Synthesis and Enantiodifferentiation of Isomeric 3,5,6,8a-Tetrahydro-2,5,5,8a-tetramethyl-2*H*-1-benzopyrans (Edulans I and II)

Gertraut Schmidt, Gerhard Full, Peter Winterhalter, and Peter Schreier*

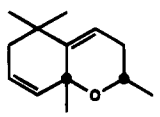
Lehrstuhl für Lebensmittelchemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

The benzopyran derivatives **1a–d** were prepared in a biomimetic-type reaction from their natural precursor 3-hydroxy-*retro*-α-ionol (**6**) which was available from α-ionol by *tert*-butyl chromate oxidation, reduction with $NaBH_4$, and subsequent rearrangement of the 7,8 double bond. The so-obtained geometrical isomers 3-oxo-*retro*-α-ionol **4a/b** were separated by preparative and analytical multilayer coil countercurrent chromatography. The racemic 3-oxo-*retro*-α-ionol **4a** was esterified with (*R*)-(−)-2-phenylpropionic acid, and the resulting diastereomeric esters (**5a/b**) were isolated in pure form (de 90%) by preparative HPLC. Configuration at C-9 was determined by ^1H NMR spectroscopy. The isomeric diols **6a/b** obtained from esters **5a/b** by $LiAlH_4$ reductive cleavage were subjected to thermal treatment (simultaneous distillation extraction), yielding two pairs of diastereomeric edulans (**1a/b** and **1c/d**) which were subsequently obtained in optically pure form by analytical HPLC. The absolute configuration at C-8a was established by NOE experiments. Using on-line coupled multidimensional gas chromatography-mass spectrometry [DB-Wax/heptakis-(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin] with selected ion monitoring mode, enantiodifferentiation of **1a–d** in a number of natural sources revealed predominance of the 2*S* enantiomers.

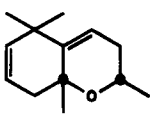
Keywords: *Edulans; enantiodifferentiation; MDGC–MS*

INTRODUCTION

There are about 400 known species of *Passiflora* of which some 30 are reported to bear edible fruit. Only a few species have achieved commercial development, and of these the best known is the purple-skinned *Passiflora edulis* Sims and its closely related yellow-skinned mutant *Passiflora edulis f. flavicarpa* Degener. The purple passion fruit has an intensely pleasant, floral-fruity aroma, whereas the yellow variety has an exotic ester aroma with a sharp sulfury note (Whitfield and Last, 1986). Many years ago, the four edulans, designated I, II, III, and IV in descending order of their



I and II



III and IV

relative concentration in the fresh juice, were recognized as important flavor compounds of the purple variety (Murray et al., 1972). Synthesis of edulans I and II (Adams et al., 1974; 1975) coupled with the determination of their relative stereochemistry (Whitfield and Stanley, 1977) showed that these substances were the isomeric (trans = I; cis = II) 3,5,6,8a-tetrahydro-2,5,5,-8a-tetramethyl-2*H*-1-benzopyrans **1**. In subsequent synthetic work edulans III and IV have been shown to be the isomeric 3,5,8,8a-tetrahydro-2,5,5,8a-tetramethyl-2*H*-1-benzopyrans (Stanley, 1979). Edulans I and II occur in amounts of approximately 1 and 0.1 mg/kg, respectively, in purple passion fruit. Since edulans III and IV are only present in trace amounts in the fresh juice, they were not included in this study. Edulans I and II have attractive roselike aromas and are considered to be key flavor components of the purple passion fruit (Whitfield and Stanley, 1977). Despite the extended synthetic work (Adams et al., 1974, 1975; Schulte-Elte et al., 1978; Etoh et al., 1980) including a biomimetic type of reaction involving prototropic dehydration of 3-hydroxy-*retro*-α-ionol (**6a/b**), the known natural precursor of edulans I and II (Herderich and Winterhalter, 1991), their absolute stereochemistry is still unknown.

In this paper, our studies on the synthesis of the edulan enantiomers **1a–d** and their enantiodifferentiation in natural sources are described.

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 Chiralizer polarimetric detector (Knauer). 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. (*R*)-(−)-2-Phenylpropionic acid [*R*-(−)-HTA] was obtained from Aldrich-Chemie GmbH, Steinheim, Germany.

