Synthesis and Enantiodifferentiation of Isomeric Theaspiranes†

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The spiro ethers **6a–d** were prepared in a biomimetic-type reaction from their natural precursor 4-hydroxy-7,8-dihydro-β-ionol (**5**) that was available from 4-oxo-β-ionone (**1**) by $NaBH_4$ and subsequent H_2/Pd reduction. The so-obtained racemic keto alcohol **3** was esterified with (*R*)-(−)-2-phenylpropionic acid, and the resulting diastereomeric esters (**4a/b**) were isolated in pure form (de > 90%) by preparative HPLC. Configuration at C-9 was determined by ^1H NMR spectroscopy. The isomeric diols **5a/b** obtained from esters **4a/b** by $LiAlH_4$ reductive cleavage were subjected to thermal treatment at pH 3.4, yielding two pairs of diastereomeric theaspiranes (**6a/b** and **6c/d**) which were subsequently obtained in optically pure form by preparative HPLC. The absolute configuration at C-5 was established by NOE experiments. The enantiomers distinctly differed in their odor properties. Whereas spiro ether **6a** showed a weak camphoraceous note, isomer **6b** exhibited an intense fresh-fruity (black currant or cassis) odor. The odor of isomer **6c** was dominated by a fresh camphoraceous note; this note almost became naphthalene-like in isomer **6d**. Using on-line coupled multidimensional gas chromatography–mass spectrometry (DB-5/C-Dex B) with SIM mode, enantiodifferentiation of **6a–d** in a number of natural sources revealed a high variation in the distribution of the enantiomers.

INTRODUCTION

Diastereomeric theaspiranes have been often found in nature, e.g., in raspberry (Winter and Enggist, 1971), yellow and purple passion fruit (Winter and Klöti, 1972; Winterhalter, 1990), black and green tea (Renold et al., 1974; Zeng et al., 1990), grapes (Schreier et al., 1976), *Osmanthus* absolute (Kaiser et al., 1978), guava (Idstein and Schreier, 1985), black chokeberry (*Aronia melanocarpa* Ell.) (Hirvi and Honkanen, 1985), and quince fruit (Tsuneya et al., 1983; Winterhalter et al., 1987). A few years ago, the pathway of theaspirane formation via prototropic dehydration of their natural precursor, 4-hydroxy-7,8-dihydro-β-ionol (**5**), was elucidated (Winterhalter and Schreier, 1988). Theaspiranes from several chemical syntheses have been described to exhibit attractive sensory properties (Skorianetz et al., 1976; Naegeli, 1977; Nakatani and Yamanishi, 1969; Ina et al., 1972; Bellas et al., 1974; Nakatani, 1976; Schulte-Elte et al., 1978; Etoh et al., 1980, 1988; Torii et al., 1981; Masuda and Mihara, 1985; Uneyama et al., 1985; Winterhalter and Schreier, 1988). Recently, enantioresolution of theaspiranes has been achieved by chirospecific complexation gas chromatography using modified cyclodextrin phases (Guichard et al., 1990; Werkhoff et al., 1991).

In this paper, we report for the first time the synthesis of the theaspirane enantiomers **6a–d**, their sensory properties, and their enantiodifferentiation in a number of natural sources.

EXPERIMENTAL PROCEDURES

General. NMR spectra were taken on Fourier transform Bruker AC 200 and WM 400 spectrometers. Vapor-phase FTIR spectra were recorded on a Hewlett-Packard IRD system (5965B with a wide band MCT detector). Optical rotation was measured with a Perkin-Elmer 241 polarimeter. All commercial chemicals used were of analytical grade quality. All solvents used were of high purity at purchase and were redistilled before use. For flash chromatography (Still et al., 1978) Merck silica gel 60 (0.032–0.063 mm) was used. Optically pure (*R*)-(−)-2-phenylpropionic acid [*R*-(−)-HTA] was obtained from Aldrich-Chemie GmbH, Steinheim, Germany. 4-Oxo-β-ionone (**1**) and *Osmanthus* absolute were donated samples from Dragoco, Holzminden, Germany.

