Chemical Structure-Odor Correlation in a Series of Synthetic *n*-Nonen-1-ols

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In order to elucidate chemical structure-odor correlation in the all isomers of *n*-nonen-1-ols, an entire series of these alcohols were synthesized stereo-selectively in high purity. For unequivocal syntheses of them, geometrically selective hydrogenation of the respective acetylenic compound was adopted. The synthesized alcohols were converted to their 3,5-dinitrobenzoate derivatives with 3,5-dinitrobenzoyl chloride, and then purified by repeated recrystallization.

Chemical structure-odor correlations in all the isomers of *n*-nonen-1-ols were elucidated by introducing a novel method to evaluate odor characteristics and by treating the obtained data statistically with the principal component analysis method (Cramer *et al.,* 1988). The odor profiles of the tested compounds were attributable largely to the positions of the carbon-double bond. The geometries of compounds had only a little effect. With the principal component analysis, the odor profiles of the series of compounds were successfully integrated into the first and the second principal components. The first component (PC-1) consisted of combined characteristics of fruity, fresh, sweet, herbal and oily-fatty, in which herbal and oily-fatty were conversely correlated each other to the position of double-bond of the tested compounds. Of these, only (6*Z*)-nonen-1-ol deviated markedly from the correlation, indicative of some special interaction between the spatial structure of this compound and the sensory machinery of human.

Introduction

(3*Z*)-Hexen-1-ol (leaf alcohol) is widely distributed in plants, and it is responsible for the green odor. This odor is known to be a repellent and an attractant of insects and an allelochemical of plants.

Recently, the relations between the characteristic odor and position and/or geometry of a double bond in various isomers of C_6-unsaturated alcohols were successfully evaluated. Interestingly, (3*Z*)-hexen-1-ol, which is known as "leaf alcohol", was found to be deviated from the relationship and showed a unique odor profile (Hatanaka *et al.,* 1992). C_9-unsaturated alcohols and aldehydes (including violet leaf aldehyde; (2*E*,6*Z*)-nonadienal, cucumber alcohol; (2*E*,6*Z*)-nonadien-1-ol *etc.*) are also known to be characteristic constituents of vegetables and fruits. Nevertheless, the chemical structure-odor correlation in the C_9-unsaturated compounds has not been explored so far. In order to reveal the correlations, an entire series of the C_9-isomers are necessary. Here, we report unequivocal syntheses of all the isomer of *n*-nonen-1-ols and chemical structure-odor correlation of them.

Materials and Methods

IR spectra were recorded on a JIR 100 FT-IR spectrometer (JEOL, Tokyo, Japan). ^1H NMR and ^{13}C NMR spectra were obtained on a JNM-EX 500 spectrometer (JEOL, Tokyo, Japan) at 500 MHz and 125 MHz, respectively. MS spectra were taken on a JMS-DX 300 spectrometer (JEOL, Tokyo, Japan).

Preparation of (2 Z)-nonen-1-ol and (2 E)-nonen-1-ol

Propargyl alcohol was protected with 3,4-dihydro-2H-pyran to give 2-(2′-propynyloxy)-tetrahydropyran in 88% yield. 2-(2′-Nonynyloxy)-tetrahydropyran was prepared by acetylenic coupling

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of 2-(2′-propynyloxy)-tetrahydropyran with hexyl bromide in 58% yield. The pyranyl ether was converted to 2-nonyn-1-ol with 30% phosphoric acid in 98% yield. The ynol was hydrogenated over Lindlar catalyst to give (2*Z*)-nonen-1-ol in 98% yield (Lindlar *et al.,* 1966). (2*E*)-Nonen-1-ol was obtained by reduction with lithium aluminum hydride in ether in 92% yield.

(2*Z*)-nonen-1-ol: b.p. 77.0–78.0 °C/2 mmHg; purity 99.2%; m.p. of 3,5-DNB 44.0–45.1 °C; IR (film) cm^{-1}: 3332 (O–H), 2956, 2925, 2856 (C–H), 1655 (double bond), 1024 (C–H), 723 (*Z*, C=C); MS (70 eV): *m/z* (%) = 124 (43), 96 (31), 95 (40), 82 (47), 81 (38), 69 (31), 68 (43), 67 (37), 57 (100), 55 (46), 54 (44), 43 (42), 41 (43); ^{13}C NMR (CDCl$_3$/TMS): δ = 14.1, 22.7, 27.5, 28.9, 29.6, 31.8, 58.5, 128.5, 133.0 ppm; ^{1}H NMR (CDCl$_3$/TMS): δ = 0.88 (t, 3H, *J* = 6.7), 1.20–1.38 (m, 8H), 2.06 (m, 2H), 2.11 (br s, 1H), 4.18 (t, 2H, *J* = 6.1), 5.49–5.61 ppm (m, 2H).

(2*E*)-nonen-1-ol: b.p. 75.0–75.2 °C/2 mmHg; purity 99.4%; m.p. of 3,5-DNB 61.2–62.0 °C; IR (film) cm^{-1}: 3328 (O–H), 2956, 2871, 2856 (C–H), 1679 (C=C), 1004 (C–O), 968 (*E*, C=C); MS (70 eV): *m/z* (%) = 142 (M$^+$, 5), 95 (39), 82 (46), 81 (32), 68 (41), 57 (100), 55 (38), 43 (39), 41 (38); ^{13}C NMR (CDCl$_3$/TMS): δ = 14.1, 22.6, 28.9, 29.1, 31.7, 32.2, 63.8, 128.9, 133.6 ppm; ^{1}H NMR (CDCl$_3$/TMS): δ = 0.88 (t, 3H, *J* = 7.3), 1.22–1.33 (m, 6H), 1.38 (m, 2H), 1.56 (br s, 1H), 4.08 (t, 2H, *J* = 5.5), 5.60–5.73 ppm (m, 2H).

