# Bakkenolide-E, a Minor Component of the Bud of *Petasites japonicus*, subsp *giganteus* Kitam.

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Their investigations of the bitter principles of the bud of *Petasites japonicus*, subsp *giganteus* Kitam., (local name; BAKKE) were reported by the present authors in previous papers,[2,3] in which the isolation of four compounds, named Bakkenolide-A(I), -B(II), -C(III) and -D(IV), was described, as were their structures.

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[2] N. Abe, R. Onoda, K. Shirahata, T. Kato, M. C. Woods and Y. Kitahara, *Tetrahedron Letters*, **1968**, 369.

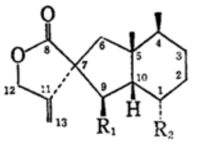
[3] N. Abe, R. Onoda, K. Shirahata, T. Kato, M. C. Woods, Y. Kitahara, K. Ro and T. Kurihara, *ibid.*, **1968**, 1993.

TABLE 1. NMR SPECTRA[a] OF II AND VII

| | $H_1$ | $C_4$-Me | $C_5$-Me | $H_6$[b] | $H_9$ | $H_{10}$ | $H_{12}$ | $H_{13}$ |
|---|---|---|---|---|---|---|---|---|
| II | *ca*5.2 (m) | 0.91(d, $J$=5.9) | 1.13(S) | 2.10 ($J$=14.2) | 5.75(d, $J$=11.2) | 2.82(d,d $J$=11.2, 5.0) | 4.67(t, $J$=2.0) | ca5.2 (m) |
| VII | *ca*5.1 (m) | 0.91(d, $J$=5.3) | 1.12(S) | 2.10 ($J$=14.2) | 5.78(d, $J$=11.2) | 2.80(d,d $J$=11.2, 4.8) | 4.65(t, $J$=2.1) | ca5.2 (m) |

a) NMR data refer to $CDCl_3$ solution, with chemical shifts given in ppm down field from internal TMS (s=singlet, d=doublet, t=triplet, m=multiplet)

b) center of AB quartet,



I $R_1$=H $R_2$=H

II $R_1$=OAc $R_2$=$OCO\overset{CH_3}{\overset{|}{C}}{=}C\begin{smallmatrix}\diagup H\\ \diagdown CH_3\end{smallmatrix}$

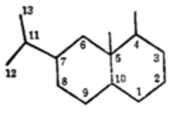
III $R_1$=OH $R_2$=$OCO\overset{CH_3}{\overset{|}{C}}{=}C\begin{smallmatrix}\diagup H\\ \diagdown CH_3\end{smallmatrix}$

IV $R_1$=OAc $R_2$=$OCO\overset{H}{\overset{|}{C}}{=}C\begin{smallmatrix}\diagup H\\ \diagdown SCH_3\end{smallmatrix}$

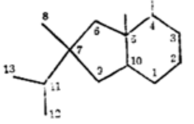
VII $R_1$=OAc $R_2$=$OCO\underset{CH_3}{\underset{|}{C}}{=}C\begin{smallmatrix}\diagup H\\ \diagdown CH_3\end{smallmatrix}$

VIII $R_1$=OH $R_2$=OH

These compounds belong to a new type of sesquiterpenoids and have the novel carbon skeleton (V), to which the authors propose to give the name "bakkane." Since many sesquiterpenoids with the eremophilane skeleton (VI) have been isolated[4,5] from the same genus, *Petasites,* the bakkane is biogenetically related with the eremophilane skeleton. The mode of the biogenesis of the bakkane might be bond fission at $C_8$ and $C_9$, with a concomitant bond formation at $C_7$ and $C_9$ of the eremophilane, but we can not yet define the direct precursor with the eremophilane skeleton and the oxidation stages at $C_8$, $C_{11}$ and $C_{12}$ of bakkenolide-A, from which the other bakkenolides might be biosynthetized. It is, therefore, desirable to make clear the components which might be expected to be biogenetically important intermediates so as to discuss the biogenesis of the bakkenolides of the plant.



VI



V

From this point of view, the minor components of the essential oil of the plant were investigated in detail.

The gas chromatograph of the oil shows the presence of at least nine components, in addition to compounds I—IV, from which the new compound, bakkenolide-E, was isolated.

Bakkenolide-E, (VII), mp 168°C (from ethanol) has the molecular formula of $C_{22}H_{30}O_6$ (found: C, 67.90; H, 8.00%). The IR spectrum (KBr) of VII suggests the presence of the following groups; $\gamma$-lactone at 1792 $cm^{-1}$, two different types of carboxylates at 1740 and 1700 $cm^{-1}$ (acetate and tiglate), and exocyclic methylene at 1650 and 910 $cm^{-1}$.

VII, when hydrolysed with 25% potassium hydroxide in aqueous methanol, affords tiglic acid (identified by comparison with an authentic sample) and 1,9-dihydroxybakkenolide-A (VIII). The latter compound was also obtained from II, III, and IV by the same treatment, thus indicating that VII is a derivative of bakkenolide-A with tiglate and acetate (from IR and NMR) groups.

The similarities of the NMR spectra of bakkenolides-E and -B (Table 1) demonstrate that the acetate and tiglate groups of VII are located at $C_9$ and $C_1$ of bakkenolide-A respectively.

The other, minor components of the oil are now being investigated.

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4) For example, L. Novotny, V. Herout and F. Sorm, *Tetrahedron Letters,* **1961**, 697.

5) K. Naya, I. Takagi, M. Hayashi, S. Nakamura and M. Kobayashi, "Symposium Papers, The 11th Symposium on the Chemistry of Natural Products" (Kyoto, 1967), p. 88, and some references therein.