Fruits. Except for raspberry fruits, which were deep-frozen, fresh ripe fruit material was used. Aroma extracts were obtained by continuous liquid–liquid extraction (pentane/dichloromethane 2:1) of fruit pulps at their natural pH and, in part, after neutralization at pH 7. For the isolation of glycosidically bound constituents from fruits and leaves the XAD method (Günata et al., 1985) with methanol elution was used. Enzymatic hydrolyses were carried out using β-D-glucosidase from sweet almond (Serva).

Preparation of Optically Pure Reference Compounds 6a–d. (*a*) *Synthesis and Separation of HTA Esters of 4-Oxo-7,8-dihydro-β-ionol* **4a/b**. For the preparation of optically pure theaspiranes **6a–d** our previously published method (Winterhalter and Schreier, 1988) was modified as outlined in Figure 1, employing HPLC separation of diastereomeric HTA esters of 4-oxo-7,8-dihydro-β-ionol (**4a/b**). The latter compounds were accessible in good yields (60%) from 4-oxo-β-ionone (**1**) by $NaBH_4$ reduction, thus yielding keto alcohol **2**, which upon selective hydrogenation (Pd/$BaSO_4$) of the side-chain double bond yielded the 7,8-dihydro analogue **3**. Spectral data of **1–3** have been published previously (Kaiser and Lamparsky, 1978). Diastereomeric HTA esters **4a/b** were obtained by adding a solution of 320 mg (1.6 mmol) of 4-oxo-7,8-dihydro-β-ionol (**3**) in dry CCl_4 (20 mL) to a stirred solution of 810 mg (4.8 mmol) of freshly prepared (*R*)-(−)-2-phenylpropionyl chloride (Helmchen and Schmierer, 1976). After 3 days of stirring at room temperature, H_2O (50 mL) was added and the water phase extracted with diethyl ether (3 × 50 mL). Combined ether extracts were washed with 0.5 N NaOH (50 mL) and H_2O (50 mL). After drying (Na_2SO_4) and concentration in vacuo, the reaction mixture was subjected to flash chromatography (Still et al., 1978) on silica gel using diethyl ether/pentane (3:7) as eluent. Final purification of diastereomeric esters **4a/b** was obtained by preparative HPLC on a LiChrospher Si60 column (5 μm, 250 × 16 mm; Knauer, Berlin; flow rate 20 mL/min; UV detection 254 nm) using diethyl ether/pentane (2:8) as eluent. Separated HTA esters **4a** and **4b** showed the following chromatographic and spectral data. First eluting isomer (HPLC retention time 21.7 min) **4a** (160 mg, white crystals, mp 70 °C): R_i (DB-5) 2519; CI-MS *m/z* (%) 360 (100, $[M + NH_4]^+$), 343 (3, $[M + H]^+$), 75 (8); FTIR (vapor phase, ν, cm^{-1}) 3072, 2980, 1740, 1690, 1607, 1461, 1329, 1167, 1071, 928, 697; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 and 0.91 (2 × 3 H, 2 s, $2CH_3$-C1), 1.17 (3 H, d, *J* = 6 Hz, CH_3-C9), 1.43 (3 H, d, *J* = 7

