3-Hydroxy-*retro*-α-ionol: A Natural Precursor of Isomeric Edulans in Purple Passion Fruit (*Passiflora edulis* Sims)

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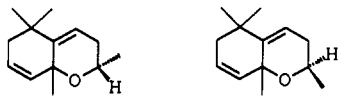
In a polar extract obtained from purple passion fruit (*Passiflora edulis* Sims) juice, capillary gas chromatography (HRGC), and coupled HRGC techniques, i.e., on-line mass spectrometry (HRGC–MS) and Fourier transform infrared spectroscopy (HRGC–FTIR), revealed for the first time the presence of 3-hydroxy-*retro*-α-ionol. The identification was verified by comparison of HRGC, HRGC–MS, and HRGC–FTIR data of the new natural product with those of an authentic reference compound synthesized from the known C_{13} keto alcohol, 3-oxo-α-ionol. Degradation studies carried out with 3-hydroxy-*retro*-α-ionol showed the easy formation of isomeric edulans under acidic conditions. Possible mechanisms for the formation of the odor active edulans, key flavor components of purple passion fruit juice, are discussed.

INTRODUCTION

In the past, the composition of volatiles from purple-skinned passion fruit (*Passiflora edulis* Sims) has been extensively studied, and approximately 150 aroma constituents have been identified to date (Maarse, 1989; Whitfield and Last, 1986). Among them, several strongly odoriferous C_{13} norisoprenoids, i.e., four isomers of megastigma-4,6,8-triene (Whitfield et al., 1977; Whitfield and Sugowdz, 1979) as well as isomeric 2,5,5,8a-tetramethyl-3,5,6,8a-tetrahydro-2*H*-1-benzopyrans **1a/b**, the so-called

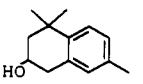


1a/b

edulans I and II (Whitfield et al., 1973; Adams et al., 1974; Whitfield and Stanley, 1977), were reported to make a specific contribution to the flavor of fresh passion fruit juice. Especially the latter ones, with attractive roselike aromas and a total concentration of approximately 1.1 mg/kg of fresh juice, are considered to be key flavor components of the purple variety (Whitfield and Last, 1986). However, in spite of the significant aroma contribution of the bicyclic ethers **1a/b**, their natural precursor in passion fruit is still unknown.

With regard to potential progenitors of **1a/b**, two classes of flavor precursors have to be considered: First, non-conjugated polyhydroxylated terpenoids, so-called polyols, upon heat treatment under acid conditions can form a great number of volatile aroma compounds (Williams et al., 1980). Second, acid-labile glycosidically bound components can also easily be transformed to free volatiles by means of acid as well as enzymatic hydrolysis (Williams et al., 1989; Günata et al., 1989). Both precursor classes have been shown to be present in purple passion fruit juice. In an earlier investigation of Engel and Tressl (1983), dealing with the monoterpenoid composition of the purple passion fruit variety, polyols as well as glycosidic conjugates have been elucidated as important precursors of the monoterpenoid volatiles under investigation.

A recent study (Winterhalter, 1990), directed at the formation of C_{13} norterpenoid volatiles in purple passion fruit, revealed for the first time the presence of 16 glycosidically bound C_{13} compounds in the juice of the purple-skinned variety, which in number and concentration clearly dominated over the monoterpenoid conjugates. Important aglycons included the acid-labile naphthalene derivative **2**, a component known to yield the off-flavor-causing



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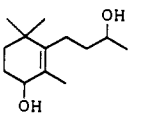

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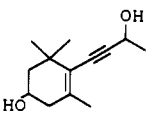

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hydrocarbon 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), upon heat treatment (Davis et al., 1976); and 4-hydroxy-7,8-dihydro-β-ionol (**3**), the natural precursor of isomeric theaspiranes (Winterhalter and Schreier, 1988). In addition, employing on-line HRGC–FTIR analysis, we succeeded most recently in identifying the glycoconjugated acetylenic diol **4** as a natural progenitor of damascenone in purple passion fruit juice (Winterhalter et al., 1991).