Preparation of (3Z)-nonen-1-ol and (3E)-nonen-1-ol

3-Butyn-1-ol was prepared by coupling of ethylene oxide with sodium acetylide in liquid ammonia. The ynol was protected with 3,4-dihydro-2H-pyran to give 2-(3′-butynyloxy)-tetrahydropyran in 90% yield. Acetylenic coupling of the tetrahydropyran with amyl bromide gave 2-(3′-nonynyloxy)-tetrahydropyran in 60% yield. The pyranyl ether was converted to 3-nonyn-1-ol with 30% (w/w) phosphoric acid-methanol in 98% yield. The ynol was hydrogenated over Lindlar catalyst to give (3*Z*)-nonen-1-ol in 88% yield. On the other hand, Birch reduction of the ynol with sodium in liquid ammonia gave (3*E*)-nonen-1-ol in 84% yield.

(3*Z*)-nonen-1-ol: b.p. 73.0–73.8 °C/2 mmHg; purity 99.7%; m.p. of 3,5-DNB 44.6–44.9 °C; IR (film) cm^{-1}: 3334 (O–H), 3008 (C=C–H), 2956, 2858 (C–H), 1654 (C=C), 1049, 1022 (C–O), 723 (*Z*, C=C); MS (70 eV): *m/z* (%) = 142 (M$^+$, 7), 124 (47), 96 (41), 95 (63), 82 (67), 81 (86), 69 (71), 68 (100), 67 (61), 55 (83), 54 (39), 41 (57); ^{13}C NMR (CDCl$_3$/TMS): δ = 14.1, 22.6, 27.4, 29.4, 30.8, 31.5, 62.3, 125.0, 133.4 ppm; ^{1}H NMR (CDCl$_3$/TMS): δ = 0.89 (t, 3H, *J* = 7.0), 1.24–1.39 (m, 6H), 1.91 (br s, 1H), 2.06 (m, 2H), 2.33 (m, 2H), 3.63 (t, 2H, *J* = 6.7), 5.36 (dt, 1H, *J* = 7.3, 11.0), 5.55 ppm (dt, 1H, *J* = 7.3, 11.0).

(3*E*)-nonen-1-ol: b.p. 73.0–73.2 °C/2 mmHg; purity 99.5%; m.p. of 3,5-DNB 50.1–50.5 °C; IR (film) cm^{-1}: 3340 (O–H), 3025 (C=C), 2956, 2856 (C–H), 1049 (C–O), 968 (*E*, C=C); MS (70 eV): *m/z* (%) = 142 (M$^+$, 6), 124 (43), 96 (37), 95 (54), 82 (62), 81 (71), 70 (34), 69 (98), 68 (94), 67 (57), 57 (31), 55 (100), 54 (41), 41 (62); ^{13}C NMR CDCl$_3$/TMS): δ = 14.1, 22.6, 27.4, 29.4, 30.8, 31.5, 62.3, 125.0, 133.4 ppm; ^{1}H NMR (CDCl$_3$/TMS): δ = 0.89 (t, 3H, *J* = 7.0), 1.24–1.39 (m, 6H), 1.91 (br s, 1H), 2.06 (m, 2H), 2.33 (m, 2H), 3.63 (t, 2H, *J* = 6.7), 5.36 (dt, 1H, *J* = 7.3, 11.0), 5.55 ppm (dt, 1H, *J* = 7.3, 11.0).

Preparation of (4Z)-nonen-1-ol and (4E)-nonen-1-ol

2-(4′-Pentynyloxy)-tetrahydropyran was obtained in 44% yield by chlorination of tetrahydrofurfuryl alcohol with thionyl chloride in pyridine, followed by cleavage of tetrahydrofurfuryl chloride with sodium amide in liquid ammonia and subsequent protection (4-pentyn-1-ol) with 3,4-dihydro-2H-pyran. 2-(4′-Nonynyloxy)-tetrahydropyran was prepared by acetylenic coupling with butyl bromide in 53% yield (Brooks *et al.,* 1955; Jones *et al.,* 1963). The pyranyl ether was converted to 4-nonyn-1-ol in 93% yield. The ynol was hydrogenated over Lindlar catalyst to give (4*Z*)-nonen-1-ol in 71% yield. On the other hand, Birch reduction of the ynol by sodium in liquid ammonia gave (4*E*)-nonen-1-ol in 75% yield.

(4*Z*)-nonen-1-ol: b.p. 74.0–74.5 °C/2 mmHg; purity 99.2%; m.p. of 3,5-DNB 13.2–14.2 °C; IR (film) cm^{-1}: 3340 (O–H), 3006 (C=C–H), 2956, 2929, 2871 (C–H), 1654 (C=C), 1060, 1020 (C–O), 713 (*Z*, C=C); MS (70 eV): *m/z* (%) = 142 (M$^+$, 10), 124 (45), 96 (48), 95 (67), 81 (100), 69 (33), 68 (87), 67 (65), 55 (63), 54 (42), 41 (47); ^{13}C NMR (CDCl$_3$/TMS): δ = 14.0, 22.4, 23.6, 26.9, 31.9, 32.7, 62.6, 128.9, 130.8 ppm; ^{1}H NMR ($CDCl_3$/TMS): δ = 0.90 (t, 3H, *J* = 7.3), 1.27–1.36 (m, 4H), 1.63 (m, 2H), 1.97 (br s, 1H), 2.05 (m, 2H), 2.11 (m, 2H), 3.64 (t, 2H, *J* = 6.4), 5.34–5.43 ppm (m, 2H).