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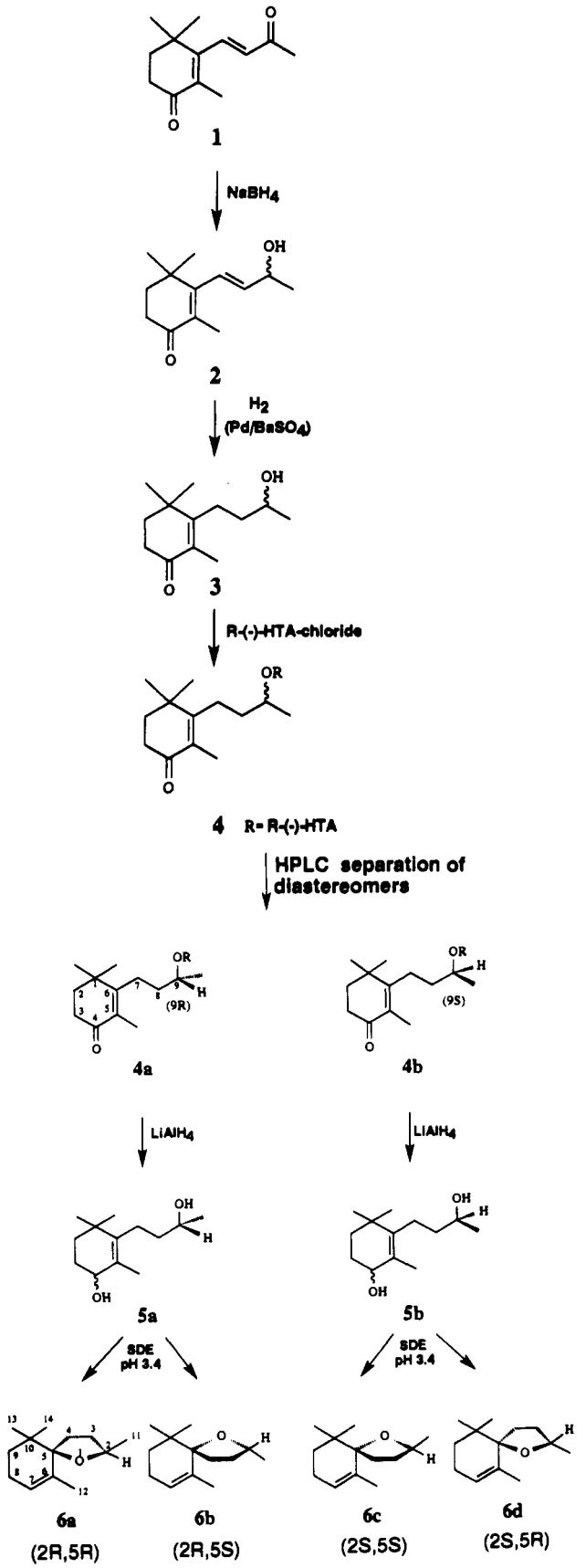

Figure 1. Preparation of (*R*)-HTA diastereomers **4** of 4-oxo-7,8-dihydro-β-ionol from 4-oxo-β-ionone (**1**) and of optically pure theaspirane isomers **6a–d** from separated (*R*)-HTA diastereomers **4a** and **4b**.

Hz, CH_3-C1′), 1.51 (3 H, s, CH_3-C5), 1.46–1.89 (4 H, m, H_2C2 and H_2C8), 2.29–2.36 (4 H, m, H_2C3 and H_2C7), 3.62 (q, J = 7 Hz, HC1′), 4.85 (1 H, m, HC9), 7.15–7.24 (5 H, m, phenyl-C1′). Second eluting isomer (23.2 min) **4b** (160 mg, viscous liquid): R_i (DB-5)

Table I. ^{13}C NMR Spectral Data (100 MHz, $CDCl_3$) of Theaspirane Enantiomers (δ Relative to TMS)

position	6a and 6c δ	DEPT	6b and 6d δ
2	76.78	CH	76.76
3[a]	35.18	CH_2	36.17
4[a]	34.26	CH_2	31.34
5	88.67	C	87.64
6	140.20	C	136.91
7	121.49	CH	123.89
8	22.80	CH_2	22.91
9[a]	34.72	CH_2	33.68
10	36.63	C	37.90
11	20.83	CH_3	21.27
12	18.46	CH_3	19.33
13[b]	21.89	CH_3	23.00
14[b]	24.80	CH_3	24.01

[a,b] Exchangeable values.

2540; CI-MS and FTIR, identical with that of isomer **4a**; ^{1}H NMR δ 1.03 and 1.04 (2 × 3 H, 2s, $2CH_3$-C1), 1.09 (3 H, d, J = 6 Hz, CH_3-C9), 1.45 (3 H, d, J = 7 Hz, CH_3-C1′), 1.64 (3 H, s, CH_3-C5), 1.51–1.74 (4 H, m, H_2C2 and H_2C8), 2.01–2.40 (4 H, m, H_2C3 and H_2C7), 3.65 (q, J = 7 Hz, HC1′), 4.84 (1 H, m, HC9), 7.13–7.26 (5 H, m, phenyl-C1′).