Fruits. Fresh ripe purple passion fruit (*Passiflora edulis* Sims) originated from Kenya, Chile, and Ivory Coast. The fruit pulp (approximately 300 g) was centrifuged at 10000*g* for 1 h. Half of the juice was subjected to liquid–liquid extraction with diethyl ether; the other part was subjected to simultaneous distillation extraction (SDE, pH 3.4).

Simultaneous Distillation Extraction (SDE). SDE was performed with pentane/diethyl ether (1:1 v/v) for 2 h using the SDE head described by Schultz et al. (1977). The extract was dried over anhydrous sodium sulfate and carefully concentrated to 1 mL using a Vigreux column.

Preparation of Optically Pure Reference Compounds 1a–d. *(a) Synthesis and Separation of HTA Esters of (E)-3-Oxo-retro-α-ionol 5a/b.* For the preparation of optically pure edulans **1a–d** a previously published method (Herderich and Winterhalter, 1991) was modified as outlined in Figure 1, employing HPLC separation of diastereomeric HTA esters of

0021-8561/95/1443-0185$09.00/0

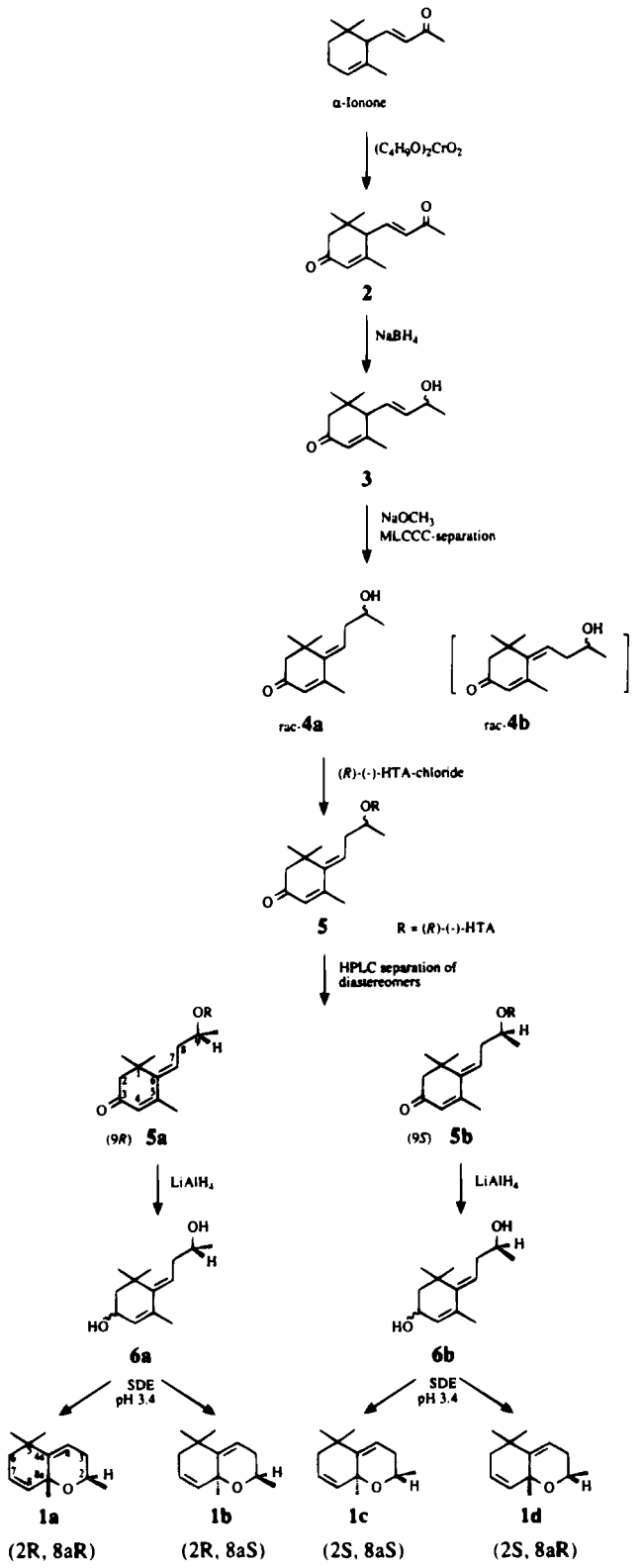


Figure 1. Preparation of (*R*)-(−)-HTA diastereomers **5** of 3-oxo-*retro*-α-ionol from α-ionone and optically pure edulan isomers **1a**−**d** from separated (*R*)-(−)-HTA diastereomers **5a** and **5b**.