(4*E*)-nonen-1-ol: b.p. 73.0–74.0 °C/2 mmHg; purity 99.4%; m.p. of 3,5-DNB 29.7–30.6 °C; IR (film) cm^{-1}: 3334 (O–H), 3020 (C=C), 2956, 2927, 1873 (C–H), 1058 (C–O), 966 (*E*, C=C); MS (70 eV): *m/z* (%) = 142 (M^+, 13), 124 (42), 96 (38), 95 (58), 82 (58), 81 (100), 69 (32), 68 (84), 67 (60), 55 (60), 54 (37), 41 (43); ^{13}C NMR ($CDCl_3$/TMS): δ = 14.0, 22.4, 23.6, 26.9, 31.9, 32.7, 62.6, 128.9, 130.8 ppm; ^{1}H NMR ($CDCl_3$/TMS): δ = 0.89 (t, 3H, *J* = 7.3), 1.26–1.36 (m, 4H), 1.62 (m, 2H), 1.96–2.00 (m, 3H), 2.07 (m, 2H), 3.63 (t, 2H, *J* = 6.4), 5.37–5.48 ppm (m, 2H).

Preparation of (5 Z)-nonen-1-ol and (5 E)-nonen-1-ol

2-(5′-Hexynyloxy)-tetrahydropyran was obtained in 48% yield by chlorination of tetrahydropyran-2-methanol with thionyl chloride in pyridine, followed by cleavage of tetrahydropyran-2-methyl chloride with sodium amide in liquid ammonia and subsequent protection (5-hexyn-1-ol) with 3,4-dihydro-2H-pyran. The pyranyl ether was converted to its lithium salt with *n*-butyllithium in tetrahydrofuran (THF) and coupled with propyl bromide in hexamethylphosphoric triamide (HMPA) to give 2-(5′-nonynyloxy)-tetrahydropyran in 57% yield. The pyranyl ether was converted to 5-nonyl-1-ol by methanolysis in a methanol solution containing 30% (w/w) phosphoric acid in 80% yield. The ynol was hydrogenated under Lindlar catalyst to give (5*Z*)-nonen-1-ol in 87% yield. On the other hand, Birch reduction of the ynol with sodium in liquid ammonia gave (5*E*)-nonen-1-ol in 71% yield.

(5*Z*)-nonen-1-ol: b.p. 75.0–76.0 °C/2 mmHg; purity 99.7%; m.p. of 3,5-DNB 29.1–29.9 °C; IR (film) cm^{-1}: 3336 (O–H), 3006 (C=C–H), 2958, 2869 (C–H), 1654 (C=C), 1064, 1041 (C–O), 713 (*Z*, C=C); MS (70 eV): *m/z* (%) = 142 (M^+, 10), 124 (48), 95 (100), 82 (79), 81 (93), 68 (71), 67 (91), 55 (70), 54 (61), 41 (56); ^{13}C NMR ($CDCl_3$/TMS): δ = 13.8, 22.9, 25.9, 26.9, 29.3, 32.4, 62.8, 129.6, 130.1 ppm; ^{1}H NMR ($CDCl_3$/TMS): δ = 0.90 (t, 3H, *J* = 7.3), 1.33–1.45 (m, 4H), 1.58 (m, 2H), 1.98–2.09 (m, 5H), 3.63 (t, 2H, *J* = 6.7), 5.33–5.41 ppm (m, 2H).

(5*E*)-nonen-1-ol: b.p. 75.0–76.0 °C/2 mmHg; purity 99.9%; m.p. of 3,5-DNB 24.3–25.6 °C; IR (film) cm^{-1}: 3340 (O–H), 3025 (C=C), 2931, 2871 (C–H), 1058, 1039 (C–O), 966 (*E*, C=C); MS (70 eV): *m/z* (%) = 142 (M^+, 15), 124 (53), 96 (81), 95 (95), 82 (77), 81 (100), 68 (71), 67 (88), 57 (32), 55 (75), 54 (68), 41 (58); ^{13}C NMR ($CDCl_3$/TMS): δ = 13.7, 22.7, 25.8, 32.2, 32.3, 34.7, 62.9, 130.1, 130.7 ppm; ^{1}H NMR ($CDCl_3$/TMS): δ = 0.88 (t, 3H, *J* = 7.3), 1.36 (m, 2H), 1.43 (m, 2H), 1.57 (m, 2H), 1.74 (br s, 1H), 1.95 (m, 2H), 2.02 (m, 2H), 3.63 (t, 2H, *J* = 6.7), 5.38–5.42 ppm (m, 2H).

Preparation of (6 Z)-nonen-1-ol and (6 E)-nonen-1-ol

Tetrahydropyran was acetylated with acetyl bromide under zinc bromide to give 5-bromopentyl acetate in 93% yield (Synerholm, 1955). 5-Bromopentan-1-ol was obtained by hydrolysis of 5-bromopentyl acetate with hydrogen bromide in ethanol. Then the pyranyl ether of 5-Bromopentan-1-ol was coupled with lithium acetylide, ethylenediamine complex in dimethyl sulfoxide (DMSO) to give 2-(6′-heptynyloxy)-tetrahydropyran in 77% yield, which was converted to a lithium salt with *n*-butyllithium in tetrahydrofuran and coupled with ethyl bromide in hexamethylphosphoric triamide to give 2-(6′-nonynyloxy)-tetrahydropyran in 88% yield. The pyranyl ether was converted to 6-nonyn-1-ol by methanolysis in a methanol solution containing 30% (w/w) phosphoric acid in 87% yield. The ynol was hydrogenated under Lindlar catalyst to give (6*Z*)-nonen-1-ol in 89% yield. On the other hand, Birch reduction of the ynol with sodium in liquid ammonia to give (6*E*)-nonen-1-ol in 79% yield.