(*b*) *Reduction of Ester* **4a** *and Subsequent Cyclization to Diastereomeric Theaspiranes* **6a/b**. Sixty-two milligrams (0.18 mmol) of HTA ester **4a** (diastereomeric excess de > 98%, HRGC control) in 20 mL of dry diethyl ether was added to a stirred suspension of 300 mg (8 mmol) of $LiAlH_4$ in 20 mL of diethyl ether at 0 °C After 2 h of stirring at room temperature and the addition of ice–water (50 mL), the organic layer was separated and the water phase extracted with Et_2O (3 × 50 mL). The combined organic phases were washed with brine (30 mL) and water (30 mL). After drying (Na_2SO_4) and careful concentration (Vigreux column), the reduction product **5a** was—without further purification—subjected to simultaneous distillation/extraction (SDE) treatment at pH 3.4 for 1 h using the distillation head described by Schultz et al. (1977) and diethyl ether/pentane (1:1) as solvent. After drying (Na_2SO_4) of the organic phase and careful concentration (Vigreux column) to 0.5 mL, the concentrate was subjected to flash chromatography on silica gel using pentane as eluent. For final purification of the thermally formed diastereomeric theaspiranes **6a/b**, preparative HPLC was employed (LiChrospher Si60 column; flow rate 10 mL/min; UV detection 205 nm; eluent pentane/diethyl ether 95:5). Separated theaspirane isomers **6a** (enantiomeric excess ee 99%) and **6b** (ee 98%) showed the following chromatographic and spectral data. 2*R*,5*R* isomer **6a**: R_i (DB-5) 1304; $[\alpha]^{20}_D$ −160°* (*c* 0.001, $CHCl_3$); MS and IR data, cf., e.g., Masuda and Mihara (1985); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 and 0.93 (2 × 3 H, 2s, $2CH_3$-C10), 1.25 (3 H, d, J = 6 Hz, CH_3-C2), 1.29–2.04 (8 H, m, H_2C3, H_2C4, H_2C8, and H_2C9), 1.70 (3 H, br s, CH_3-C6), 4.10 (1 H, m, HC2), 5.25 (1 H, m, HC7); ^{13}C NMR cf. Table I. 2*R*,5*S* isomer **6b**: R_i (DB-5) 1321; $[\alpha]^{20}_D$ −221°*; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.84 and 0.97 (2 × 3 H, 2s, $2CH_3$-C10), 1.26 (3 H, d, J = 6 Hz, CH_3-C2), 1.54–2.15 (8 H, m, H_2C3, H_2C4, H_2C8, and H_2C9), 1.70 (3 H, br s, CH_3-C6), 4.00 (1 H, m, HC2), 5.40 (1 H, m, HC7); ^{13}C NMR, cf. Table I. *[α] values are still tentative, due to the small concentration of optically pure theaspiranes available for the determination of the optical rotation.

(*c*) *Reduction of Ester* **4b** *and Subsequent Cyclization of Diastereomeric Theaspiranes* **6c/d**. (9*S*)-HTA ester **4b** (de 88%, HRGC control) was treated as described for the 9*R* isomer **4a**. SDE treatment yielded the diastereomeric theaspiranes **6c/d**. LC purification (flash chromatography and subsequent HPLC) provided diastereomers **6c** (ee 85%) and **6d** (ee 84%), showing identical chromatographic and spectral data as obtained for the corresponding enantiomers **6a/b**.

