secretions showed a trinervitene distribution characteristic of the field-collected Voi minor soldiers. These preliminary data suggest genetic patterning of the enzymes responsible for trinervitene biosynthesis. Furthermore, the discovery of the new trinervitene **II** lends support to a hypothetical biosynthesis from intramolecular cyclization of cembrene-like precursors followed by specific hydroxylation at C-2, C-3, C-9, C-13,[2,e and f] or C-17[2,b].

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The scent scale substances of male *Pieris* butterflies *(Pieris melete* and *Pieris napi)*

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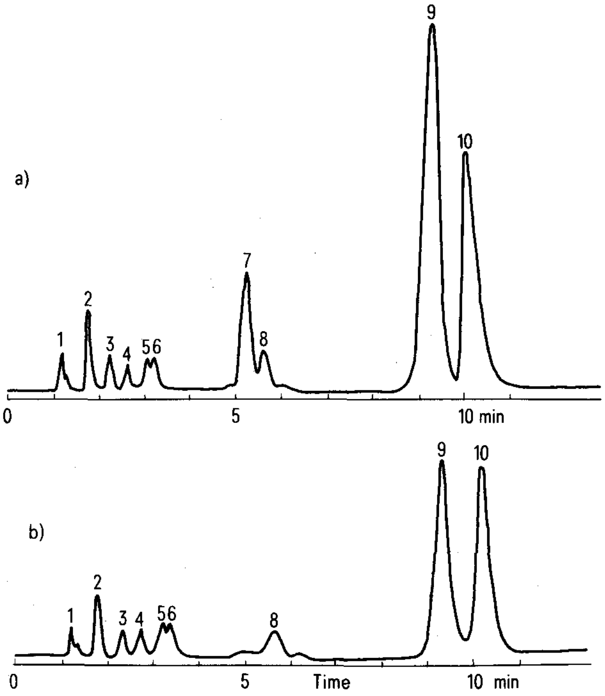
Summary. 7 monoterpenes, *α*-pinene, *β*-pinene, myrcene, p-cymene, limonene, neral and geranial, were identified together with n-undecane in the scent scales of *P. melete,* and also, together with considerable amounts of linalool, in the scent scales of *P. napi.* Content ratio of neral to geranial in *P. melete* ranged from 0.77 to 1.04, and that in *P. napi* from 1.84 to 2.43. The present chemotaxonomic approach shows the 2 species of *Pieris* to be distinct.

Some studies on the chemical structure and physiological functions of scent scale substances of male butterflies have been reported: e.g. the presence of neral, geranial and geraniol in the scent scales of *P. napi* found by Bergström et al.[3], and the presence of nonan-1-al, hexadecan-1-ol, hexadecan-1-ol acetate and muurol (or amorphol) in the scent scales of *Lycalides argyrognomone* observed by Lundgren et al.[4]. It was said that these substances function as an aphrodisiac[3], like the hair pencil secretions of Danoid butterflies[5-8]. The scent scale substances[9] of 2 species (*Pieris melete* Ménétriès and *Pieris napi japonica* Shirôzu) of Pieridae in Japan are investigated in this paper.

Material and method. The butterflies were collected in the mountainous district in Hiroshima Prefecture. The wings of 3 male adults were extracted with n-pentane (5 ml) at room temperature. The extracts were concentrated to 10 µl under nitrogen stream at room temperature. 2 µl of each sample were injected into gas chromatograph-mass spectrometer. The JGC-20KP gas chromatograph equipped with columns was coupled with the JMS-D 100 mass spectrometer (JEOL Co. Ltd., Japan) and was operated under the following conditions: column, 3% OV-1 gas-chrom Q (100-200 mesh) glass column (1 m×3 mm); column temperature programmed 50-150 °C (5 °C/min); injection temperature 200 °C; ionizing voltage 20 and 70 eV. From each of the mass spectra determined, the mass units and intensity of 3 abundant ions, base (H_1), 2-highest (H_2), and 3-highest (H_3) ions, together with molecular ion (M^+), were obtained (table). Based on agreement of these spectral patterns with authentic ones, identification was carried out. For quantitative analysis of geranial and neral, the Hitachi 063 type gas chromatograph equipped with flame ionization detector was used. The gas chromatograph was operated at 120 °C, using PEGS (polyethylene glycol succinate on chromosorb WAW (60-80 mesh) 15%) column (2 m×3 mm). The relative percentage of individual constituents were determined by integration and summation of peak area with electric digital integrator. The individual variation of the content ratio of neral to geranial was obtained from 12 heads of *P. melete* and 9 heads of *P. napi.*



Gas chromatogram of the scent scale substances of *P. napi* (a) and *P. melete* (b). 1. Unknown, 2. *α*-pinene, 3. *β*-pinene, 4. myrcene, 5. p-cymene, 6. limonene, 7. linalool, 8. n-undecane, 9. neral, 10. geranial.