(*E*)-3-oxo-*retro*-α-ionol (**5a/b**). The latter compounds were accessible from α-ionone by oxidation with *tert*-butyl chromate in CCl_4, thus yielding 3-oxo-α-ionone (**2**). Subsequent reduction with $NaBH_4$ and rearrangement of the 7,8 double bond ($NaOCH_3$) yielded 3-oxo-*retro*-α-ionols (**4a/b**). Spectral data of **2** and **3** have been published previously (Sefton et al., 1989). The *E*-configured isomer (**4a**) was purified using multilayer coil countercurrent chromatography (MLCCC) (Ito et al., 1982). Hexane/ethyl acetate/methanol/water (70:30:14:10) was used as solvent with the more dense layer acting as stationary phase (flow rate 2 mL/min; simultaneous UV detection at λ = 300 and 254 nm). After preseparation on a preparative MLCCC coil (2.6 mm i.d., 68 m, PTFE tubing), analytical MLCCC (1.6 mm i.d., 162 m, PTFE tubing) yielded pure isomer **4a**. Retention times were 14.5 (**4a**) and 11.5 h (**4b**) for preparative separations and 13 (**4a**) and 11 h (**4b**) for analytical separations, respectively. Spectral data of **4a** and **4b** have been reported previously (Herderich and Winterhalter, 1991). HTA esters **5a/5b** were obtained by adding a solution of 40 mg (1.9×10^{-1} mmol) of (*E*)-3-oxo-*retro*-α-ionol (**4a**) in dry CCl_4 (10 mL) to a stirred solution of 97.7 mg (5.8×10^{-1} mmol) of freshly prepared (*R*)-(−)-2-phenylpropionyl chloride (Helmchen and Schmierer, 1976). After 3 days of stirring at room temperature (TLC monitoring), H_2O (20 mL) was added and the water phase extracted with diethyl ether (3 × 20 mL). Combined ether extracts were washed with 0.5 N NaOH (20 mL) and H_2O (20 mL). After drying (Na_2SO_4) and concentration *in vacuo*, the reaction mixture was subjected to flash chromatography on silica gel using diethyl ether/pentane (3:7) as eluent. Final purification of diastereomeric esters **5a/b** was obtained by preparative HPLC on an Eurospher Si100 column (7 μm, 250 × 16 mm; Knauer, Berlin; flow rate 10 mL/min; UV detection 254 nm) using MTBE/pentane (2:8) as eluent. Separated HTA esters **5a** and **5b** showed the following chromatographic and spectral data: first eluting isomer (HPLC retention time 18.7 min) **5a** (5 mg) Ri (DB-5) 2565; CI-MS *m/z* (%) 358 (100, $[M + NH4]^+$), 341 (8, $[M + H]^+$), 208 (2), 190 (3), 103 (3); ^1H NMR (200 MHz, $CDCl_3$, ppm) δ 1.18 and 1.20 (2 × 3 H, 2 s, $2CH_3$-C1), 1.29 (3 H, d, J = 6 Hz, CH_3-C9), 1.48 (3 H, d, J = 7 Hz, CH_3-C1′), 1.72 (3 H, d, J = 1 Hz, CH_3-C5), 2.26 (2 H, br s, H_2C2), 2.59 (2 H, m, H_2C8), 3.68 (1 H, q, J = 7 Hz, HC1′), 5.04 (1 H, m, HC9), 5.64 (1 H, t, J = 6 Hz, HC7), 5.81 (1 H, br s, HC4), 7.25 (5 H, m, phenyl-C1′); second eluting isomer (19.8 min) **5b** (5 mg) Ri (DB-5) 2587; CI-MS identical with that of isomer **5a**; ^1H NMR δ 1.20 (3 H, d, J = 6 Hz, CH_3-C9), 1.27 (6 H, s, $2CH_3$-C1), 1.49 (3 H, d, J = 7 Hz, CH_3-C1′), 1.92 (3 H, d, J = 1 Hz, CH_3-C5), 2.33 (2 H, s, H_2C2), 2.65 (2 H, m, H_2C8), 3.69 (1 H, q, J = 7 Hz, HC1′), 5.04 (1 H, m, HC9), 5.81 (1 H, t, J = 6 Hz, HC7), 5.88 (1 H, br s, HC4), 7.26 (5 H, m, phenyl-C1′).