Capillary Gas Chromatography (HRGC). For HRGC a Hewlett-Packard 5890 gas chromatograph equipped with a J&W fused silica DB-5 capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm) was used. Split injection was employed. The temperature program was from 60 to 300 °C at 5 °C/min. The flow rates for the carrier gas were 1.6 mL/min of He, for the makeup gas 30 mL/min of N_2, and for the detector gases 30 mL/

Table II. Enantiomeric Composition of Theaspiranes 6a–d in Various Natural Sources

source	6a (2R,5R), %	6c (2S,5S), %	ee, %	6d (2S,5R), %	6b (2R,5S), %	ee, %
free theaspiranes						
guava (Brazil)	1	99	98	99	1	98
quince (Germany)	5	95	90	94	6	88
Osmanthus	16	84	68	88	12	76
gooseberry (Germany)	29	71	42	74	26	38
raspberry (France)	37	63	26	60	40	20
raspberry (France)	75	25	50	20	80	60
raspberry (Yugoslavia)	90	10	80	85	15	70
bound theaspiranes						
purple passion fruit (Australia)	14	86	72	85	15	70
blackberry leaves (Germany)	35	65	30	64	36	28
green tea (Japan)	14	86	72	84	16	68

min of H_2 and 300 mL/min of air. The injector temperature was kept at 250 °C and the detector temperature at 280 °C. Linear retention index (R_i) is based on a series of *n*-hydrocarbons.

Capillary Gas Chromatography–Mass Spectrometry (HRGC–MS). A Varian 3300 gas chromatograph equipped with a split injector was combined by direct coupling to a Finnigan MAT 44 mass spectrometer with PCDS data system. The same type of column and the same temperature program as mentioned above for HRGC analysis were used. Temperature of ion source and all connection parts was 220 °C, electron energy was 70 eV, and cathodic current was 0.7 mA.

Multidimensional Gas Chromatography–Mass Spectrometry (MDGC–MS). A Siemens Sichromat 2 double-oven gas chromatograph with split injection (250 °C, 1:20) and flame ionization detectors on ovens 1 and 2 (250 °C each) was used. Preseparation was achieved in oven 1 on a J&W DB-5 fused silica capillary column (25 m × 0.25 mm i.d.; film thickness 0.25 μm). The temperature was programmed from 60 to 300 °C at 10 °C/min and held isothermally at 300 °C for 25 min. A "live" switching device (Schomburg et al., 1984) in oven 1 was used to perform effluent cuts onto column 2 in oven 2 (J&W C-Dex B, permethylated β-cyclodextrin; 25 m × 0.25 mm i.d.; df = 0.25 μm). The temperature was isothermal at 80 °C for 20 min and then programmed from 80 to 220 °C at 2 °C/min. A 36-s cut was carried out. Helium was used as the carrier gas at 0.66 mL/min in oven 1 and at 1.96 mL/min in oven 2. The flow rates for the detector gases were each 30 mL/min of hydrogen and 300 mL/min of air. The coupling of the MDGC system with a Finnigan MAT 44 quadrupole mass spectrometer was achieved by a variable effluent splitter (Siemens) working as a second live switching device. The temperature of the ion source and the transfer line was 200 °C. The electron energy was 70 eV and the cathodic current 0.7 mA. Injection volumes of 1.0 μL were used. Results of analyses were verified by comparison of MDGC–MS (SIM mode) data of authentic optically pure theaspiranes.

Chemical Ionization Mass Spectrometry (CI-MS). For CI-MS analyses a Finnigan 8200 mass spectrometer was used (reactant gas NH_3; pressure 0.3 mbar). Positive ions over a range *m/z* 70–800 were scanned.

RESULTS AND DISCUSSION

In Figure 1, a scheme of the synthesis of theaspirane enantiomers is outlined. The spiro ethers **6a–d** were prepared from their natural precursor 4-hydroxy-7,8-dihydro-β-ionol (**5a/b**) which was available from 4-oxo-β-ionone (1) by $NaBH_4$ and subsequent H_2/Pd reduction. The racemic keto alcohol **3** was subsequently esterified with (*R*)-(−)-2-phenylpropionic acid, and the resulting diastereomeric esters (**4a** and **4b**) were isolated in pure form by preparative HPLC. The absolute configuration at C9 was established according to the method of Helmchen correlating stereochemistry of chiral secondary alcohols with ^1H NMR spectroscopic behavior of their diastereomeric esters prepared from optically pure (*R*)-2-phenylpropionic acid (Helmchen, 1974; Helmchen and Schmierer, 1976). Comparison of the ^1H NMR data of the separated esters **4a** and **4b** showed inter alia that the resonance of CH_3-C9 in ester **4a** was downfield shifted, thus indicating *R* configuration at C9. Accordingly, due to the upfield shift for the resonance of CH_3-C9 in ester **4b**, *S* configuration was deduced.