(6*Z*)-nonen-1-ol: b.p. 77.5–78.0 °C/2 mmHg; purity 99.6%; m.p. of 3,5-DNB 26.5–27.6 °C; IR (film) cm^{-1}: 3336 (O–H), 3004, 2962 (C=C–H), 2933, 2873 (C–H), 1652 (C=C), 1052, 1025 (C–O), 713 (*Z*, C=C); MS (70 eV): *m/z* (%) = 142 (M^+, 6), 124 (39), 96 (36), 95 (100), 82 (89), 81 (55), 69 (34), 68 (78), 67 (94), 55 (56), 54 (33), 41 (63); ^{13}C NMR ($CDCl_3$/TMS): δ = 14.4, 20.5, 25.4, 27.1, 29.6, 32.7, 62.9, 129.0, 131.8 ppm; ^{1}H NMR ($CDCl_3$/TMS): δ = 0.95 (t, 3H, *J* = 7.3), 1.36–1.38 (m, 4H), 1.57 (m, 2H), 2.00–2.07 (m, 4H), 2.09 (br s, 1H), 3.62 (t, 2H, *J* = 6.7), 5.29–5.40 ppm (m, 2H).

(6*E*)-nonen-1-ol: b.p. 75.5–76.2 °C/2 mmHg; purity 99.9%; m.p. of 3,5-DNB 49.1–50.9 °C; IR (film) cm^{-1}: 3338 (O–H), 3023 (C=C), 2931, 2871 (C–H), 1054, 1012 (C–O), 966 (*E*, C=C); MS (70 eV): *m/z* (%) = 142 (M^+, 9), 124 (39), 96 (38), 95 (100), 82 (83), 81 (53), 69 (39), 68 (66), 67 (87), 55 (52), 41 (61); ^{13}C NMR ($CDCl_3$/TMS): δ = 14.0, 25.3, 25.6, 29.5, 32.5, 32.7, 62.9, 129.1, 132.2 ppm; ^{1}H NMR ($CDCl_3$/TMS): δ = 0.96 (t, 3 H, *J* = 7.3), 1.31–1.41 (m, 4 H), 1.56 (m, 2 H), 1.97–2.04 (m, 5 H), 3.61 (t, 2 H, *J* = 6.7), 5.35–5.48 ppm (m, 2 H).

Preparation of (7Z)-nonen-1-ol and (7E)-nonen-1-ol

1,6-Hexanediol was converted to 6-bromohexan-1-ol by a mild bromination using hydrogen bromide under the condition of continuous extraction with hot toluene (Campbell, *et al.,* 1955). Then the bromohydrin was protected with 3,4-dihydro-2 H-pyran to give 2-(6′-bromohexanyloxy)-tetrahydropyran in 60% yield. The pyranyl ether was coupled with lithium acetylide in dimethyl sulfoxide to give 2-(7′-octynyloxy)-tetrahydropyran in 68% yield. The pyranyl ether was converted to a lithium acetylide with *n*-butyllithium in tetrahydrofuran which was coupled with methyl iodide in hexamethylphosphoric triamide to give 2-(7′-nonynyloxy)-tetrahydropyran in 99% yield. The nonynyl pyranyl ether was converted to 7-nonyn-1-ol by methanolysis in a methanol solution containing 30% (w/w) phosphoric acid in 97% yield. The ynol was hydrogenated under Lindlar catalyst to give (7*Z*)-nonen-1-ol in 81% yield. On the other hand, Birch reduction of the ynol with sodium in liquid ammonia gave (7*E*)-nonen-1-ol in 78% yield.

(7*Z*)-nonen-1-ol: b. p. 78.0–78.5 °C/2 mmHg; purity 99.4%; m. p. of 3,5-DNB 30.6–32.5 °C; IR (film) cm^{-1}: 3338 (O–H), 3012 (C=C–H), 2931, 2856 (C–H), 1657 (C=C), 1056, 1033 (C–O), 702 (*Z*, C=C); MS (70 eV): *m/z* (%) = 142 (M^+, 3), 124 (28), 95 (50), 82 (57), 81 (43), 69 (32), 68 (100), 67 (60), 55 (51), 41 (46); ^{13}C NMR ($CDCl_3$/TMS): δ = 12.7, 25.7, 26.8, 29.1, 29.5, 32.8, 62.9, 123.8, 130.7 ppm; ^{1}H NMR ($CDCl_3$/TMS): δ = 1.34–1.40 (m, 6 H), 1.55 (m, 2 H), 1.60 (d, 3 H), *J* = 6.7), 1.92 (br s, 1 H), 2.03 (m, 2 H), 3.62 (t, 2 H, *J* = 6.7), 5.36–5.46 ppm (m, 2 H).

(7*E*)-nonen-1-ol: b. p. 77.0–78.0 °C/2 mmHg; purity 99.6%; m. p. of 3,5-DNB 39.0–40.0 °C; IR (film) cm^{-1}: 3336 (O–H), 3022 (C=C), 2929, 1856 (C–H), 1057 (C–O), 964 (*E*, C=C); MS (70 eV): *m/z* (%) = 142 (M^+, 5), 124 (32), 95 (56), 82 (62), 81 (48), 69 (33), 68 (100), 67 (62), 55 (60), 41 (45); ^{13}C NMR ($CDCl_3$/TMS): δ = 17.9, 25.7, 29.0, 29.6, 32.5, 32.8, 62.9, 124.7, 131.5 ppm; ^{1}H NMR ($CDCl_3$/TMS): δ = 1.29–1.38 (m, 6 H), 1.56 (m, 2 H), 1.64 (dd, 3 H, *J* = 1.2, *J* = 4.9), 1.91 (br s, 1 H), 1.97 (m, 2 H), 3.62 (t, 2 H, *J* = 6.7), 5.39–5.42 ppm (m, 2 H).