(b) Reduction of Ester 5a and Subsequent Cyclization to Diastereomeric Edulans 1a/b. Five milligrams (1.47×10^{-2} mmol) of (9*R*)-HTA ester **5a** (diastereomeric excess, de > 97%; HRGC control) in 5 mL of dry diethyl ether was added to a stirred suspension of 2.8 mg (7.5×10^{-2} mmol) of $LiAlH_4$ in 5 mL of diethyl ether at 0 °C. After stirring (2 h) at room temperature and the addition of ice−water (10 mL), the organic layer was separated and the water phase extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with brine (10 mL) and water (10 mL). After drying (Na_2SO_4) and careful concentration (Vigreux column), the reduction product **6a** was—without further purification—subjected to simultaneous distillation extraction treatment at pH 3.4. 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 edulans **1a/b**, analytical HPLC was employed (Eurospher Si100 column; flow rate 2 mL/min; UV detection 205 nm; eluent pentane/MTBE 97:3). Separated edulan isomers **1a** (enantiomeric excess ee 94%) and **1b** (ee 91%) showed the following chromatographic and spectral data: 2*R*,-8a*R* isomer **1a**: Ri (DB-5) 1298; Ri (DB-Wax) 1472; UV λ_{max} = 192.5 nm; MS and IR data, cf., e.g., Whitfield and Stanley (1977); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 1.15 (6 H, s, $2CH_3$-C5), 1.19 (3 H, d, J = 6.1 Hz, CH_3-C2), 1.40 (3 H, br s, CH_3-C8a), 1.8−2.0 (4 H, m, H_2C3, H_2C6), 3.42 (1 H, qdd, J = 6.2 Hz, 9.6 Hz, 2.8 Hz, HC2), 5.57 (1 H, dq, J = 10 Hz, 1 Hz, HC8), 5.65 (1 H, ddd, J = 10 Hz, 4.9 Hz, 2.6 Hz, HC7), 5.75 (1 H, dd, J = 7.6 Hz, 2.8 Hz, HC4); 2*R*,8a*S* isomer **1b**: Ri (DB-5) 1359; Ri (DB-Wax) 1601; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 1.09 and 1.11 (6 H, 2s, $2CH_3$-C5), 1.2 (3 H, d, J = 6.2 Hz, CH_3-C2), 1.50 (3 H, s, CH_3-C8a), 1.9 −2.2 (4 H, m, H_2C3, H_2C6), 4.03 (1 H, qdd, J = 6.2 Hz, 10.4 Hz, 4.6 Hz, HC2), 5.48 (1 H, t, J = 3.7 Hz, HC4), 5.62 (1 H, dd, J = 10 Hz, J = 2.2 Hz, HC8), 5.66

Table 1. Enantiomeric Composition of Edulans 1a–d in Purple Passion Fruits of Various Origins

source	**1a** (2*R*,8a*R*), %	**1c** (2*S*,8a*S*), %	ee, %	**1d** (2*S*,8a*R*), %	**1b** (2*R*,8a*S*), %	ee, %
Ivory Coast[a]	10	90	80	94	6	88
Kenya[a]	10	90	80	91	9	82
Chile[a]	16	84	68	90	10	80
Ivory Coast[b]	10	90	80	85	15	70
Kenya[b]	20	80	60	89	11	78
Chile[b]	t	t		89	11	78

[a] Liquid/liquid extraction. [b] SDE, pH 3.4; t, trace (value for ee not determinable).

(1 H, ddd, J = 10 Hz, 4.6 Hz, 2.2 Hz, HC7); ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ 26.7 and 27.0 C10/11 (CH_3), 29.2 and 29.3 C9/C12 (CH_3), 33.5 C3 (CH_2), 35.4 C5 (C), 42.0 C6 (CH_2), 62.5 C2 (CH), 72.8 C8a (C), 116.1 C4 (CH), 125.9 C7 (CH), 132.7 C8 (CH), 147.0 C4a (C). Due to the small concentration of optically pure edulans available for the determination of the optical rotation, only the sense of rotation of isomers **1b** and **1d** could be determined. The assignments were (−) for edulan isomer **1b** and (+) for isomer **1d**.