However, there was no evidence for the presence of edulan generating compounds among the glycosidically bound constituents. Consequently, on the basis of these results, more intense studies into the polyol fraction of the purple fruit became necessary. In the present paper we report on the synthesis and the identification of a natural precursor of isomeric edulans **1a/b** in purple passion fruit juice.

EXPERIMENTAL PROCEDURES

Chemicals. All commercial chemicals used were of analytical grade quality. Sodium dihydridobis(2-methoxyethoxy)aluminate (SDMA) was obtained from Sigma Chemie GmbH, Deisenhofen, Germany. All solvents used were of high purity at purchase and were redistilled before use. 3-Oxo-α-ionol (**9**) was a donated sample from Dragoco GmbH, Holzminden, Germany.

Fruits. Fresh purple passion fruit (*P. edulis* Sims) was obtained by air-freight from Adelaide, South Australia.

Isolation of Glycosidically Bound Compounds from Passion Fruit Juice (cf. Scheme I). The pulp of 1 kg of ripe passion fruit was centrifuged at 10000*g* for 1 h. The clear juice obtained was diluted with the same volume of H_2O and, after the

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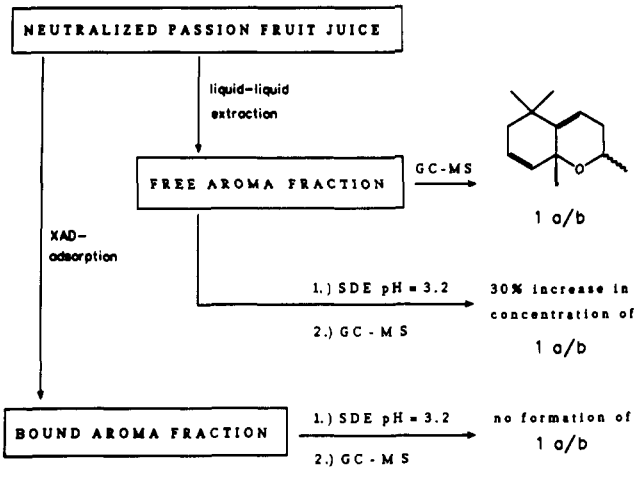
Scheme I. Screening for Edulan 1a/b Generating Precursors



pH was adjusted to 7 (2 N NaOH) and a further centrifugation, passed through a column (20 cm × 3 cm i.d.) of Amberlite XAD-2 resin (Günata et al., 1985). After the column was rinsed with H_2O (1000 mL), the glycosidic fraction was eluted with MeOH (500 mL). The solvent was carefully removed in vacuo, and the residue was liquid–liquid extracted with diethyl ether (24 h) to ensure removal of any volatiles prior to simultaneous distillation–extraction (SDE) treatment. SDE was carried out at pH 3.5 (0.2 M citric acid/phosphate buffer, 50 mL) for 1 h by using the apparatus designed by Schultz et al. (1977) with pentane–diethyl ether (1:1 v/v; 60 mL) as solvent. After drying (Na_2SO_4), and careful concentration (Vigreux column), the aroma extract was subjected to HRGC and HRGC–MS analyses.

Liquid–Liquid Extraction of Purple Passion Fruit Juice (cf. Scheme I). The pulp of 5 kg of passion fruit (approximately 1.2 L) was centrifuged at 10000*g* for 1 h. The clear juice obtained (0.7 L), possessing a pH value of 3.5, was first neutralized by adding an aqueous solution of NaOH (2 N) and then continuously liquid–liquid extracted (24 h) with diethyl ether. After drying over Na_2SO_4, one aliquot of the extract ($^1/_{10}$ part) was concentrated (Vigreux column) and after addition of an external standard (2-decanol) analyzed by HRGC and HRGC–MS. A further aliquot ($^1/_{10}$ part) of the ether extract was also concentrated and subjected to heat treatment (SDE, 1 h; pH 3.5) prior to standard-controlled HRGC and HRGC–MS analyses. The remaining ether extract was used for the identification of the edulan generating precursor.