Preparation of 8-nonen-1-ol

1,7-Heptanediol was converted to 7-bromoheptan-1-ol by a mild bromination using hydrogen bromide under the condition of continuous extraction with hot toluene (Campbell *et al.,* 1955). Then the bromohydrin was protected with 3,4-dihydro-2 H-pyran to give 2-(7′-bromoheptanyloxy)-tetrahydropyran in 56% yield. The pyranyl ether was coupled with lithium acetylide in dimethyl sulfoxide to give 2-(8′-nonynyloxy)-tetrahydropyran in 81% yield. The pyranyl ether was converted to 8-nonyn-1-ol by methanolysis in a methanol solution containing 30% (w/w) phosphoric acid in 93% yield. Birch reduction of the ynol with sodium in liquid ammonia gave 8-nonen-1-ol in 70% yield.

8-nonen-1-ol: b. p. 76.0–76.8 °C/2 mmHg; purity 99.8%; m. p. of 3,5-DNB 49.2–50.3 °C; IR (film) cm^{-1}: 3334 (O–H), 3077 (C=C), 2927, 2856 (C–H), 1641 (C=C), 1057 (C–O); MS (70 eV): *m/z* (%) = 124 (8), 96 (38), 95 (54), 82 (86), 81 (66), 68 (86), 67 (87), 55 (100), 54 (80), 41 (67); ^{13}C NMR ($CDCl_3$/TMS): δ = 15.7, 28.9, 29.1, 29.3, 32.8, 33.8, 62.9, 114.2, 139.1 ppm; ^{1}H NMR ($CDCl_3$/TMS): δ = 1.30–1.42 (m, 8 H), 1.55 (m, 2 H), 2.01–2.07 (m, 3 H), 3.61 (t, 2 H, *J* = 6.7), 4.93 (dd, 1 H, *J* = 1.2, *J* = 10.4), 4.99 (ddd, 1 H, *J* = 1.8, 3.7, 16.1), 581 ppm (ddt, 1 H, *J* = 6.7, 10.4, 16.1).

Purification of n-nonen-1-ols

General procedure: A C_9-unsaturated alcohol (10.0 g, 70.4 mmol) synthesized as above was added into a solution of 3,5-dinitrobenzoyl chloride (17.8 g, 77.4 mmol) in benzene (100 ml). Then pyridine (6.1 ml) was added into the mixture and stirred at room temperature. The reaction mixture was extracted with diethyl ether. The extract was washed with sat. $NaHCO_3$ soln. and brine, dried over Na_2SO_4 (anhydrous), and evaporated *in vacuo* to give a crude 3,5-dinitrobenzoate. It was repeatedly recrystallized from ethanol to give pure 3,5-dinitrobenzoate derivatives in 84–99% yield.

The purified 3,5-dinitrobenzoate derivative (4.0 g, 11.9 mmol) was added into 10% NaOH soln. (150 ml) and then stirred at room temperature. Then the mixture was extracted with ether and washed with brine. The extract was dried over Na_2SO_4 (anhydrous) and concentrated *in vacuo* to give highly pure *n*-nonen-1-ols (over 99.2% purity) in 82–92% yield (1.4–1.6 g, 97.5–11.0 mmol).

Odor Characteristics

Sensory evaluation

Three trained flavorists sniffed paper strips dipped in 1% triethyl citrate solutions of the synthesized alcohols. They were asked to describe the sensory characteristics using eight sensory descriptive terms: leaf of grassy green an image of grasses, stems, and leaves; vegetable-like an image of vegetable, *i. e.,* tomatoes, green peppers, cabbages etc; fruity an image of fruits, *i. e.* apples, berries, pears etc; sweet degree of sweetness; fresh degree of freshness; spicy an image of pepper, nutmeg, cinnamon etc; oily-fatty oily-fatty, waxy, rancid; herbal an image reminiscent of bitterness of crude drugs. Score sheets with four-point scale ranging from threshold to very intense: *i. e.* 0 = threshold, 1 = very weak, 2 = intense, 3 = very intense, were used for the evaluation of the test samples. The average scores of three panellers were adopted as the odor-strength of the sensory attributes.

Statistical analysis

The average scores from sensory evaluation were subjected to principal component analysis using "ANALYST" (analyzer programs for statistical data, Fujitsu, Tokyo, Japan) on a FACOM M-308 computer (Fujitsu, Tokyo, Japan).

The data from sensory evaluation were statistically analyzed using principal component analysis, one of the multivariate analyses, to characterize the odor profiles of the tested compounds. The analysis was carried out with all the 13 compounds using the eight explanatory variables.

Results

Odor specificity analysis: Odor characteristic of each *n*-nonen-1-ol was described by using the eight sensory descriptive terms of leaf or grassy, vegetable-like, fruity, sweet, fresh, spicy, oily and herbal. The odor strength in each descriptive term was scored as 0 threshold; 1 very weak; 2 intense; 3 very intense. The average of three trained flavorists was plotted on the radar chart (Figs. 1 and 2). This analysis showed that, if the position of double bond was the same, the odor characteristic quite resembled, irrespective of its geometry, while the position of double bond affected the characteristic so much. As the position of double bond was shifted to the ω-terminal, the oily factor was weakened. The least oily note was observed with nonen-1-ols having a double bond at position 5 or 6. With (7*E*)- and 8-nonen-1-ols, the factor again appeared. Vegetable-like factor was strongest with (3*Z*)- and (4*Z*)-nonen-1-ols. The vegetable-like factor was also weakened, as the position of double bond was shifted to both the terminal ends. Among *n*-nonen-1-ols (6*Z*)-nonen-1-ol showed pleasant flavor having high fruity, sweet and fresh factors.