Mass spectra of the scent scale substances of *P. melete* and *P. napi*

Peak No.	Component	R_t	M^+	H_1	H_2	H_3	*P. melete* (%)	*P. napi* (%)
1	Unknown	0.60	104	104	78	43	5.0	2.1
2	α-Pinene	1.00	136	93	77	41	8.7	5.4
3	β-Pinene	1.28	136	93	41	69	4.0	3.0
4	Myrcene	1.44	136	41	93	69	4.3	4.2
5	p-Cymene	1.72	134	119	134	91	3.7	4.3
6	Limonene	1.87	136	68	93	67	3.6	3.6
7	Linalool	2.88	154	71	41	93	–	8.8
8	n-Undecane	3.11	156	57	43	71	4.0	1.1
9	Neral	5.27	152	69	41	94	35.4	44.3
10	Geranial	5.72	152	69	41	84	31.1	23.2

R_t: α-pinene = 1.00, M^+; molecular ion, H_1; base ion, H_2; 2nd-highest ion, H_3; 3rd-highest ion.

Results. The results are shown in the table and the figure. 7 monoterpenes (α-pinene, β-pinene, myrcene, p-cymene, limonene, neral and geranial) were identified together with n-undecane from the scent scales of *P. melete*, while these 7 and considerable amounts of linalool were identified in the scent scales of *P. napi* (figure). Content ratio of neral to geranial in *P. melete* was 0.77–1.04 and that in *P. napi* was 1.84–2.43. Although it is difficult to distinguish the 2 species, since morphological differences between them are slight, the present results suggest them to be tentatively identified by the ratio of neral to geranial and the presence or absence of linalool in the scent scales.

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The association between N-acetyl-neuraminic acid and calcium ions in aqueous solution

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Summary. The conductances of aqueous solutions of the calcium salt of N-acetyl-neuraminic acid (NANA) an important constituent of glycolipids and glycoproteins have been measured over a range of temperature. The data are consistent with the formation of the $Ca(NANA)^+$ ion-pair. Dissociation constants and thermodynamic parameters for the ion-pair have been derived.

N-acetyl-neuraminic acid (NANA) is an important constituent of membrane glycolipids and glycoproteins and it has been shown to be responsible for a large proportion of the surface charge of erythrocytes[1]. The interaction of calcium ions with NANA has been implicated in a variety of physiological and biochemical processes[2-4]. Behr and Lehn[5] investigated the interaction between alkali and alkaline-earth cations using ion selective electrodes and the binding of calcium ions at high concentrations (0.1-4 M) to NANA and its derivatives has been studied using ^{13}C NMR[6,7].

In this communication a conductimetric study of the calcium salt of NANA in aqueous solution over a range of temperature is reported. Conductivity measurements afford a sensitive means of detecting ion-pair formation at physiological Ca^{2+} ion concentrations. The data show that there are considerable deviations from the Onsager limiting law for conductivity. The results can be interpreted in terms of the formation of the $Ca(NANA)^+$ ion-pair for which the dissociation constant and thermodynamic parameters are derived.

Synthetic 'pure' NANA was obtained from Koch-Light Laboratories Ltd., and was used as supplied. Aqueous solutions of the calcium salt were prepared by conductimetric titrations of standardized calcium hydroxide solutions (nominally 6 mM) with NANA solutions (nominally 12 mM). The conductivities were measured in the range 0.1-2.5 mM using specially constructed

Table 1. Calculation of dissociation constants for the $Ca(NANA)^+$ ion-pair from conductance measurements at 25 °C

Molarity (moles/l) × 10^3	Λ_e ($cm^2\ \Omega^{-1}\ equiv^{-1}$)	$[Ca(NANA)^+] \times 10^3$ (moles/l)	$I \times 10^3$	f*	$K_{diss} \times 10^3$ (moles/l)
2.768	70.65	1.157	5.99	0.6944	4.241
2.666	70.71	1.118	5.76	0.6994	4.076
1.596	79.57	0.4975	3.79	0.7482	4.452
0.9108	87.48	0.1988	2.33	0.7964	4.628
0.9072	87.80	0.1937	2.33	0.7964	4.754
0.4112	94.84	0.06063	1.11	0.8550	3.718
0.4088	94.16	0.05668	1.12	0.8541	4.092
0.2316	98.51	0.02304	0.65	0.8869	3.536

* Calculated from $\log f\pm = -4 \times 0.5115\sqrt{I}$.