Synthesis of 3-Hydroxy-*retro*-α-ionols 5a/b. (*a*) *Preparation of 3-Oxo-retro-α-ionols* **10a/b** (*Sefton et al., 1989*). 3-Oxo-α-ionol (**9**) (1.03 g) in distilled MeOH (10 mL) was treated for 48 h with a solution of sodium methoxide in methanol (1 M, 10 mL) at room temperature under nitrogen. The reaction mixture was acidified with glacial acetic acid and subsequently extracted with 3 × 100 mL of diethyl ether. The ether extract was washed with a saturated solution of $NaHCO_3$ (200 mL) and H_2O (2 × 100 mL). After drying (Na_2SO_4), HRGC and HRGC–MS analyses showed that the reaction mixture consisted of starting material **9** (41%), the first-eluting isomer of keto alcohol **10** (18%), and the second-eluting isomer of **10** (41%). From this mixture the major isomer of **10** (140 mg) was isolated by preparative HPLC with diethyl ether as eluent, flow rate of 10 mL/min, UV detection at 240 nm, and a LiChrospher Si100 column (5 μm, 250 × 16 mm, Knauer, Berlin): R_i (DB-5) 1792; MS (*m/z*, %) 208 (M^+, 3), 193 (2), 190 (6), 175 (3), 164 (56), 149 (100), 136 (11), 135 (8), 122 (22), 121 (19), 108 (11), 107 (17), 105 (11), 93 (11), 91 (17), 79 (14), 77 (14), 45 (61), 43 (23); FTIR (vapor phase, ν, cm^{-1}) 3653, 3040, 2973, 2887, 1693, 1632, 1597, 1456, 1380, 1250, 1113; ^1H NMR (WM 400, $CDCl_3$, ppm) 1.28 (3 H, d, *J* = 6 Hz, CH_3-C9), 1.29 and 1.31 (2 × 3 H, 2 s, 2CH_3-C1), 1.84 (H, br s, O*H*), 2.08 (3 H, d, *J* = 1 Hz, CH_3-C5), 2.35 (2 H, s, 2H-C2), 2.60 (2 H, m, 2H-C8), 3.96 (H, m, H-C9), 5.91 (H, br s, H-C4), 6.06 H, t, *J* = 6 Hz, H-C7); ^{13}C NMR (AC 200, $CDCl_3$, ppm) 22.4, 23.5, 29.0, 29.1 (4 × CH_3 at C1, C1, C5, C9), 38.3 (C1), 39.3 (C8), 53.9 (C2), 68.1 (C9), 125.6 (C7), 131.3 (C4), 143.4 (C6), 155.3 (C5), 199.3 (C3). ^{13}C chemical shifts were assigned on the basis of a DEPT experiment. Nuclear Overhauser effect (NOE) experiments: irradiation of the protons of the methyl group at C5 resulted in a NOE (27%) at the proton at C7, vice versa NOE (9%); irradiation of the protons at C8 gave a NOE (14%) at the methyl groups at C1, vice versa NOE (14%). On the basis of these results the second-eluting isomer of keto alcohol **10** was assigned as the *E* isomer **10b**.

The first-eluting *Z* isomer **10a**, which could not be completely separated from starting material **9**, showed the following chromatographic and spectral data: R_i (DB-5) 1739; MS (*m/z*, %) 208 (M^+, 3), 193 (3), 190 (3), 164 (59), 149 (100), 136 (9), 135 (5), 122 (22), 121 (19), 108 (15), 107 (16), 105 (12), 93 (9), 91 (16), 79 (13), 77 (13), 45 (72), 43 (25); FTIR (vapor phase, ν, cm^{-1}) 3653, 3040, 2973, 2897, 1694, 1628, 1597, 1451, 1379, 1249, 1111.