(c) Reduction of Ester 5b and Subsequent Cyclization to Diastereomeric Edulans 1c/d. (9*S*)-HTA ester **5b** (de 89%, HRGC control) was treated as described for the 9*R* isomer **5a**. SDE treatment yielded diastereomeric edulans **1c/d**. LC purification (flash chromatography and subsequent HPLC) provided diastereomers **1c** (ee 94%) and **1d** (ee 91%), showing identical chromatographic and spectral data as obtained for the corresponding enantiomers **1a/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) and a Carlo Erba Fractovap 4100 gas chromatograph equipped with a J&W fused silica DB-Wax capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm) were used. Split injection was employed. The temperature program was from 60 to 300 °C at 5 °C/min for DB-5 and from 50 (3 min isotherm) to 240 °C at 4 °C/min for DB-Wax. 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/min of H_2 and 300 mL/min of air. The injector temperature was kept at 250 °C and the detector temperature at 280 (DB-5), 220 and 260 °C (DB-Wax), respectively. Linear retention index (Ri) 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 a 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-Wax fused silica capillary column (25 m × 0.25 mm i.d.; film thickness 0.25 μm). The temperature was programmed from 60 to 240 °C (5 °C/min). A "live" switching device (Schomburg et al., 1984) in oven 1 was used to perform effluent cuts onto column 2 in oven 2 [heptakis(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin; 25 m × 0.25 mm i.d.; film thickness 0.25 μm]. The temperature was isothermal at 60 °C for 20 min and then programmed from 60 to 200 °C at 2 °C/min. Two 18-s cuts were carried out. The flow rates for the detector gases were each 30 mL/min of hydrogen and 300 mL/min of air. The MDGC system was directly coupled to a Finnigan MAT 44 quadrupole mass spectrometer using a heated transfer line. 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 edulans.

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 edulan enantiomers **1a–d** is outlined. The benzopyran derivatives **1a–d** were prepared from their natural precursor 3-hydroxy-*retro*-α-ionol (**6a/b**) which was available from α-ionone by *tert*-butyl chromate oxidation, $NaBH_4$ reduction, and subsequent rearrangement of the 7,8 double bond with $NaOCH_3$. The two geometrical isomers (*E*/*Z*)-3-oxo-*retro*-α-ionols (**4a/b**) (yield 10%) were first separated by preparative MLCCC and then by analytical MLCCC. In the first step, the *E* isomer (**4a**) was preseparated from 3-oxo-α-ionol (**3**); in the second step, final purification of **4a** was achieved. The racemic keto alcohol **4a** was subsequently esterified with (*R*)-(−)-2-phenylpropionic acid; the resulting diastereomeric esters (**5a** and **5b**) 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 **5a** and **5b** showed *inter alia* that the resonance of CH_3-C9 in ester **5a** was downfield shifted, thus indicating *R* configuration at C9. Accordingly, due to the upfield shift for the resonance of CH_3-C9 in ester **5b**, *S* configuration was deduced.

The isomeric diols **6a** and **6b** obtained from **5a/b** by reductive cleavage with $LiAlH_4$ were subjected to simultaneous distillation extraction (pH 3.4), yielding two pairs of diastereomeric edulans **1a/b** and **1c/d** which were subsequently isolated in pure form by preparative HPLC. The absolute configuration at C8a of the separated benzopyran derivatives was established by NOE NMR experiments. Thus, e.g., for enantiomer **1d** irradiation of the protons at the methyl group at C8a resulted in a NOE at the C2 methine proton, implicating 2*S*,8a*R* configuration for this isomer. The enantiomer **1b** showed the same effect in the NOE experiment, thus revealing 2*R*,8a*S* configuration. Interpretation of the NOE NMR experiments performed with isomers **1a** and **1c** was not possible, since the synthesized amounts of these isomers were too small. However, from the synthetic route chosen (cf. Figure 1), which defines stereochemistry at the chiral center at C2, it is obvious that the corresponding isomers **1a** and **1c** show the absolute configuration 2*R*,8a*R*-**1a** and 2*S*,8a*S*-**1c**, respectively. Compared with the major isomers **1b/d**, isomers **1a/c** are only formed in a ratio of 4:1 (Adams et al., 1974). Concerning the reaction mechanism, it can be assumed that the acid-catalyzed cyclization of the diol (**6a/b**) and the equilibration of the edulans take place through the common pentadienyl carbonium ion. Edulan **1b/d** with the 2-methyl group equatorial in a

