

NMR: (δ , H_2), 2.01 (s, 3H). *ursa-20-en-3-one*. Plates, m.p., 162–1963° (*Anal.* Found: C, 84.44; H, 10.96; O, 4.28. Cald. for $C_{30}H_{48}O$: C, 84.84; H, 11.39 O, 3.77%. Soln $CHCl_3$ $[\alpha]_{589} + 49^\circ$ $[\alpha]_{578} + 51.0^\circ$ $[\alpha]_{546} + 60.3^\circ$; $[\alpha]_{436} + 114.3^\circ$ $[\alpha]_{365} + 207.0^\circ$ $[\alpha]_{316} + 222.4^\circ$. $\nu_{\max}^{KBr}$ 1700 cm^{-1} . *3 β -hydroxy-ursane*. m.p. 204–206°. (*Anal.* Found, C, 84.26, H, 12.23, O, 4.02. Cald. for $C_{30}H_{52}O$: C, 84.04, H, 12.23; O, 3.73%) Soln $CHCl_3$ $[\alpha]_{589}^{25} - 12.9$; $[\alpha]_{578} - 13.4^\circ$; $[\alpha]_{546} - 13.8^\circ$; $[\alpha]_{436} - 22.8$; $[\alpha]_{363} - 31.1^\circ$.

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SESQUITERPENES FROM THE ROOTS OF *LIGULARIA HODGSONII*

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Key Word Index—*Ligularia hodgsonii*; Compositae; sesquiterpene; furanoeremophilane; bakkenolide A (fukinanolide); eremophilanolide.

Plant. *Ligularia hodgsonii* Hook. f. (Compositae). *Source.* Mt. Yakeishi-dake, Iwate prefecture, Japan. Voucher specimen is kept in the Herbarium of National Science Museum, Tokyo (TNS 201645). *Previous work.* On roots (furanoeremophilan-14 β ,6 α -olide).¹

Present work. Dried roots (1.7 kg) were extracted with hot C_6H_6 . The solvent was evaporated to give the residue (54 g) which was dissolved in warm light petrol. The soluble material was sublimed at 100° under reduced pressure (1 mmHg) and the material sublimed (11 g) was chromatographed on silica gel. Elution with light petrol. gave a colourless oil (48 mg), $C_{15}H_{22}O$ (M^+ at m/e 218), $[\alpha]_D - 12^\circ$ ($CHCl_3$). UV: $\lambda_{\max}^{MeOH}$ 221 nm (ϵ 7000). IR: (liquid film) 1649, 1568, 1094 cm^{-1} ; PMR ($CDCl_3$) δ 0.95 (3H, s; tert-Me), δ 0.99 (3H, d, J 7 Hz; sec-Me), δ 1.99 (3H, d, J 1 Hz; $-\underline{CH=C=Me}$), δ 7.13 ppm (1H, m; $-\underline{O-CH=C=Me}$), identical ($[\alpha]_D$, IR, PMR, MS) with furanoeremophilane.² Elution with light petrol.– Et_2O (100:3) afforded a crystalline compound, which was recrystallized from light petrol. to give 690 mg of bakkenolide A³ (fukinolide⁴), m.p. 80.5–81.5°, $C_{15}H_{22}O_2$ (M^+ at m/e 234), $[\alpha]_D + 20^\circ$ (MeOH). IR: (Nujol) 1780, 1665, 900 cm^{-1} . PMR: (C_6D_6) δ 0.68 (3H, d, J 6

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² HOCHMANNOVÁ, J., NOVOTNÝ, L. and HEROUT, V. (1962) *Coll. Czech. Chem. Commun.* **27**, 1870; ISHII, H., TOZYO, T. and MINATO, H. (1966) *J. Chem. Soc. C*, 1545.

Hz; sec-Me), δ 0.87 (3H, s; tert-Me), δ 4.17 (2H, quartet of triplets, J 13, J 2, J 2 Hz; $\text{H}_2\text{C}=\text{C}=\text{CH}_2-\text{O}-\text{CO}-$), δ 4.42 and δ 4.72 ppm (each 1H, each t , J 2, J 2 Hz; $\text{H}_2\text{C}=\text{C}=\text{CH}_2-$), identical with a genuine sample in all respects (m.p., m.m.p., $[\alpha]_D$, IR, PMR, MS). Successive elution with light petrol.- Et_2O (20:3) gave 10 mg of eremophileno-
lide,⁵ m.p. 124°, $\text{C}_{15}\text{H}_{22}\text{O}_2$ (M^+ at m/e 234), $[\alpha]_D + 202^\circ$ (MeOH). UV: $\lambda_{\text{max}}^{\text{MeOH}}$ 221 nm (ϵ 19 900). IR: (Nujol) 1750, 1693 cm^{-1} . PMR: (CDCl_3) δ 0.80 (3H, d , J 6 Hz; sec-Me), δ 1.05 (3H, s; tert-Me), δ 1.81 (3H, s; $=\text{C}=\text{C}=\text{Me}$), δ 4.63 ppm (1H, m ; $=\text{CH}-\text{O}-\text{CO}-$). Identification with the authentic specimen was effected on m.p., m.m.p. and IR.

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lide.

* The reported $[\alpha]_D$ value $+16.6^\circ$ (CHCl_3)⁵ seems to be erroneous. The authentic sample supplied by Dr. Novotný showed $[\alpha]_D + 177^\circ$ (CHCl_3).

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⁵ NOVOTNÝ, L., JIZBA, J., HEROUT, V. and SÖRM, F. (1962) *Coll. Czech. Chem. Commun.* **27**, 1393; NOVOTNÝ, L., JIZBA, J., HEROUT, V., SÖRM, F., ZALKOW, L. H., HU, S. and DJERASSI, C. (1963) *Tetrahedron* **19**, 1101; HORÁK, M., MOTL, O., PLIVA, J. and SÖRM, F. (1963) *Terpenspektren*, Teil II, S I 28, Akademie, Berlin; KABUTO, C., TAKEDA, N., MAEDA, S. and KITAHARA, Y. (1973) *Chemistry Letters* 371.

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LA CANADALINE: NOUVEL ALCALOÏDE D'*HYDRASTIS CANADENSIS*

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La canadaline est l'un des plus abondants des alcaloïdes mineurs d'*Hydrastis canadensis* à structures encore indéterminées: $\text{C}_{21}\text{H}_{23}\text{NO}_5$ (M^+ 369); F (éther): 117–118°; $[\alpha]_D + 43^\circ$ (c 0.5, CHCl_3). Le pic moléculaire du spectre de masse est d'intensité très faible (1%); cependant le pic de base (m/e : 190) suggère un enchaînement de type dihydrohydrastinine.¹



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¹ HABERMEHL, G. et SCHUNCK, J. (1971) *J. L. Ann. Chem.* **750**, 120.