(*b*) *Reduction to (E)-3-Hydroxy-retro-α-ionol* **5b**. To 100 mg of keto alcohol **10b** in dry THF (20 mL) was added with stirring at 0 °C a 70% solution of $NaAlH_2(OCH_2CH_2OCH_3)_2$ in toluene (0.3 mL). The mixture was then warmed to 25 °C and held at this temperature for 16 h. After cooling, the mixture was treated cautiously with 2 N NaOH (1 mL) and the product extracted with diethyl ether (2 × 50 mL). The organic layer was washed with distilled H_2O (2 × 50 mL) and brine (50 mL). After drying (Na_2SO_4) and concentration in vacuo, a mixture of diastereoisomeric diols **5b** was obtained, which could clearly be separated on a polar Stabilwax HRGC column. The diols **5b** were purified by preparative HPLC with diethyl ether as eluent, flow rate of 12 mL/min, UV detection at 240 nm, and a LiChrosorb diol column (5 μm, 250 × 16 mm i.d., Knauer, Berlin) and showed the following chromatographic and spectral data: R_i (Stabilwax) 2797 and 2803; R_i (DB-5) 1703 (no separation of diastereoisomers); MS, cf. Figure 3; FTIR, cf. Figure 4; ^1H NMR (AC 200, $CDCl_3$, ppm) 1.14[a] and 1.36[a] (2 × 3 H, 2 s, 2CH_3-C1), 1.25[a] (3 H, d, *J* = 6 Hz, CH_3-C9), 1.53 (H, dd, *J* = 12 Hz, 10 Hz; H_a-C2), 1.77 (H, ddd, *J* = 12 Hz, 6 Hz, 1 Hz; H_b-C2), 1.85 (3 H, d, *J* = 1 Hz, CH_3-C5), 2.53 (2 H, m, 2H-C8), 3.90 (H, m, H-C9), 4.30 (H, m, H-C3), 5.56 (H, m, H-C7), 5.65 (H, br s, H-C4); ^{13}C NMR (AC 200, $CDCl_3$, ppm) 22.2, 23.9[a], 27.4[a], 31.6, 35.9, 40.4, 50.7, 66.3, 69.3[a], 124.1, 124.3, 130.3, 135.4 ([a]splitting of the signals indicated the occurrence of diastereoisomers).

(*c*) *Reduction to (Z)-3-Hydroxy-retro-α-ionol* **5a**. Keto alcohol **10a**, which still included starting material **9** as impurity, was treated analogously and gave diastereoisomer diols **5a**: R_i (DB-5) 1696 (no separation of diastereoisomers); MS, cf. Figure 3.

Degradation Studies. Two milligrams of each of the diols **5a** and **5b** in 5 mL of diethyl ether was treated with formic acid (2 drops) over 2 h. After neutralization with a saturated aqueous solution of $NaHCO_3$, the reaction mixture was extracted with diethyl ether (3 × 10 mL). The combined ether extracts were dried over Na_2SO_4, carefully concentrated (Vigreux column), and subjected to HRGC and HRGC–MS analyses.

Capillary Gas Chromatography (HRGC). A Carlo Erba Fractovap 4160 gas chromatograph equipped with FID was used. Two types of fused silica columns were employed: (a) J&W DB-5 (30 m, 0.25 mm i.d., film thickness 0.25 μm); (b) Analyt Stabilwax DA (30 m, 0.25 mm i.d., film thickness 0.25 μm). Split injection was used (1:20). The temperature programs were 60 °C up to 300 °C at 5 °C/min (a) and 3-min isothermal at 50 °C and then increased at 4 °C/min to 280 °C (b). The flow rate for the carrier gas was 2.0 mL/min of He, for the make-up gas 30 mL/min of N_2, and for the detector gases 30 mL/min of H_2 and 300 mL/min of air, respectively. The injector temperature was kept at 220 °C and the detector temperature at 300 °C.

Capillary Gas Chromatography–Mass Spectrometry (HRGC–MS). A Varian Aerograph 1440 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 types of columns as mentioned above for HRGC analysis were used. The conditions were as follows: temperature programs, (a) from 60 to 300 °C at 5 °C/min and (b) 3-min isothermal at 50 °C and then increased at 4 °C/min to 260 °C and 10-min isothermal at 260 °C; carrier gas flow rate, 2.5 mL/min of He; temperature of ion source and all connection parts, 200 °C; electron energy, 70 eV; cathodic current, 0.7 mA.

