH_2$$
1

$$Me\text{–}(CH_2)_4\text{–}CH{=}CH\text{–}CH_2\text{–}CH{=}CH\text{–}(CH_2)_5\text{–}CH{=}CH_2$$
2

$$Me\text{–}(CH_2)_7\text{–}CH{=}CH\text{–}(CH_2)_5\text{–}CH{=}CH_2$$
3

$$Me\text{–}(CH_2)_{14}\text{–}CH{=}CH_2$$
4

Because May is the flowering time and a biologically important month, the contents of the four hydrocarbons found this month are expressed as 1.00 and the monthly contents are recalculated accordingly (Fig. 1). The values for aplotaxene **1** are 1.00–1.11 and a large change is not observed. On the other hand, the other three hydrocarbons show a large decrease in February and March before flowering; 0.74 and 0.72 (relative content of **2**), 0.57 and 0.55 (**3**), 0.44 and 0.44 (**4**), respectively. It is, therefore, concluded that this decrease in the relative contents of dihydroaplotaxene **2**, tetrahydroaplotaxene **3** and hexahydroaplotaxene **4** may be related to flowering.

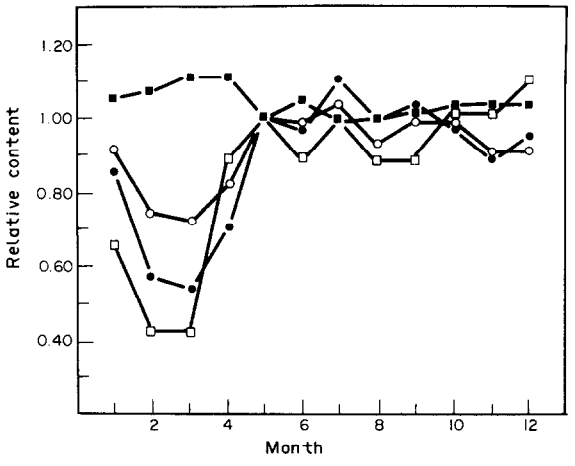

Fig. 1. Variation relative contents of aplotaxene **1** (■), dihydroaplotaxene **2** (○), tetrahydroaplotaxene **3** (●) and hexahydroaplotaxene **4** (□). The contents of the four hydrocarbons are taken as one in May.

EXPERIMENTAL

Fr. roots of *C. japonicum* were collected monthly at Fukuoka prefecture. Extraction was as described in our previous paper [1]. January: root 450 g, extracted oil 1.33 g. February: 470 g, 0.86 g. March: 370 g, 0.75 g. April: 610 g, 1.48 g. May: 540 g, 1.44 g. June: 920 g, 2.30 g July: 410 g, 1.43 g. August: 370 g, 1.34 g. September: 310 g, 1.19 g. October: 300 g, 1.13 g. November: 350 g, 1.25 g. December: 400 g, 1.39 g. To analyse volatile constituents, GC was carried out using a column of 25% PEG 6000-Shimalite (BT) 60–80 mesh, 3 mm × 2.1 m, 180°, He 30 ml/min. Peaks of aplotaxene **1** (R_t 22.0 min), dihydroaplotaxene **2** (17.7), tetrahydroaplotaxene **3** (15.3) and hexahydroaplotaxene **4** (13.6) were identified by comparison with authentic compounds.

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