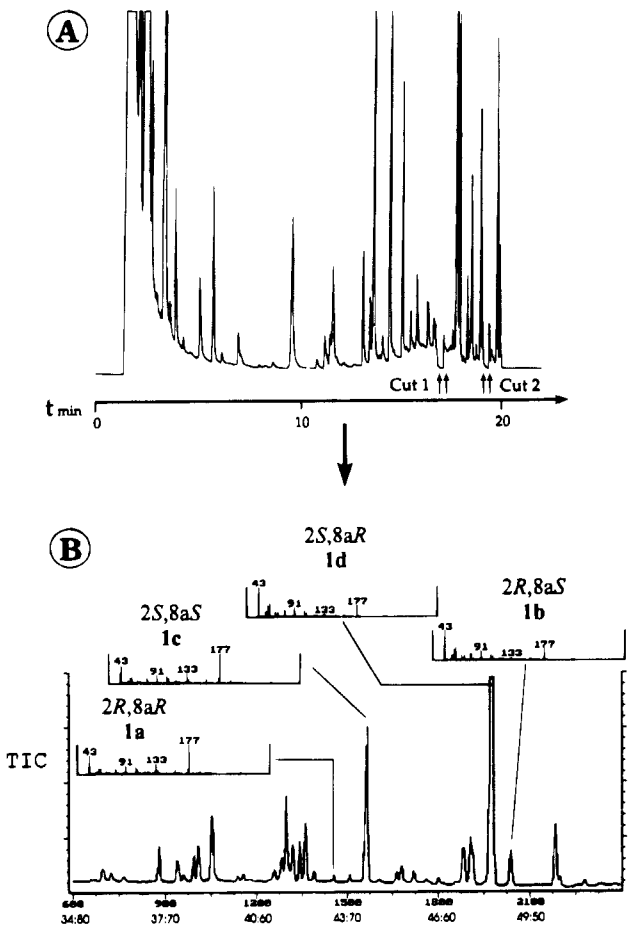


Figure 2. MDGC–MS enantiodifferentiation of edulans **1a–d** in an extract of purple passion fruit from Chile: (A) preseparation on an achiral column (J&W DB-Wax), cut 1, 16.8–17.1 min, Cut 2, 19.0–19.3 min; (B) separation on a chiral column [heptakis(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin].

distorted chair conformation of the dihydropyran ring is more stable than edulan **1a/c** with the 2-methyl group equatorial in a distorted boat conformation.

Using on-line coupled multidimensional gas chromatography–mass spectrometry (MDGC–MS) (Bernreuther and Schreier, 1991) with SIM mode, enantiodifferentiation of **1a–d** in natural sources was carried out. The results of these studies are summarized in Table 1. The order of elution of the four edulan isomers **1a–d** on a chiral column [heptakis(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin] was found to be **1a** (2*R*,8a*R*), **1c** (2*S*,8a*S*), **1d** (2*S*,8a*R*), **1b** (2*R*,8a*S*). As a representative example in Figure 2 the MDGC–MS separation of **1a–d** in an extract of purple passion fruit is outlined. In all samples examined (cf. Table 1) the 2*S* isomers **1c** and **1d** predominated (enantiomeric excess, ee 70%). Since the formation proceeds via the precursor diols **6a/b**, this result also implies prevailing *S* configuration at the C9 chiral center.

ACKNOWLEDGMENT

We gratefully acknowledge the skillful assistance of T. Rückert. We are indebted to Dr. Scheutzow and E. Ruckdeschel (Institut für Organische Chemie, Würzburg) for recording the 400-MHz NMR spectra. We thank Dr. G. Lange for recording the CI-MS. We also thank The Deutsche Forschungsgemeinschaft, Bonn, for funding the research.