Capillary Gas Chromatography–Fourier Transform Infrared Spectroscopy (HRGC–FTIR). A HP-IRD system

(5965B with a wide band MCT detector) interfaced by a HP 5890 Series II gas chromatograph equipped with FID was used. A HP-5 fused silica capillary column (25 m × 0.32 mm i.d.; film thickness 0.52 μm) was employed. On-column injection was used. The temperature program was 60 to 280 °C at 4 °C/min. Light pipe and transfer line were held at 250 °C. He (2.5 mL/min) was used as carrier gas. Vapor-phase spectra were recorded from 550 to 4000 cm^{-1} with a resolution of 8 cm^{-1}.

Nuclear Magnetic Resonance (NMR) Spectroscopy. ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz on a Bruker WM 400 and at 200 MHz on a Bruker AC 200 instrument, respectively, with $CDCl_3$ as solvent and Me_4Si as reference standard.

RESULTS AND DISCUSSION

Location of the Edulan 1a/b Generating Precursor. As a first step in this study it was necessary to examine whether the isomeric edulans **1a/b** are formed by degradation of glycosidically bound components or by acid-catalyzed reactions of free polyols. For this purpose, the bound aroma fraction of purple passion fruit juice was isolated by adsorption on XAD-2 resin (Günata et al., 1985). The glycosidic fraction was subsequently eluted with methanol and after evaporation of the solvent subjected to a SDE treatment (Schultz et al., 1977) at natural pH conditions (pH 3.5) of purple passion fruit juice (cf. Scheme I). Since HRGC and HRGC–MS analyses of the SDE extracts revealed no formation of isomeric edulans **1a/b**, a glycosidically bound precursor form was excluded as natural source of the attractive aroma compounds **1a/b**. Consequently, our attention was directed to the free aroma fraction. For the examination of the nonconjugated constituents in passion fruit the neutralized juice was continuously (24 h) liquid–liquid extracted (cf. Scheme I). One aliquot of the aroma extract obtained was immediately analyzed by standard-controlled HRGC and HRGC–MS analyses; a second aliquot was subjected to heat treatment (SDE) under natural pH conditions of the juice prior to HRGC and HRGC–MS analyses. In the latter case, standard-controlled HRGC analysis revealed a 30% increase in concentration of isomeric edulans **1a/b**, indicating the presence of an acid-labile progenitor among the free aroma constituents.

Polyhydroxylated C_{13} Norisoprenoids as Possible Precursors of Edulans. On the basis of the earlier results of our group concerning the formation of related C_{13} norisoprenoids, the so-called theaspiranes (Winterhalter and Schreier, 1988), several polyhydroxylated C_{13} compounds came under consideration as potential progenitors of bicyclic ethers **1a/b**. Among them, the previously unknown diol **5** was the most likely one. In analogy to theaspirane formation by an acid-catalyzed cyclization of 4-hydroxy-7,8-dihydro-β-ionol, the tetrahydropyran derivatives **1a/b** should theoretically be accessible via prototropic dehydration and subsequent cyclization of the allyl-1,7-diol **5**. Precedent for this type of reaction can be found in earlier work on the dehydration of monoterpenoid allyl-1,7-diols (Ohloff et al., 1964). This assumption was further supported by a previous paper on the synthesis of isomeric dihydroedulans from a 6,7-saturated analogue of diol **5** (Prestwich et al., 1976), although the latter diol has never been identified in a natural tissue. Other polyols, like dienediol **6** (Adams et al., 1975), trienol **7** (Schulte-Elte et al., 1978), and triol **8** (Etoh et al., 1980) (cf. Figure 1), which have been previously reported as synthetic precursors of edulans **1a/b**, were to our best knowledge never detected in any natural substrate.