Principal analysis: Previous result of principal analyses concerning about C_6-unsaturated alcohols and aldehydes suggested that this analytical system can be properly used for the odor evaluation (Hatanaka *et al.*, 1992). After the analysis of the tested compounds using the eight explanatory variables, *i. e.,* descriptive terms, Eigenvalues, Eigenvectors and the proportions of the correlation matrixs from the first principal component (PC-1) to the fifth (PC-5) were obtained (Table I). Fresh, fruity and sweet factors were found to contribute to PC-1, on the other hand, herbal, vegetable-like and leaf or grassy were found to contribute to PC-2. As the Table shows, the portion of PC-1 and PC-2 summed up to nearly 70%. The portions of PC-3, PC-4, and PC-5 were small. Thus, further analysis was made on PC-1 and PC-2 to summarize the odor images. As shown in Fig. 3, it was indicated that 5-, 6- and 7-nonen-1-ols, which contain a double bond in ω side had a positive value of PC-1, on the other hand, 2-, 3-, and 4-nonen-1-ols which contain a double bond in the α-terminal functional group side did a negative one. Interestingly, 4- and 6-nonen-1-ols, and 3- and 7-nonen-1-ols were respectively located in opposite positions respective to PC-1. Relative localization of each set of the two geometrical isomers of nonen-1-ols having the same position of double

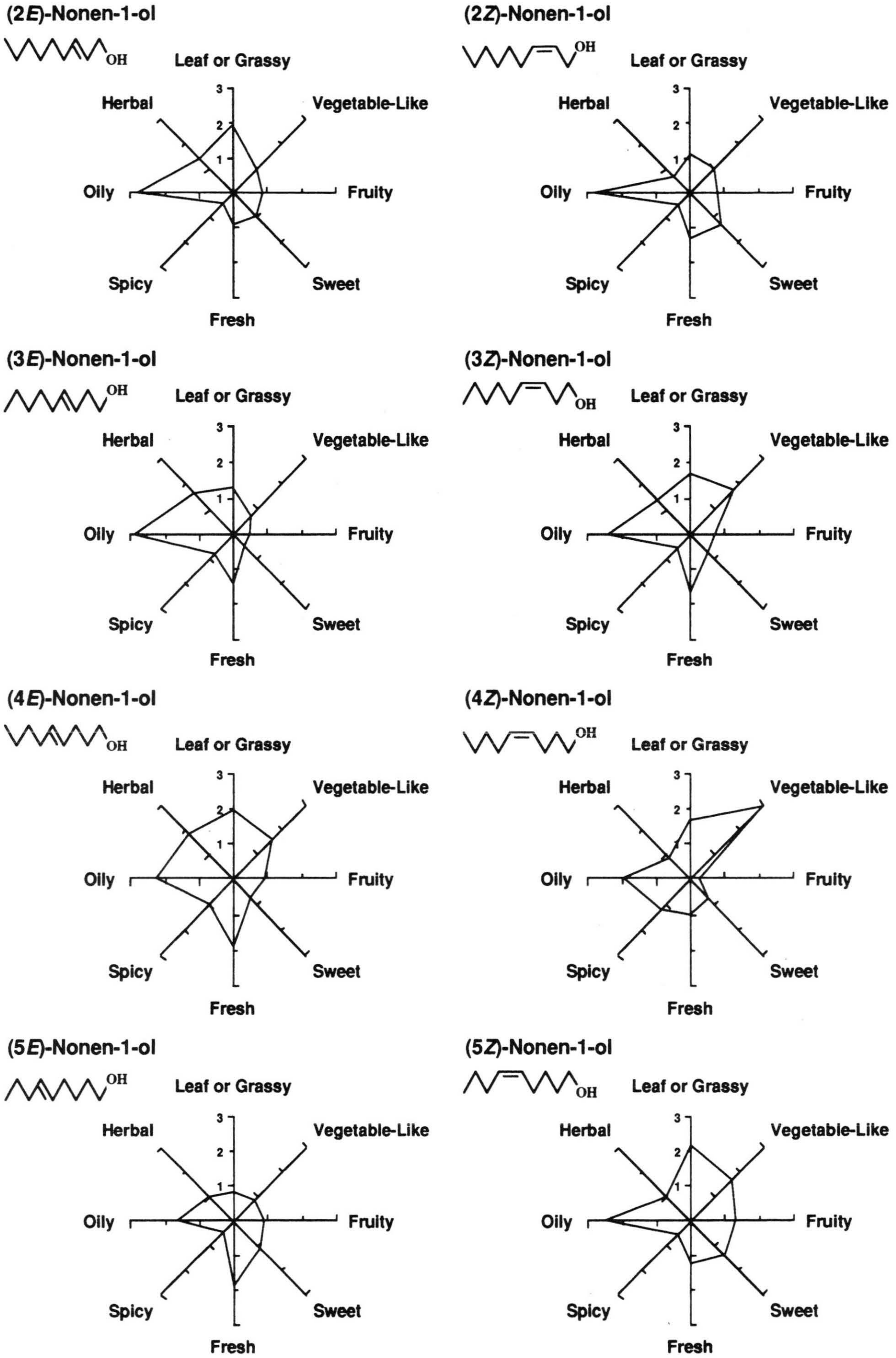
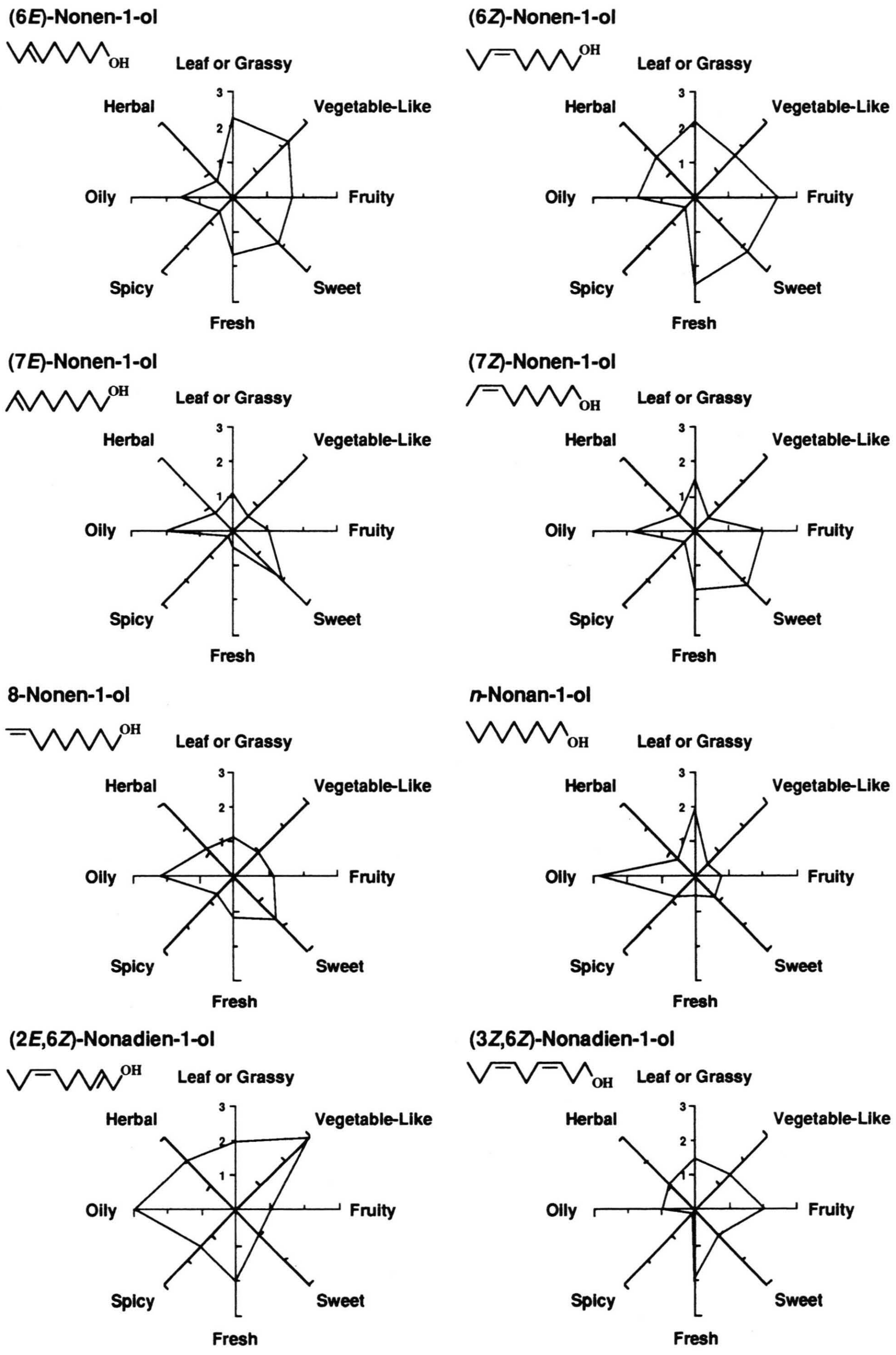