LITERATURE CITED

Adams, D. R.; Bhatnagar, S. P.; Cookson, R. C.; Stanley, G.; Whitfield, F. B. Synthesis and structures of edulan I and II. *J. Chem. Soc., Chem. Commun.* **1974**, 469–470.

Adams, D. R.; Bhatnagar, S. P.; Cookson, R. C. Synthesis and structure of edulan I and II. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1736–1739.

Bernreuther, A.; Schreier, P. Multidimensional gas chromatography-mass spectrometry: A powerful tool for the direct chiral evaluation of aroma compounds in plant tissues. II. Linalool in essential oils and fruits. *Phytochem. Anal.* **1991**, *2*, 167–170.

Etoh, H.; Ina, K.; Iguchi, M. New synthesis of edulans and theaspiranes from α-ionone. *Agric. Biol. Chem.* **1980**, *44*, 2871–2876.

Helmchen, G. New method for the determination of the absolute configuration of chiral secondary alcohols and amines. NMR spectroscopy of diastereoisomeric esters and amides of α-phenylbutyric and hydratropic acid. *Tetrahedron Lett.* **1974**, *16*, 1527–1530.

Helmchen, G.; Schmierer, R. Determination of the absolute configuration of chiral thiols by proton NMR spectroscopy of diastereomeric thiol esters. *Angew. Chem.* **1976**, *88*, 770–771.

Herderich, M.; Winterhalter, P. 3-Hydroxy-*retro*-α-ionol: a natural precursor of isomeric edulans in purple passion fruit (*Passiflora edulis* Sims). *J. Agric. Food Chem.* **1991**, *39*, 1270–1274.

Ito, Y.; Sandlin, J.; Bowers, W. G. High-speed preparative countercurrent chromatography with a coil planet centrifuge. *J. Chromatogr.* **1982**, *244*, 247–258.

Murray, K. E.; Shipton, J.; Whitfield, F. B. The chemistry of food flavor; I. Volatile constituents of passionfruit, *Passiflora edulis*. *Aust. J. Chem.* **1972**, *25*, 1921–1933.

Schomburg, G.; Husmann, H.; Podmaniczky, L.; Weeke, F. Coupled gas chromatographic methods for separation, identification, and quantitative analysis of complex mixtures: MDGC, GC-IR, LC-GC. In *Analysis of Volatiles*; Schreier, P., Ed.; de Gruyter: Berlin, 1984; pp 121–150.

Schulte-Elte, K. H.; Gautschi, F.; Renold, W.; Hauser, A.; Fankhauser, P.; Limacher, J.; Ohloff, G. Vitispiranes, important constituents of vanilla aroma. *Helv. Chim. Acta* **1978**, *61*, 1125–1133.

Schultz, T. H.; Flath, R. A.; Mon, T. R.; Eggling, S. B.; Teranishi, R. Isolation of volatile components from a model system. *J. Agric. Food Chem.* **1977**, *25*, 446–449.

Sefton, M. A.; Skouroumounis, G. K.; Massy-Westropp, R. A.; Williams, P. J. Norisoprenoids in *Vitis vinifera* white wine grapes and the identification of a precursor of damascenone in these fruits. *Aust. J. Chem.* **1989**, *42*, 2071–2084.

Stanley, G. Reaction gas chromatography in sealed glass capillaries; dehydration, reduction and oxidation reactions, and the synthesis of reference compounds. *J. Chromatogr.* **1979**, *178*, 487–493.

Still, W. C.; Kahn, M.; Mitra, A. Rapid chromatographic technique for preparative separations with moderate resolutions. *J. Org. Chem.* **1978**, *43*, 2923–2925.

Whitfield, F. B.; Last, J. H. The flavor of the passion fruit—a review. In *Progress in Essential Oil Research*; Brunke, E. J., Ed.; de Gruyter: Berlin, 1986; pp 3–48.

Whitfield, F. B; Stanley, G. The structure and stereochemistry of edulan I and II and the stereochemistry of the 2,5,5,8a-tetramethyl-3,4,4a,5,6,7,8,8a-octahydro-2*H*-1-benzopyrans. *Aust. J. Chem.* **1977**, *30*, 1073–1091.

Received for review July 6, 1994. Accepted October 12, 1994.[⊗]

JF940367L

[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1994.