Synthesis of 3-Hydroxy-*retro*-α-ionols 5a/b. The synthesis was performed as outlined in Figure 2. Isomeric

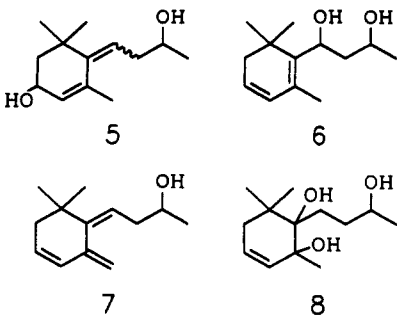


Figure 1. Proposed structure for the edulan generating precursor **5** and structures **6–8** of known synthetic progenitors of edulans **1a/b**.

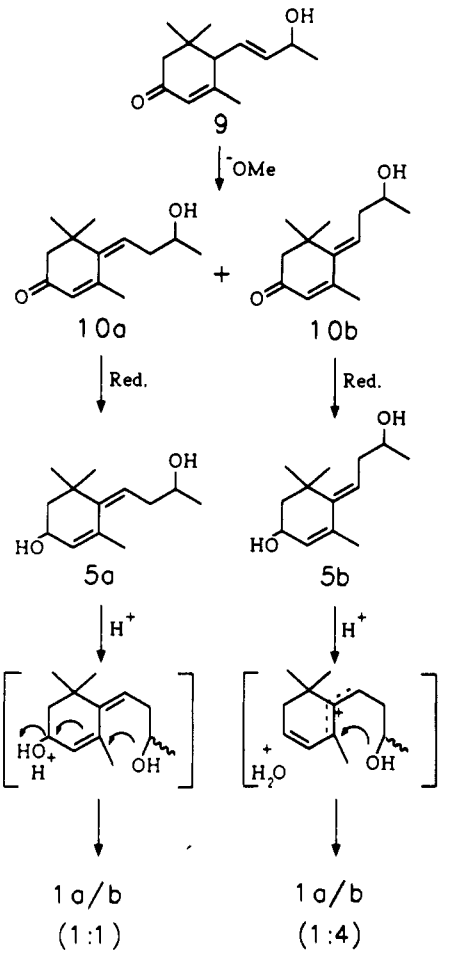


Figure 2. Synthesis of 3-hydroxy-*retro*-α-ionols **5a/b** from 3-oxo-α-ionol **9** and proposed mechanisms for the formation of isomeric edulans **1a/b**.

hydroxydienones **10a/b** were obtained in a ratio of approximately 1:2 by base treatment of 3-oxo-α-ionol (**9**) (Sefton et al., 1989). Purification using preparative HPLC provided the longer retention time isomer in a pure state, whose structure was assigned as the *E* isomer **10b** on the basis of ^1H and ^{13}C NMR data in combination with nuclear Overhauser effect (NOE) experiments. Subsequent reduction of keto alcohol **10b** using sodium dihydridobis-(2-methoxyethoxy)aluminate (Prestwich et al., 1976) gave a mixture of diastereoisomeric diols **5b**. In the same way the *Z* isomer **10a**, which could not be completely separated from starting material **9**, gave a mixture of diols **5a**.

Identification of 3-Hydroxy-*retro*-α-ionol (5b) in Purple Passion Fruit Juice. With the chromatographic and spectral data of diols **5a/b** in hand, we investigated the free aroma fraction of purple passion fruit juice, in which, on the basis of the results of the above-mentioned

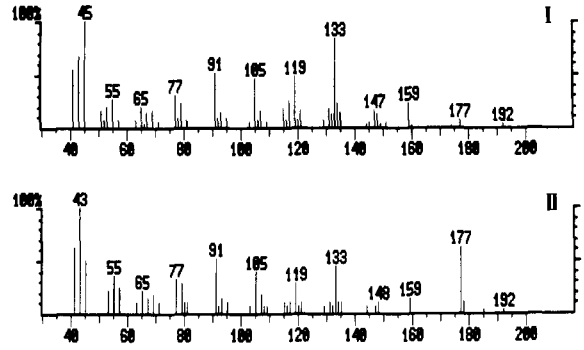


Figure 3. Mass spectra (70 eV) of (*E*)-3-hydroxy-*retro*-α-ionol (**5b**) (I) and (*Z*)-3-hydroxy-*retro*-α-ionol (**5a**) (II).