Fig. 1. Odor profiles of *n*-nonen-1-ols (from 2-nonen-1-ols to 5-nonen-1-ols). Eight sensory descriptive terms were used for the sensory characteristics: leaf or grassy green an image of grasses, stems, and leaves; vegetable-like an image of vegetable, *i. e.*, tomatoes, green peppers, cabbages etc; fruity an image of fruits, *i. e.*, apples, berries, pears etc; sweet degree of sweetness; fresh degree of freshness; spicy an image of pepper, nutmeg, cinnamon etc; oily-fatty oily-fatty, waxy, rancid; herbal an image reminiscent of bitterness of crude drugs. Score sheets with four-point scale ranging from threshold to very intense: *i. e.* 0 = threshold, 1 = very weak, 2 = intense, 3 = very intense, were used for the evaluation of the test samples. The average scores of three panellers were adopted as the odor-strength of the sensory attributes.


(6*E*)-Nonen-1-ol

(6*Z*)-Nonen-1-ol

(7*E*)-Nonen-1-ol

(7*Z*)-Nonen-1-ol

8-Nonen-1-ol

n-Nonan-1-ol

(2*E*,6*Z*)-Nonadien-1-ol

(3*Z*,6*Z*)-Nonadien-1-ol

Fig. 2. Odor profiles of *n*-nonen-1-ols (from 6-nonen-1-ols to 8-nonen-1-ol), *n*-nonanol, (2*E*, 6*Z*)-nonadien-1-ol, and (3*Z*, 6*Z*)-nonadien-1-ol.

Table I. The principal component analyses of the odor of the *n*-nonen-1-ols, *n*-nonanol, and (2*E*, 6*Z*)- and (3*Z*, 6*Z*)-nonadien-1-ols.

Odor description	PC-1	PC-2	PC-3	PC-4	PC-5
Fresh	−0.55123	0.63329	−0.48884	−0.06496	0.13029
Fruity	−0.84830	0.41553	0.07473	0.23991	−0.08724
Leaf of grassy	0.10557	0.75117	0.51601	0.24290	−0.29752
Herbal	0.43771	0.64501	−0.51532	0.29810	0.09741
Oily-fatty	0.76864	−0.20249	0.02398	0.54174	0.17516
Spicy	0.81220	0.37998	0.07797	−0.08575	0.31900
Sweet	−0.79911	0.06975	0.23509	0.26810	0.46241
Vegetable-like	0.30784	0.78845	0.23099	−0.39282	0.15480
Eigenvalue	3.21001	2.36590	0.89164	0.73666	0.49282
Proportion	40.1	29.6	11.1	9.2	6.2
Cumulative proportion	40.1	69.7	80.8	90.0	96.2

PC: Principal component.