The isomeric diols **5a** and **5b** obtained from **4a/b** by reductive cleavage with $LiAlH_4$ were subjected to simultaneous distillation extraction (SDE) (Schultz et al., 1977) at pH 3.4, yielding two pairs of diastereomeric theaspiranes **6a/b** and **6c/d** that were subsequently isolated in pure form by preparative HPLC. The absolute configuration at C5 of the separated spiro ethers was established by NOE NMR experiments. Thus, e.g., for enantiomer **6a** irradiation of the protons at the methyl group at C6 resulted in a NOE at the C2 methine protone, whereas for enantiomer **6b** a NOE at the methyl group at C2 was observed.

The theaspirane enantiomers distinctly differed in their sensory properties. Whereas spiro ether **6a** showed a weak camphoraceous note, isomer **6b** exhibited a highly attractive, intense fresh-fruity (black currant or cassis) odor. The odor of isomer **6c** was dominated by a fresh camphoraceous note; this note almost became naphthalene-like in isomer **6d**.

Using on-line coupled multidimensional gas chromatography–mass spectrometry (MDGC–MS) (Bernreuther and Schreier, 1991) with SIM mode, enantiodifferentiation of **6a–d** in a number of natural sources was carried out. The results of these studies are summarized in Table II. As a representative example, in Figure 2 the MDGC–MS separation of **6a–d** in an aglycon fraction from purple passion fruit is outlined. In this case—as well as for blackberry and green tea leaves—the formation of isomeric theaspiranes **6a–d** can be explained by a partial acid-catalyzed cyclization of the extremely labile natural precursor 4-hydroxy-7,8-dihydro-β-ionol **5a/b**, which was identified among the aglycons (Winterhalter, 1990). As shown in Table II, a high variation in the distribution of **6a–d** was observed. Generally, the 2*S* isomers **6c** and **6d** predominated; however, in raspberry fruits of various origin a considerable variation in enantiomeric distribution was determined. At present, there are no experimental data to explain the reasons for these findings. An explanation

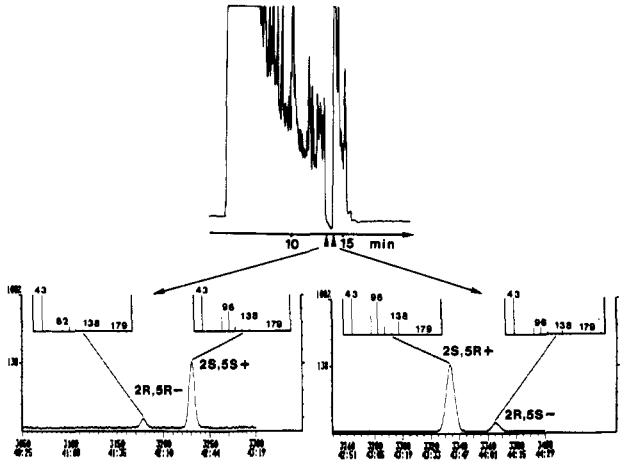

Figure 2. MDGC-MS enantiodifferentiation of theaspiranes **6a–d** in an aglycon fraction of purple passion fruit.

may be given by different enzyme selectivities responsible for the reduction at C9 of a still hypothetic natural ketone precursor of diol **5a/b**.

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Registry No. 1, 117048-10-9; 2, 141556-16-3; 3, 113832-46-5; 4a, 141556-17-4; 4b, 141556-18-5; (4*R*,9*R*)-5a, 141556-19-6; (4*S*,9*R*)-5a, 141583-44-0; (4*S*,9*S*)-5b, 141583-45-1; (4*R*,9*S*)-5b, 141556-20-9; 6a, 130404-01-2; 6b, 66537-40-4; 6c, 66537-39-1; 6d, 130404-02-3; (*R*)-(−)-2-phenylpropionyl chloride, 36240-11-6.