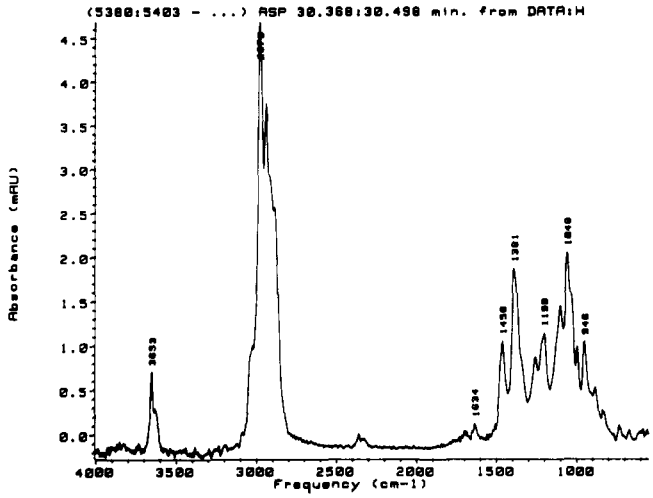


Figure 4. Vapor-phase FTIR spectrum of (*E*)-3-hydroxy-*retro*-α-ionol (**5b**).

screening, the precursor of isomeric edulans **1a/b** was located. Hence, a polar extract of the juice was obtained by continuous liquid–liquid extraction using diethyl ether as solvent. Subsequent HRGC, HRGC–MS, and HRGC–FTIR analyses of the extract revealed for the first time the presence of one diastereoisomer of 3-hydroxy-*retro*-α-ionol (**5b**) with still undefined stereochemistry in the 3- and 9-positions. The mass and FTIR spectra of this new natural compound were identical with those obtained for synthetic **5b** (cf. Figure 3 and 4). Quantitatively, approximately 0.1 mg of diol **5b** was determined per kilogram of fresh passion fruit juice.

Degradation Studies. Acid treatments of solutions of diols **5a** and **5b**, respectively, were carried out according to the procedure of Prestwich et al. (1976). For diol **5a** a complete conversion to isomeric edulans **1a/b** (ratio approximately 1:1) was observed. The presumed mechanism is outlined in Figure 2, a classical example for a "prototropic dehydration of an allyl-1,7-diol" giving rise to the formation of tetrahydropyran derivatives as previously described by Ohloff et al. (1964). Diol **5a** was even so unstable that, when injected in the hot injector block of the gas chromatograph, a considerable amount of edulans **1a/b** was formed. The easy cyclization to bicyclic ethers **1a/b** is also apparent from the mass spectrum (70 eV) obtained for diol **5a** (cf. Figure 3), which strongly resembles those of edulans **1a/b**, thus indicating a formation of the latter compounds during fragmentation in the mass spectrometer.

The mass spectrum of the natural precursor compound **5b** differs from that obtained for **5a**. The most prominent ion is *m/z* 45, which is characteristic of 2-alkanols. This indicates that in the case of the sterically hindered *E* isomer **5b** a direct cyclization to edulans **1a/b** is not possible. A presumed mechanism for edulan formation may start with a dehydration in the 3,4-position, generating a carbonium ion as outlined in Figure 2. Subsequent *Z* isomerization allows then a cyclization to the target compounds **1a/b**. Again, an almost complete conversion to isomeric edulans **1a/b** was observed under the experimental conditions used. However, for the conversion of diol **5b** the ratio of isomeric edulans formed was approximately 1:4, with the longer retention time isomer (edulan I) being the main component. Thus, a similar ratio of edulans **1a/b** was obtained, as has been previously reported for authentic purple passion fruit juice (Whitfield et al., 1973).

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