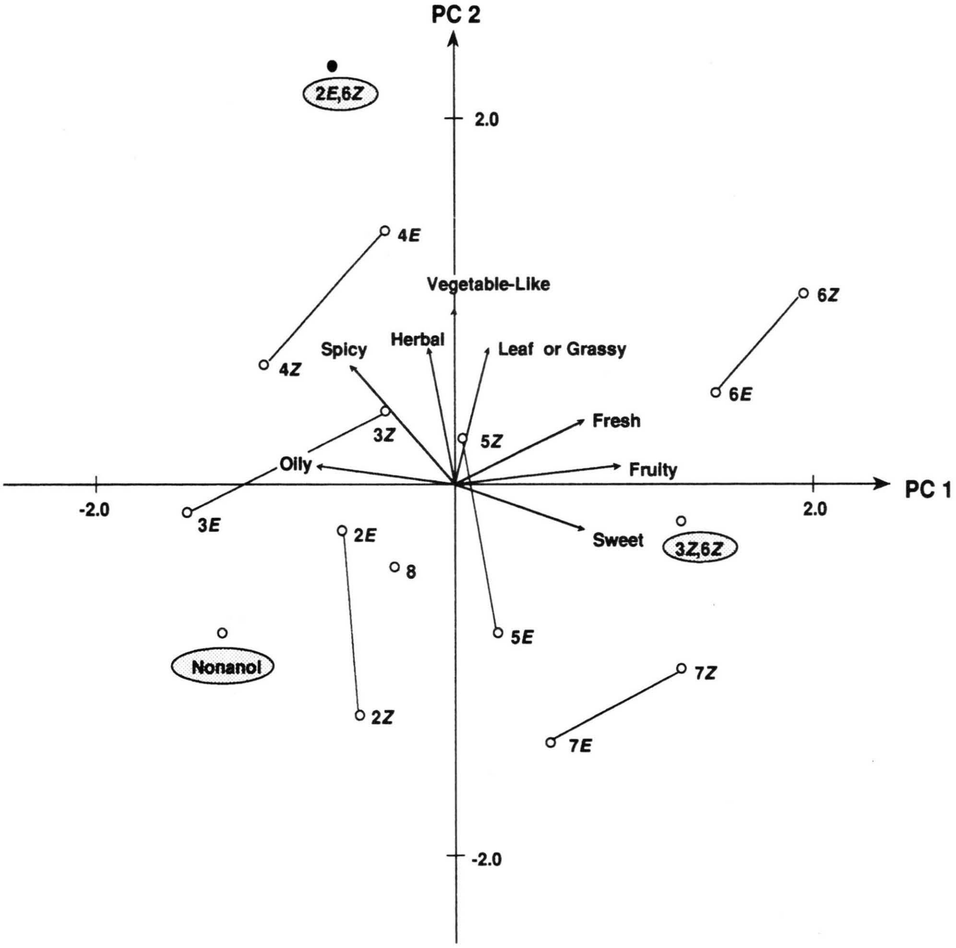


Fig. 3. The score plots and the vectors of the eigenvalues on the plane of the first principal component *vs.* the second principal component in *n*-nonen-1-ols, *n*-nonanol, and (2*E*, 6*Z*)- and (3*Z*, 6*Z*)-nonadien-1-ols.

bond did not show significant regulatory tendency, but the each distance between the two points of the corresponding geometrical isomers, *i. e.*, $(\Delta PC\text{-}1)^2 + (\Delta PC\text{-}2)^2$, was almost the same. Interestingly, the locations of (3*Z*, 6*Z*)- and (2*E*, 6*Z*)-nonadien-1-ol in the figure were not a simple algorithm of the corresponding monoenols, *e. g.*, (6*Z*)-, (2*E*)-, or (3*Z*)-nonen-1-ol. Among these *n*-nonen-1-ols, (6*Z*)-nonen-1-ol, which has a *Z*-double bond at ω 3 position had highest values of both the first and the second principal components. This was also observed with (3*Z*)-hexen-1-ol, which contains an ω 3*Z* double bond. Probably, an ω 3*Z* structure in volatile alcohols has a specific interaction with a sensory system of humans.

Discussion

All the isomers of *n*-nonen-1-ols were synthesized stereo-selectively, and they were highly purified by recrystallization of their 3,5-dinitrobenzoate derivatives.

In the study of the chemical structure-odor correlations we introduced a new system for the evaluation of odor characteristics. The statistical analyses led to the very interesting results. The quantitative structure-activity relationships (QSAR) have been established in the fields of drugs and pesticides (Martin, 1978). Although the sensory tests to determine the strengths of odor characteristics are semi-quantitative, the correlations between the chemical structures and odor characteristics could be explained very clearly after the statistical analyses. The odor profiles of the tested compounds were dominated mainly by two integrated odor parameters, PC-1 and PC-2, derived from statistical treatment. The odor-characteristics of each compound could be expressed in numbers steadily by means of the scores of PC-1 and PC-2, and thus, QSAR analysis was applied successfully to the chemical structure-odor correlation. (3*Z*, 6*Z*)-, (2*E*, 6*Z*)- nonadien-1-ols, and (6*Z*)-nonen-1-ol, which exist in nature, differed strongly in the principal elements of their odor from the other C_9-alcohols. All of them have the structure of ω3*Z*. The structure may be recognized specifically by the human sense of smell. This strategy for evaluating chemical structure-odor correlations must be applicable to clarify those of the other series of compounds.

Acknowledgements

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